Combining electronic and steric effects to generate hindered propargylic alcohols in high enantiomeric excess

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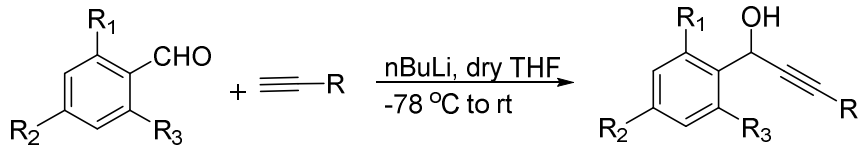
Contents.

All reagents and solvents were used as purchased and without further purification. All reactions were carried out under a nitrogen atmosphere unless otherwise specified. Reactions at elevated temperature were maintained by thermostatically controlled aluminium heating blocks or in oil baths. A temperature of 0 °C refers to an ice slush bath. NMR spectra were recorded on a Bruker AV (250 MHz), Bruker DPX (300 or 400MHz) or Bruker DRX (500 MHz) instrument. All chemical shifts are reported in ppm and are referenced to the solvent chemical shift, and coupling constants are given in Hz. Mass spectra were recorded on an Esquire 2000 and high resolution mass spectra were recorded on a Bruker Micro ToF or MaXis. IR spectra were recorded on a PerkinElmer spectrum100. Optical rotations were measured on an Optical Activity Ltd. AA-1000. The chiral GC measurements were carried out on a PerkinElmer 8500 or Hewlett-Packard 1050 instrument linked to PC running DataApex Clarity software. HPLC was carried out on a Hewlett-Packard 1050 HPLC system. Melting points were determined on a Stuart scientific melting point apparatus and are uncorrected. Flash column chromatography was performed using silica gel of mesh size 230-400, Thin layer chromatography was carried out on aluminium backed silica gel 60 (F254) plates, visualized using 254nm UV light or iodine stains as appropriate.

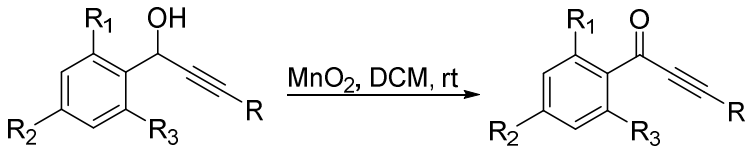
General procedures for the syntheses.

Procedure A: Synthesis of Racemic Alcohols.



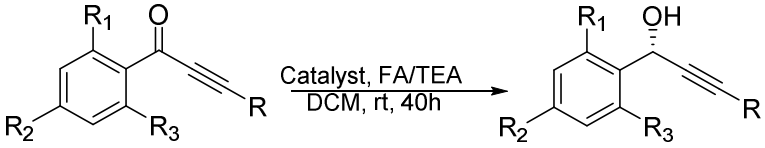
To a solution of acetylene (6.0 mmol, 1.2 equiv) in dry THF (25 mL) was added *n*BuLi (2.5 M in *n*-hexane, 2.0 mL, 5.0 mmol, 1.0 equiv) dropwise at –78 ºC under nitrogen atmosphere. After the reaction mixture had been stirred at –78 ºC for 1 h, aldehyde (5.0 mmol, 1.0 equiv) was added dropwise at -78 ºC. Upon stirring at same temperature for 1 h, the reaction mixture was stirred at ambient temperature for 1 h. It was then concentrated under reduced pressure, extracted with ethyl acetate (3 x 50 mL), washed with brine (50 mL), dried over Na_2SO_4, filtered, concentrated, and purified by column chromatography on silica gel to yield the alcohol product.

Procedure B: Oxidation of alcohols to ketones.



To a stirred solution of alkynol (4 mmol) in DCM (15 mL) was added activated manganese dioxide (2.40 g, 28 mmol, 7.0 equiv) at rt under nitrogen atmosphere. After 24 h, the reaction mixture was filtered through a Celite pad with CH_2Cl_2. The filtrate was concentrated and purified by column chromatography on silica gel to yield the ketone.

Procedure C: Asymmetric Transfer Hydrogenation (ATH) of ketones.

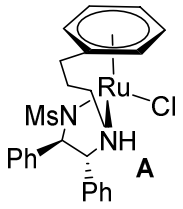


The ketone (0.2 mmol), catalyst (2.0 x 10^{-3} mmol), DCM (2 mL) and FA/TEA (0.2 mL) azeotrope was added sequentially to the reaction tube and stirred at rt. The reaction was monitored by TLC. After the completion of reaction, it was quenched by water (10 mL) and extracted with ethyl acetate (2 x 10 mL). The organic layer was dried with Na_2SO_4 and concentrated to obtain a residue. The residue was purified with a silica gel column eluted with petroleum ether and ethyl acetate to obtain the pure desired product. Reaction time at rt is ca 40h.

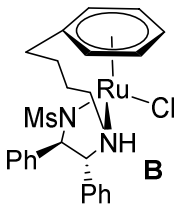
ATH of o-OMe ketone to give alcohol **16** using other catalysts and conditions not listed in main paper.

Entry	Catalyst	Conv./%	Ee/%	Notes
1	RR-DENEB 4	70	53 (*S*)	
2	RR 3C Ms Teth A	100	20 (*S*)	
3	RR C4 tris teth B	100	20 (*S*)	
4	RR 3C teth 2	100	60 (*S*)	40 °C
5	RR 3C teth 2	100	64 (*S*)	40 °C, no DCM
6	RR 3C teth 2	100	60 (*S*)	60 °C
7	RR-DENEB 4	93	35 (*S*)	40 °C

Conditions; 1 mol% catalyst, rt, DCM, 24h.



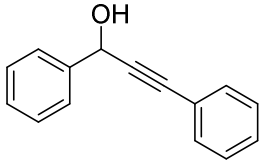
A

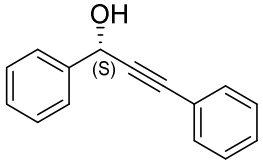


B

Data for alcohols and ketones.

Racemic and (*S*)-1,3-diphenylprop-2-yn-1-ol (7).





This compound is known and has been fully characterized:

Zheng, B.; Li, Z.; Liu, F.; Wu, Y.; Shen, J.; Bian, Q.; Hou, S.; Wang, M. *Molecules,* **2013,** *18,* 15422-15433.

This compound was prepared in racemic form following procedure A using: phenyl acetylene (0.65 mL, 6.0 mmol, 1.2 equiv), benzaldehyde (0.51 mL, 5.0 mmol, 1.0 equiv), nBuLi, 2.5 M in hexane (2.0 mL, 5.0 mmol, 1.0 equiv) and dry THF (25 mL). 1,3-Diphenylprop-2-yn-1-ol was isolated by flash chromatography (pet ether/ EtOAc: 80:20) as a colourless oil (408 mg, 2.0 mmol, 39.6%).

This compound was prepared in enantiomerically-enriched form following procedure C, using 1,3-diphenylprop-2-yn-1-one (50 mg, 0.24 mmol, 1.0 equiv), FA/TEA (0.2 mL), [(*R,R*)Teth-TsDpenRuCl] (1.5 mg, 2.4 x 10^{-3} mmol, 1 mol%) and DCM (2 mL). (*S*)-1,3-Diphenylprop-2-yn-1-ol was formed in 17 % conversion (HPLC data) and was not isolated. The data was obtained using the mixture.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (2H, dd, J = 7.2, 1.8 Hz, ArH), 7.47 – 7.43 (2H, m, ArH), 7.41 – 7.28 (6H, m, ArH), 5.67 (1H, d, J = 5.9 Hz, CH), 2.52 (1H, d, J = 6.1 Hz, OH);

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.6, 131.7, 128.7, 128.6, 128.4, 128.3, 128.2, 126.7, 122.4, 88.8, 86.6, 65.1;

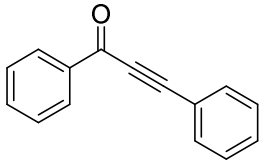
m/z (ESI) 230.0 ($[M+Na]^+$, 100%)

Enantiomeric excess determined by HPLC analysis (CHIRALPAK IB column, hexane 90:10 iPrOH, 0.7 mL/min, T = 30°C, λ = 250 nm, Ketone 7.5 min, *R* enantiomer 12.1 min, *S*-enantiomer 17.7 min). 35.4% ee (*S*).

Using [(MeO)(*R,R*)Teth-TsDpenRuCl] as catalyst, the conversion was 8% and the ee was 29%.

Major product configuration was established by comparison of elution of HPLC peaks - order matched that reported under conditions in the paper cited above, and which are substantiated by reports in other papers. See Table at end of SI.

1,3-Diphenylprop-2-yn-1-one.



This compound has been reported and fully characterised.

Liu, J.; Peng, X.; Sun, W.; Zhao, Y.; Xia, C. *Org. Lett.*, **2008**, *10*, 3933–3936.

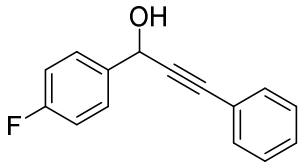
This compound was prepared following procedure B using 1,3-diphenylprop-2-yn-1-ol (350 mg, 1.68 mmol, 1.0 equiv), MnO_2 (910 mg, 10.6 mmol, 7.0 equiv) and DCM (15 mL). 1,3-Diphenylprop-2-yn-1-one was isolated by flash chromatography (pet ether/ EtOAc: 90:10) as a yellow solid (297 mg, 1.45 mmol, 86.3%)

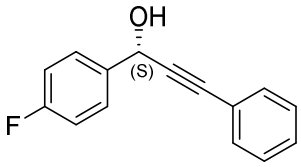
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 – 8.18 (2H, m, ArH), 7.73 – 7.58 (3H, m, ArH), 7.55 – 7.38 (5H, m, ArH).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.0, 136.9, 134.1, 133.0, 130.8, 129.5, 128.7, 128.6, 120.1, 93.1, 86.9.

m/z (ESI) 228.0 ($[M+Na]^+$, 100%).

Racemic and (*S*)-1-(4-fluorophenyl)-3-phenylprop-2-yn-1-ol (8).





This compound is known and has been fully characterized:

Zheng, B.; Li, Z.; Liu, F.; Wu, Y.; Shen, J.; Bian, Q.; Hou, S.; Wang, M. *Molecules*, **2013,** *18*, 15422-15433.

This compound was prepared in racemic form following procedure A using: phenyl acetylene (0.65 mL, 6.0 mmol, 1.2 equiv), p-fluoro benzaldehyde (0.53 mL, 5.0 mmol, 1.0 equiv), nBuLi, 2.5 M in hexane (2.0 mL, 5.0 mmol, 1.0 equiv) and dry THF (25 mL). 1-(4-Fluorophenyl)-3-phenylprop-2-yn-1-ol was isolated by flash chromatography (pet ether/ EtOAc: 80:20) as a colourless oil (250 mg, 1.1 mmol, 22.1%).

This compound was prepared in enantiomerically-enriched form following procedure C, 1-(4-fluorophenyl)-3-phenylprop-2-yn-1-one (40 mg, 0.18 mmol, 1.0 equiv), FA/TEA (0.2 mL),

[(*R*,*R*)Teth-TsDpen RuCl] (1.1 mg, 1.8 x 10^{-3} mmol, 1 mol%) and DCM (2 mL). (*S*)- 1-(4-Fluorophenyl)-3-phenylprop-2-yn-1-ol was formed in 15 % conversion (HPLC data) and was not isolated. The data was obtained using the mixture.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (2H, dd, *J* = 8.5, 5.4 Hz, ArH), 7.49 – 7.43 (2H, m, ArH), 7.39 – 7.26 (3H, m, ArH), 7.08 (2H, t, *J* = 8.7 Hz, ArH), 5.67 (1H, s, CH) 2.18 (1H, s, OH).

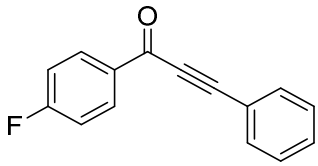
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7 (d, *J* = 247.0 Hz), 136.5, 131.7, 128.7, 128.6, 128.5, 128.3, 115.5 (d, *J* = 21.6 Hz), 88.4, 86.9, 64.4.

m/z (ESI) 248.0 ($[M+Na]^+$, 100%).

Enantiomeric excess determined by HPLC analysis (CHIRALCEL OD-H column, hexane 80:20 iPrOH, 1.0 mL/min, T = 30°C, λ = 250 nm, Ketone 5.1 min, *R* enantiomer 6.1 min, *S*-enantiomer 13.5 min). 14.0% ee (*S*).

Not screened with OMe catalyst. Major product configuration was established by comparison of elution of HPLC peaks - order matched that under reported conditions in the paper cited above, and which are substantiated by reports in other papers. See Table at end of SI.

1-(4-Fluorophenyl)-3-phenylprop-2-yn-1-one.



This compound has been reported and fully characterised.

Bai, C.; Jian, S.; Yao, X.; Li, Y. *Catal. Sci. Technol.*, **2014**, *4*, 3261.

This compound was prepared following procedure B using 1-(4-fluorophenyl)-3-phenylprop-2-yn-1-ol (200 mg, 0.889 mmol, 1.0 equiv), MnO_2 (550 mg, 6.4 mmol, 7.0 equiv), DCM (10 mL). 1-(4-Fluorophenyl)-3-phenylprop-2-yn-1-one was isolated by flash chromatography (pet ether/ EtOAc: 90:10) as a white solid (151 mg, 0.67 mmol, 76.1%)

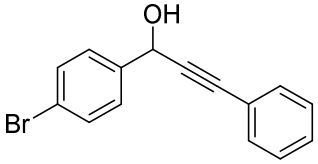
mp: 65-67 ^{o}C

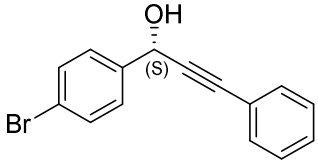
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (2H, dd, *J* = 8.5, 5.5 Hz, ArH), 7.73 – 7.65 (2H, m, ArH), 7.53 – 7.39 (3H, m, ArH), 7.19 (2H, t, *J* = 8.5 Hz, ArH).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.3, 166.4 (d, *J* = 256.5 Hz), 133.4, 133.0, 132.2, 130.9, 128.7, 119.9, 115.8 (d, *J* = 22.2 Hz), 93.3, 86.6.

m/z (ESI) 246.0 ($[M+Na]^+$, 100%).

Racemic and (*S*)-1-(4-Bromophenyl)-3-phenylprop-2-yn-1-ol (9).





This compound is known and has been fully characterized:

Zhong, J.-C.; Hou, S.-C.; Bian, Q.-H.; Yin, M.-M.; Na, R.-S.; Zheng, B.; Li, Z.-Y.; Liu, S.-Z.; Wang, M. *Chem. Eur. J.* 2009, *15,* 3069 – 3071.

This compound was prepared in racemic form following procedure A using: phenyl acetylene (0.65 mL, 6.0 mmol, 1.2 equiv), *p*-bromo benzaldehyde (0.50 mL, 5.0 mmol, 1.0 equiv), nBuLi, 2.5 M in hexane (2.0 mL, 5.0 mmol, 1.0 equiv) and dry THF (25 mL). 1-(4-Bromophenyl)-3-phenylprop-2-yn-1-ol was isolated by flash chromatography (pet ether/ EtOAc: 80:20) as a yellow oil (442 mg, 1.5 mmol, 31.0%).

This compound was prepared in enantiomerically-enriched form following procedure C, using 1-(4-bromophenyl)-3-phenylprop-2-yn-1-one (40 mg, 0.14 mmol, 1.0 equiv), FA/TEA (0.2 mL), [(*R,R*)Teth-TsDpen RuCl] (0.9 mg, 1.4 x 10^{-3} mmol, 1 mol%) and DCM (2 mL). (*S*)- 1-(4-Bromophenyl)-3-phenylprop-2-yn-1-ol was formed in 48% conversion (HPLC data) and was not isolated. The data was obtained using the mixture.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.45 (6H, m, ArH), 7.37 – 7.27 (3H, m, ArH), 5.65 (1H, s, CH), 2.28 (1H, s, OH).

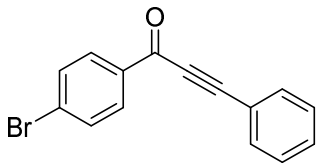
^{13}C NMR (101 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.6, 131.7, 131.4, 128.8, 128.4, 128.3, 122.4, 122.1, 88.1, 87.0, 64.4.

m/z (ESI) 308.7 ([M + Na]+, 68 %), 310.7 ([M + 2+ $Na]^+$, 70 %)

Enantiomeric excess determined by HPLC analysis (CHIRALCEL OD-H column, hexane 80:20 iPrOH, 1.0 mL/min, T = 30°C, λ = 250 nm, Ketone 5.7 min, *R* enantiomer 6.6 min, *S*-enantiomer 15.7 min). 8.4% ee (*S*).

Not screened with OMe catalyst. Major product configuration was established by comparison of elution of HPLC peaks - order matched that reported under conditions in the paper cited above, and which are substantiated by reports in other papers. See Table at end of SI.

1-(4-Bromophenyl)-3-phenylprop-2-yn-1-one.



This compound has been reported and fully characterised.

Bai, C.; Jian, S.; Yao, X.; Li, Y. *Catal. Sci. Technol.* **2014**, *4*, 3261.

This compound was prepared following procedure B using 1-(4-bromophenyl)-3-phenylprop-2-yn-1-ol (400 mg, 1.4 mmol, 1.0 equiv), MnO_2 (850 mg, 9.9 mmol, 7.0 equiv) and DCM (10 mL) 1-(4-Bromophenyl)-3-phenylprop-2-yn-1-one was isolated by flash chromatography (pet ether/ EtOAc: 90:10) as a white solid (231 mg, 0.82 mmol, 58.2%).

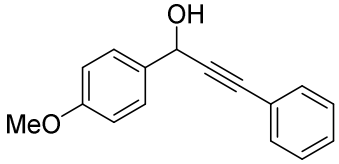
mp: 112-114 ^{o}C.

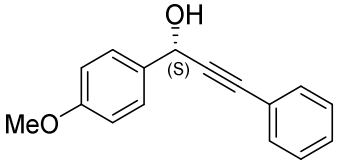
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (2H, d, *J* = 8.3 Hz, ArH), 7.68 (4H, t, *J* = 7.7 Hz, ArH), 7.54 – 7.38 (3H, m, ArH).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.8, 135.7, 133.1, 132.0, 131.0, 130.9, 129.5, 128.7, 119.8, 93.7, 86.5.

m/z (ESI) 306.7 ([M + Na]+, 100 %), 308.7 ([M + 2+ Na]$^{+}$, 98 %).

Racemic and (*S*)-1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-ol (10).





This compound is known and has been fully characterized:

Zheng, B.; Li, Z.; Liu, F.; Wu, Y.; Shen, J.; Bian, Q.; Hou, S.; Wang, M. *Molecules* **2013,** *18,* 15422-15433.

This compound was prepared in racemic form following procedure A using: phenyl acetylene (0.65 mL, 6.0 mmol, 1.2 equiv), p-methoxy benzaldehyde (0.61 mL, 5.0 mmol, 1.0 equiv), nBuLi, 2.5 M in hexane (2.0 mL, 5.0 mmol, 1.0 equiv) and dry THF (25 mL). 1-(4-Methoxyphenyl)-3-phenylprop-2-yn-1-ol was isolated by flash chromatography (pet ether/ EtOAc: 80:20) as a white solid (978 mg, 4.1 mmol, 83.0%).

This compound was prepared in enantiomerically-enriched form following procedure C, 1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-one (42 mg, 0.18 mmol, 1.0 equiv), FA/TEA (0.2 mL),

[(*R*,*R*)Teth-TsDpenRuCl] (1.1 mg, 1.8 x 10^{-3} mmol, 1 mol%) and DCM (2 mL). (*S*)- 1-(4-Methoxyphenyl)-3-phenylprop-2-yn-1-ol was formed in 24% conversion (HPLC data) and was not isolated. The data was obtained using the mixture.

mp 94-96 ^{o}C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.51 (2H, m, ArH), 7.50 – 7.42 (2H, m, ArH), 7.36 – 7.26 (2H, m, ArH), 6.96 – 6.89 (2H, m, ArH), 5.64 (1H, d, J = 5.9 Hz, CH), 3.81 (3H, s, OCH_3), 2.31 (1H, d, J = 6.0 Hz, OH).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 133.0, 131.7, 128.5, 128.3, 128.1, 122.5, 114.0, 88.9, 86.5, 64.7, 55.3.

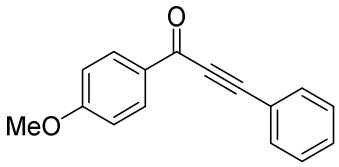
m/z (ESI) 260.8 ([M + Na]+, 100 %).

Enantiomeric excess determined by HPLC analysis (CHIRALCEL OD-H column, hexane 90:10 iPrOH, 1.0 mL/min, T = 30°C, λ = 250 nm, Ketone 12.1 min, *R* enantiomer 15.3 min, *S*-enantiomer 32.3 min). 39.0% ee (*S*).

Using [(MeO)(*R*,*R*)Teth-TsDpenRuCl] as catalyst, the conversion was 6% and the ee was 37%.

Major product configuration was established by comparison of elution of HPLC peaks - order matched that reported under conditions in the paper cited above, and which are substantiated by reports in other papers. See Table at end of SI.

1-(4-Methoxyphenyl)-3-phenylprop-2-yn-1-one.



This compound has been reported and fully characterised.

Cai, S.; Yang, K.; Wang, D. Z. *Org. Lett*, **2014**, *16*, 2606 – 2609.

This compound was prepared following procedure B using 1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-ol (950 mg, 4.0 mmol, 1.0 equiv), MnO_2 (2.40 g, 28.0 mmol, 7.0 equiv) and DCM (15 mL). 1-(4-Methoxyphenyl)-3-phenylprop-2-yn-1-one was isolated by flash chromatography (pet ether/ EtOAc: 90:10) as a yellow solid (597 2.54 mmol, 63.0%)

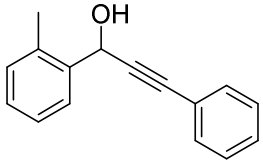
mp: 90-92 ^{o}C.

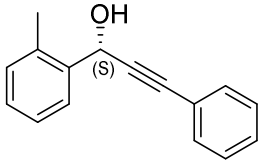
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 – 8.16 (2H, m, ArH), 7.70 – 7.62 (2H, m, ArH), 7.52 – 7.36 (3H, m, ArH), 7.03 – 6.94 (2H, m, ArH), 3.90 (3H, s, OCH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.68, 164.49, 132.96, 131.99, 130.59, 130.34, 128.66, 120.38, 113.90, 92.31, 86.94, 55.62.

m/z (ESI) 260.8 ([M + Na]+, 100 %).

Racemic and (*S*)-3-phenyl-1-(o-tolyl)prop-2-yn-1-ol (11).





This compound is known and has been fully characterized:

Zheng, B.; Li, Z.; Liu, F.; Wu, Y.; Shen, J.; Bian, Q.; Hou, S.; Wang, M. *Molecules*, **2013,** *18,* 15422-15433.

This compound was prepared in racemic form following procedure A using: phenyl acetylene (0.65 mL, 6.0 mmol, 1.2 equiv), o-tolualdehyde (0.6 mL, 5.0 mmol, 1.0 equiv), nBuLi, 2.5 M in hexane (2.0 mL, 5.0 mmol, 1.0 equiv) and dry THF (25 mL). 3-Phenyl-1-(o-tolyl)prop-2-yn-1-ol was isolated by flash chromatography (pet ether/ EtOAc: 80:20) as a colourless oil (1050 mg, 4.70 mmol, 95.5%).

This compound was prepared in enantiomerically-enriched form following procedure C, 3-phenyl-1-(o-tolyl)prop-2-yn-1-one (42 mg, 0.19 mmol, 1.0 equiv), FA/TEA (0.2 mL), [(*R,R*)Teth-TsDpen RuCl] (1.2 mg, 1.9 x 10^{-3} mmol, 1 mol%) and DCM (2 mL). (*S*)- 3-Phenyl-1-(o-tolyl)prop-2-yn-1-ol was formed in 27% conversion (HPLC data) and was not isolated. The data was obtained using the mixture.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.66 (1H, m, ArH), 7.48 – 7.40 (2H, m, ArH), 7.32 – 7.14 (6H, m, ArH), 5.79 (1H, s, CH), 2.46 (3H, s, CH_3), 2.45 (1H, s, OH).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.4, 136.0, 131.7, 130.8, 128.5, 128.5, 128.3, 126.6, 126.2, 122.5, 88.6, 86.5, 62.9, 19.0.

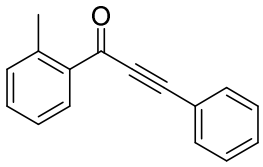
m/z (ESI) 244.8 ([M + Na]+, 100 %).

Enantiomeric excess determined by HPLC analysis (CHIRALCEL OD-H column, hexane 80:20 iPrOH, 1.0 mL/min, T = 30°C, λ = 250 nm, Ketone 4.7 min, *R* enantiomer 6.4 min, *S*-enantiomer 11.1 min). 14.4% ee (*S*).

Using [(MeO)(*R,R*)Teth-TsDpenRuCl] as catalyst, the conversion was 17% and the ee was 35%.

Major product configuration was established by comparison of elution of HPLC peaks - order matched that reported under reported conditions in the paper cited above, and which are substantiated by reports in other papers. See Table at end of SI.

3-Phenyl-1-(o-tolyl)prop-2-yn-1-one.



This compound has been reported and fully characterised.

Cai, S.; Yang, K.; Wang, D. Z. *Org. Lett*, **2014**, *16*, 2606 – 2609.

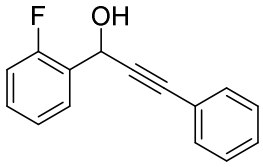
This compound was prepared following procedure B using 3-phenyl-1-(o-tolyl)prop-2-yn-1-ol (1.00 g, 4.5 mmol, 1.0 equiv), MnO_2 (2.70 g, 31.0 mmol, 7.0 equiv) and DCM (15 mL). 3-Phenyl-1-(o-tolyl)prop-2-yn-1-one was isolated by flash chromatography (pet ether/ EtOAc: 90:10) as a colourless oil (768 mg, 3.5 mmol, 70.0%)

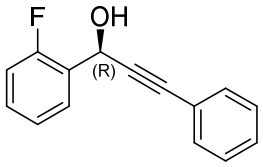
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (1H, dd, *J* = 7.7, 1.4 Hz, ArH), 7.67 – 7.61 (2H, m, ArH), 7.49 – 7.33 (5H, m, ArH), 7.30 – 7.24 (1H, m, ArH), 2.68 (3H, s, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 179.77, 140.49, 135.75, 133.18, 132.93, 132.91, 132.19, 130.60, 128.65, 125.90, 120.37, 91.82, 88.41, 21.96.

m/z (ESI) 242.8 ([M + Na]+, 100 %).

Racemic and (*R*)-1-(2-fluorophenyl)-3-phenylprop-2-yn-1-ol (12).





This compound is known and has been fully characterized:

lit:- Zhong, J.-C.; Hou, S.-C.; Bian, Q.-H.; Yin, M.-M.; Na, R.-S.; Zheng, B.; Li, Z.-Y.; Liu, S.-Z.; Wang, M. *Chem. Eur. J.* **2009**, *15*, 3069 – 3071.

This compound was prepared in racemic form following procedure A using: phenyl acetylene (0.65 mL, 6.0 mmol, 1.2 equiv), o-fluoro benzaldehyde (0.53 mL, 5.0 mmol, 1.0 equiv), nBuLi, 2.5 M in hexane (2.0 mL, 5.0 mmol, 1.0 equiv) and dry THF (25 mL). 1-(2-Fluorophenyl)-3-

phenylprop-2-yn-1-ol was isolated by flash chromatography (pet ether/ EtOAc: 80:20) as a colourless oil (1060 mg, 4.7 mmol, 93.8%).

This compound was prepared in enantiomerically-enriched form following procedure C, 31-(2-fluorophenyl)-3-phenylprop-2-yn-1-one (40 mg, 0.18 mmol, 1.0 equiv), FA/TEA (0.2 mL), [(*R,R*)Teth-TsDpen RuCl] (1.1 mg, 1.8 x 10^{-3} mmol, 1 mol%) and DCM (2 mL). *(R)*-1-(2-Fluorophenyl)-3-phenylprop-2-yn-1-ol was isolated by flash chromatography (pet ether/ EtOAc: 80:20) as a colourless oil (38 mg, 0.17 mmol, 94%).

$[\alpha]_D^{25}$ -28.3° (c 0.21 in $CHCl_3$) 62.6 % ee (*R*) (lit $[\alpha]^D$ +6.5° (c 0.71 in $CHCl_3$, 94% ee (*S*)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.68 (1H, m, ArH), 7.50 – 7.43 (2H, m, ArH), 7.38 – 7.26 (4H, m, ArH), 7.23 – 7.14 (1H, m, ArH), 7.14 – 7.04 (1H, m, ArH), 5.96 (1H, s, CH), 2.50 (1H, s, OH).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.27 (d, *J* = 248.3 Hz), 131.80, 130.32, 128.71, 128.46, 128.32, 124.44, 122.26, 115.79, 115.58, 87.09 (d, J = 96.5 Hz), 59.57.

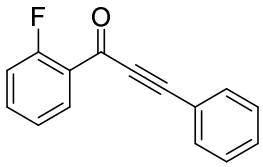
m/z (ESI) 248.8 ([M + Na]+, 100 %).

Enantiomeric excess determined by HPLC analysis (CHIRALCEL OD-H column, hexane 80:20 iPrOH, 1.0 mL/min, T = 30°C, λ = 250 nm, Ketone 5.2 min, *R* enantiomer 6.0 min, *S*-enantiomer 7.4 min). 62.6% ee (*R*).

Using [(MeO)(*R,R*)Teth-TsDpenRuCl] as catalyst, the conversion was 100%, yield 95% and the ee was 59%.

Major product configuration was established by comparison of elution of HPLC peaks - order matched that reported under reported conditions in the paper cited above, linking configuration to HPLC. This was also supported by a comparison of the reported optical rotation. See Table at end of SI.

1-(2-Fluorophenyl)-3-phenylprop-2-yn-1-one.



This compound has been reported and fully characterised.

Fuchs, F. C.; Eller, G. A.; Holzer, W. *Molecules,* **2009,** *14*, 3814 – 3832.

This compound was prepared following procedure B using 1-(2-fluorophenyl)-3-phenylprop-2-yn-1-ol (1.00 g, 4.4 mmol, 1.0 equiv), MnO_2 (2.70 g, 31.0 mmol, 7.0 equiv) and DCM (15 mL) 1-(2-Fluorophenyl)-3-phenylprop-2-yn-1-one was isolated by flash chromatography (pet ether/ EtOAc: 90:10) as a yellow viscous oil (636 mg, 2.8 mmol, 63.0%).

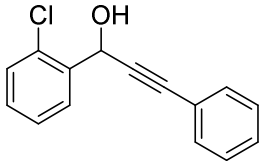
ν_{max}: 3063, 2195, 1627, 1605, 1482, 1306, 1203, 1010, 747, 685 cm^{-1}.

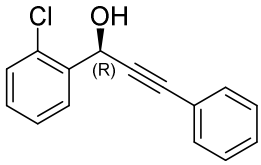
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.06 (1H, m, ArH), 7.71 – 7.55 (3H, m, ArH), 7.51 – 7.38 (3H, m, ArH), 7.32 – 7.24 (1H, m, ArH), 7.23 – 7.13 (1H, m, ArH).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.22, 162.15 (d, *J* = 261.7 Hz), 135.63, 133.23, 131.84, 130.94, 128.68, 124.24, 120.11, 117.13 (d, *J* = 21.9 Hz), 93.05, 88.52.

m/z (ESI) 246.8 ([M + Na]+, 100 %).

Racemic and (*R*)-1-(2-Chlorophenyl)-3-phenylprop-2-yn-1-ol (13).





This compound is known and has been fully characterized:

Lit. - Boobalan, R.; Chen, C.; Lee, G.-H. *Org. Biomol. Chem.*, **201**2, *10*, 1625–1638.

This compound was prepared in racemic form following procedure A using: phenyl acetylene (0.65 mL, 6.0 mmol, 1.2 equiv), o-chloro benzaldehyde (750 mg, 5.0 mmol, 1.0 equiv), nBuLi, 2.5 M in hexane (2.0 mL, 5.0 mmol, 1.0 equiv) and dry THF (25 mL). 1-(2-chlorophenyl)-3-phenylprop-2-yn-1-ol was isolated by flash chromatography (pet ether/ EtOAc: 80:20) as a colourless oil (1069 mg, 4.40 mmol, 89.1%).

This compound was prepared in enantiomerically-enriched form following procedure C, 1-(2-chlorophenyl)-3-phenylprop-2-yn-1-one (40 mg, 0.16 mmol, 1.0 equiv), FA/TEA (0.2 mL), [(*R*,*R*)Teth-TsDpen RuCl] (1.0 mg, 1.6 x 10^{-3} mmol, 1 mol%), DCM (2 mL). *(R)*-1-(2-chlorophenyl)-3-phenylprop-2-yn-1-ol was isolated by flash chromatography (pet ether/ EtOAc: 80:20) as a colourless oil (39 mg, 0.16 mmol, 97%).

$[\alpha]_D^{25}$ -26.8^o (c 0.14 in $CHCl_3$) 62.2 % ee (*R*) (lit $[\alpha]^D$ -49.7^o (c 0.5 in $CHCl_3$, 91% ee, (*R*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (1H, dd, *J* = 7.5, 1.9 Hz, ArH), 7.49 – 7.40 (2H, m, ArH), 7.35 – 7.17 (6H, m, ArH), 6.01 (1H, s, CH), 2.98 (1H, s, OH).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0, 132.8, 131.8, 129.8, 129.7, 128.7, 128.5, 128.3, 127.3, 122.4, 87.8, 86.6, 62.4.

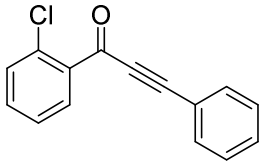
m/z (ESI) 264.7 ([M + Na]+, 100%), 266.7 ([M + 2+ Na]$^+$, 35%).

Enantiomeric excess determined by HPLC analysis (CHIRALCEL OD-H column, hexane 97:3 iPrOH, 1.0 mL/min, T = 30°C, λ = 250 nm, Ketone 10.7 min, *R* enantiomer 34.5 min, *S*-enantiomer 53.7 min). 62.2% ee.

Using [(MeO)(*R,R*)Teth-TsDpenRuCl] as catalyst, the conversion was 100%, yield 94% and the ee was 68.4% (*R*).

Major product configuration was established by comparison of elution of HPLC peaks - order matched that under reported conditions in the paper cited above, and which are substantiated by reports in other papers. This was also supported by a comparison of the reported optical rotation. See Table at end of SI.

1-(2-Chlorophenyl)-3-phenylprop-2-yn-1-one.



This compound has been reported and fully characterised.

Zhao, T.; Xu, B. *Org. Lett.*, **2010**, *12*, 212–215.

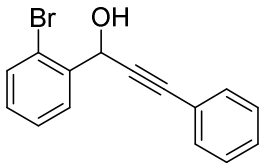
This compound was prepared following procedure B using 1-(2-chlorophenyl)-3-phenylprop-2-yn-1-ol (1.04 mg, 4.3 mmol, 1.0 equiv), MnO_2 (2.70 mg, 31.0 mmol, 7.0 equiv) and DCM (15 mL) 1-(2-chlorophenyl)-3-phenylprop-2-yn-1-one was isolated by flash chromatography (pet ether/ EtOAc: 90:10) as a yellow oil (731 mg, 3.04 mmol, 70.7%)

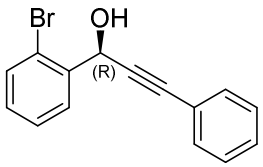
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.04 (1H, m, ArH), 7.69 – 7.61 (2H, m, ArH), 7.52 – 7.38 (6H, m, ArH).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.80, 135.89, 133.56, 133.38, 133.12, 132.53, 131.54, 130.96, 128.69, 126.81, 120.05, 93.96, 88.33.

m/z (ESI) 262.7 ([M + Na]+, 100%), 264.7 ([M + 2+ Na]$^+$, 35%)

Racemic and (*R*)-1-(2-Bromophenyl)-3-phenylprop-2-yn-1-ol (14).





This compound is known and has been fully characterized:

Lit. - Boobalan, R.; Chen, C.; Lee, G.-H. *Org. Biomol. Chem.*, **201**2, *10*, 1625–1638.

This compound was prepared in racemic form following procedure A using: phenyl acetylene (0.33 mL, 3 mmol, 1.2 equiv), o-bromo benzaldehyde (0.3 mL, 2.5 mmol, 1.0 equiv), nBuLi, 2.5 M in hexane (1.0 mL, 2.5 mmol, 1.0 equiv) and dry THF (16 mL). 1-(2-bromophenyl)-3-phenylprop-2-yn-1-ol was isolated by flash chromatography (pet ether/ EtOAc: 80:20) as a colourless oil (631 mg, 2.2 mmol, 88.5%).

This compound was prepared in enantiomerically-enriched form following procedure C, 1-(2-bromophenyl)-3-phenylprop-2-yn-1-one (40 mg, 0.14 mmol, 1.0 equiv), FA/TEA (0.2 mL), [(*R*,*R*)Teth-TsDpen RuCl] (0.9 mg, 1.4 x 10^{-3} mmol, 1 mol%), DCM (2 mL). *(R)*-1-(2-bromophenyl)-3-phenylprop-2-yn-1-ol was isolated by flash chromatography (pet ether/ EtOAc: 80:20) as a colourless oil (40 mg, 0.14 mmol, 99%).

$[\alpha]_D^{25}$ -22.6º (c 0.23 in $CHCl_3$) 52.8 % ee (*R*) (lit $[\alpha]_D^{22.1}$ -53.9º (c 0.5 in $CHCl_3$, 88% ee (*R*))

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (1H, dd, *J* = 7.7, 1.7 Hz, ArH), 7.51 (1H, dd, *J* = 8.0, 1.3 Hz, ArH), 7.43 – 7.36 (2H, m, ArH), 7.33 – 7.11 (5H, m, ArH), 5.94 (1H, d, *J* = 4.9 Hz, CH), 2.52 (1H, d, *J* = 5.3 Hz, OH).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.5, 133.1, 131.8, 130.0, 128.7, 128.4, 128.3, 127.9, 122.8, 122.3, 87.6, 86.8, 64.7.

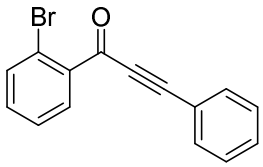
m/z (ESI) 308.7 ([M + Na]+, 100%), 310.7 ([M + 2+ Na]$^+$, 85%).

Enantiomeric excess determined by HPLC analysis (CHIRALCEL OD-H column, hexane 97:3 iPrOH, 1.0 mL/min, T = 30°C, λ = 250 nm, Ketone 16.0 min, *R* enantiomer 34.6 min, *S*-enantiomer 44.9 min). 52.8% ee (*R)*.

Using [(MeO)(*R*,*R*)Teth-TsDpenRuCl] as catalyst, the conversion was 100%, yield 99% and the ee was 68.4%.

Major product configuration was established by comparison of elution of HPLC peaks - order matched that reported under conditions in the paper cited above, This was also supported by a comparison of the reported optical rotation. See Table at end of SI.

1-(2-Bromophenyl)-3-phenylprop-2-yn-1-one.



This compound has been reported and fully characterised.

Zhao, T.; Xu, B. *Org. Lett.*, **2010**, *12*, 212–215.

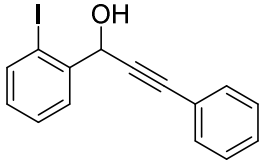
This compound was prepared following procedure B using 1-(2-bromophenyl)-3-phenylprop-2-yn-1-ol (600 mg, 1.7 mmol, 1.0 equiv), MnO_2 (1.00 g, 12.0 mmol, 7.0 equiv) and DCM (10 mL) 1-(2-bromophenyl)-3-phenylprop-2-yn-1-one was isolated by flash chromatography (pet ether/ EtOAc: 90:10) as a colorless oil (340 mg, 1.20 mmol, 57.1%)

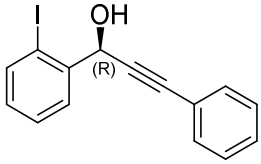
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (1H, dd, J = 7.7, 1.8 Hz, ArH), 7.67 – 7.55 (3H, m, ArH), 7.46 – 7.28 (5H, m, ArH).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.7, 137.6, 134.9, 133.3, 133.1, 132.7, 131.0, 128.7, 127.4, 121.2, 119.6, 94.2, 87.9.

m/z (ESI) 306.7 ([M + Na]+, 100%), 308.7 ([M + 2+ Na]$^{+}$, 85%).

Racemic and (*R*)-1-(2-Iodophenyl)-3-phenylprop-2-yn-1-ol (15).





This compound has been reported but not fully characterized:

Cai, Q.; Zhou, F.; Xu, T.; Fu, L.; Ding, K. *Org. Lett.*, **2011**, *13*, 340–343.

This compound was prepared in racemic form following procedure A using: phenyl acetylene (0.65 mL, 6.0 mmol, 1.2 equiv), o-iodo benzaldehyde (1000 mg, 5.0 mmol, 1.0 equiv), nBuLi, 2.5 M in hexane (2.0 mL, 5.0 mmol, 1.0 equiv) and dry THF (25 mL). 1-(2-iodophenyl)-3-phenylprop-2-yn-1-ol was isolated by flash chromatography (pet ether/ EtOAc: 80:20) as a colourless oil (1129 mg, 3.4 mmol, 78.9%).

This compound was prepared in enantiomerically-enriched form following procedure C, 1-(2-iodophenyl)-3-phenylprop-2-yn-1-one (40 mg, 0.12 mmol, 1.0 equiv), FA/TEA (0.2 mL), [(*R*,*R*)Teth-TsDpen RuCl] (0.7 mg, 1.2 x 10^{-3} mmol, 1 mol%), DCM (2 mL). *(R)*-1-(2-iodophenyl)-

3-phenylprop-2-yn-1-ol was isolated by flash chromatography (pet ether/ EtOAc: 80:20) as a colourless oil (16 mg, 0.048 mmol, 42%).

$[\alpha]_D^{25}$ -30.5º (c 0.1 in $CHCl_3$) 40.0 % ee (*R*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.77 (2H, m, ArH), 7.49 – 7.38 (3H, m, ArH), 7.31 (3H, d, *J* = 4.5 Hz, ArH), 7.08 – 6.99 (1H, m, ArH), 5.88 (1H, s, CH), 2.59 (1H, s, OH).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5, 139.8, 131.8, 130.2, 128.8, 128.7, 128.3, 128.2, 122.3, 98.1, 87.9, 87.0, 69.0.

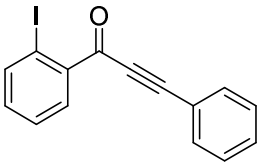
m/z (ESI) 356.7 ([M + Na]+, 100 %).

Enantiomeric excess determined by HPLC analysis (CHIRALCEL OD-H column, hexane 97:3 iPrOH, 1.0 mL/min, T = 30°C, λ = 250 nm, Ketone 11.2 min, *R* enantiomer 44.6 min, *S*-enantiomer 58.9 min). 40.0% ee (*R*).

Using [(MeO)(*R*,*R*)Teth-TsDpenRuCl] as catalyst, the conversion was 47% and the ee was 69%.

There is no report of an assigned configuration for this compound therefore HPLC and optical rotations could not be compared. The configuration was assigned by analogy with closely-related substrates.

1-(2-Iodophenyl)-3-phenylprop-2-yn-1-one.



This compound has been reported and fully characterised.

Cai, Q.; Zhou, F.; Xu, T.; Fu, L.; Ding, K. *Org. Lett.*, **2011**, *13*, 340–343.

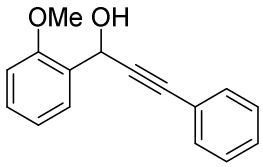
This compound was prepared following procedure B using 1-(2-iodophenyl)-3-phenylprop-2-yn-1-ol (1.05 mg, 3.2 mmol, 1.0 equiv), MnO_2 (1.90 mg, 22.0 mmol, 7.0 equiv) and DCM (15 mL) 1-(2-iodophenyl)-3-phenylprop-2-yn-1-one was isolated by flash chromatography (pet ether/ EtOAc: 90:10) as a colorless oil (853 mg, 2.53 mmol 81.2%)

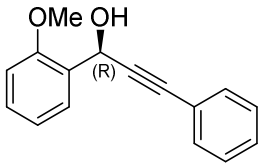
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (1H, dd, *J* = 7.8, 1.6 Hz, ArH), 8.06 (1H, dd, *J* = 7.9, 1.1 Hz, ArH), 7.69 – 7.62 (2H, m, ArH), 7.54 – 7.37 (4H, m, ArH), 7.24 – 7.18 (1H, m, ArH).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.1, 142.1, 139.4, 133.4, 133.1, 133.0, 131.0, 128.7, 128.1, 119.9, 94.4, 92.8, 87.2.

m/z (ESI) 354.7 ([M + Na]+, 100 %).

Racemic and (*R*)-1-(2-Methoxyphenyl)-3-phenylprop-2-yn-1-ol (16).





This compound is known and has been fully characterized:

Lit. - Boobalan, R.; Chen, C.; Lee, G.-H. *Org. Biomol. Chem.*, **2012**, *10*, 1625–1638.

This compound was prepared in racemic form following procedure A using: phenyl acetylene (0.65 mL, 6.0 mmol, 1.2 equiv), o-methoxy benzaldehyde (0.61 mL, 5.0 mmol, 1.0 equiv), nBuLi, 2.5 M in hexane (2.0 mL, 5.0 mmol, 1.0 equiv) and dry THF (25 mL). 1-(2-methoxyphenyl)-3-phenylprop-2-yn-1-ol was isolated by flash chromatography (pet ether/ EtOAc: 70:30) as a colourless oil (1117 mg, 4.7 mmol, 94.7%).

This compound was prepared in enantiomerically-enriched form following procedure C, 1-(2-metoxyphenyl)-3-phenylprop-2-yn-1-one (50 mg, 0.21 mmol, 1.0 equiv), FA/TEA (0.2 mL), [(*R,R*)Teth-TsDpen RuCl] (1.3 mg, 2.1 x 10^{-3} mmol, 1 mol%)), DCM (2 mL). *(R)*-1-(2-methoxyphenyl)-3-phenylprop-2-yn-1-ol was isolated by flash chromatography (pet ether/ EtOAc: 80:20) as a colourless oil (47 mg, 0.20 mmol, 95%).

$[\alpha]_D^{25}$ -7.6º (c 0.15 in $CHCl_3$) 79.2 % ee (*R*) (lit $[\alpha]_D^{20.7}$ -10.5º (c 1.2 in $CHCl_3$, 92% ee (*R*))

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (1H, dd, *J* = 7.5, 1.7 Hz, ArH), 7.47 (2H, dd, *J* = 6.6, 3.1 Hz, ArH), 7.33 – 7.26 (4H, m, ArH), 7.03 – 6.94 (1H, m, ArH), 6.93 – 6.88 (1H, m, ArH), 5.93 (1H, d, *J* = 6.1 Hz, CH), 3.88 (3H, s, OCH_3), 3.15 (1H, d, *J* = 6.2 Hz, OH).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9, 131.8, 129.7, 128.8, 128.4, 128.3, 128.1, 122.8, 120.9, 110.9, 88.5, 86.1, 61.6, 55.6.

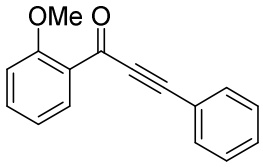
m/z (ESI) 260.8 ([M + Na]+, 100 %).

Enantiomeric excess determined by HPLC analysis (CHIRALPAK IB column, hexane 90:10 iPrOH, 0.7 mL/min, T = 30°C, λ = 250 nm, Ketone 11.2 min, *R* enantiomer 14.2 min, *S*-enantiomer 16.3 min). 79.2% ee (*R*).

Using [(MeO)(*R,R*)Teth-TsDpenRuCl] as catalyst, the conversion was 97.2%, yield 91.2% and the ee was 59.3%.

Major product configuration was established by comparison of elution of HPLC peaks - order matched that reported under conditions in the papers cited above and in other papers. This was also supported by a comparison of the reported optical rotation. See Table at end of SI.

1-(2-Methoxyphenyl)-3-phenylprop-2-yn-1-one.



This compound has been reported and fully characterised.

Sun, G.; Lei, M.; Hu, L. *RSC Adv.*, **2016**, *6*, 28442.

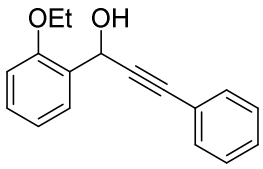
This compound was prepared following procedure B using 1-(2-methoxyphenyl)-3-phenylprop-2-yn-1-ol (1.05 mg, 4.4 mmol, 1.0 equiv), MnO_2 (2.70 g, 31.0 mmol, 7.0 equiv) and DCM (15 mL) 1-(2-methoxyphenyl)-3-phenylprop-2-yn-1-one was isolated by flash chromatography (pet ether/ EtOAc: 90:10) as a colourless oil (702 mg, 2.97 mmol, 66.7%).

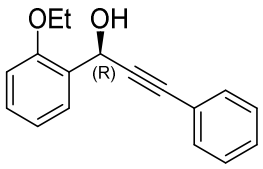
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (1H, dd, *J* = 7.8, 1.8 Hz, ArH), 7.67 – 7.59 (2H, m, ArH), 7.57 – 7.50 (1H, m, ArH), 7.47 – 7.36 (3H, m, ArH), 7.08 – 7.00 (2H, m, ArH), 3.96 (s, OCH_3).

13C NMR (101 MHz, CDCl3) δ 176.7, 159.8, 135.0, 132.9, 132.6, 130.5, 128.6, 126.8, 120.7, 120.3, 112.2, 91.6, 89.2, 55.9.

m/z (ESI) 260.8 ([M + Na]+, 100 %).

Racemic and (*R*)-1-(2-Ethoxyphenyl)-3-phenylprop-2-yn-1-ol (17).





This compound is known and has been fully characterized:

Lit. - Liu, L.; Pu, L. *Tetrahedron*, **2004**, **60**, 7427 – 7430.

This compound was prepared in racemic form following procedure A using: phenyl acetylene (0.65 mL, 6.0 mmol, 1.2 equiv), o-ethoxy benzaldehyde (0.7 mL, 5.0 mmol, 1.0 equiv), nBuLi, 2.5 M in hexane (2.0 mL, 5.0 mmol, 1.0 equiv) and dry THF (25 mL). 1-(2-ethoxyphenyl)-3-

phenylprop-2-yn-1-ol was isolated by flash chromatography (pet ether/ EtOAc: 80:20) as a colourless oil (863 mg, 3.4 mmol, 66.9%).

This compound was prepared in enantiomerically-enriched form following procedure C, 1-(2-etoxyphenyl)-3-phenylprop-2-yn-1-one (40 mg, 0.16 mmol, 1.0 equiv), FA/TEA (0.2 mL), [OMe (*R*,*R*)Teth-TsDpen RuCl] (1.0 mg, 1.5 x 10^{-3} mmol, 1 mol%), DCM (2 mL). *(R)*-1-(2-ethoxyphenyl)-3-phenylprop-2-yn-1-ol was isolated by flash chromatography (pet ether/ EtOAc: 80:20) as a colourless oil (38 mg, 0.15 mmol, 94%).

$[\alpha]_D^{25}$ -3.6º (c 0.34 in $CHCl_3$) 58.4 % ee (*R*). Lit. $[\alpha]_D^{24}$ +2.92 (c 1.38, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (1H, dd, *J* = 7.6, 1.6 Hz, ArH), 7.47 (2H, dd, *J* = 6.6, 2.9 Hz, ArH), 7.33 – 7.26 (4H, m, ArH), 7.01 – 6.89 (2H, m, ArH), 5.90 (1H, d, *J* = 6.1 Hz, CH), 4.15 (CH_2, qd, *J* = 7.0, 2.9 Hz, ArH), 3.24 (1H, d, *J* = 6.4 Hz, OH), 1.47 (3H, t, *J* = 7.0 Hz, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3, 131.7, 129.6, 129.0, 128.3, 128.2, 128.0, 122.8, 120.8, 111.8, 88.5, 85.9, 64.0, 62.0, 14.9.

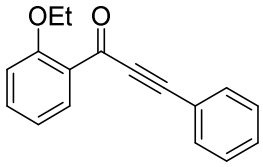
Enantiomeric excess determined by HPLC analysis (CHIRALCEL OD-H column, hexane 90:10 iPrOH, 1.0 mL/min, T = 30°C, λ = 250 nm, Ketone 7.5 min, *R* enantiomer 10.6 min, *S*-enantiomer 16.3 min). 58.4% ee (*R*).

m/z (ESI) 274.8 ([M + Na]+, 100 %).

Using [(*R*,*R*)Teth-TsDpenRuCl] as catalyst, the conversion was 69%, yield 52.5% and the ee was 58.4%.

Major product configuration was assigned by analogy with the o-OMe product.

1-(2-Ethoxyphenyl)-3-phenylprop-2-yn-1-one.



This compound has been reported and fully characterised.

Renault, J.; Qian, Z.; Uriac, P.; Gouault, N. *Tetrahedron Lett.*, 2011 , 52, 2476 – 2479.

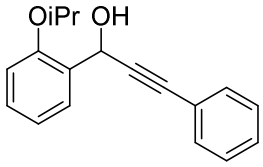
This compound was prepared following procedure B using 1-(2-ethoxyphenyl)-3-phenylprop-2-yn-1-ol (815 mg, 3.3 mmol, 1.0 equiv), MnO_2 (1.80 mg, 21.0 mmol, 7.0 equiv) and DCM (15 mL) 1-(2-ethoxyphenyl)-3-phenylprop-2-yn-1-one was isolated by flash chromatography (pet ether/ EtOAc: 90:10) as a colourless oil (579 mg, 2.30 mmol, 70.8%).

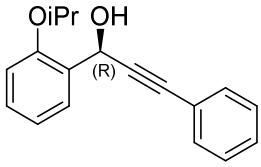
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (1H, dd, *J* = 7.8, 1.8 Hz, ArH), 7.66 – 7.37 (6H, m, ArH), 7.06 – 6.93 (2H, m, ArH), 4.17 (2H, q, *J* = 7.0 Hz, CH_2), 1.46 (3H, t, *J* = 7.0 Hz, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.9, 159.2, 134.8, 132.7, 131.9, 130.3, 128.6, 127.1, 120.8, 120.2, 113.1, 91.5, 89.6, 64.5, 14.8.

m/z (ESI) 272.8 ([M + Na]+, 100 %).

Racemic and (*R*)-1-(2-isopropoxyphenyl)-3-phenylprop-2-yn-1-ol (18).





This compound is novel.

This compound was prepared in racemic form following procedure A using: phenyl acetylene (0.65 mL, 6.0 mmol, 1.2 equiv), o-isopropoxy benzaldehyde (0.80 mL, 5.0 mmol, 1.0 equiv), nBuLi, 2.5 M in hexane (2.0 mL, 5.0 mmol, 1.0 equiv) and dry THF (25 mL). 1-(2-isopropoxyphenyl)-3-phenylprop-2-yn-1-ol was isolated by flash chromatography (pet ether/ EtOAc: 80:20) as a colourless oil (718 mg, 2.7 mmol, 54.4%).

This compound was prepared in enantiomerically-enriched form following procedure C, 1-(2-isopropoxyphenyl)-3-phenylprop-2-yn-1-one (40 mg, 0.15 mmol, 1.0 equiv), FA/TEA (0.2 mL), [(*R*,*R*)Teth-TsDpen RuCl] (0.94 mg, 1.5 x 10^{-3} mmol, 1 mol%), DCM (2 mL). *(R)*-1-(2-ethoxyphenyl)-3-phenylprop-2-yn-1-ol was formed in 37% conversion (HPLC data) and was not isolated. The data was obtained using the mixture.

(found (ESI) [M+Na]+, 289.1201. $C_{18}H_{18}NaO_2$ requires 289.1199).

ν_{max}: 3404 (broad), 2976, 1598, 1486, 1235, 1115, 1014, 949, 749, 690 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (1H, dd, *J* = 7.5, 1.7 Hz, ArH), 7.49 – 7.43 (2H, m, ArH), 7.32 – 7.25 (4H, m, ArH), 6.98 – 6.91 (2H, m, ArH), 5.85 (1H, d, *J* = 6.5 Hz, CH), 4.68 (1H, hept, *J* = 5.8 Hz, CH), 3.36 (1H, d, *J* = 6.6 Hz, OH), 1.40 (6H, dd, *J* = 6.0, 4.9 Hz, $2CH_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.2, 131.7, 129.7, 129.5, 128.8, 128.3, 128.2, 122.9, 120.7, 113.0, 88.7, 85.8, 70.6, 62.4, 22.2.

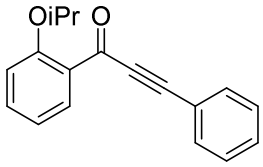
Enantiomeric excess determined by HPLC analysis (CHIRALCEL OD-H column, hexane 90:10 iPrOH, 1.0 mL/min, T = 30°C, λ = 250 nm, Ketone 5.8 min, *R* enantiomer 7.4 min, *S*-enantiomer 17.8 min). 40.4% ee (*R*).

m/z (ESI) 288.8 ([M + Na]+, 100 %).

Using [(*R*,*R*)Teth-TsDpenRuCl] as catalyst, no reduction was observed.

Major product configuration was assigned by analogy with o-OMe and other ortho-substituted products. There are no reports of chiral HPLC or optical rotation data for this compound.

1-(2-Isopropoxyphenyl)-3-phenylprop-2-yn-1-one.



This compound is novel.

This compound was prepared following procedure B using 1-(2-isopropoxyphenyl)-3-phenylprop-2-yn-1-ol (670 mg, 2.5 mmol, 1.0 equiv), MnO_2 (1.55 mg, 18.0 mmol, 7.0 equiv) and DCM (15 mL) 1-(2-isopropoxyphenyl)-3-phenylprop-2-yn-1-one was isolated by flash chromatography (pet ether/ EtOAc: 90:10) as a yellow solid (491 mg, 1.86 mmol, 73.8%).

(found (ESI) [M+Na]+, 287.1038. $C_{18}H_{16}NaO_2$ requires 287.1099)

ν_{max}: 2978, 2198, 1587, 1450, 1306, 1244, 1099, 944, 753, 690 cm^{-1}.

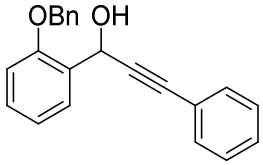
mp: 44-46 ^oC

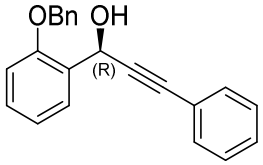
^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (1H, dd, *J* = 7.9, 1.8 Hz, ArH), 7.64 – 7.58 (2H, m, ArH), 7.52 – 7.36 (4H, m, ArH), 7.03 – 6.96 (2H, m, ArH), 4.69 (1H, hept, *J* = 5.9 Hz, CH), 1.40 (6H, d, *J* = 6.1 Hz, $2CH_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.2, 158.2, 134.6, 132.7, 131.8, 130.2, 128.6, 128.2, 120.9, 120.2, 114.6, 91.5, 89.9, 71.3, 22.0.

m/z (ESI) 286.8 ([M + Na]+, 100 %).

Racemic and (*R*)-1-(2- benzyloxyphenyl)-3-phenylprop-2-yn-1-ol (19).





This compound is known and has been fully characterized:

Lit. - Semenova, I. S.; Yarovenko, V. N.; Levchenko, K. S.; Krayushkin, M. M. *Russian Chemical Bulletin*, **2013**, *62*, 1022 – 1025.

This compound was prepared in racemic form following procedure A using: phenyl acetylene (0.65 mL, 6.0 mmol, 1.2 equiv), o-benzyloxy benzaldehyde (1060 mg, 5.0 mmol, 1.0 equiv), nBuLi, 2.5 M in hexane (2.0 mL, 5.0 mmol, 1.0 equiv) and dry THF (25 mL). 1-(2- benzyloxy phenyl)-3-phenylprop-2-yn-1-ol was isolated by flash chromatography (pet ether/ EtOAc: 80:20) as a colourless oil (1231 mg, 3.7 mmol, 82.2%).

This compound was prepared in enantiomerically-enriched form following procedure C, 1-(2-benzyloxyphenyl)-3-phenylprop-2-yn-1-one (40 mg, 0.12 mmol, 1.0 equiv), FA/TEA (0.2 mL), [(*R,R*)Teth-TsDpen RuCl] (0.8 mg, 1.3 x 10^{-3} mmol, 1 mol%), DCM (2 mL). *(R)*-1-(2- benzyloxy phenyl)-3-phenylprop-2-yn-1-ol was isolated by flash chromatography (pet ether/ EtOAc: 80:20) as a colourless oil (40 mg, 0.13 mmol, 99%).

$[\alpha]_D^{25}$ -6.7^o (c 0.5 in $CHCl_3$) 79.4 % ee (*R*).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 136.6, 131.7, 129.7, 129.3, 128.7, 128.4, 128.3, 128.2, 128.1, 127.3, 122.8, 121.2, 112.3, 88.7, 85.9, 70.3, 62.1.

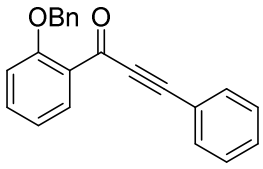
Enantiomeric excess determined by HPLC analysis (CHIRALCEL OD-H column, hexane 80:20 iPrOH, 1.0 mL/min, T = 30°C, λ = 250 nm, Ketone 5.8 min, *R* enantiomer 11.1 min, *S*-enantiomer 19.4 min). 79.4% ee (*R*).

m/z (ESI) 336.9 ([M + Na]+, 100 %).

Using [(MeO)(*R,R*)Teth-TsDpenRuCl] as catalyst, the conversion was 100%, yield 93% and the ee was 51.4%.

Major product configuration was assigned by analogy with o-OMe and other ortho-substituted products. There are no reports of chiral HPLC or optical rotation data for this compound.

1-(2-(Benzyloxyphenyl)-3-phenylprop-2-yn-1-one.



This compound has been reported and fully characterised.

Semenova, I. S.; Yarovenko, V. N.; Levchenko, K. S.; Krayushkin, M. M. *Russian Chemical Bulletin*, **2013**, *62*, 1022 – 1025.

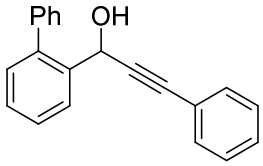
This compound was prepared following procedure B using 1-(2-ethoxyphenyl)-3-phenylprop-2-yn-1-ol (1.13 mg, 3.5 mmol, 1.0 equiv), MnO_2 (2.06 mg, 24.0 mmol, 7.0 equiv), DCM (15 mL) 1-(2-benzyloxyphenyl)-3-phenylprop-2-yn-1-one was isolated by flash chromatography (pet ether/ EtOAc: 90:10) as a colourless oil (952 mg, 3.04 mmol, 84.0%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (1H, dd, *J* = 7.9, 1.8 Hz, ArH), 7.53 – 7.47 (3H, m, ArH), 7.42 – 7.37 (3H, m, ArH), 7.32 – 7.23 (5H, m, ArH), 7.10 – 7.01 (2H, m, ArH), 5.23 (2H, s, CH_2).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.8, 158.8, 136.3, 134.8, 132.9, 132.2, 130.3, 128.6, 128.4, 127.9, 127.4, 127.2, 120.7, 120.6, 113.5, 91.9, 89.6, 70.7.

m/z (ESI) 334.9 ([M + Na]+, 100 %).

1-([1,1'-biphenyl]-2-yl)-3-phenylprop-2-yn-1-ol (20).



This compound is known and has been fully characterized:

Wadhwa, K.; Chintareddy, V. R.; Verkade, J. G. *J. Org. Chem.*, **2009**, *74*, 6681–6690.

This compound was prepared in racemic form following procedure A using: phenyl acetylene (0.65 mL, 6.0 mmol, 1.2 equiv), o-phenyl benzaldehyde (940 mg, 5.0 mmol, 1.0 equiv), nBuLi, 2.5 M in hexane (2.0 mL, 5.0 mmol, 1.0 equiv) and dry THF (25 mL). 1-([1,1'-biphenyl]-2-yl)-3-phenylprop-2-yn-1-ol was isolated by flash chromatography (pet ether/ EtOAc: 80:20) as a yellow oil (1268 mg, 4.5 mmol, 90.0%).

This compound was prepared in enantiomerically-enriched form following procedure C, 1-([1,1'-biphenyl]-2-yl)-3-phenylprop-2-yn-1-one (40 mg, 0.14 mmol, 1.0 equiv), FA/TEA (0.2 mL), [(*R,R*)Teth-TsDpen RuCl] (0.9 mg, 1.4 x 10^{-3} mmol, 1 mol%), DCM (2 mL). 1-([1,1'-biphenyl]-2-yl)-3-phenylprop-2-yn-1-one was not converted into corresponding product and remained unreacted and data was obtained using racemic compound.

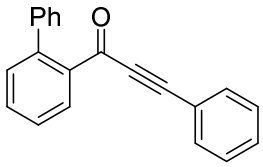
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (1H, dd, *J* = 7.7, 1.4 Hz, ArH), 7.49 – 7.37 (10H, m, ArH), 7.30 – 7.28 (3H, m, ArH), 5.68 (1H, s, CH), 2.03 (1H, s, OH).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.0, 140.2, 138.4, 131.7, 130.3, 129.5, 128.5, 128.4, 128.3, 128.1, 128.0, 127.6, 127.5, 122.6, 89.6, 86.4, 62.3.

m/z (ESI) 306.8 ([M + Na]+, 100 %).

No asymmetric product was formed from this substrate.

1-([1,1'-Biphenyl]-2-yl)-3-phenylprop-2-yn-1-one.



This compound has been reported and fully characterised.

Chen, Y.; Huang, C.; Liu, X.; Perl, E.; Chen, Z.; Namgung, J.; Subramaniam, G.; Zhang, G.; Hersh, W. H. *J. Org. Chem.*, **2014**, *79*, 3452–3464.

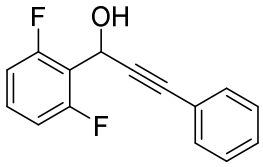
This compound was prepared following procedure B using 1-([1,1'-biphenyl]-2-yl)-3-phenylprop-2-yn-1-ol (1.20 mg, 4.2 mmol, 1.0 equiv), MnO_2 (2.60 mg, 30.0 mmol, 7.0 equiv), DCM (15 mL) 1-([1,1'-biphenyl]-2-yl)-3-phenylprop-2-yn-1-one was isolated by flash chromatography (pet ether/ EtOAc: 90:10) as a yellow oil (989 mg, 3.49 mmol, 83.1%).

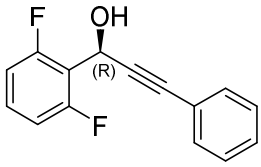
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (1H, dd, *J* = 7.7, 1.3 Hz, ArH), 7.63 – 7.54 (1H, m, ArH), 7.49 – 7.24 (12H, m, ArH).

^{13}C NMR (101 MHz, $CDCl_3$) δ 180.6, 142.7, 140.4, 138.0, 132.9, 132.1, 131.0, 130.4, 130.0, 129.5, 128.4, 128.3, 127.8, 127.4, 120.1, 93.8, 88.8.

m/z (ESI) 304.8 ([M + Na]+, 100 %).

Racemic and (*R*)-1-(2,6-difluorophenyl)-3-phenylprop-2-yn-1-ol (21).





This compound is known but not fully characterized:

Hyacinth, M.; Chruszcz, M.; Lee, K. S.; Sabat, M.; Gao, G.; Pu, L. *Angew. Chem. Int. Ed.* **2006,** *45,* 5358 –5360.

This compound was prepared in racemic form following procedure A using: phenyl acetylene (0.65 mL, 6.0 mmol, 1.2 equiv), 2,6-difluoro benzaldehyde (0.54 mL, 5.0 mmol, 1.0 equiv), nBuLi, 2.5 M in hexane (2.0 mL, 5.0 mmol, 1.0 equiv) and dry THF (25 mL). 1-(2,6-difluorophenyl)-3-

phenylprop-2-yn-1-ol was isolated by flash chromatography (pet ether/ EtOAc: 80:20) as a white solid (960 mg, 3.9 mmol, 78.7%).

This compound was prepared in enantiomerically-enriched form following procedure C, 1-(2,6-difluorophenyl)-3-phenylprop-2-yn-1-one (41 mg, 0.17 mmol, 1.0 equiv), FA/TEA (0.2 mL), [(*R*,*R*)Teth-TsDpen RuCl] (1.1 mg, 1.8 x 10^{-3} mmol, 1 mol%), DCM (2 mL). *(R)*- 1-(2,6-difluorophenyl)-3-phenylprop-2-yn-1-ol was isolated by flash chromatography (pet ether/ EtOAc: 80:20) as a white solid (40 mg, 0.16 mmol, 94.0%).

$[\alpha]_D^{25}$ -21.9º (c 0.26 in $CHCl_3$) 94.0 % ee (*R*).

mp: 51-53 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (2H, dd, *J* = 7.4, 2.2 Hz, ArH), 7.33 – 7.26 (4H, m, ArH), 6.93 (2H, t, *J* = 8.2 Hz, ArH), 5.98 (1H, d, *J* = 8.6 Hz, CH), 2.79 (1H, d, *J* = 8.9 Hz, OH).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6 (d, *J* = 257.8 Hz), 130.1 (t, *J* = 10.6 Hz), 129.9, 128.7, 128.2, 122.2, 117.6, 111.9 (d, *J* = 25.3 Hz), 87.1, 85.5, 55.6 (t, *J* = 5.4 Hz).

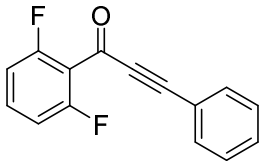
Enantiomeric excess determined by HPLC analysis (CHIRALCEL OD-H column, hexane 90:10 iPrOH, 1.0 mL/min, T = 30°C, λ = 250 nm, Ketone 5.9 min, *R* enantiomer 7.2 min, *S*-enantiomer 10.6 min). 94.0% ee (*R*).

m/z (ESI) 266.7 ([M + Na]+, 100 %).

Using [(MeO)(*R*,*R*)Teth-TsDpenRuCl] as catalyst, the conversion was 100%, yield 94% and the ee was 93.8%.

Major product configuration was established by X-ray crystallographic analysis of a diastereoiosomeric derivative, described herein. There are no reports of chiral HPLC or optical rotation data for this compound.

1-(2,6-Difluorophenyl)-3-phenylprop-2-yn-1-one.



This compound is known and has been fully characterized:

Iaroshenko, V. O.; Mkrtchyan, S.; Villinger, A. *Synthesis* **2013**, *45*. 205-218.

This compound was prepared following procedure B using 1-(2,6-difluorophenyl)-3-phenylprop-2-yn-1-ol (893 mg, 3.6 mmol, 1.0 equiv), MnO_2 (2.25 mg, 26.0 mmol, 7.0 equiv) and DCM (15

mL) 11-(2,6-difluorophenyl)-3-phenylprop-2-yn-1-ol was isolated by flash chromatography (pet ether/ EtOAc: 90:10) as a brown solid (989 mg, 2.93 mmol, 80.3%).

mp: 45-47 ^{o}C

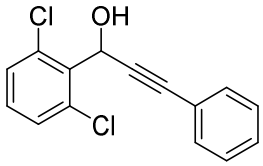
ν_{max}: 3084, 2194, 1636, 1618, 1489, 1023, 991, 796, 753, 681 cm^{-1}.

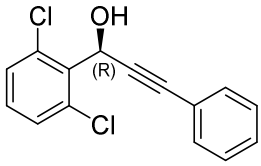
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.59 (2H, m, ArH), 7.51 – 7.36 (4H, m, ArH), 7.00 (2H, t, *J* = 8.4 Hz, ArH).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 160.9 (d, *J* = 264.2 Hz), 133.7 (t, *J* = 10.8 Hz), 133.3, 131.1, 128.7, 119.8, 117.6. 112.3 (d, *J* = 25.6 Hz), 93.4, 89.2.

m/z (ESI) 264.7 ([M + Na]+, 100 %).

Racemic and (*R*)-1-(2,6-dichlorophenyl)-3-phenylprop-2-yn-1-ol (22).





This compound is known and has been fully characterized:

lit: Liu, L.; Pu, L. *Tetrahedron*, **2004,** *60*, 7427-7430.

This compound was prepared in racemic form following procedure A using: phenyl acetylene (0.65 mL, 6.0 mmol, 1.2 equiv), 2,6-dichloro benzaldehyde (875 mg, 5.0 mmol, 1.0 equiv), nBuLi, 2.5 M in hexane (2.0 mL, 5.0 mmol, 1.0 equiv) and dry THF (25 mL). 1-(2,6-dichlorophenyl)-3-phenylprop-2-yn-1-ol was isolated by flash chromatography (pet ether/ EtOAc: 80:20) as a colourless oil (1310 mg, 4.7 mmol, 94.2%).

This compound was prepared in enantiomerically-enriched form following procedure C, 1-(2,6-dichlorophenyl)-3-phenylprop-2-yn-1-one (32 mg, 0.116 mmol, 1.0 equiv), FA/TEA (0.2 mL), [(*R,R*)Teth-TsDpen RuCl] (0.7 mg, 1.2 x 10^{-3} mmol, 1 mol%), DCM (1 mL). *(R)*- 1-(2,6-dichlorophenyl)-3-phenylprop-2-yn-1-ol was isolated by flash chromatography (pet ether/ EtOAc: 80:20) as a colourless oil (3.3 mg, 0.012 mmol, 10%). The major product was 1-(2,6-dichlorophenyl)-3-phenylpropanone (28 mg, 0.101 mmol, 87%).

$[\alpha]_D^{25}$ -16.8^{o} (c 0.3 in $CHCl_3$) 96.0 % ee (*R*) (lit $[\alpha]_D^{24}$ 3.67^{o} (c 1.26 in $CHCl_3$, 87% ee (*S*))

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.40 (2H, m, ArH), 7.37 – 7.23 (5H, m, ArH), 7.19 (1H, dd, *J* = 8.6, 7.5 Hz, ArH), 6.40 (1H, s, CH), 3.34 (1H, s, OH).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.5, 134.5, 131.8, 129.7, 129.3, 128.7, 128.3, 122.4, 86.7, 86.2, 61.5.

Enantiomeric excess determined by HPLC analysis (CHIRALCEL OD-H column, hexane 90:10 iPrOH, 1.0 mL/min, T = 30°C, λ = 250 nm, Ketone 5.9 min, *R* enantiomer 7.4 min, *S*-enantiomer 10.3 min). 96.0% ee (*R*).

m/z (ESI) 298.7 ([M + Na]+, 100%), 300.7 ([M + 2+ Na]+, 70%).

Using [(OMe)(*R*,*R*)Teth-TsDpenRuCl] as catalyst, the conversion was 8% (NMR) and the ee was 96% (*R*), and the major product was 1-(2,6-dichlorophenyl)-3-phenylpropanone (92% conversion by NMR).

Configuration assigned in analogy with 1,6-difluoro reduction product, for which configuration was confirmed by X-ray crystallography.

1-(2,6-Dichlorophenyl)-3-phenylpropanone.

(found (ESI) [M+Na]+, 301.0155, $C_{15}H_8{}^{35}Cl_2ONa$ requires 301.0157; 303.0126, $C_{15}H_8{}^{35}Cl{}^{35}Cl$ ONa requires 303.0128; 305.0097, $C_{15}H_8{}^{37}Cl_2ONa$ requires 305.0098)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40-7.20 (6H, nm, ArH), 3.15-3.05 (4H, m, CH_2CH_2) ppm.

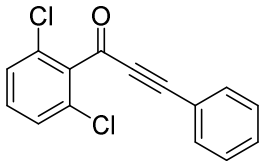
^{13}C NMR (101 MHz, $CDCl_3$) δ 201.4, 140.5 (C), 139.7 (C), 130.5, 129.7 (C), 129.3, 128.7, 128.5, 126.2, 45.27, 29.1 ppm.

ν_{max}: 1715, 1560, 1496, 1102, 777, 696 cm^{-1}.

m/z (ESI); 301 (M+Na, 2 x ^{35}Cl), 303 (M+Na, ^{35}Cl, ^{37}Cl), 305 (M+Na, 2 x ^{37}Cl).

HPLC analysis (CHIRALCEL OD-H column, hexane 90:10 iPrOH, 1.0 mL/min, T = 30°C, λ = 250 nm, Ketone 6.56 min.

1-(2,6-Dichlorophenyl)-3-phenylprop-2-yn-1-one.



This compound is novel.

This compound was prepared following procedure B using 1-(2,6-dichlorophenyl)-3-phenylprop-2-yn-1-ol (1.25 mg, 4.5 mmol, 1.0 equiv), MnO_2 (2.70 mg, 31.0 mmol, 7.0 equiv), DCM (15 mL)

11-(2,6-dichlorophenyl)-3-phenylprop-2-yn-1-ol was isolated by flash chromatography (pet ether/ EtOAc: 90:10) as a white solid (1.14 mg, 4.16 mmol, 91.8%).

(found (ESI) [M+Na]+, 296.9843. $C_{15}H_8Cl_2NaO$ requires 296.9844).

mp: 72-74 ^oC.

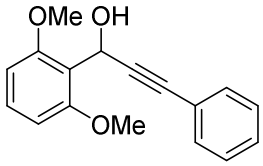
ν_{max}: 3059, 2185, 1653, 1430, 1283, 1100, 1069, 756, 683 cm^{-1}.

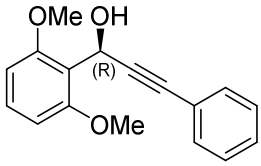
^1H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.57 (2H, m, ArH), 7.51 – 7.45 (1H, m, ArH), 7.42 – 7.29 (5H, m, ArH).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.15, 133.43, 131.64, 131.30, 131.06, 128.67, 128.43, 119.58, 95.27, 88.15.

m/z (ESI) 296.7 ([M + Na]+, 100%), 298.7 ([M + 2+ Na]+, 70%).

Racemic and (*R*)-1-(2,6-dimethoxyphenyl)-3-phenylprop-2-yn-1-ol (23).





This compound is known and has been fully characterized:

Trost, B. M.; Bartlett, M. J.; Weiss, A. H.; Vonwangelin, A. J.; Chan, V. S. *Chem. Eur. J.* **2012,** *18,* 16498 – 16509.

This compound was prepared in racemic form following procedure A using: phenyl acetylene (0.65 mL, 6.0 mmol, 1.2 equiv), 2,6-dimethoxy benzaldehyde (830 mg, 5.0 mmol, 1.0 equiv), nBuLi, 2.5 M in hexane (2.0 mL, 5.0 mmol, 1.0 equiv) and dry THF (25 mL). 1-(2,6-dimethoxyphenyl)-3-phenylprop-2-yn-1-ol was isolated by flash chromatography (pet ether/ EtOAc: 70:30) as a white solid (1130 mg, 4.2 mmol, 84.3%).

This compound was prepared in enantiomerically-enriched form following procedure C, 1-(2,6-dimethoxyphenyl)-3-phenylprop-2-yn-1-one (40 mg, 0.15 mmol, 1.0 equiv), FA/TEA (0.2 mL), [(*R,R*)Teth-TsDpen RuCl] (0.9 mg, 1.5 x 10^{-3} mmol, 1 mol%), DCM (2 mL). *(R)*- 1-(2,6-dimethoxyphenyl)-3-phenylprop-2-yn-1-ol was formed in 8% conversion (HPLC data) and was not isolated. The data was obtained using the mixture.

^1H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.37 (2H, m, ArH), 7.29 – 7.21 (4H, m, ArH), 6.60 (2H, d, *J* = 8.3 Hz, ArH), 6.12 (1H, d, *J* = 11.5 Hz, CH), 4.09 (1H, d, *J* = 11.5 Hz, OH), 3.89 (6H, s, $2OCH_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6, 131.7, 129.4, 128.1, 128.0, 123.3, 117.7, 104.7, 90.2, 83.0, 56.9, 56.1.

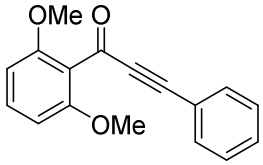
m/z (ESI) 290.8 ([M + Na]+, 100 %).

Enantiomeric excess determined by HPLC analysis (CHIRALCEL OD-H column, hexane 80:20 iPrOH, 1.0 mL/min, T = 30°C, λ = 250 nm, Ketone 14.8 min, *R* enantiomer 20.6 min, *S*-enantiomer 26.3 min). 20.4% ee (*R*).

Using [(MeO)(*R*,*R*)Teth-TsDpenRuCl] as catalyst, the conversion was 0%.

Major product configuration was tentatively assigned by comparison of order of HPLC elution times by HPLC with those reported for this compound. However very low conversion coupled to overlaps in the HPLC of our product make the unambiguous assignment of the configuration of this product uncertain. See Table at end of SI.

1-(2,6-Dimethoxyphenyl)-3-phenylprop-2-yn-1-one.



This compound is known and has been fully characterized:

Waldo, J. P.; Larock, R. C. *J. Org. Chem.*, **2007**, *72*, 9643 – 9647.

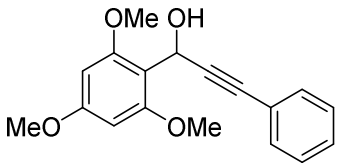
This compound was prepared following procedure B using 1-(2,6-dimethoxyphenyl)-3-phenylprop-2-yn-1-ol (1.09 g, 4.06 mmol, 1.0 equiv), MnO_2 (2.70 g, 31.0 mmol, 7.0 equiv), DCM (15 mL) 1-(2,6-methoxyphenyl)-3-phenylprop-2-yn-1-ol was isolated by flash chromatography (pet ether/ EtOAc: 90:10) as a yellow oil (0.84 g, 3.16 mmol, 77.8%).

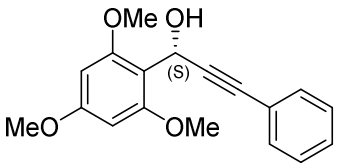
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.52 (2H, m, ArH), 7.44 – 7.30 (4H, m, ArH), 6.60 (2H, d, *J* = 8.4 Hz, ArH), 3.85 (6H, s, 2OCH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.4, 158.2, 133.0, 132.0, 130.4, 128.5, 120.7, 119.1, 104.3, 90.5, 90.0, 56.1.

m/z (ESI) 288.8 ([M + Na]+, 100 %).

Racemic and (*S*)-3-phenyl-1-(2,4,6-trimethoxyphenyl)prop-2-yn-1-ol (24).





This compound is known and has been fully characterized:

Batt, D. G.; Goodman, R.; Jones, D. G.; Kerr, J. S.; Mantegna, L. R.; McAllister, C.; Newton, R. C.; Nurnberg, S.; Welch, P. K.; Covington, M. B. *J. Med. Chem.* **1993**, *36*, 1434-1442.

This compound was prepared in racemic form following procedure A using: phenyl acetylene (0.65 mL, 6.0 mmol, 1.2 equiv), 2,4,6-trimethoxy benzaldehyde (980 mg, 5.0 mmol, 1.0 equiv), nBuLi, 2.5 M in hexane (2.0 mL, 5.0 mmol, 1.0 equiv) and dry THF (25 mL). 3-phenyl-1-(2,4,6-trimethoxyphenyl)prop-2-yn-1-ol was isolated by flash chromatography (pet ether/ EtOAc: 70:30) as a white solid (1070 mg, 3.6 mmol, 72.3%).

This compound was prepared in enantiomerically-enriched form following procedure C, 3-phenyl-1-(2,4,6-trimethoxyphenyl)prop-2-yn-1-one (42 mg, 0.14 mmol, 1.0 equiv), FA/TEA (0.2 mL), [(*R*,*R*)Teth-TsDpen RuCl] (0.9 mg, 1.4 x 10^{-3} mmol, 1 mol%), DCM (2 mL). *(S)*- 3-phenyl-1-(2,4,6-trimethoxyphenyl)prop-2-yn-1-ol was formed in 20% conversion (HPLC data) and was not isolated. The data was obtained using the mixture.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.37 (2H, m, ArH), 7.27 (3H, d, *J* = 1.3 Hz, ArH), 6.17 (2H, s, ArH), 6.02 (1H, d, *J* = 11.3 Hz, CH), 3.89 (6H, s, 2OCH_3), 3.87 (1H, s, OH), 3.82 (3H, s, OCH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1, 158.3, 131.7, 128.0, 127.9, 123.4, 111.3, 91.3, 90.5, 82.5, 56.7, 56.0, 55.4.

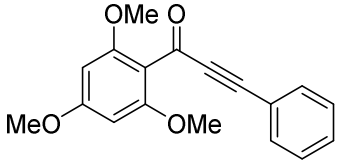
Enantiomeric excess determined by HPLC analysis (CHIRALCEL OD-H column, hexane 80:20 iPrOH, 1.0 mL/min, T = 30°C, λ = 250 nm, Ketone 8.9 min, *R* enantiomer 9.6 min, *S*-enantiomer 12.2 min). 20% ee (*R*).

m/z (ESI) 320.8 ([M + Na]+, 100 %).

Using [(MeO)(*R*,*R*)Teth-TsDpenRuCl] as catalyst, the conversion was 19.1% and the ee was 74.4%.

This product has not been reported in asymmetric form, therefore the configuration was tentatively assigned by analogy with the 2,6-disubstituted products. However very low conversion coupled to overlaps in the HPLC of our product make the unambiguous assignment of the configuration of this product uncertain.

3-Phenyl-1-(2,4,6-trimethoxyphenyl)prop-2-yn-1-one.



This compound is known but not fully characterized:

Zhou, C.; Dubrovsky, A. V.; Larock, R. C. *J. Org. Chem.* **2006**, *71*, 1626-1632.

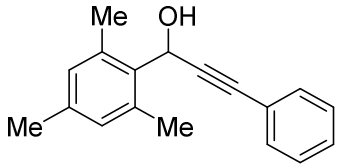
This compound was prepared following procedure B using 3-phenyl-1-(2,4,6-trimethoxyphenyl)prop-2-yn-1-ol (950 mg, 3.2 mmol, 1.0 equiv), MnO_2 (1.90 mg, 22.0 mmol, 7.0 equiv) and DCM (15 mL) 3-phenyl-1-(2,4,6-trimethoxyphenyl)prop-2-yn-1-one was isolated by flash chromatography (pet ether/ EtOAc: 70:30) as a yellow oil (720 mg, 2.45 mmol, 76.3%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.53 (2H, m, ArH), 7.43 – 7.32 (3H, m, ArH), 6.13 (2H, s, ArH), 3.86 (9H, s, 3OCH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.6, 163.7, 160.3, 132.8, 130.0, 128.4, 121.0, 115.5, 90.8, 89.1, 56.0, 55.4.

m/z (ESI) 318.8 ([M + Na]+, 100 %).

1-Mesityl-3-phenylprop-2-yn-1-ol (25).



This compound is novel.

This compound was prepared in racemic form following procedure A using: phenyl acetylene (0.65 mL, 6.0 mmol, 1.2 equiv), mesitaldehyde (740 mg, 5.0 mmol, 1.0 equiv), nBuLi, 2.5 M in hexane (2.0 mL, 5.0 mmol, 1.0 equiv) and dry THF (25 mL). 1-mesityl-3-phenylprop-2-yn-1-ol-ol was isolated by flash chromatography (pet ether/ EtOAc: 80:20) as a yellow oil (1125 mg, 4.5 mmol, 90.7%).

This compound was prepared in enantiomerically-enriched form following procedure C, 1-mesityl-3-phenylprop-2-yn-1-one (40 mg, 0.16 mmol, 1.0 equiv), FA/TEA (0.2 mL), [(*R,R*)Teth-TsDpen RuCl] (1.0 mg, 1.6 x 10^{-3} mmol, 1 mol%), DCM (2 mL). *(S)*-1-mesityl-3-phenylprop-2-

yn-1-ol was not converted into the corresponding product and remained unreacted and data was obtained using racemic compound.

(found (ESI) [M+Na]+, 273.1254. $C_{18}H1_8NaO$ requires 273.1250)

ν_{max}: 3419(broad), 3060, 2194, 1653, 1487, 1201, 1008, 754, 729, 687 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.39 (2H, m, ArH), 7.28 (3H, dd, *J* = 5.3, 2.4 Hz, ArH), 6.88 – 6.84 (2H, m, ArH), 6.10 (1H, d, *J* = 9.8 Hz, CH), 2.44 (6H, s, $2CH_3$), 2.26 (3H, s, CH_3) 1.62 (1H, s, OH).

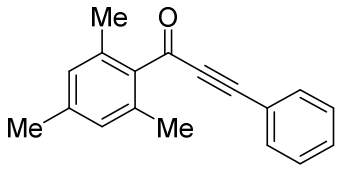
^{13}C NMR (101 MHz, $CDCl_3$) δ 137.7, 131.7, 131.7, 130.0, 129.7, 128.2, 128.2, 123.0, 87.6, 86.3, 64.3, 20.9, 20.3.

m/z (ESI) 272.8 ([M + Na]+, 100 %).

Using [(MeO)(*R,R*)Teth-TsDpenRuCl] as catalyst, the conversion was 0%

This product has not been reported, and no reduction product was formed in the ATH reaction.

1-Mesityl-3-phenylprop-2-yn-1-one.



This compound is known and has been fully characterized:

Yuan, H.; Shen, Y.; Yu, S.; Shan, L.; Sun, Q.; Zhang, W. Synth. Comm., **2013** , *43*, 2817 – 2823.

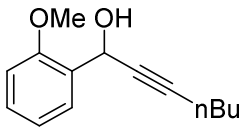
This compound was prepared following procedure B using 1-mesityl-3-phenylprop-2-yn-1-ol (1.07 mg, 4.3 mmol, 1.0 equiv), MnO_2 (2.60 mg, 30.0 mmol, 7.0 equiv) and DCM (15 mL) 1-mesityl-3-phenylprop-2-yn-1-one was isolated by flash chromatography (pet ether/ EtOAc: 90:10) as a yellow oil (809 mg, 3.26 mmol, 75.6%)

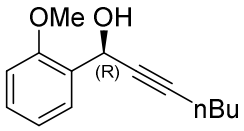
^1H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.54 (2H, m, ArH), 7.47 – 7.42 (1H, m, ArH), 7.37 (2H, dd, *J* = 8.2, 6.7 Hz, ArH), 6.89 (2H, s, ArH), 2.41 (6H, s, CH_3), 2.31 (3H, s, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 184.2, 139.8, 137.4, 135.1, 133.1, 130.8, 129.0, 128.6, 120.1, 93.2, 89.6, 21.2, 19.8.

m/z (ESI) 270.8 ([M + Na]+, 100 %).

Racemic and (*R*)-1-(2-methoxyphenyl)hept-2-yn-1-ol (27).





This compound is known and has been fully characterized:

Scheidt, K. A.; Lettan, R. B. *Org. Lett.* **2005**, *7*, 3227-3230.

This compound was prepared in racemic form following procedure A using: 1-hexyne (0.4 mL, 6.0 mmol, 1.2 equiv), o-methoxy benzaldehyde (0.61 mL, 5.0 mmol, 1.0 equiv), nBuLi, 2.5 M in hexane (2.0 mL, 5.0 mmol, 1.0 equiv) and dry THF (25 mL). 1-(2-methoxyphenyl)hept-2-yn-1-ol was isolated by flash chromatography (pet ether/ EtOAc: 85:15) as a colourless oil (781 mg, 3.6 mmol, 71.6%).

This compound was prepared in enantiomerically-enriched form following procedure C, 1-(2-methoxyphenyl)hept-2-yn-1-one (40 mg, 0.18 mmol, 1.0 equiv), FA/TEA (0.2 mL), [OMe(*R,R*)Teth-TsDpen RuCl] (1.2 mg, 1.8 x 10^{-3} mmol, 1 mol%), DCM (2 mL). *(R)*-1-(2-methoxyphenyl)hept-2-yn-1-ol was formed in 15% conversion (HPLC data) and was not isolated. The data was obtained using the mixture.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (1H, dd, *J* = 7.5, 1.7 Hz, ArH), 7.32 – 7.24 (1H, m, ArH), 7.02 – 6.93 (1H, m, ArH), 6.89 (1H, dd, *J* = 8.3, 1.0 Hz, ArH), 5.71 (1H, d, *J* = 2.4 Hz, CH), 3.88 (3H, s, OCH_3), 2.92 (1H, d, *J* = 4.2 Hz, OH), 2.28 (2H, td, *J* = 7.1, 2.0 Hz, CH_2), 1.58 – 1.37 (4H, m, $2CH_2$), 0.91 (3H, t, *J* = 7.2 Hz, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7, 129.4, 129.3, 127.9, 120.7, 110.7, 87.2, 79.1, 61.2, 55.5, 30.7, 21.9, 18.5, 13.6.

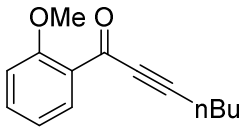
Enantiomeric excess determined by HPLC analysis (CHIRALPAK AD-H column, hexane 90:10 iPrOH, 1.0 mL/min, T = 30°C, λ = 250 nm, Ketone 7.7 min, *S* enantiomer 10.2 min, *R*-enantiomer 14.4 min). 86% ee (*R*).

m/z (ESI) 240.8 ([M + Na]+, 100 %).

Using [(*R,R*)Teth-TsDpenRuCl] as catalyst, the conversion was 33.7% and the ee was 59.4%.

Major product configuration was assigned by analogy with related products in this study. There are no reports of the asymmetric synthesis of this product.

1-(2-Methoxyphenyl)hept-2-yn-1-one.



This compound is snown and has been fully characterized:

Liang, B.; Huang, M.; You, Z.; Xiong, Z.; Lu, K.; Fathi, R.; Chen, J.; Yang, Z. *J. Org. Chem.*, **2005**, *70*, 6097 – 6100.

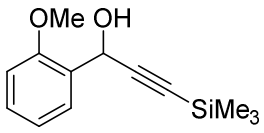
This compound was prepared following procedure B using 1-(2-methoxyphenyl)hept-2-yn-1-ol (731 mg, 3.3 mmol, 1.0 equiv), MnO_2 (2.00 mg, 23.0 mmol, 7.0 equiv) and DCM (15 mL) 1-(2-methoxyphenyl)hept-2-yn-1-one was isolated by flash chromatography (pet ether/ EtOAc: 90:10) as a yellow oil (625 mg, 2.92 mmol, 87.2%).

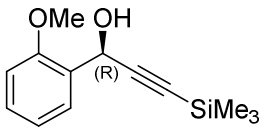
1H NMR (400 MHz, $CDCl_3$) δ 8.01 (1H, dd, J = 7.8, 1.8 Hz, ArH), 7.54 – 7.46 (1H, m, ArH), 7.07 – 6.92 (2H, m, ArH), 3.91 (3H, s, OCH_3), 2.46 (2H, t, J = 7.1 Hz, CH_2), 1.67 – 1.57 (2H, m, CH_2), 1.54 – 1.43 (2H, m, CH_2), 0.95 (3H, t, J = 7.3 Hz, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.1, 159.6, 134.6, 132.9, 126.8, 120.1, 112.1, 95.3, 81.7, 55.8, 29.8, 22.0, 18.9, 13.5.

m/z (ESI) 238.8 ([M + Na]+, 100 %).

Racemic and *(R)*-1-(2-methoxyphenyl)-3-(trimethylsilyl)prop-2-yn-1-ol (28).





This compound is known and has been fully characterized:

lit: Li, Z.-Y.; Wang, M.; Bian, Q.-H.; Zheng, B.; Mao, J.-Y.; Li, S.-N.; Liu, S.-Z.; Wang, M.-A.; Zhong, J.-C.; Guo, H.-C. *Chem. Eur. J.* **2011**, *17*, 5782–5786.

This compound was prepared in racemic form following procedure A using: trimethylsilylacetylene (0.8 mL, 6.0 mmol, 1.2 equiv), o-methoxy benzaldehyde (0.61 mg, 5.0 mmol, 1.0 equiv), nBuLi, 2.5 M in hexane (2.0 mL, 5.0 mmol, 1.0 equiv) and dry THF (25 mL). 1-(2-methoxyphenyl)-3-(trimethylsilyl)prop-2-yn-1-ol was isolated by flash chromatography (pet ether/ EtOAc: 80:20) as a colourless oil (767 mg, 3.3 mmol, 65.5%).

This compound was prepared in enantiomerically-enriched form following procedure C, 1-(2-methoxyphenyl)-3-(trimethylsilyl)prop-2-yn-1-one (40 mg, 0.17 mmol, 1.0 equiv), FA/TEA (0.2 mL), [(*R,R*)Teth-TsDpen RuCl] (1.1 mg, 1.8 x 10^{-3} mmol, 1 mol%), DCM (2 mL). *(R)*- 1-(2-

methoxyphenyl)-3-(trimethylsilyl)prop-2-yn-1-ol was isolated by flash chromatography (pet ether/ EtOAc: 80:20) as a colourless oil (39 mg, 0.16 mmol, 94%).

$[\alpha]_D^{25}$ 17.8° (c 0.21 in $CHCl_3$) 96.0 % ee (*R*) (lit $[\alpha]_D^{20}$ -15.4° (c 1.1 in $CHCl_3$, 94% ee (*S*))

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (1H, dd, *J* = 7.6, 1.6 Hz, ArH), 7.15 – 7.06 (1H, m, ArH), 6.83 – 6.74 (1H, m, ArH), 6.70 (1H, dd, *J* = 8.2, 1.0 Hz, ArH), 5.51 (1H, s, CH), 3.68 (3H, s, OCH_3), 2.73 (1H, s, OH), 0.00 (9H, s, $Si(CH_3)_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0, 129.8, 128.6, 128.1, 120.9, 110.9, 104.5, 91.0, 61.5, 55.6, 0.0.

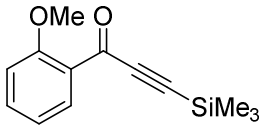
Enantiomeric excess determined by HPLC analysis (CHIRALPAK AD-H column, hexane 90:10 iPrOH, 1.0 mL/min, T = 30°C, λ = 220 nm, Ketone 7.2 min, *S* enantiomer 15.3 min, *R*-enantiomer 16.9 min). 96% ee (*R*).

m/z (ESI) 256.8 ([M + Na]+, 100 %).

Using [(MeO)(*R*,*R*)Teth-TsDpenRuCl] as catalyst, the conversion was 82.4% and the ee was 96%.

Major product configuration was established by comparison of elution of HPLC peaks - order matched that reported under conditions in the paper cited above. The configuration was also confirmed through comparison of the optical rotation with that quoted. The configuration was also assigned by analogy with the o-Br alcohol used in the formal synthesis in the paper. See Table at end of SI.

1-(2-Methoxyphenyl)-3-(trimethylsilyl)prop-2-yn-1-one.



This compound is known and has been fully characterized:

Zhou, C.; Dubrovsky, A. V.; Larock, R. C. *J. Org. Chem.* **2006**, *71*, 1626-1632.

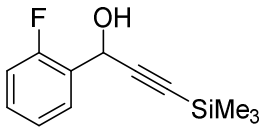
This compound was prepared following procedure B using 1-(2-methoxyphenyl)-3-(trimethylsilyl)prop-2-yn-1-ol (720 mg, 3.1 mmol, 1.0 equiv), MnO_2 (1.90 mg, 22.0 mmol, 7.0 equiv) and DCM (15 mL) 1-(2-methoxyphenyl)-3-(trimethylsilyl)prop-2-yn-1-one was isolated by flash chromatography (pet ether/ EtOAc: 90:10) as a yellow oil (546 mg, 2.37 mmol, 77.2%).

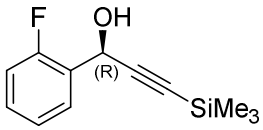
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (1H, dd, *J* = 7.7, 1.8 Hz, ArH), 7.57 – 7.48 (1H, m, ArH), 7.05 – 6.95 (2H, m, ArH), 3.92 (3H, s, OCH_3), 0.27 (9H, s, $Si(CH_3)_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.0, 160.5, 135.7, 133.4, 126.9, 120.8, 112.8, 103.5, 99.1, 56.3, 0.0.

m/z (ESI) 254.8 ([M + Na]+, 100 %).

Racemic and *(R)*-1-(2-fluorophenyl)-3-(trimethylsilyl)prop-2-yn-1-ol (29).





This compound is known and has been fully characterized:

lit: Li, Z.-Y.; Wang, M.; Bian, Q.-H.; Zheng, B.; Mao, J.-Y.; Li, S.-N.; Liu, S.-Z.; Wang, M.-A.; Zhong, J.-C.; Guo, H.-C. *Chem. Eur. J.* **2011**, *17*, 5782–5786.

This compound was prepared in racemic form following procedure A using: trimethylsilylacetylene (0.8 mL, 6.0 mmol, 1.2 equiv), o-fluoro benzaldehyde (0.6 mL, 5.0 mmol, 1.0 equiv), nBuLi, 2.5 M in hexane (2.0 mL, 5.0 mmol, 1.0 equiv) and dry THF (25 mL). 1-(2-fluorophenyl)-3-(trimethylsilyl)prop-2-yn-1-ol was isolated by flash chromatography (pet ether/ EtOAc: 80:20) as a colourless oil (570 mg, 3.3 mmol, 51.3%).

This compound was prepared in enantiomerically-enriched form following procedure C, 1-(2-fluorophenyl)-3-(trimethylsilyl)prop-2-yn-1-one (44 mg, 0.20 mmol, 1.0 equiv), FA/TEA (0.2 mL), [(*R,R*)Teth-TsDpen RuCl] (1.2 mg, 1.9 x 10^{-3} mmol, 1 mol%), DCM (2 mL). *(R)*-1-(2-fluorophenyl)-3-(trimethylsilyl)prop-2-yn-1-ol was isolated by flash chromatography (pet ether/ EtOAc: 80:20) as a colourless oil (43 mg, 0.19 mmol, 95%).

$[\alpha]_D^{25}$ +14.8^{o} (c 0.21 in $CHCl_3$) 94.8 % ee (*R*) (lit $[\alpha]_D^{20}$ -12.8^{o} (c 1.17 in $CHCl_3$, 94% ee (*S*)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.40 (1H, m, ArH), 7.16 – 7.08 (1H, m, ArH), 7.02 – 6.93 (1H, m, ArH), 6.91 – 6.81 (1H, m, ArH), 5.53 (1H, d, *J* = 5.5 Hz, CH), 2.18 (1H, d, *J* = 5.8 Hz, OH), 0.00 (9H, s, $Si(CH_3)_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5 (d, *J* = 248.5 Hz), 130.4 (d, *J* = 8.2 Hz), 128.6 (d, *J* = 3.3 Hz), 127.7 (d, *J* = 13.3 Hz), 124.5 (d, *J* = 3.6 Hz), 115.8 (d, *J* = 21.3 Hz), 103.8, 91.9, 59.6 (d, *J* = 4.9 Hz).

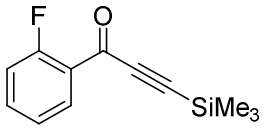
Enantiomeric excess determined by GC analysis (CROMPAC CYCLODEXTRIN- β-236M-19, 50m × 0.25mm × 0.25µm, gas: hydrogen, T=125°C, P = 18 psi, FID = 250 °C, inj = 220 °C), ketone 66.3 min, S isomer 96.2 min, R isomer 98.6 min. 94.8% ee (*R*).

m/z (ESI) 244.6 ([M + Na]+, 100 %).

Using [(MeO)(*R,R*)Teth-TsDpenRuCl] as catalyst, the conversion was 100%, yield 96% and the ee was 95%.

The configuration was also confirmed through comparison of the optical rotation with that quoted. The configuration was also assigned by analogy with the o-Br alcohol used in the formal synthesis. See Table at end of SI.

1-(2-Fluorophenyl)-3-(trimethylsilyl)prop-2-yn-1-one.



This compound is known but not fully characterized:

Willy, B.; Frank, W.; Mueller, T. J. J. *Org. Biomol. Chem*., **2010**, *8*, 90–95.

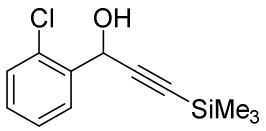
This compound was prepared following procedure B using 1-(2-fluorophenyl)-3-(trimethylsilyl)prop-2-yn-1-ol (516 mg, 2.3 mmol, 1.0 equiv), MnO_2 (1.40 mg, 16.0 mmol, 7.0 equiv) and DCM (15 mL) 1-(2-fluorophenyl)-3-(trimethylsilyl)prop-2-yn-1-one was isolated by flash chromatography (pet ether/ EtOAc: 90:10) as a yellow oil (389 mg, 1.77 mmol, 75.6%).

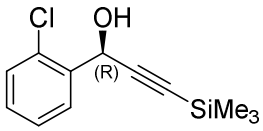
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.84 (1H, m, ArH), 7.48 – 7.37 (1H, m, ArH), 7.15 – 7.06 (1H, m, ArH), 7.05 – 6.95 (m, ArH), 0.00 (9H, s, $Si(CH_3)_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.8, 162.89 (d, *J* = 262.7 Hz), 136.42 (d, *J* = 9.2 Hz), 132.9, 126.07 (d, *J* = 7.6 Hz), 124.93 (d, *J* = 4.0 Hz), 117.88 (d, *J* = 21.7 Hz) 102.7, 101.3, 0.0.

m/z (ESI) 242.6 ([M + Na]+, 100 %).

Racemic and 1-(2-chlorophenyl)-3-(trimethylsilyl)prop-2-yn-1-ol (30).





This compound is known but not in enantiomerically-pure form:

Ghosh, N.; Nayak, S.; Sahoo, A. K. *J. Org. Chem.*, **2011**, *76*, 500-511.

This compound was prepared in racemic form following procedure A using: trimethylsilylacetylene (0.8 mL, 6.0 mmol, 1.2 equiv), o-chloro benzaldehyde (0.8 mL, 5.0 mmol, 1.0 equiv), nBuLi, 2.5 M in hexane (2.0 mL, 5.0 mmol, 1.0 equiv) and dry THF (25 mL). 1-(2-chlorophenyl)-3-(trimethylsilyl)prop-2-yn-1-ol was isolated by flash chromatography (pet ether/ EtOAc: 80:20) as a colourless oil (1.05 g, 4.4 mmol, 88.9%).

This compound was prepared in enantiomerically-enriched form following procedure C, 1-(2-chlorophenyl)-3-(trimethylsilyl)prop-2-yn-1-one (40 mg, 0.17 mmol, 1.0 equiv), FA/TEA (0.2 mL), [(*R,R*)Teth-TsDpen RuCl] (1.1 mg, 1.8 x 10^{-3} mmol, 1 mol%), DCM (2 mL). *(R)*-1-(2-chlorophenyl)-3-(trimethylsilyl)prop-2-yn-1-ol was isolated by flash chromatography (pet ether/ EtOAc: 80:20) as a colourless oil (40 mg, 0.17 mmol, 99%).

This compound was also prepared in enantiomerically-enriched form on a scale of > 1 mmol following procedure C, 1-(2-chlorophenyl)-3-(trimethylsilyl)prop-2-yn-1-one (355 mg, 1.5 mmol, 1.0 equiv), FA/TEA (1.5 mL), [(*R,R*)Teth-TsDpen RuCl] (9.3 mg, 0.015 mmol, 1 mol%), DCM (1.5 mL). *(R)*-1-(2-chlorophenyl)-3-(trimethylsilyl)prop-2-yn-1-ol was isolated by flash chromatography (pet ether/ EtOAc: 80:20) as a colourless oil (237 mg, 1.0 mmol, 67%).

$[\alpha]_D^{25}$ 2.7° (c 0.2 in $CHCl_3$) 93.8 % ee (*R*).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (1H, dd, *J* = 7.5, 1.8 Hz, ArH), 7.21 – 7.02 (3H, m, ArH), 5.62 (1H, d, *J* = 5.6 Hz, CH), 2.30 (1H, brs,, OH), 0.00 (9H, s, $Si(CH_3)_3$).

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.7, 133.1, 129.9, 129.9 (overlapped), 128.6, 127.4, 103.8, 92.1, 62.5, 0.0.

Enantiomeric excess determined by HPLC analysis (CHIRALCEL OD-H column, hexane 97:03 iPrOH, 1.0 mL/min, T = 30°C, λ = 220 nm, Ketone 4.4 min, *S* enantiomer 8.2 min, *R*-enantiomer 10.0 min). 93.8% ee (*R*).

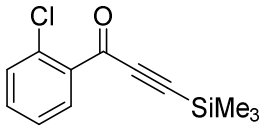
Enantiomeric excess for >1 mmol scale reaction determined by HPLC analysis (CHIRALCEL OD-H column, hexane 97:03 iPrOH, 0.5 mL/min, T = 30°C, λ = 220 nm, Ketone 8.4 min, *S* enantiomer 16.6 min, *R*-enantiomer 19.2 min). 94.2% ee. The lower flow rate gave improved separation, although the peak shape was unchanged.

m/z (ESI) 260.6 ([M + Na]+, 100%), 262.6 ([M + 2+ Na]+, 40%).

Using [(MeO)(*R,R*)Teth-TsDpenRuCl] as catalyst, the conversion was 100% and the ee was 90.6% but the alcohol was not isolated..

Major product configuration was assigned by analogy to related compounds as no asymmetric preparations of this compound have been reported. The configuration was also assigned by analogy with the o-Br alcohol used in the formal synthesis.

1-(2-Chlorophenyl)-3-(trimethylsilyl)prop-2-yn-1-one.



This compound is novel.

This compound was prepared following procedure B using 1-(2-chlorophenyl)-3-(trimethylsilyl)prop-2-yn-1-ol (456 mg, 1.9 mmol, 1.0 equiv), MnO_2 (1.10 mg, 13.0 mmol, 7.0 equiv) and DCM (15 mL) 1-(2-chlorophenyl)-3-(trimethylsilyl)prop-2-yn-1-one was isolated by flash chromatography (pet ether/ EtOAc: 90:10) as a yellow oil (223 mg, 0.93 mmol, 48.2%).

(found (ESI) [M+Na]+, 259.0312. $C_{12}H_{13}ClNaOSi$ requires 259.0316).

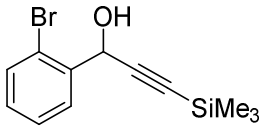
ν_{max}: 2961, 2095, 1651, 1434, 1225, 1011, 841, 739, 624 cm^{-1}.

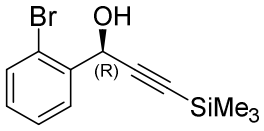
^1H NMR (400 MHz, $CDCl_3$) δ 8.06 – 8.02 (1H, m, ArH), 7.48 – 7.44 (2H, m, ArH), 7.41 – 7.36 (1H, m, ArH), 0.29 (9H, s, $Si(CH_3)_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.1, 136.0, 134.4, 134.2, 133.7, 132.3, 127.5, 102.6, 102.2, 0.0.

m/z (ESI) 258.6 ([M + Na]+, 100%), 260.5 ([M + 2+ Na]+, 40%).

Racemic and 1-(2-bromophenyl)-3-(trimethylsilyl)prop-2-yn-1-ol (31).





This compound is known and has been fully characterized:

Wienhold, F.; Claes, D.; Graczyk, K.; Maison, W. *Synthesis* **2011**, 4059–4067.

This compound was prepared in racemic form following procedure A using: trimethylsilylacetylene (0.8 mL, 6.0 mmol, 1.2 equiv), o-bromo benzaldehyde (0.6 mL, 5.0 mmol, 1.0 equiv), nBuLi, 2.5 M in hexane (2.0 mL, 5.0 mmol, 1.0 equiv) and dry THF (25 mL). 1-(2-bromophenyl)-3-(trimethylsilyl)prop-2-yn-1-ol was isolated by flash chromatography (pet ether/ EtOAc: 80:20) as a colourless oil (1076 mg, 3.8 mmol, 76.3%).

This compound was prepared in enantiomerically-enriched form following procedure C, 1-(2-bromophenyl)-3-(trimethylsilyl)prop-2-yn-1-one (45 mg, 0.16 mmol, 1.0 equiv), FA/TEA (0.2 mL), [OMe(*R,R*)Teth-TsDpen RuCl] (1 mg, 1.5 x 10^{-3} mmol, 1 mol%), DCM (2 mL). *(R)*-1-(2-bromophenyl)-3-(trimethylsilyl)prop-2-yn-1-ol was isolated by flash chromatography (pet ether/ EtOAc: 80:20) as a colourless oil (43 mg, 0.15 mmol, 94%).

$[\alpha]_D^{25}$ 11.7° (c 0.4 in $CHCl_3$) 96.2 % ee (*R*)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (1H, dd, *J* = 7.8, 1.7 Hz, ArH), 7.36 (1H, dd, *J* = 8.0, 1.1 Hz, ArH), 7.20 – 7.12 (1H, m, ArH), 7.04 – 6.95 (1H, m, ArH), 5.58 (1H, d, *J* = 5.5 Hz, CH), 2.32 (1H, d, *J* = 5.5 Hz, OH), 0.0 (9H, s, $Si(CH_3)_3$)..

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.4, 133.2, 130.1, 128.9, 128.0, 123.2, 103.8, 92.2, 64.7, 0.0.

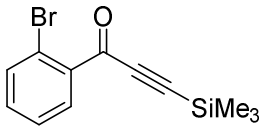
Enantiomeric excess determined by HPLC analysis (CHIRALCEL OD-H column, hexane 97:03 iPrOH, 1.0 mL/min, T = 30°C, λ = 220 nm, Ketone 4.6 min, *S* enantiomer 8.5 min, *R*-enantiomer 10.9 min). 96.2% ee (*R*).

m/z (ESI) 304.6 ([M + Na]+, 100%), 306.5 ([M + 2+ Na]+, 98%).

Using [(*R,R*)Teth-TsDpenRuCl] as catalyst, the conversion was 100%, yield 98% and the ee was 91.8%.

Major product configuration was assigned by result obtained from the subsequent formal synthesis as no asymmetric preparations of this compound have been reported.

1-(2-Bromophenyl)-3-(trimethylsilyl)prop-2-yn-1-one.



This compound is known and has been fully characterized:

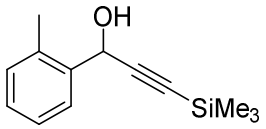
Carmichael, R. A.; Sophanpanichkul, P.; Chalifoux, W. A. *Org. Lett.*, **2017**, *19*, 259 –2595.

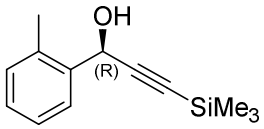
This compound was prepared following procedure B using 1-(2-bromophenyl)-3-(trimethylsilyl)prop-2-yn-1-ol (1.01 mg, 3.6 mmol, 1.0 equiv), MnO_2 (2.10 mg, 24.0 mmol, 7.0 equiv) and DCM (15 mL) 1-(2-bromophenyl)-3-(trimethylsilyl)prop-2-yn-1-one was isolated by flash chromatography (pet ether/ EtOAc: 90:10) as a yellow oil (818 mg, 2.93 mmol, 81.8%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (1H, dd, *J* = 7.7, 1.8 Hz, ArH), 7.68 (1H, dd, *J* = 7.8, 1.1 Hz, ArH), 7.47 – 7.33 (2H, m, ArH), 0.29 (9H, s, $Si(CH_3)_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.7, 137.6, 135.8, 134.2, 134.0, 128.0, 122.0, 102.4, 102.2, 0.0.
m/z (ESI) 302.6 ([M + Na]+, 98%), 304.6 ([M + 2+ Na]+, 100%).

Racemic and *(R)*-1-(o-tolyl)-3-(trimethylsilyl)prop-2-yn-1-ol (32).





This compound is known and has been fully characterized:

Li, Z.-Y.; Wang, M.; Bian, Q.-H.; Zheng, B.; Mao, J.-Y.; Li, S.-N.; Liu, S.-Z.; Wang, M.-A.; Zhong, J.-C.; Guo, H.-C. *Chem. Eur. J.* **2011**, *17*, 5782–5786.

This compound was prepared in racemic form following procedure A using: trimethylsilylacetylene (0.8 mL, 6.0 mmol, 1.2 equiv), o-tolualdehyde (0.6 mL, 5.0 mmol, 1.0 equiv), nBuLi, 2.5 M in hexane (2.0 mL, 5.0 mmol, 1.0 equiv) and dry THF (25 mL). 1-(o-tolyl)-3-(trimethylsilyl)prop-2-yn-1-ol was isolated by flash chromatography (pet ether/ EtOAc: 80:20) as a colourless oil (813 mg, 3.7 mmol, 74.6%).

This compound was prepared in enantiomerically-enriched form following procedure C, 1-(o-tolyl)-3-(trimethylsilyl)prop-2-yn-1-one (42 mg, 0.19 mmol, 1.0 equiv), FA/TEA (0.2 mL), [(*R,R*)Teth-TsDpen RuCl] (1.2 mg, 1.9 x 10^{-3} mmol, 1 mol%), DCM (2 mL). *(R)*- 1-(o-tolyl)-3-(trimethylsilyl)prop-2-yn-1-ol was formed in 36% conversion (HPLC data) and was not isolated. The data was obtained using the mixture.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.41 (1H, m, ArH), 7.07 – 6.95 (3H, m, ArH), 5.39 (1H, d, *J* = 5.6 Hz, CH), 2.24 (3H, s, CH_3), 1.97 (1H, d, *J* = 5.7 Hz, OH), 0.00 (9H, s, $Si(CH_3)_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.2, 136.2, 130.9, 128.5, 126.7, 126.3, 104.9, 91.6, 63.0, 19.1, 0.0.

Enantiomeric excess determined by HPLC analysis (CHIRALCEL OD-H column, hexane 97:03 iPrOH, 1.0 mL/min, T = 30°C, λ = 220 nm, Ketone 3.8 min, *S* enantiomer 9.0 min, *R*-enantiomer 10.8 min). 58.8% ee (*R*).

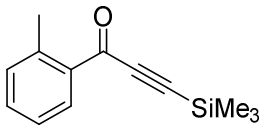
m/z (ESI) 240.6 ([M + Na]+, 100 %).

Using [(MeO)(*R,R*)Teth-TsDpenRuCl] as catalyst, the conversion was 21% and the ee was 43%.

Major product configuration was established by comparison of elution of HPLC peaks - order matched that reported under reported conditions in the paper cited above. The configuration was

also assigned by analogy with the o-Br alcohol used in the formal synthesis. See Table at end of SI.

1-(o-Tolyl)-3-(trimethylsilyl)prop-2-yn-1-one.



This compound is known and has been fully characterized:

Friscourt, F.; Boons, G.-J. *Org. Lett*., **2010**, *12*, 4936 – 4939.

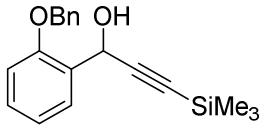
This compound was prepared following procedure B using 1-(o-tolyl)-3-(trimethylsilyl)prop-2-yn-1-ol (756 mg, 3.5 mmol, 1.0 equiv), MnO_2 (2.10 mg, 24.0 mmol, 7.0 equiv) and DCM (15 mL) 1-(o-tolyl)-3-(trimethylsilyl)prop-2-yn-1-one was isolated by flash chromatography (pet ether/ EtOAc: 90:10) as a yellow oil (403 mg, 1.85 mmol, 53.0%).

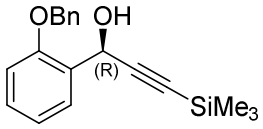
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (1H, dd, *J* = 7.8, 1.4 Hz, ArH), 7.33 – 7.26 (1H, m, ArH), 7.18 (1H, t, *J* = 7.5 Hz, ArH), 7.09 (1H, d, *J* = 7.6 Hz, ArH), 2.47 (3H, s, CH_3), 0.15 (9H, s, $Si(CH_3)_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 180.0, 141.2, 135.9, 134.0, 133.6, 132.7, 126.5, 102.9, 99.6, 22.5, 0.0.

m/z (ESI) 238.5 ([M + Na]+, 100 %).

Racemic and *(R)*-1-(2-benzyloxyphenyl)-3-(trimethylsilyl)prop-2-yn-1-ol (33).





This compound is novel:

This compound was prepared in racemic form following procedure A using: trimethylsilylacetylene (0.8 mL, 6.0 mmol, 1.2 equiv), o-benzyloxy benzaldehyde (1060 mg, 5.0 mmol, 1.0 equiv), nBuLi, 2.5 M in hexane (2.0 mL, 5.0 mmol, 1.0 equiv) and dry THF (25 mL). 1-(2-benzylphenyl)-3-(trimethylsilyl)prop-2-yn-1-ol was isolated by flash chromatography (pet ether/ EtOAc: 80:20) as a colourless oil (1289 mg, 4.1 mmol, 83.2).

This compound was prepared in enantiomerically-enriched form following procedure C, 1-(2-benzylphenyl)-3-(trimethylsilyl)prop-2-yn-1-one (44 mg, 0.14 mmol, 1.0 equiv), FA/TEA (0.2 mL), [(*R*,*R*)Teth-TsDpen RuCl] (0.9 mg, 1.4 x 10^{-3} mmol, 1 mol%), DCM (2 mL). *(R)*- 1-(2-

benzylphenyl)-3-(trimethylsilyl)prop-2-yn-1-ol was isolated by flash chromatography (pet ether/ EtOAc: 80:20) as a colourless oil (44 mg, 0.14 mmol, 99%).

(found (ESI) [M+Na]+, 333.1283. $C_{19}H_{22}NaO_2Si$ requires 333.1281).

$[\alpha]_D^{25}$ 5.1° (c 0.3 in $CHCl_3$) 93.4 % ee (*R*).

ν_{max}: 3453 (broad), 2959, 2170, 1597, 1247, 1026, 839, 750, 695 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 7.37 (1H, dd, *J* = 7.5, 1.6 Hz, ArH), 7.27 (2H, d, *J* = 7.2 Hz, ArH), 7.22 – 7.04 (4Hm, ArH), 6.83 – 6.74 (2H, m, ArH), 5.53 (1H, d, *J* = 6.5 Hz, CH), 4.96 (2H, d, *J* = 3.6 Hz, CH_2), 2.83 (1H, d, *J* = 6.6 Hz, OH), 0.00 (9H, s, $Si(CH_3)_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 136.6, 129.7, 129.1, 128.7, 128.2, 128.1, 127.3, 121.2, 112.3, 104.8, 90.8, 70.3, 62.0, 0.0.

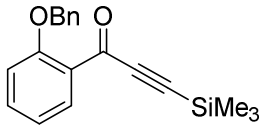
Enantiomeric excess determined by HPLC analysis (CHIRALCEL OD-H column, hexane 97:03 iPrOH, 1.0 mL/min, T = 30°C, λ = 220 nm, Ketone 9.3 min, *S* enantiomer 19.6 min, *R*-enantiomer 24.2 min). 93.4% ee (*R*).

m/z (ESI) 332.7 ([M + Na]+, 100 %).

Using [(MeO)(*R*,*R*)Teth-TsDpenRuCl] as catalyst, the conversion was 100% and the ee was 88.0% but the alcohol was not isolated.

Major product configuration was assigned by analogy to related compounds as no asymmetric preparations of this compound have been reported. The configuration was also assigned by analogy with the o-Br alcohol used in the formal synthesis.

1-(2-Benzylphenyl)-3-(trimethylsilyl)prop-2-yn-1-one



This compound is novel:

This compound was prepared following procedure B using 1-(2-benzylphenyl)-3-(trimethylsilyl)prop-2-yn-1-ol (1.21 mg, 3.9 mmol, 1.0 equiv), MnO_2 (2.30 mg, 27.0 mmol, 7.0 equiv) and DCM (15 mL) 1-(2-benzylphenyl)-3-(trimethylsilyl)prop-2-yn-1-one was isolated by flash chromatography (pet ether/ EtOAc: 90:10) as a yellow oil (941 mg, 3.05 mmol, 78.2%).

(found (ESI) [M+Na]+, 331.1126. $C_{19}H_{20}NaO_2Si$ requires 331.1125).

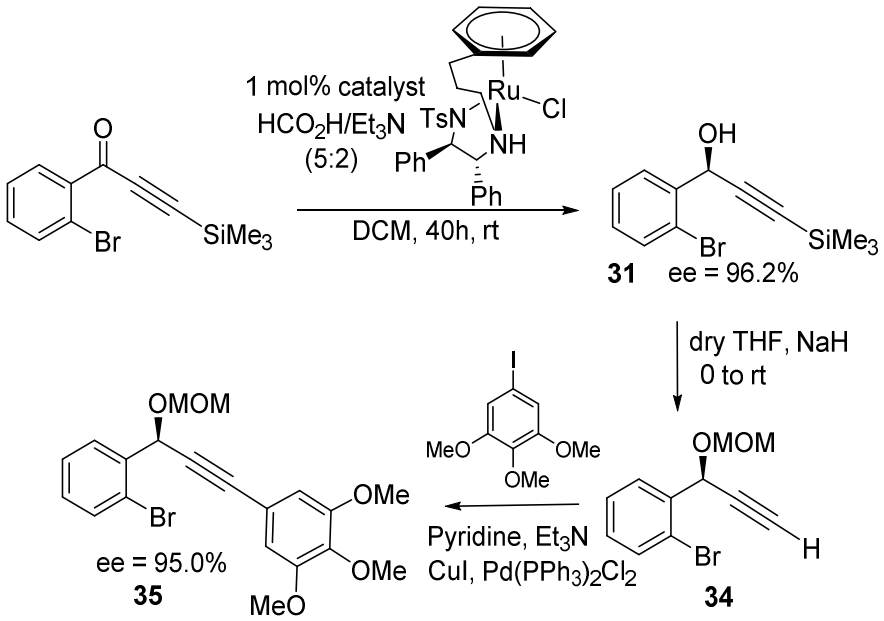
ν_{max}: 2960, 2151, 1644, 1594, 1221, 1004, 840, 753, 693 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (1H, dd, *J* = 7.8, 1.8 Hz, ArH), 7.33 – 7.06 (6H, m, ArH), 6.85 – 6.75 (2H, m, ArH), 5.01 (2H, s, CH_2), 0.00 (9H, s, $Si(CH_3)_3$).

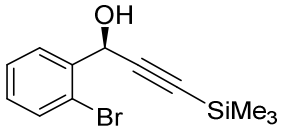
^{13}C NMR (101 MHz, $CDCl_3$) δ 177.4, 159.4, 137.1, 135.5, 133.4, 129.2, 128.5, 127.8, 127.5, 121.3, 114.3, 103.7, 99.4, 71.0, 0.0.

m/z (ESI) 330.7 ([M + Na]+, 100 %).

Catalytic Synthesis of the key intermediate in the synthesis of Allocolchicine.

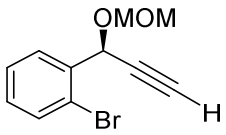


(*R*)-1-(2-bromophenyl)-3-(trimethylsilyl)prop-2-yn-1-ol 31.



This compound was prepared in enantiomerically-enriched form following procedure C, 1-(2-bromophenyl)-3-(trimethylsilyl)prop-2-yn-1-one (200 mg, 0.71 mmol, 1.0 equiv), FA/TEA (0.5 mL), [OMe(*R,R*)Teth-TsDpen RuCl] (4.6 mg, 7.1 x 10^{-3} mmol, 1 mol%), DCM (5 mL). *(R)*-1-(2-bromophenyl)-3-(trimethylsilyl)prop-2-yn-1-ol was isolated by flash chromatography (pet ether/ EtOAc: 80:20) as a colourless oil (191 mg, 0.68 mmol, 96%). 96% ee**.**

***(R)*-1-Bromo-2-(1-(methoxymethoxy)prop-2-yn-1-yl)benzene 34.**



This compound is novel:

To a solution of (*R*)-1-(2-bromophenyl)-3-(trimethylsilyl)prop-2-yn-1-ol **31** (180 mg, 0.63 mmol) in 28 mL of dry THF was added sodium hydride 60% in mineral oil (60 mg, 1.5 mmol) at 0°C. The resulting mixture was stirred at rt for 1h. Bromo(methoxy)methane (90 mg, 0.06 mL, 0.72

mmol) was added and the resulting mixture was stirred at 0 °C for 15 min before letting the solution warm to rt and stir overnight. Water was added slowly and THF was removed under rotary evaporator. The resulting thick oil was extracted twice with ether. The organic layer was dried over $NaSO_4$, filtered and concentrated. The colourless oil was purified by column chromatography on silica gel using 30% EtOAc/hexane to give (S)-1-bromo-2-(1-(methoxymethoxy)prop-2-yn-1-yl)benzene as a colourless oil (80 mg, 0.31 mmol, 48%).

(found (ESI) [M+Na]+, 276.9829. $C_{11}H_{11}BrNaO_2$ requires 276.9835).

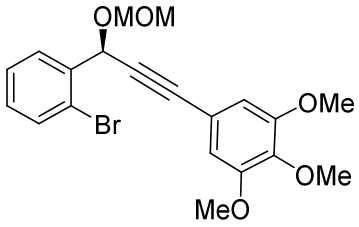
ν_{max}: 2938, 1575, 1502, 1463, 1409, 1234, 1123, 1004, 831, 754, 630 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (1H, dd, *J* = 7.9, 1.6 Hz, ArH), 7.42 – 7.34 (1H, m, ArH), 7.23 – 7.14 (1H, m, ArH), 7.06 – 6.95 (1H, m, ArH), 5.60 (1H, d, *J* = 2.1 Hz, CH), 4.88 – 4.73 (1H, m, CH_2), 4.68 – 4.49 (1H, m, CH_2), 3.26 (3H, s, CH_3), 2.44 – 2.40 (1H, m, CH).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.5, 132.9, 130.1, 129.4, 127.9, 123.0, 94.3, 89.1, 75.4, 66.6, 56.2.

m/z (ESI) 292.5 ([M+K]+, 98%), 294.5 ([M+ K]+, 100%).

***(R)*-5-(3-(2-Bromophenyl)-3-(methoxymethoxy)prop-1-yn-1-yl)-1,2,3-trimethoxybenzene 35.**



This compound is known and has been fully characterized:

Leblanc, M.; Fagnou, K. *Org. Lett.*, **2005**, *7*, 2849–2852.

A mixture of (*R*)-1-bromo-2-(1-(methoxymethoxy)prop-2-yn-1-yl)benzene **34** (80 mg, 0.31 mmol, 1.0 equiv), $Pd(PPh_3)_2Cl_2$ (11 mg, 0.016 mmol, 5 mol%), CuI (5 mg, 0.026 mmol, 8 mol%) and 5-Bromo-1,2,3-trimethoxybenzene (80 mg, 0.32 mmol, 1.0 equiv) was dissolved in pyridine (2 mL) and Et_3N (5 mL) under nitrogen atmosphere. The reaction was heated at 90 °C for 18 hours. The reaction was allowed to cool to ambient temperature, filtered through celite and washed with EtOAc. The reaction mixture was acidified to pH 7 with 10% $HCl_{(aq)}$, extracted with EtOAc, dried over Na_2SO_4, and solvent removed in vacuo. The residue was purified by column chromatography (pet ether/ EtOAc: 90:10) as a yellow oil (92 mg, 0.22 mmol, 73%).

$[\alpha]_D^{25}$ 19.0° (c 0.1 in CH_2Cl_2) 95.0 % ee (*R*); lit: $[\alpha]_D^{22}$ -22.5 (c 1, CH_2Cl_2) 95.4% ee (*S*)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (1H, dd, *J* = 7.8, 1.7 Hz, ArH), 7.59 (1H, dd, *J* = 8.0, 1.2 Hz, ArH), 7.44 – 7.35 (1H, m, ArH), 7.26 – 7.17 (1H, m, ArH), 6.70 (2H, s, ArH), 6.00 (1H, s, CH), 5.12 (1H, d, *J* = 6.8 Hz, CH_2), 4.75 (1H, d, *J* = 6.8 Hz, CH_2), 3.84 (9H, s, $3OCH_3$), 3.48 (3H, s, CH_3).

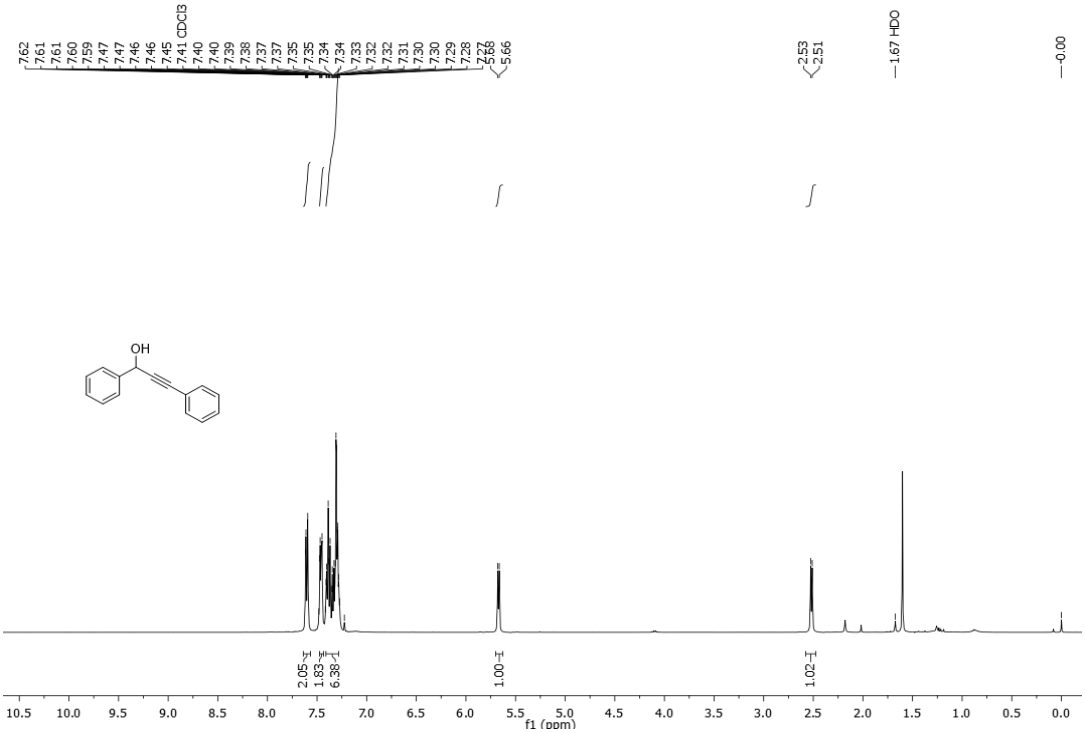
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.0, 138.0, 132.9, 130.0, 129.5, 127.9, 123.1, 117.3, 109.0, 94.3, 87.2, 85.1, 67.3, 60.9, 56.2.

m/z (ESI) 442.8 ([M + Na]+, 100%), 444.8 ([M + 2+ Na]+, 100%).

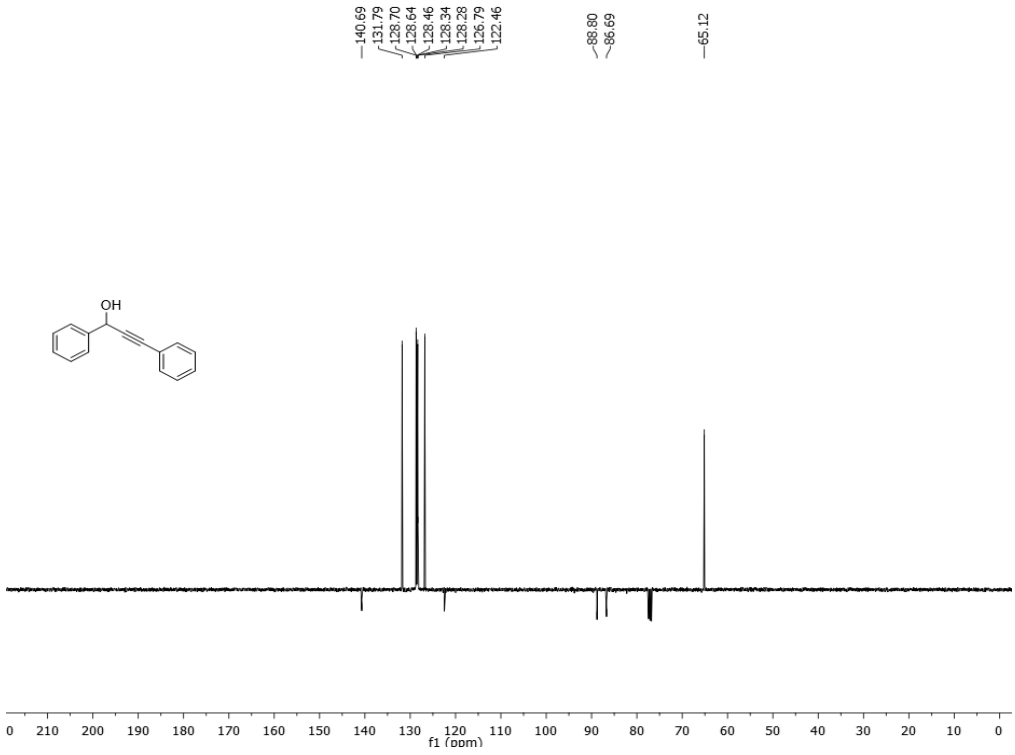
Enantiomeric excess determined by HPLC analysis (CHIRALPAK AD-H column, hexane 90:10 iPrOH, 1.0 mL/min, T = 30°C, λ = 250 nm, Ketone 4.6 min, *R* enantiomer 10.6 min, *S*-enantiomer 11.8 min). 95.0% ee (*R*). This matches the reported data on the same column and conditions by LeBlanc and Fagnou.

1,3-Diphenylprop-2-yn-1-ol (7).

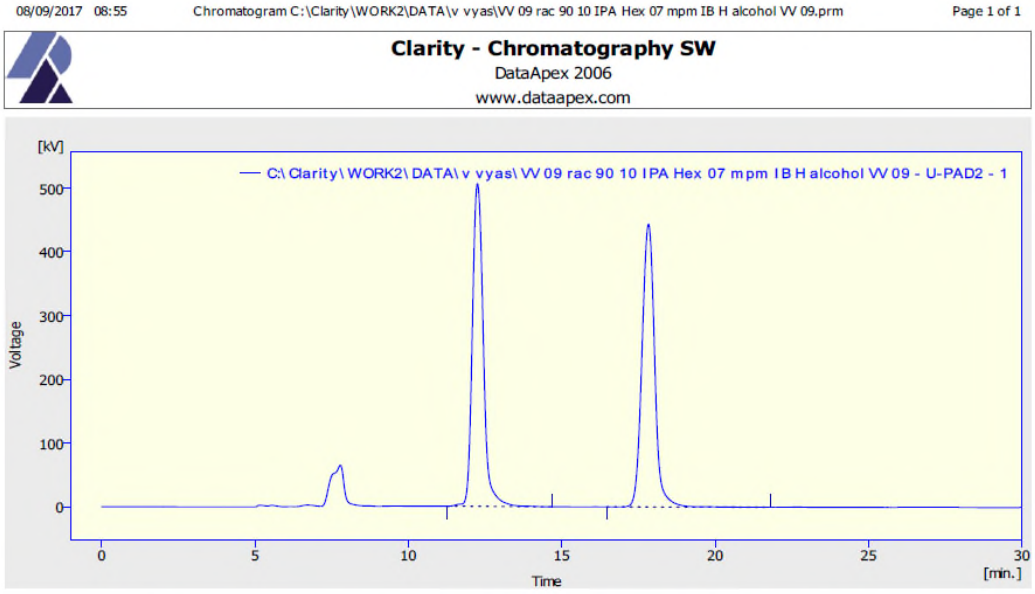
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



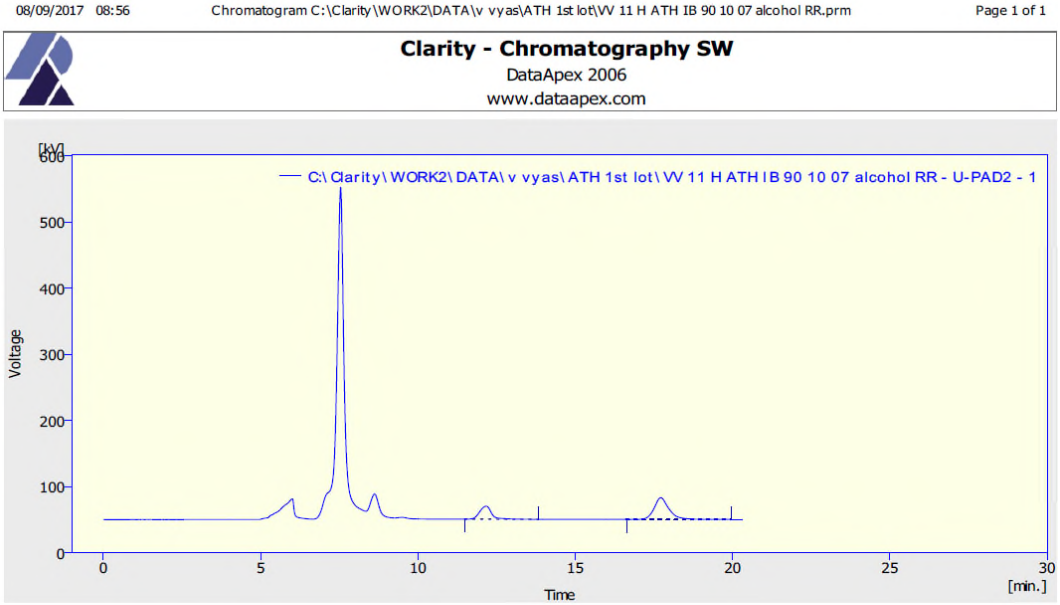
Racemic HPLC of 1,3-diphenylprop-2-yn-1-ol (**7**).



Result Table (Uncal - C:\Clarity\WORK2\DATA\v vyas\VV 09 rac 90 10 IPA Hex 07 mpm IB H alcohol VV 09 - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	12.252	12586.235	506.240	49.7	53.3	0.38	
2	17.828	12736.231	443.763	50.3	46.7	0.44	
	Total	25322.466	950.004	100.0	100.0		

HPLC after ATH 1,3-diphenylprop-2-yn-1-ol (**7**) (17% conversion, 35.4% ee).

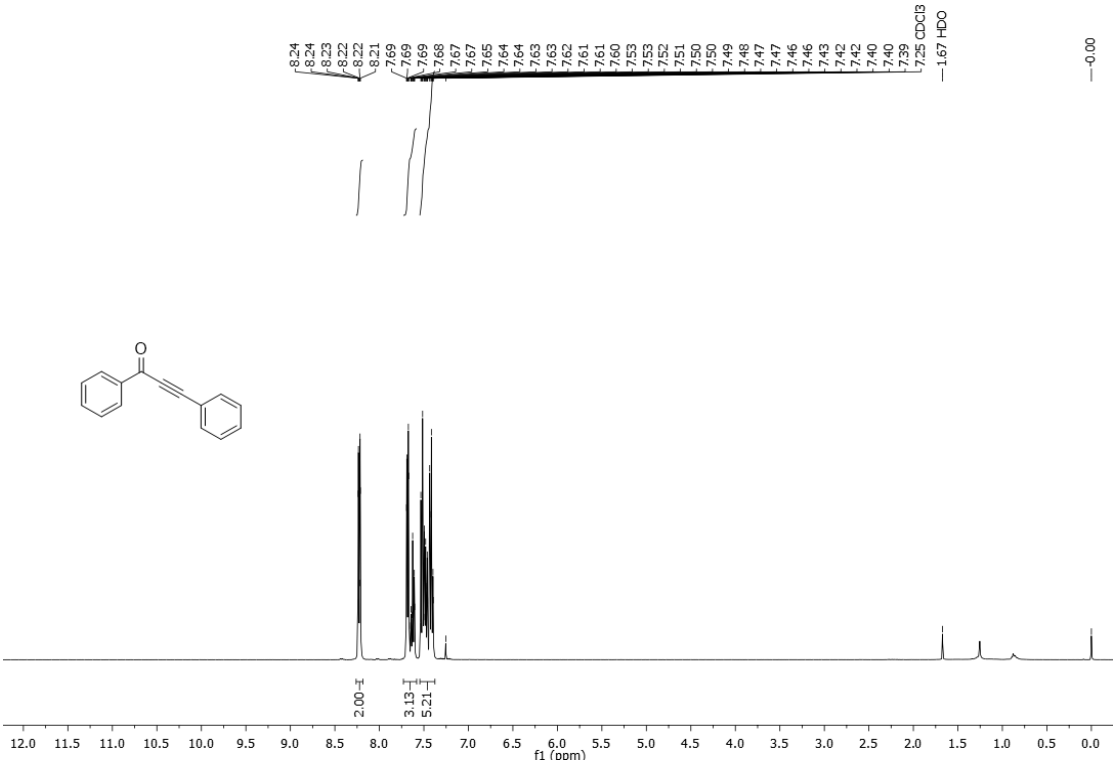


Result Table (Uncal - C:\Clarity\WORK2\DATA\v vyas\ATH 1st lot\VV 11 H ATH IB 90 10 07 alcohol RR - U-PAD2 - 1)

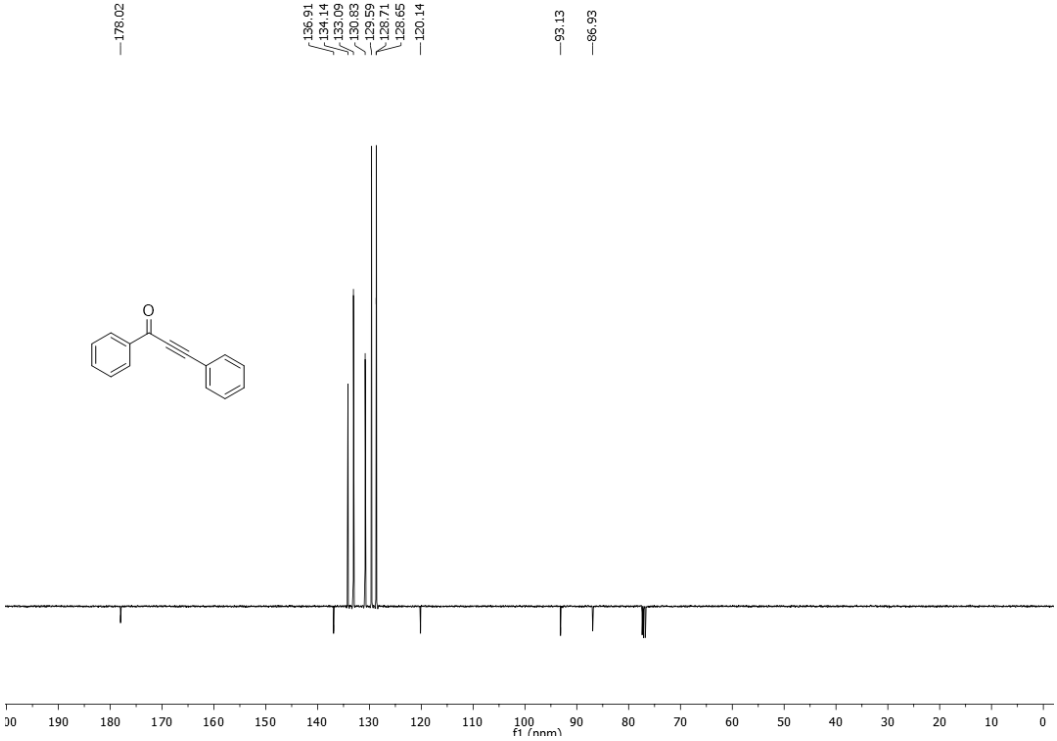
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	12.168	513.588	19.706	32.3	37.4	0.39	
2	17.720	1077.507	32.929	67.7	62.6	0.48	
	Total	1591.096	52.635	100.0	100.0		

1,3-Diphenylprop-2-yn-1-one.

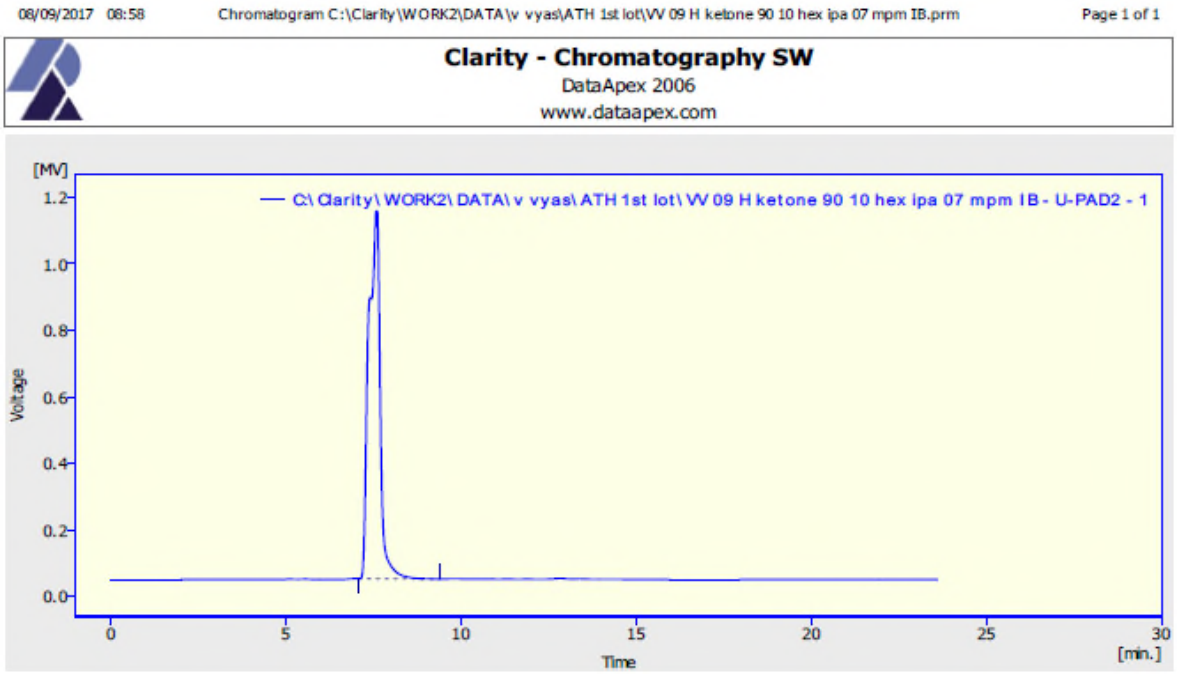
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



Ketone HPLC of 1,3-diphenylprop-2-yn-1-one.

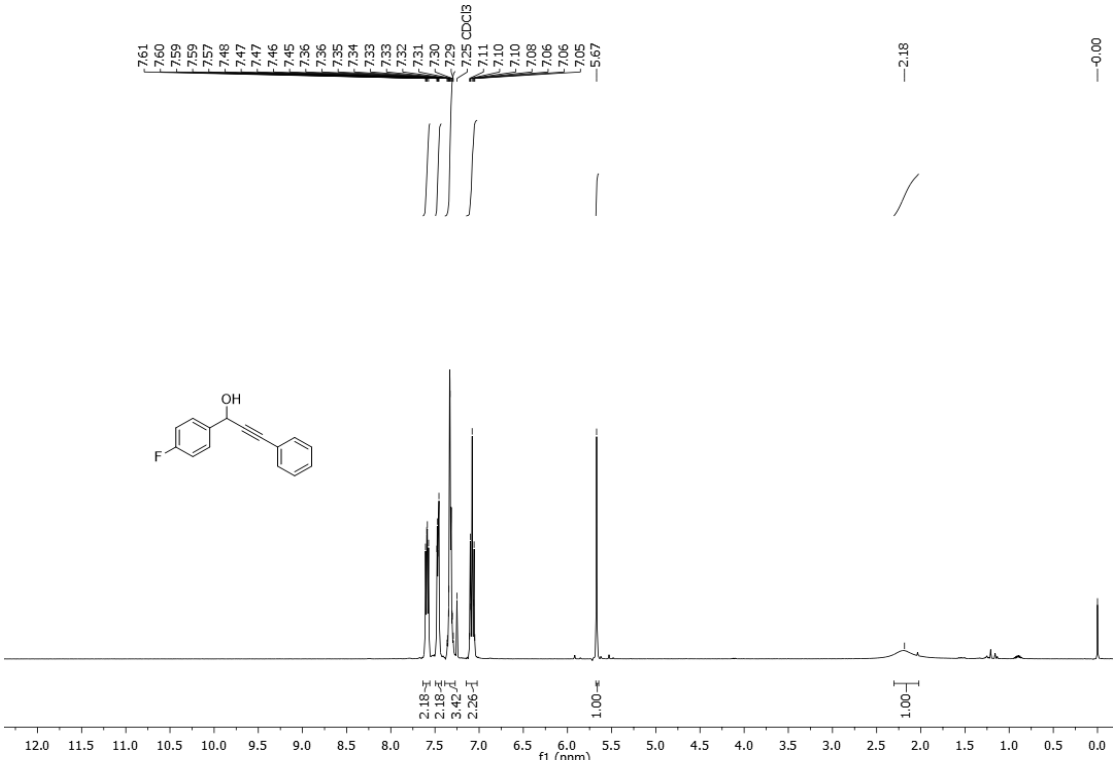


Result Table (Uncal - C:|Clarity|WORK2|DATA|v vyas|ATH 1st lot|VV 09 H ketone 90 10 hex ipa 07 mpm IB - U-PAD2 - 1)

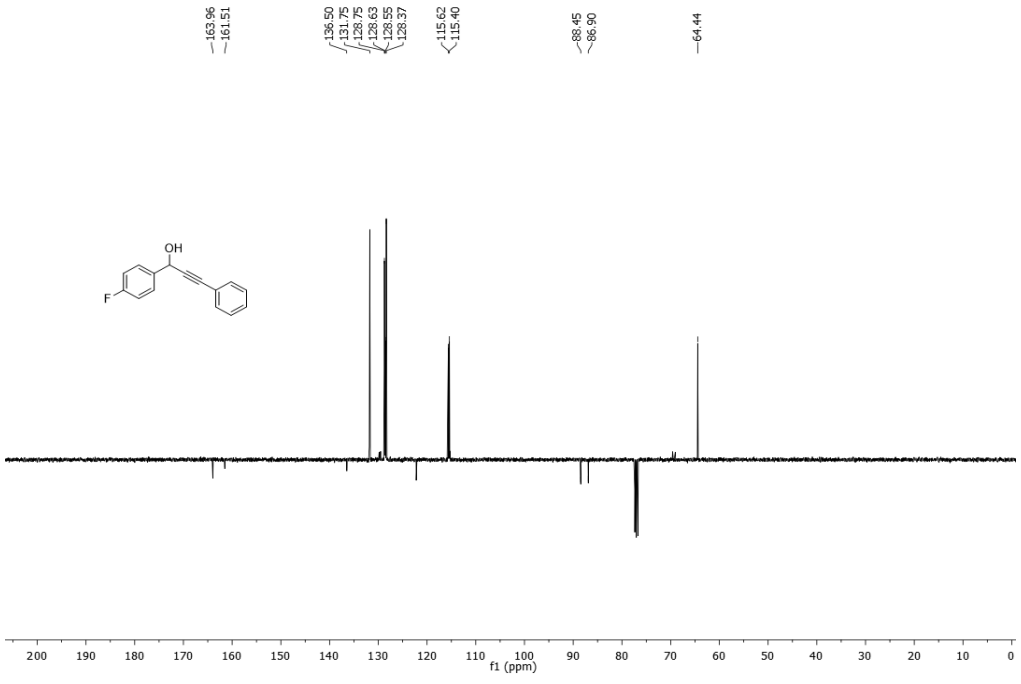
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	7.596	25231.392	1105.821	100.0	100.0	0.39	
	Total	25231.392	1105.821	100.0	100.0		

1-(4-Fluorophenyl)-3-phenylprop-2-yn-1-ol (8).

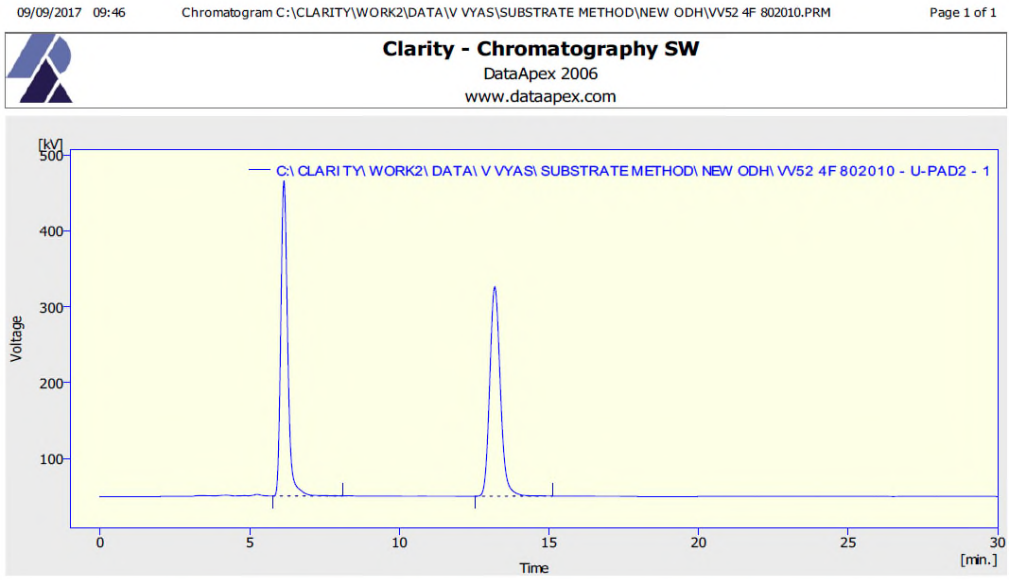
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



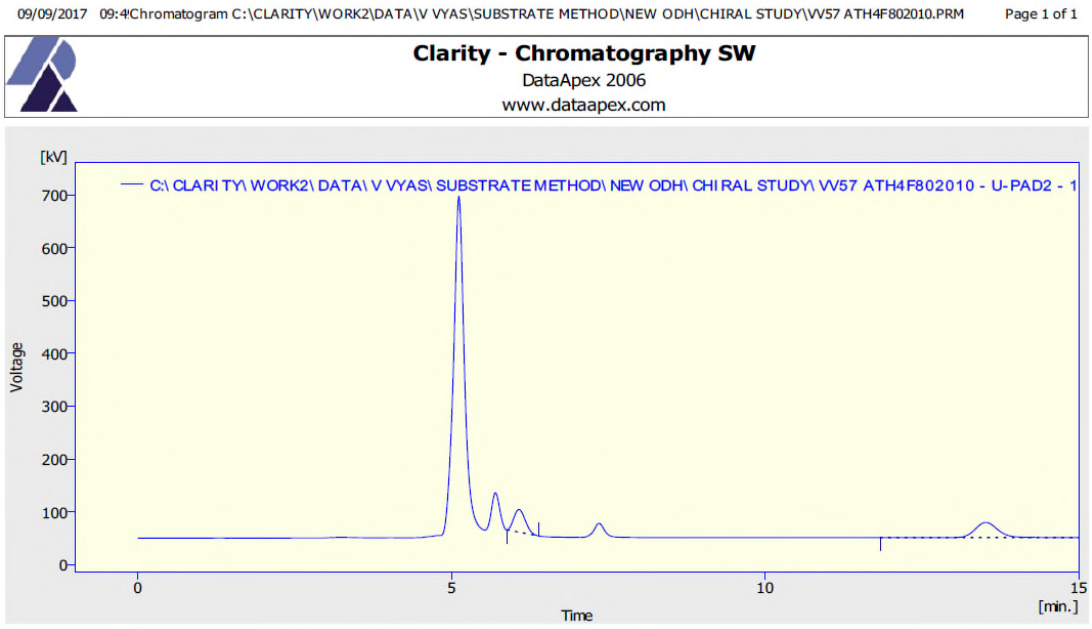
Racemic HPLC of 1-(4-fluorophenyl)-3-phenylprop-2-yn-1-ol (**8**).



Result Table (Uncal - C:\CLARITY\WORK2\DATA\V VYAS\SUBSTRATE METHOD\NEW ODH\VV52 4F 802010 - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	6.144	6639.210	415.131	49.4	60.1	0.24	
2	13.188	6803.697	275.899	50.6	39.9	0.38	
	Total	13442.908	691.030	100.0	100.0		

HPLC after ATH of 1-(4-fluorophenyl)-3-phenylprop-2-yn-1-ol (**8**) (15% conversion, 14% ee).

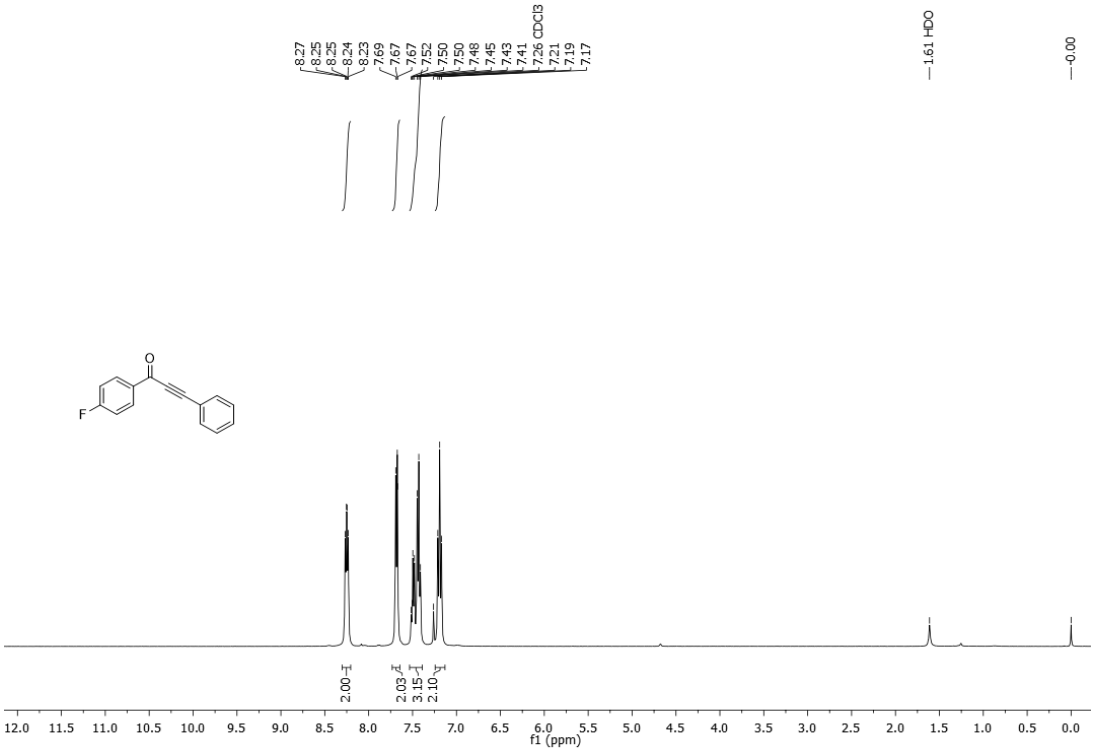


Result Table (Uncal - C:\CLARITY\WORK2\DATA\V VYAS\SUBSTRATE METHOD\NEW ODH\CHIRAL STUDY\VV57 ATH4F802010 - U-PAD2 - 1)

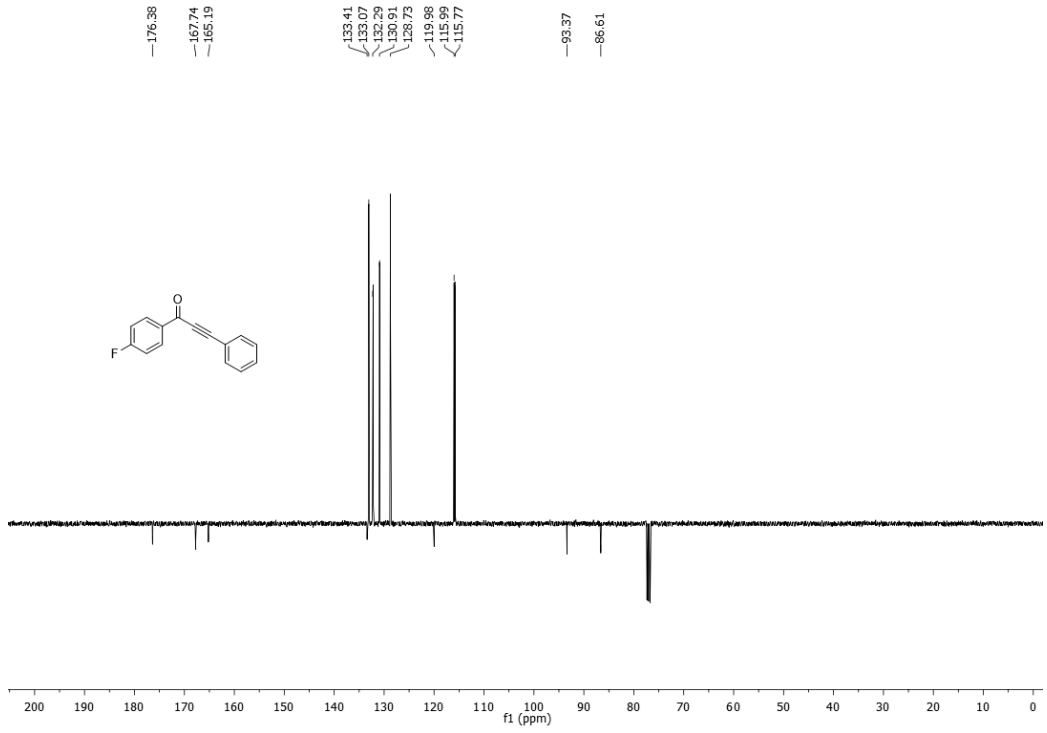
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	6.076	551.516	43.012	43.1	59.9	0.21	
2	13.520	728.850	28.825	56.9	40.1	0.38	
	Total	1280.366	71.837	100.0	100.0		

1-(4-Fluorophenyl)-3-phenylprop-2-yn-1-one.

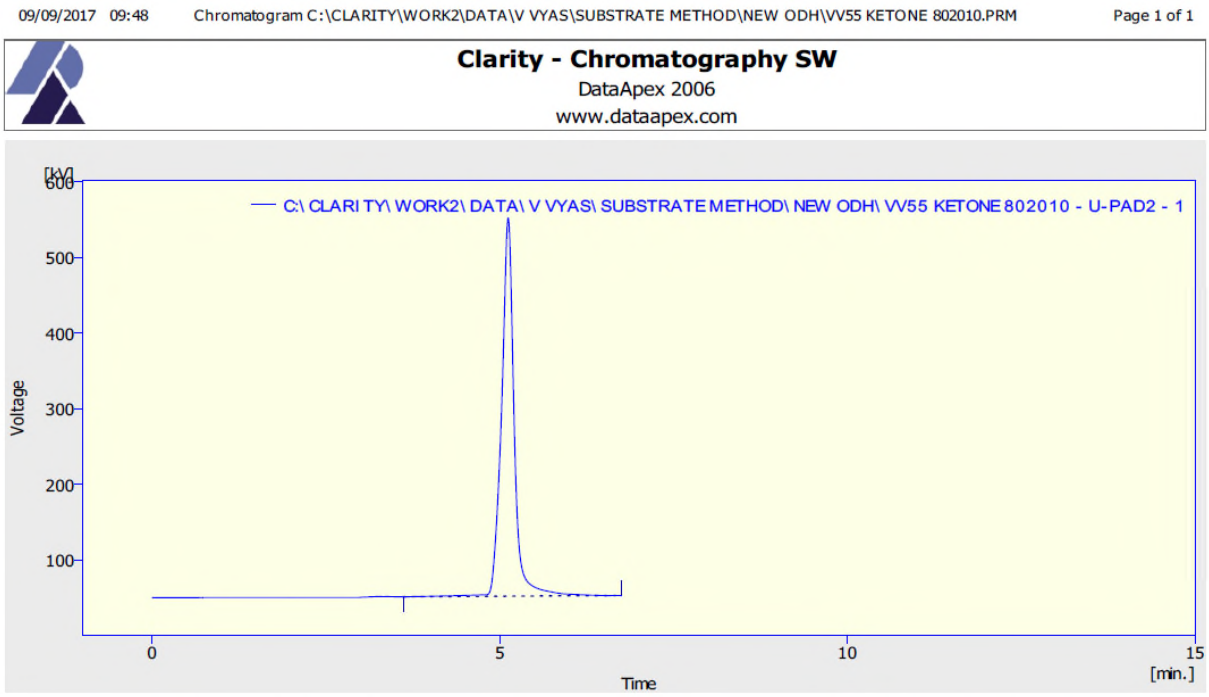
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



Ketone HPLC of 1-(4-fluorophenyl)-3-phenylprop-2-yn-1-one.

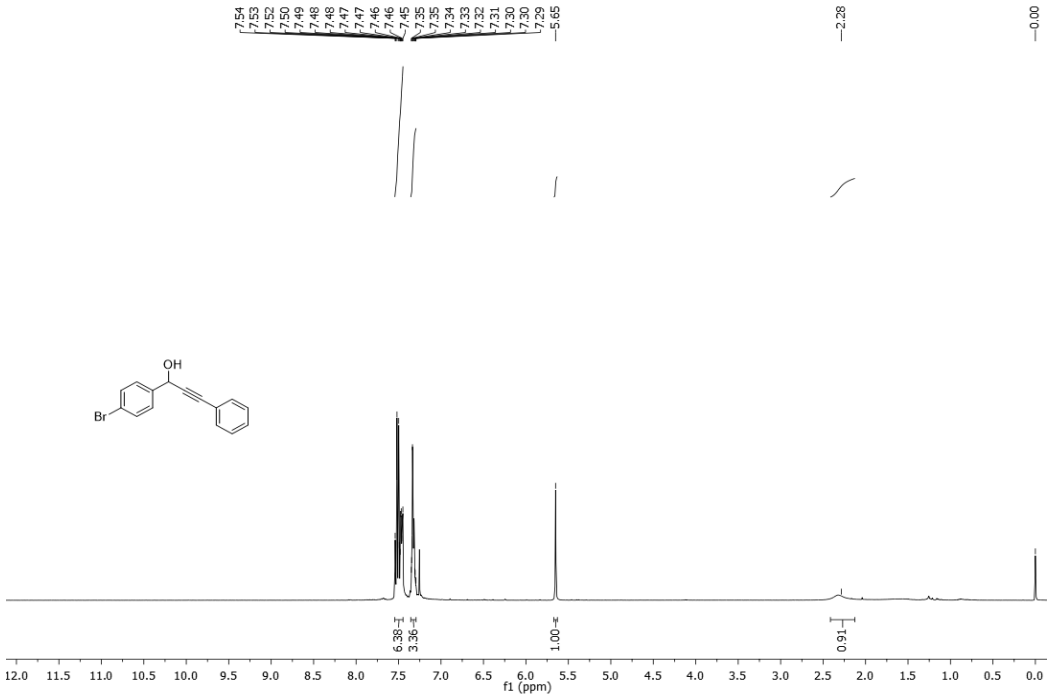


Result Table (Uncal - C:|CLARITY|WORK2|DATA|V VYAS|SUBSTRATE METHOD|NEW ODH|VV55 KETONE 802010 - U-PAD2 - 1)

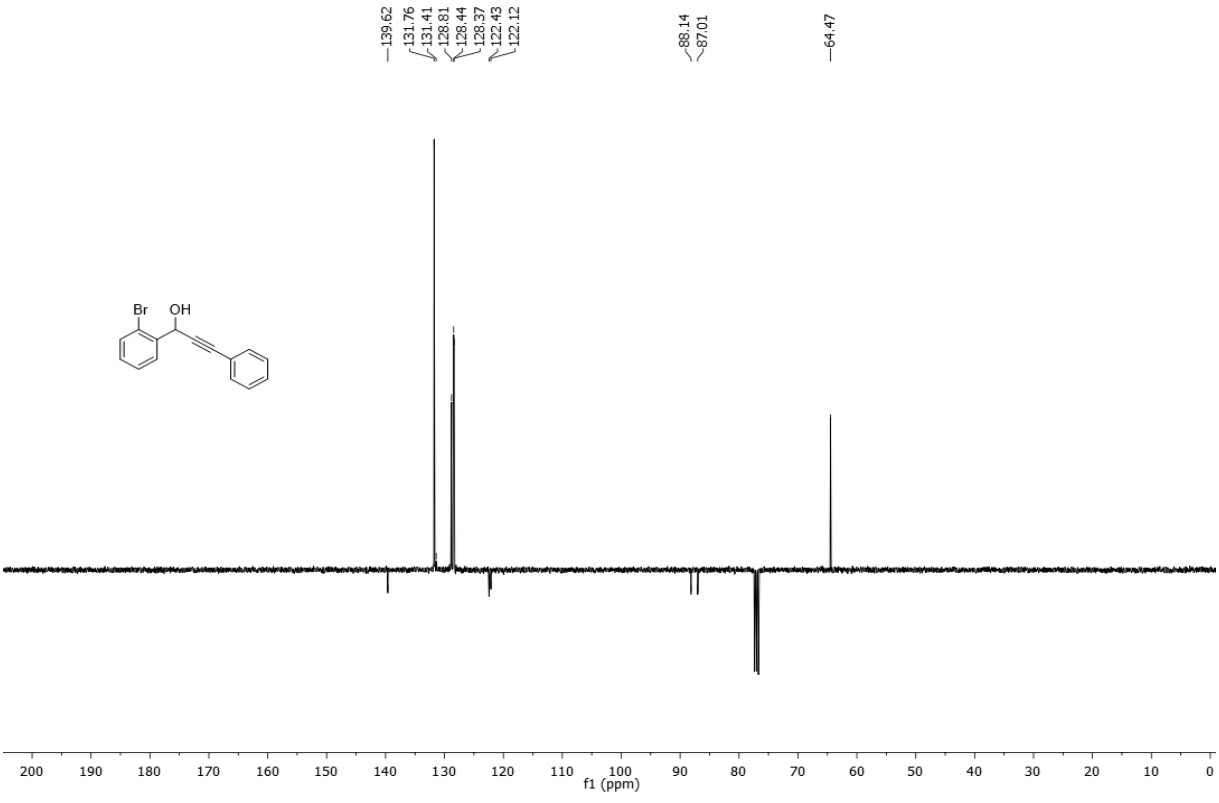
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	5.124	6376.013	500.155	100.0	100.0	0.18	
	Total	6376.013	500.155	100.0	100.0		

1-(4-Bromophenyl)-3-phenylprop-2-yn-1-ol (9).

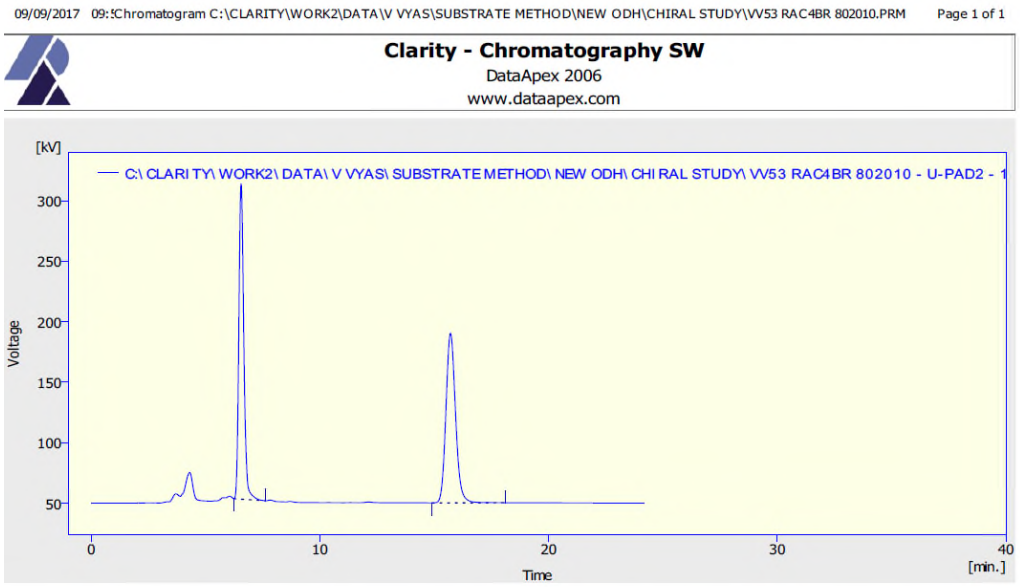
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



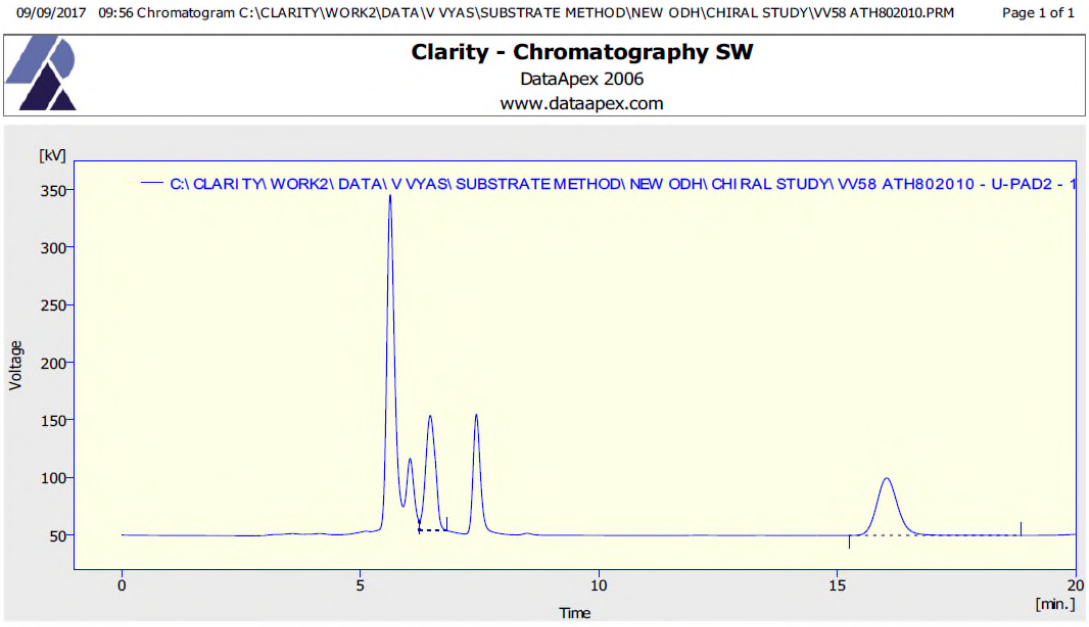
Racemic HPLC of 1-(4-bromophenyl)-3-phenylprop-2-yn-1-ol (**9**).



Result Table (Uncal - C:\|CLARITY\|WORK2\|DATA\|V VYAS\|SUBSTRATE METHOD\|NEW ODH\|CHIRAL STUDY\|VV53 RAC4BR 802010 - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	6.552	3928.191	260.641	48.9	65.0	0.23	
2	15.712	4098.607	140.172	51.1	35.0	0.45	
	Total	8026.799	400.813	100.0	100.0		

HPLC after ATH of 1-(4-bromophenyl)-3-phenylprop-2-yn-1-ol (**9**) (48% conversion, 8.4% ee).

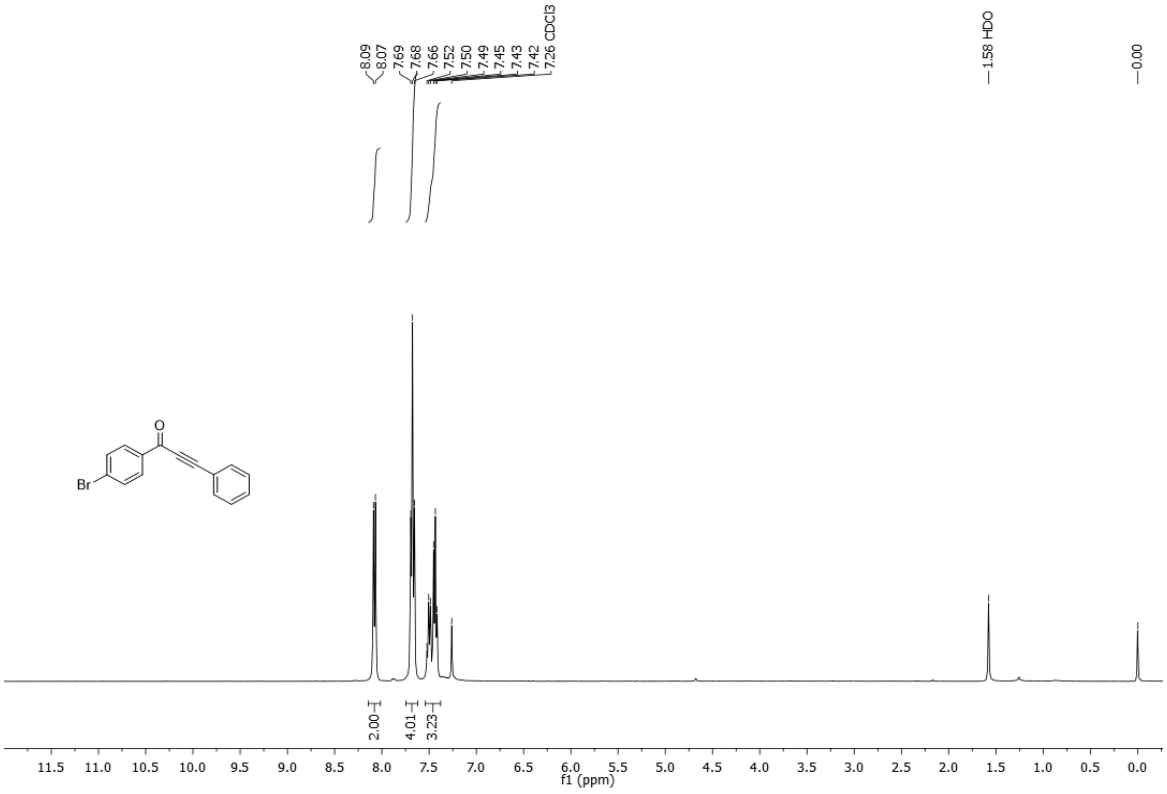


Result Table (Uncal - C:\|CLARITY\|WORK2\|DATA\|V VYAS\|SUBSTRATE METHOD\|NEW ODH\|CHIRAL STUDY\|VV58 ATH802010 - U-PAD2 - 1)

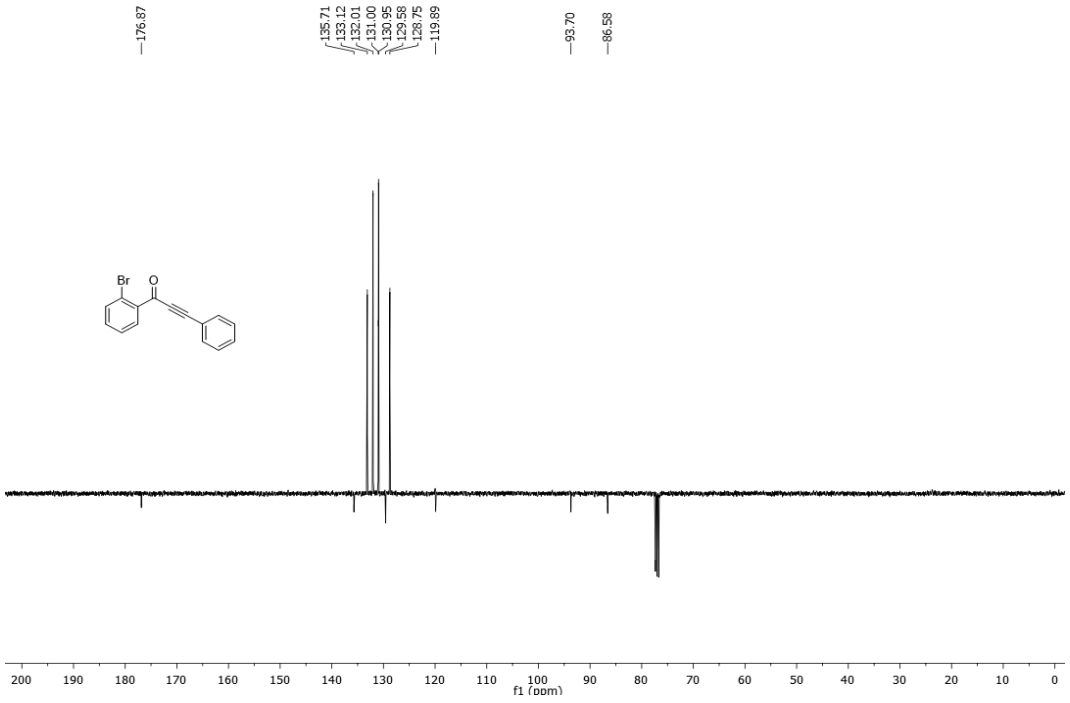
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	6.472	1423.177	99.951	48.4	66.7	0.24	
2	16.036	1514.721	49.904	51.6	33.3	0.46	
	Total	2937.898	149.855	100.0	100.0		

1-(4-Bromophenyl)-3-phenylprop-2-yn-1-one.

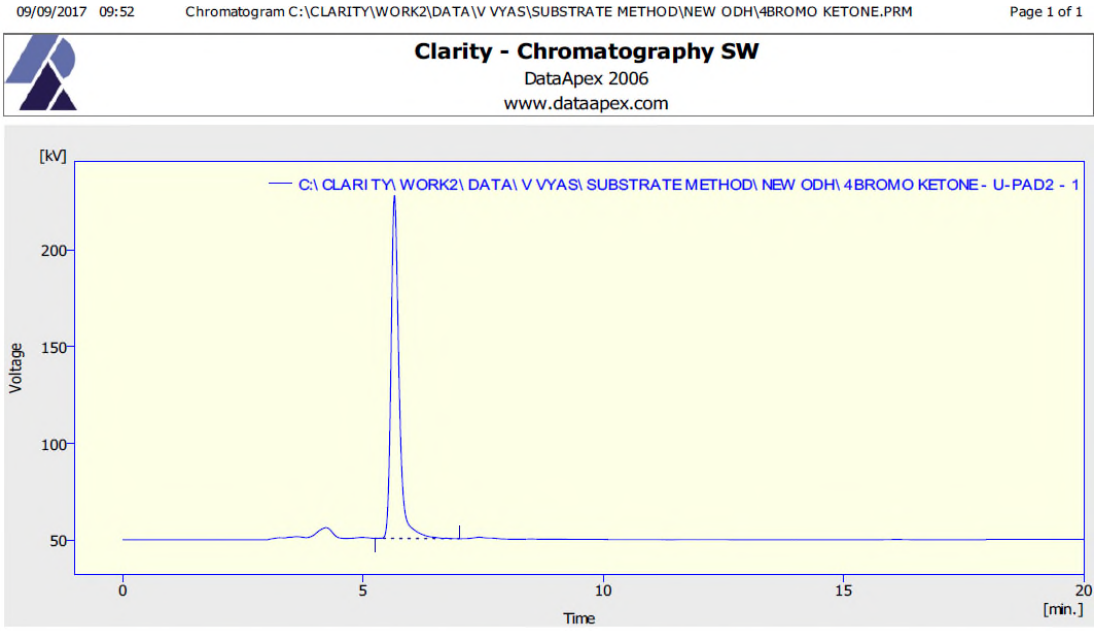
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



Ketone HPLC of 1-(4-bromophenyl)-3-phenylprop-2-yn-1-one.

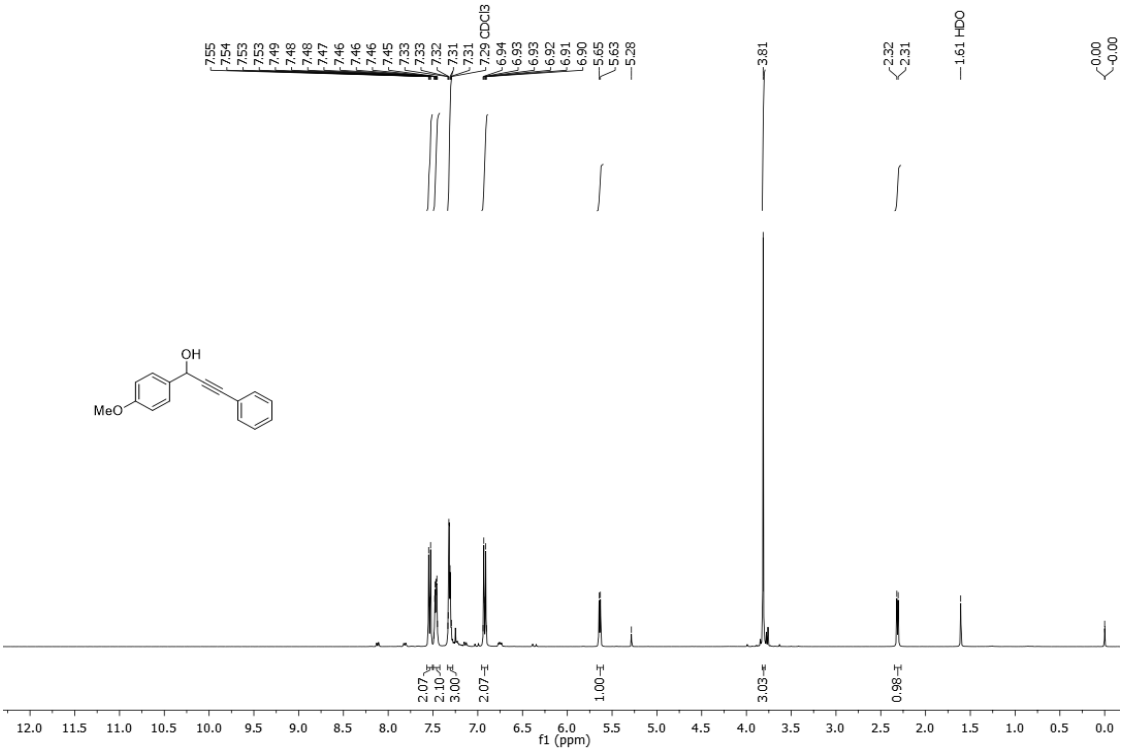


Result Table (Uncal - C:\|CLARITY\|WORK2\|DATA\|V VYAS\|SUBSTRATE METHOD\|NEW ODH\|4BROMO KETONE - U-PAD2 - 1)

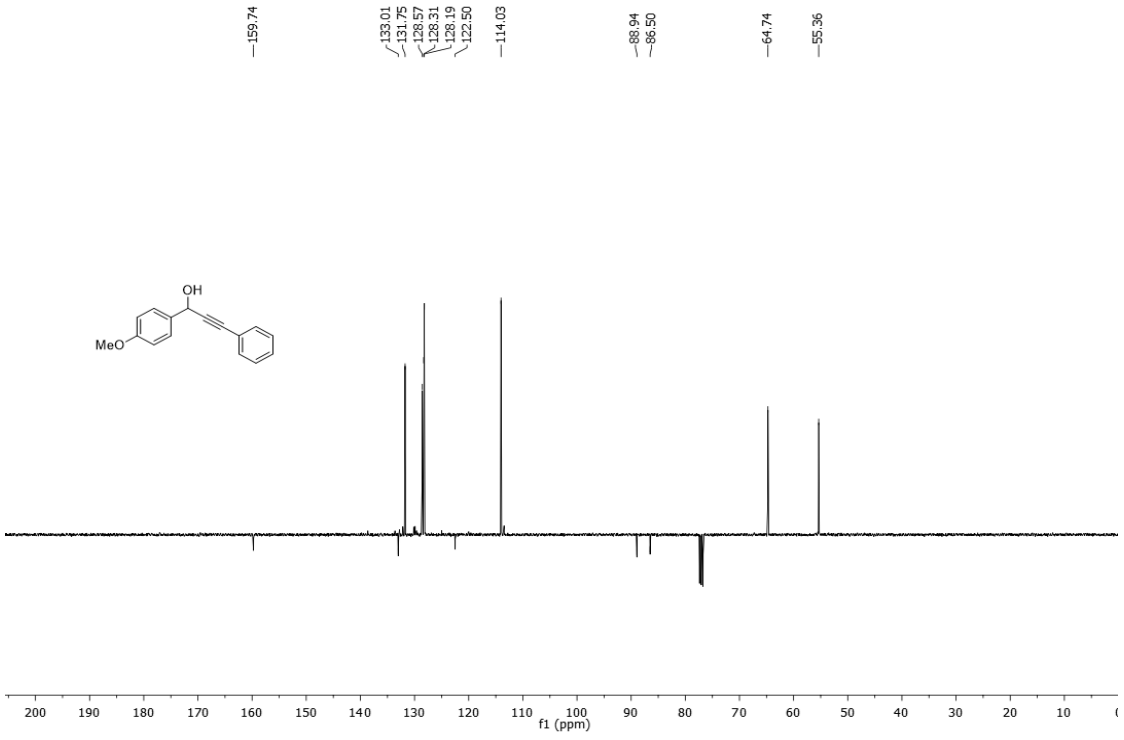
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	5.660	2069.467	177.156	100.0	100.0	0.17	
	Total	2069.467	177.156	100.0	100.0		

1-(4-Methoxyphenyl)-3-phenylprop-2-yn-1-ol (10).

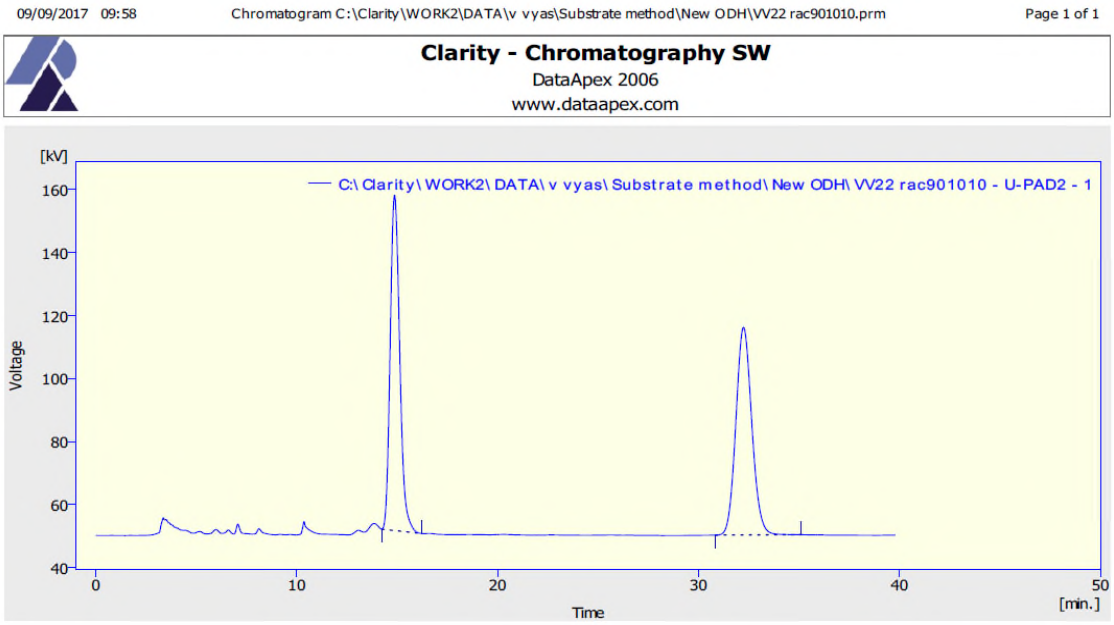
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



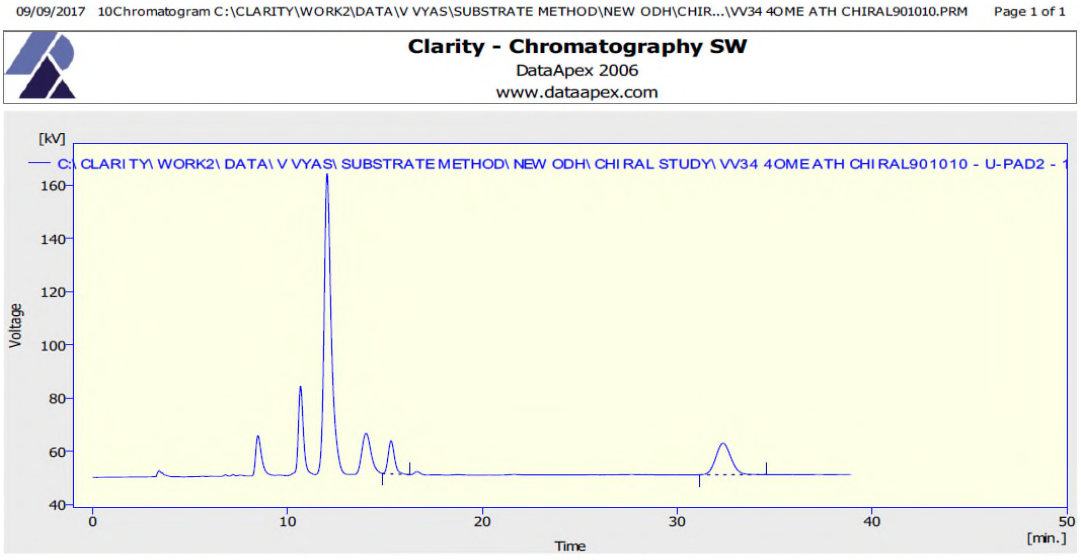
Racemic HPLC of 1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-ol (**10**).



Result Table (Uncal - C:\|Clarity\|WORK2\|DATA\|v vyas\|Substrate method\|New ODH\|VV22 rac901010 - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	14.868	3514.228	106.489	49.2	61.8	0.51	
2	32.236	3631.474	65.952	50.8	38.2	0.85	
	Total	7145.702	172.441	100.0	100.0		

HPLC after ATH of 1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-ol (**10**) (24% conversion, 39% ee).

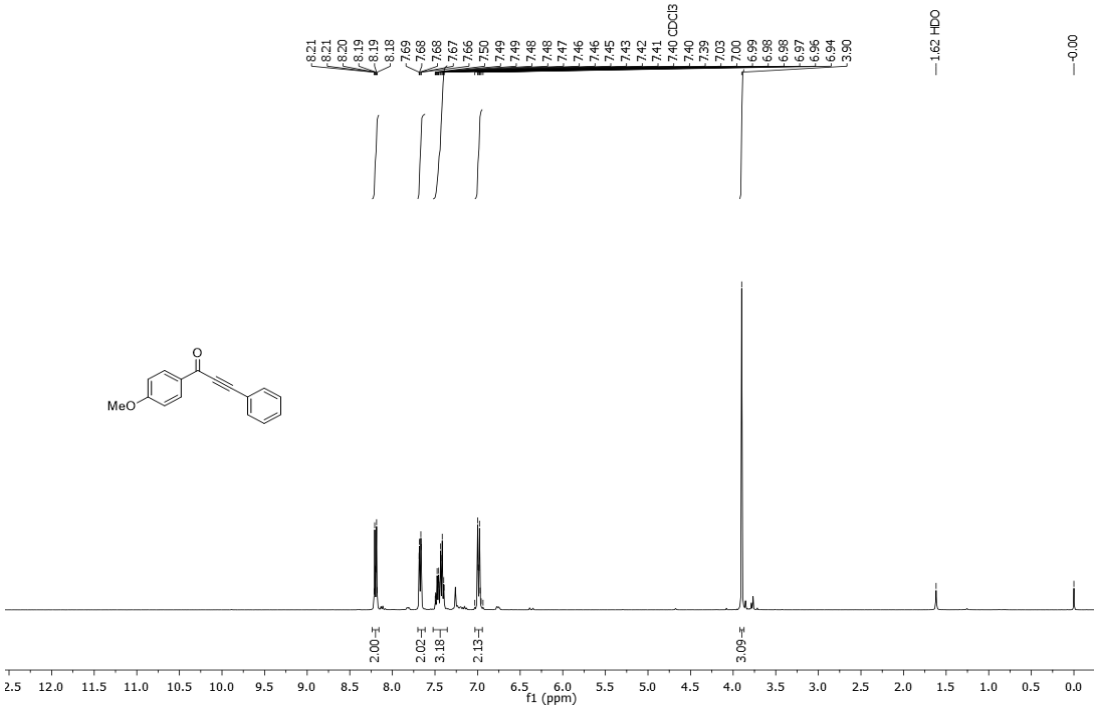


Result Table (Uncal - C:\|CLARITY\|WORK2\|DATA\|V VYAS\|SUBSTRATE METHOD\|NEW ODH\|CHIRAL STUDY\|VV34 4OME ATH CHIRAL901010 - U-PAD2 - 1)

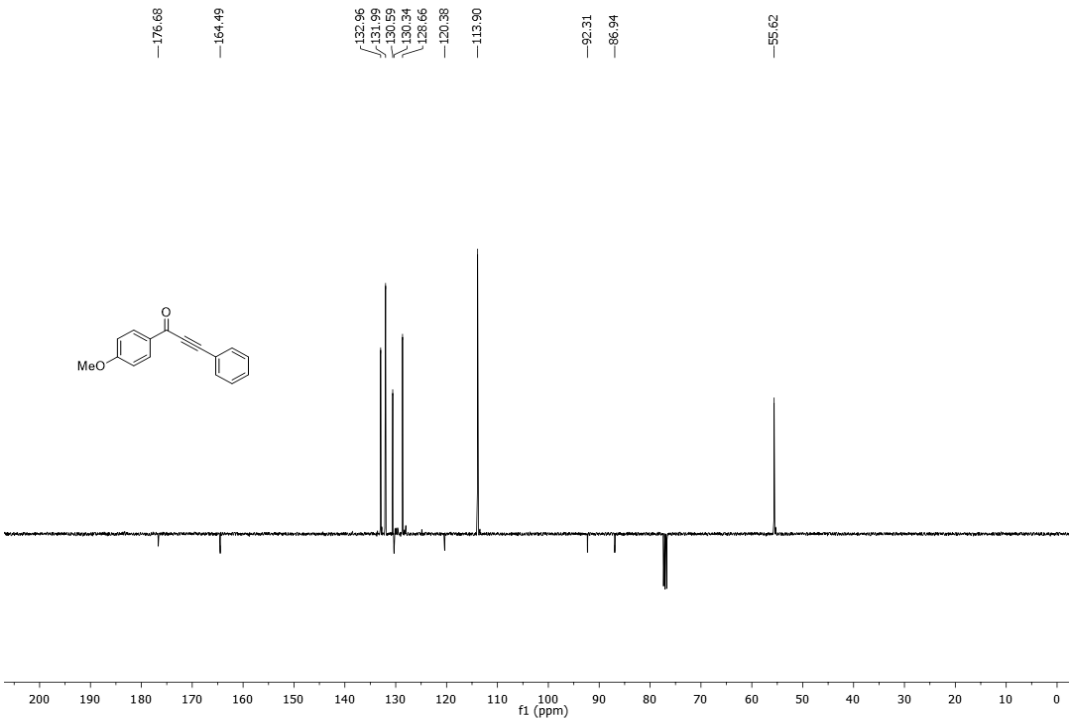
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	15.312	280.582	12.384	30.5	51.1	0.34	
2	32.356	638.734	11.836	69.5	48.9	0.84	
	Total	919.316	24.220	100.0	100.0		

1-(4-Methoxyphenyl)-3-phenylprop-2-yn-1-one.

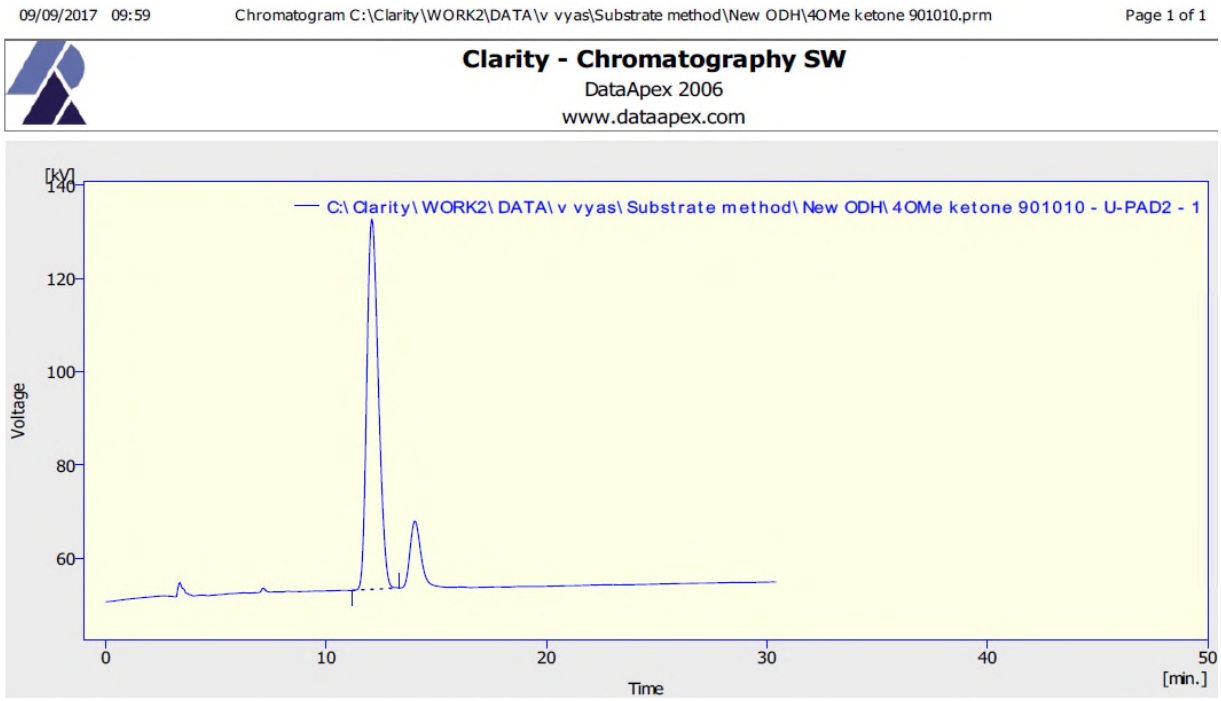
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



Ketone HPLC of 1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-one.

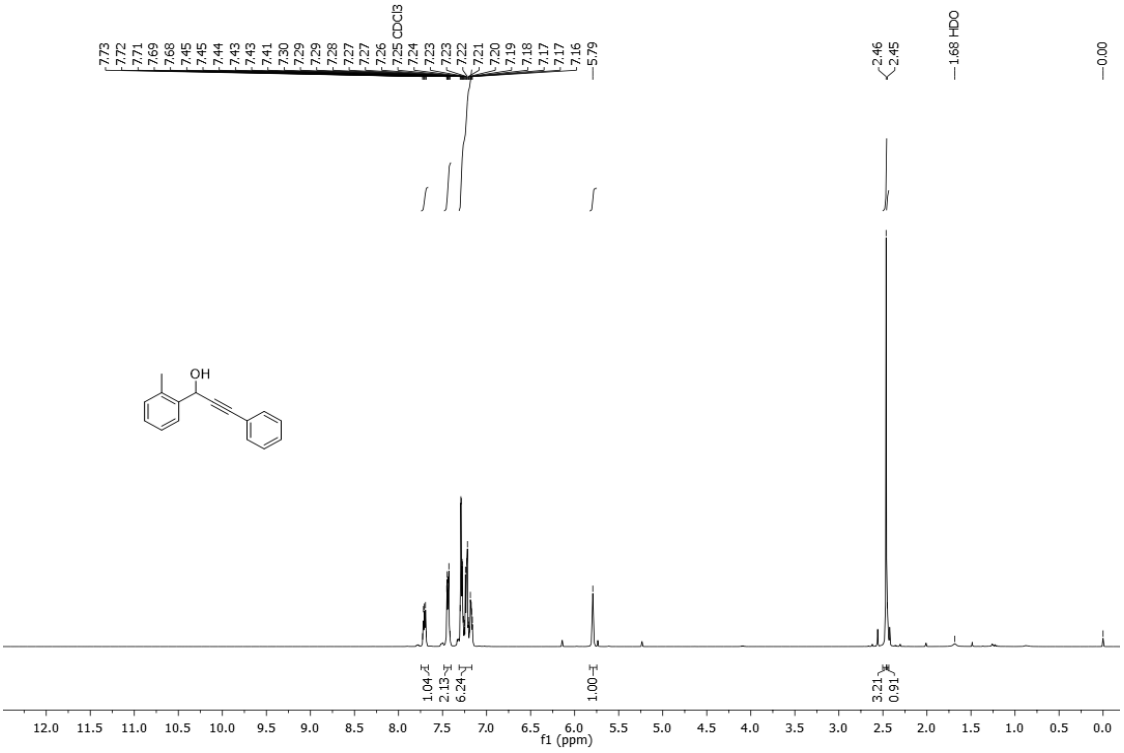


Result Table (Uncal - C:|Clarity|WORK2|DATA|v vyas|Substrate method|New ODH|4OMe ketone 901010 - U-PAD2 - 1)

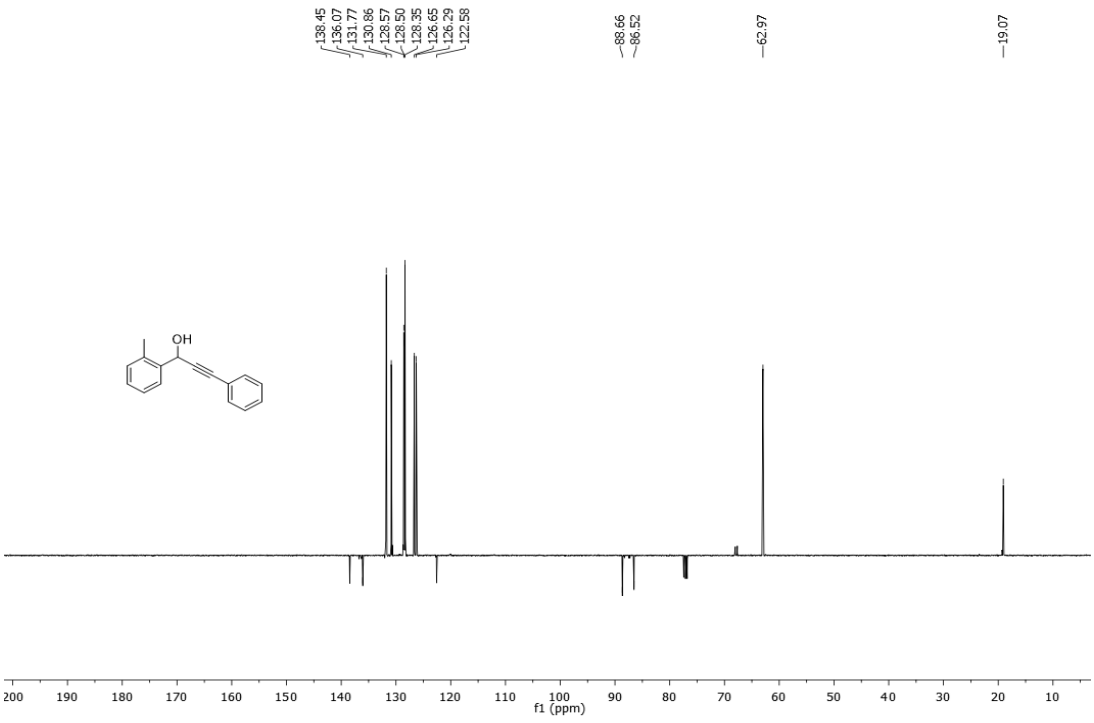
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	12.072	2882.004	79.283	100.0	100.0	0.58	
	Total	2882.004	79.283	100.0	100.0		

3-Phenyl-1-(o-tolyl)prop-2-yn-1-ol (11).

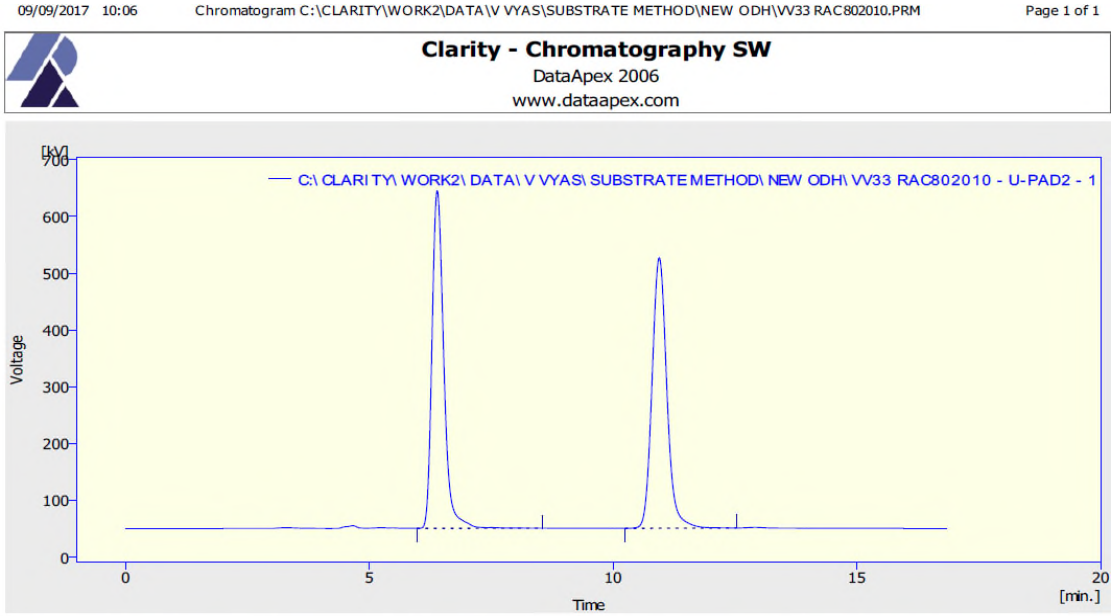
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



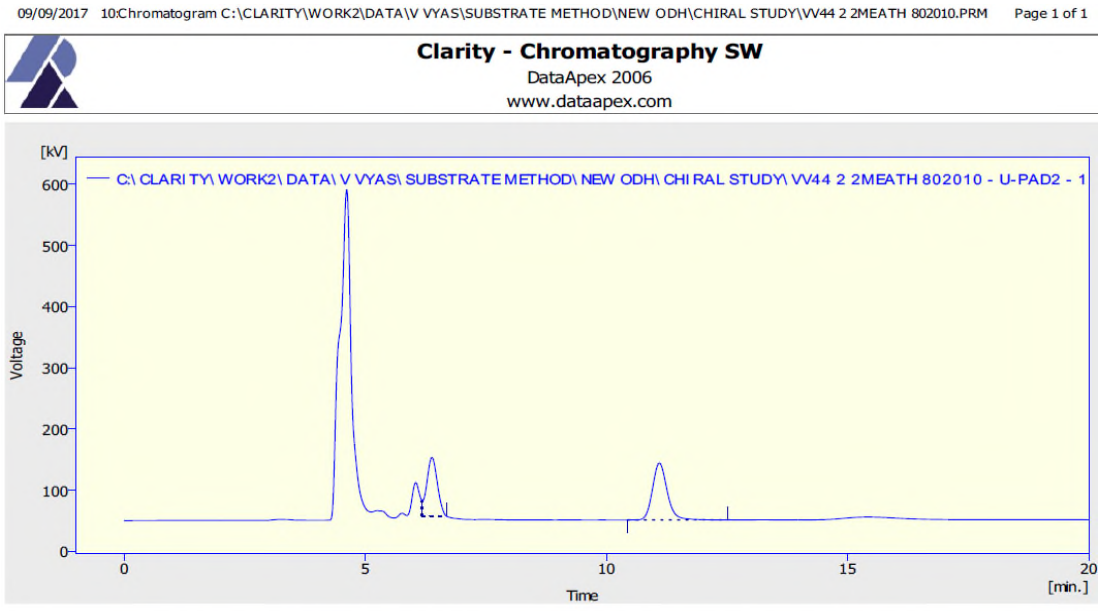
Racemic HPLC of 3-phenyl-1-(o-tolyl)prop-2-yn-1-ol (**11**).



Result Table (Uncal - C:\CLARITY\WORK2\DATA\V VYAS\SUBSTRATE METHOD\NEW ODH\VV33 RAC802010 - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	6.396	9982.239	594.951	49.8	55.5	0.25	
2	10.948	10063.185	476.648	50.2	44.5	0.32	
	Total	20045.423	1071.599	100.0	100.0		

HPLC after ATH of 3-phenyl-1-(o-tolyl)prop-2-yn-1-ol (**11**) (27% conversion, 14.4% ee).

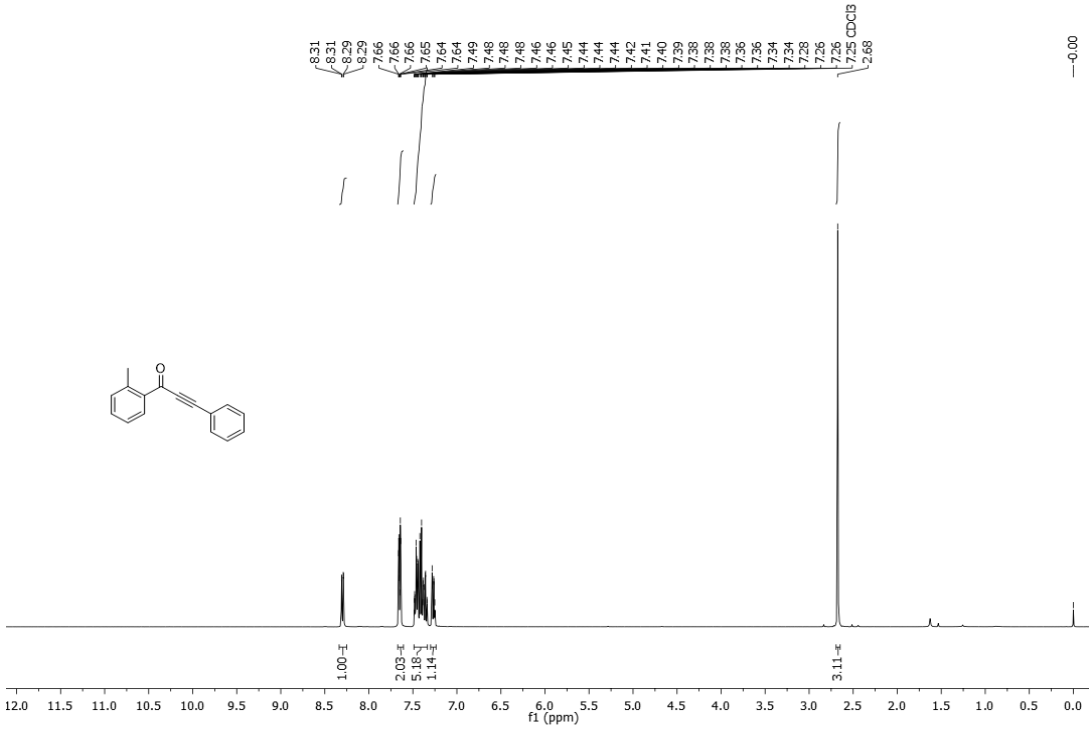


Result Table (Uncal - C:\CLARITY\WORK2\DATA\V VYAS\SUBSTRATE METHOD\NEW ODH\CHIRAL STUDY\VV44 2 2MEATH 802010 - U-PAD2 - 1)

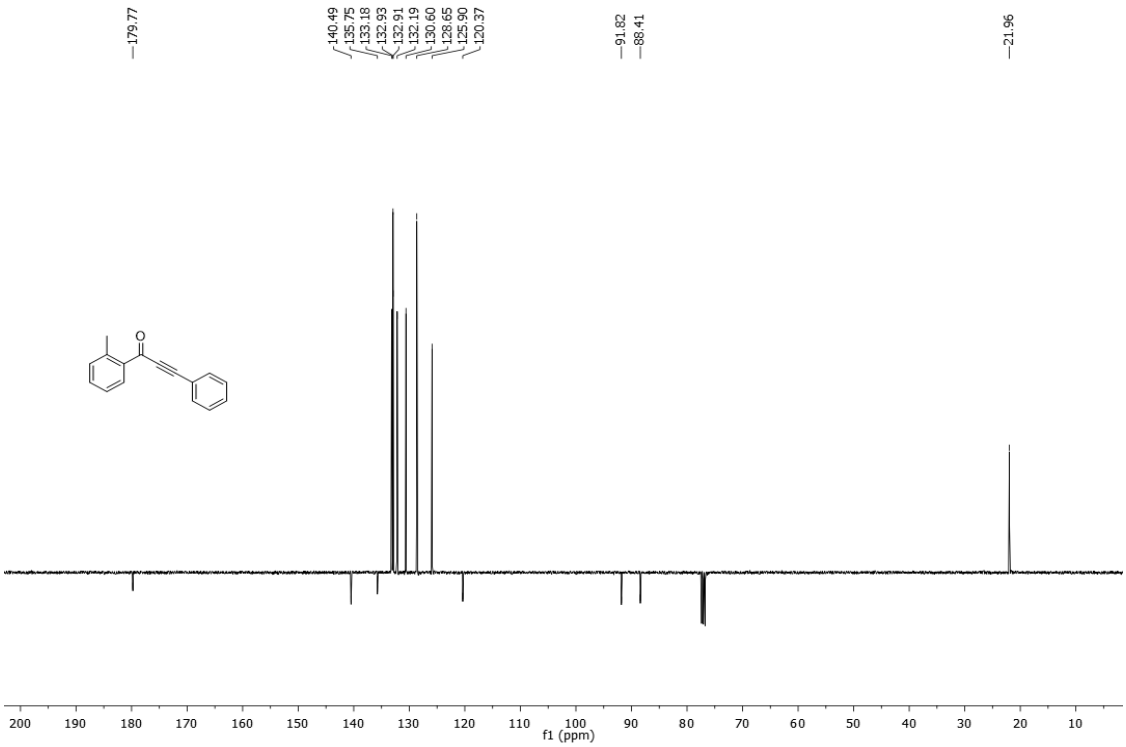
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	6.384	1469.190	95.857	42.8	50.8	0.25	
2	11.100	1965.760	93.010	57.2	49.2	0.32	
	Total	3434.950	188.868	100.0	100.0		

3-Phenyl-1-(o-tolyl)prop-2-yn-1-one.

^{1}H NMR (400 MHz, $CDCl_3$)



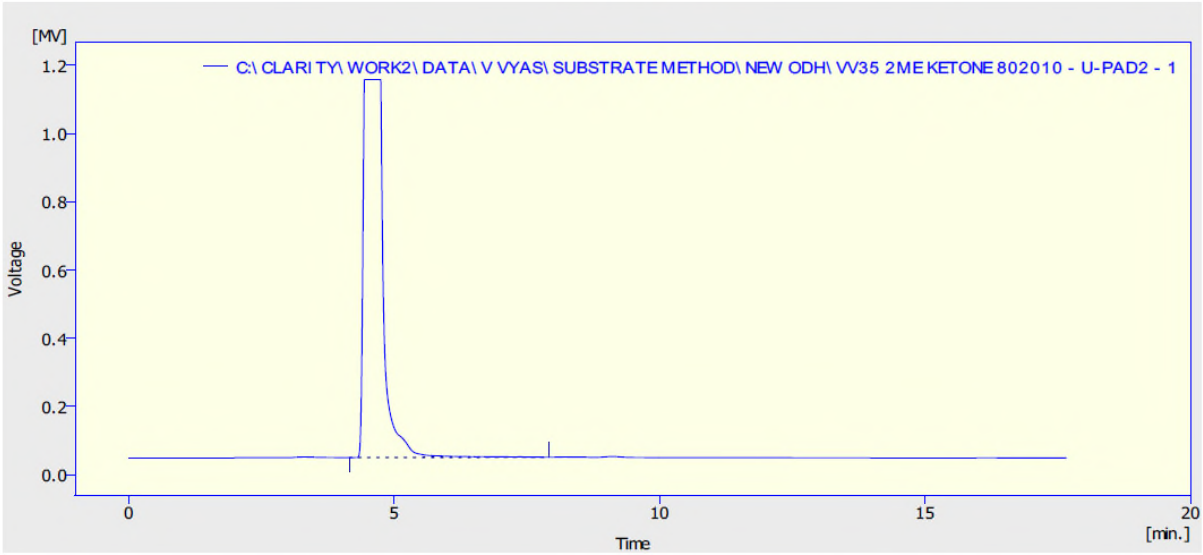
^{13}C NMR (101 MHz, $CDCl_3$)



Ketone HPLC of 3-phenyl-1-(o-tolyl)prop-2-yn-1-one.

09/09/2017 10:07 Chromatogram C:\CLARITY\WORK2\DATA\V VYAS\SUBSTRATE METHOD\NEW ODH\VV35 2ME KETONE 802010.PRM Page 1 of 1

Clarity - Chromatography SW
DataApex 2006
www.dataapex.com

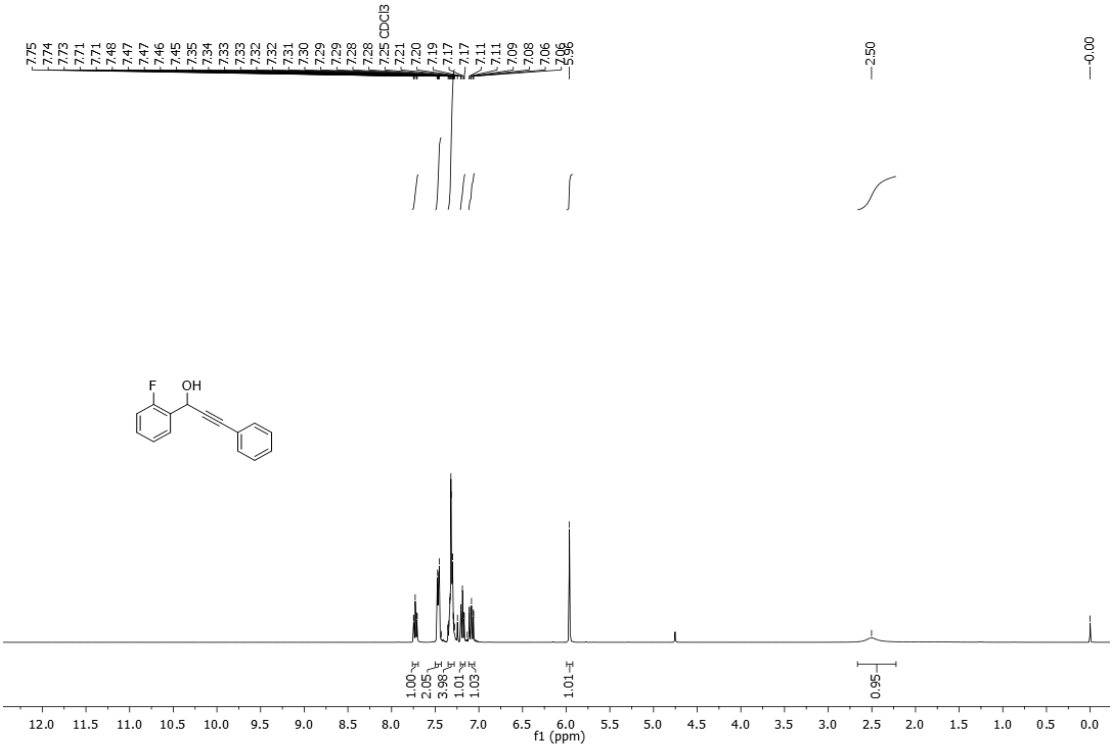


Result Table (Uncal - C:\CLARITY\WORK2\DATA\V VYAS\SUBSTRATE METHOD\NEW ODH\VV35 2ME KETONE 802010 - U-PAD2 - 1)

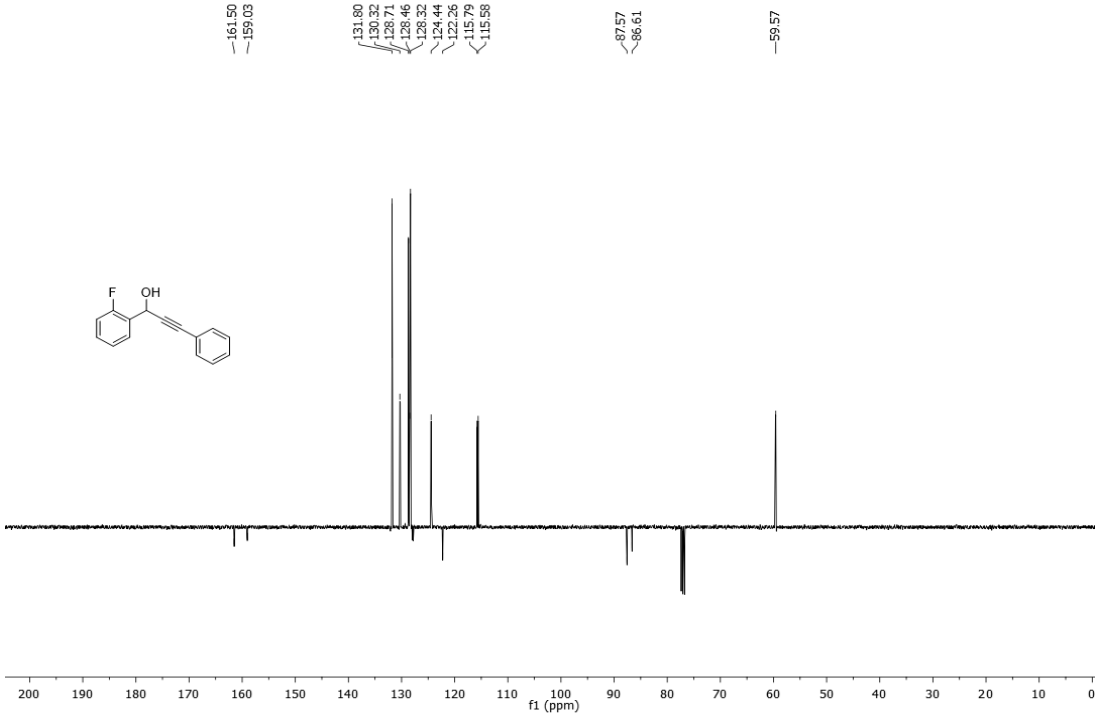
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	4.736	28888.930	1107.995	100.0	100.0	0.38	
	Total	28888.930	1107.995	100.0	100.0		

1-(2-Fluorophenyl)-3-phenylprop-2-yn-1-ol (12).

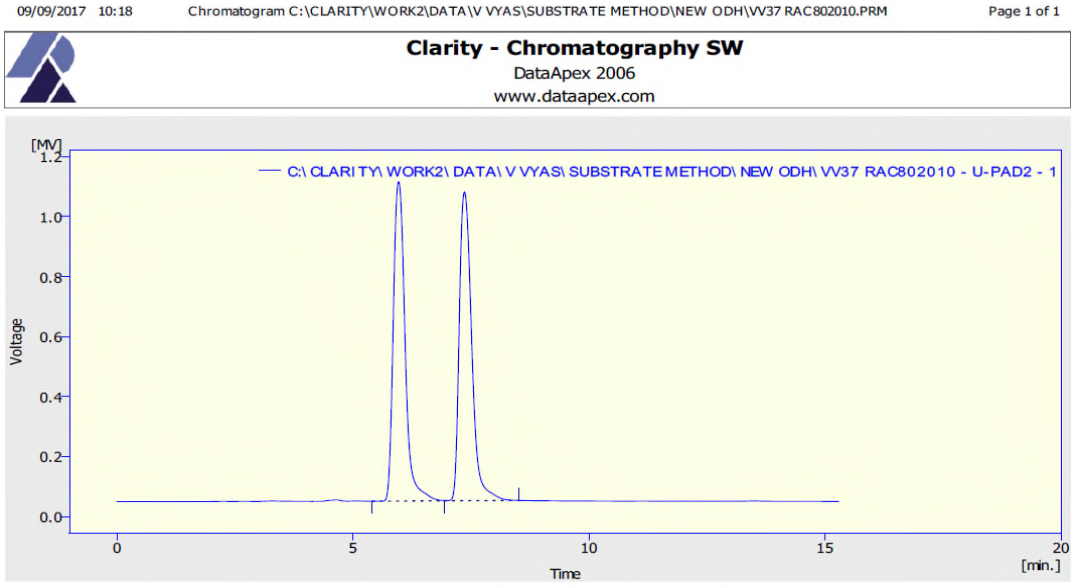
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



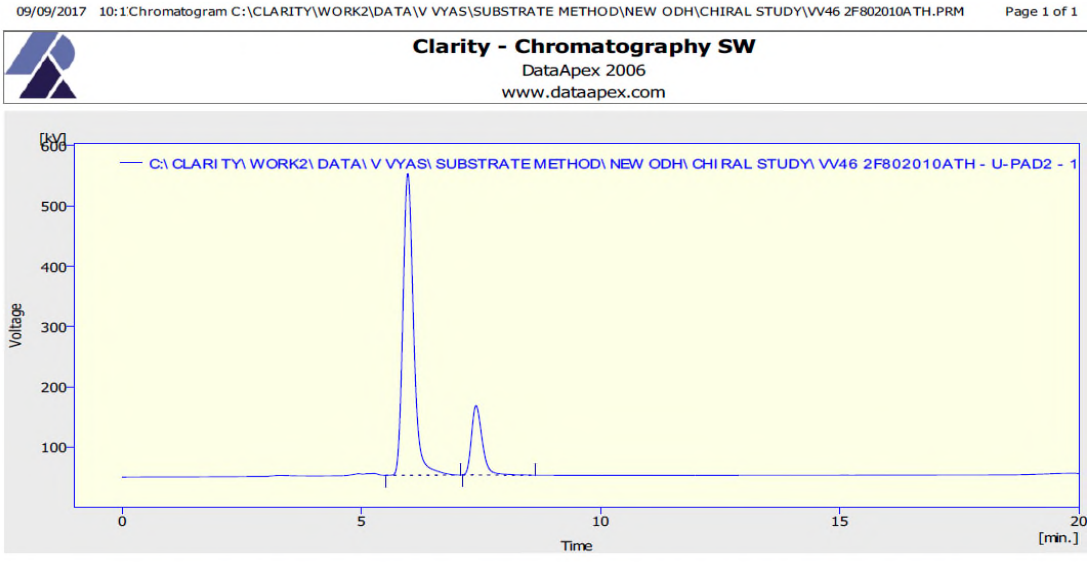
Racemic HPLC of 1-(2-fluorophenyl)-3-phenylprop-2-yn-1-ol (**12**).



Result Table (Uncal - C:\|CLARITY\|WORK2\|DATA\|V VYAS\|SUBSTRATE METHOD\|NEW ODH\|VV37 RAC802010 - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	5.968	18469.350	1065.115	49.5	50.9	0.26	
2	7.364	18852.687	1029.368	50.5	49.1	0.28	
	Total	37322.037	2094.482	100.0	100.0		

HPLC after ATH of 1-(2-fluorophenyl)-3-phenylprop-2-yn-1-ol (**12**) (100% conversion, 62.6% ee).

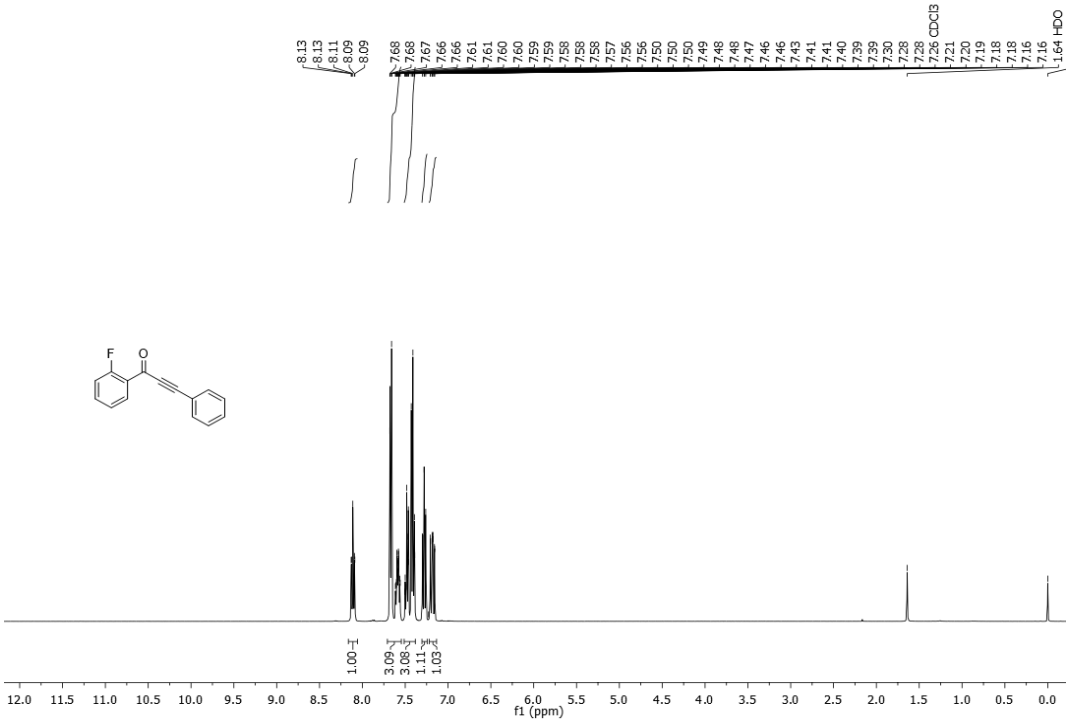


Result Table (Uncal - C:\|CLARITY\|WORK2\|DATA\|V VYAS\|SUBSTRATE METHOD\|NEW ODH\|CHIRAL STUDY\|VV46 2F802010ATH - U-PAD2 - 1)

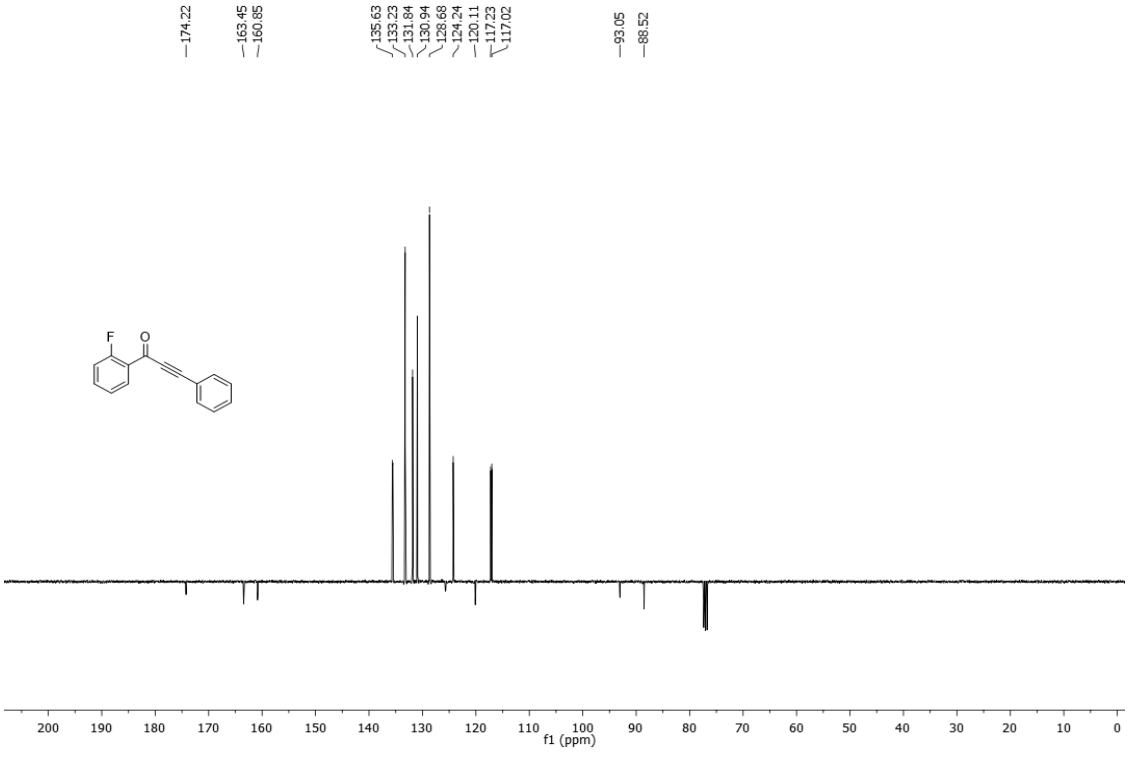
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	5.972	7763.708	500.239	81.3	81.3	0.23	
2	7.400	1789.165	115.052	18.7	18.7	0.24	
	Total	9552.873	615.291	100.0	100.0		

1-(2-Fluorophenyl)-3-phenylprop-2-yn-1-one.

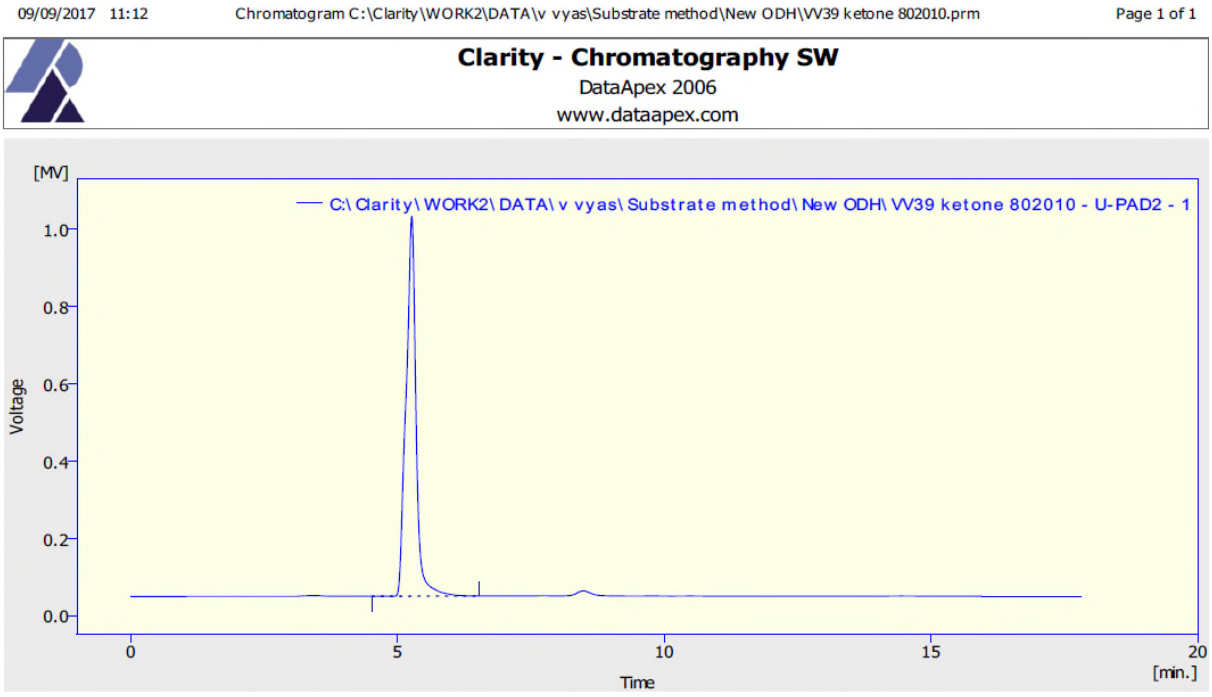
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



Ketone HPLC of 1-(2-fluorophenyl)-3-phenylprop-2-yn-1-one.

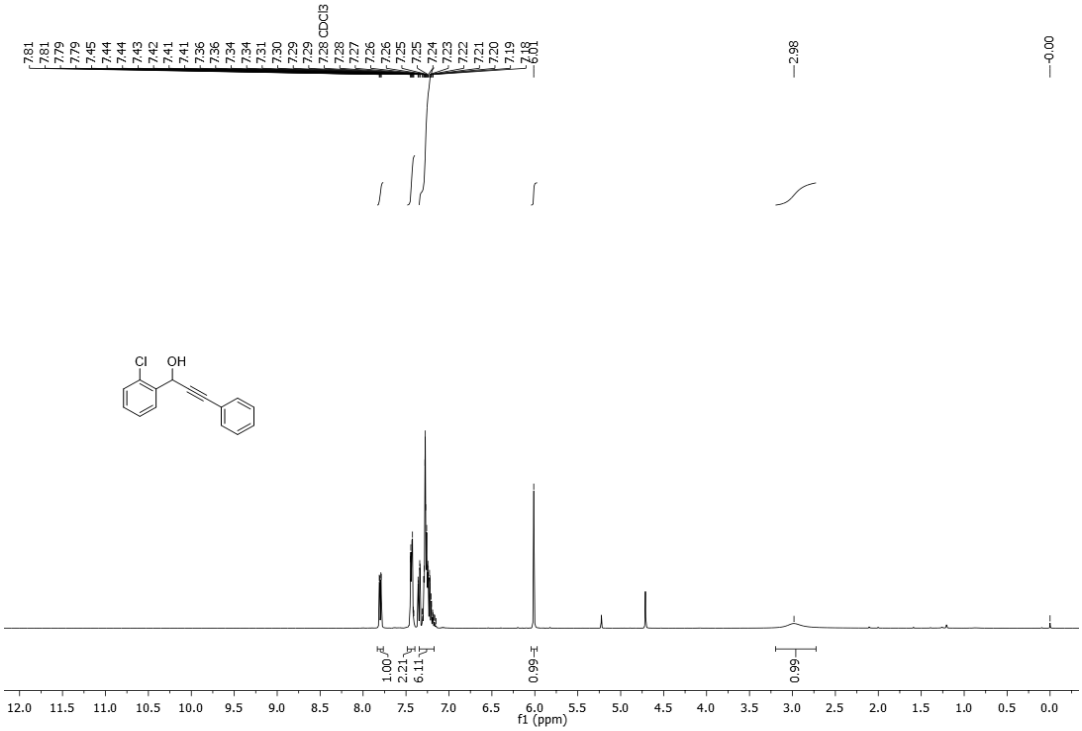


Result Table (Uncal - C:\Clarity\WORK2\DATA\v vyas\Substrate method\New ODH\VV39 ketone 802010 - U-PAD2 - 1)

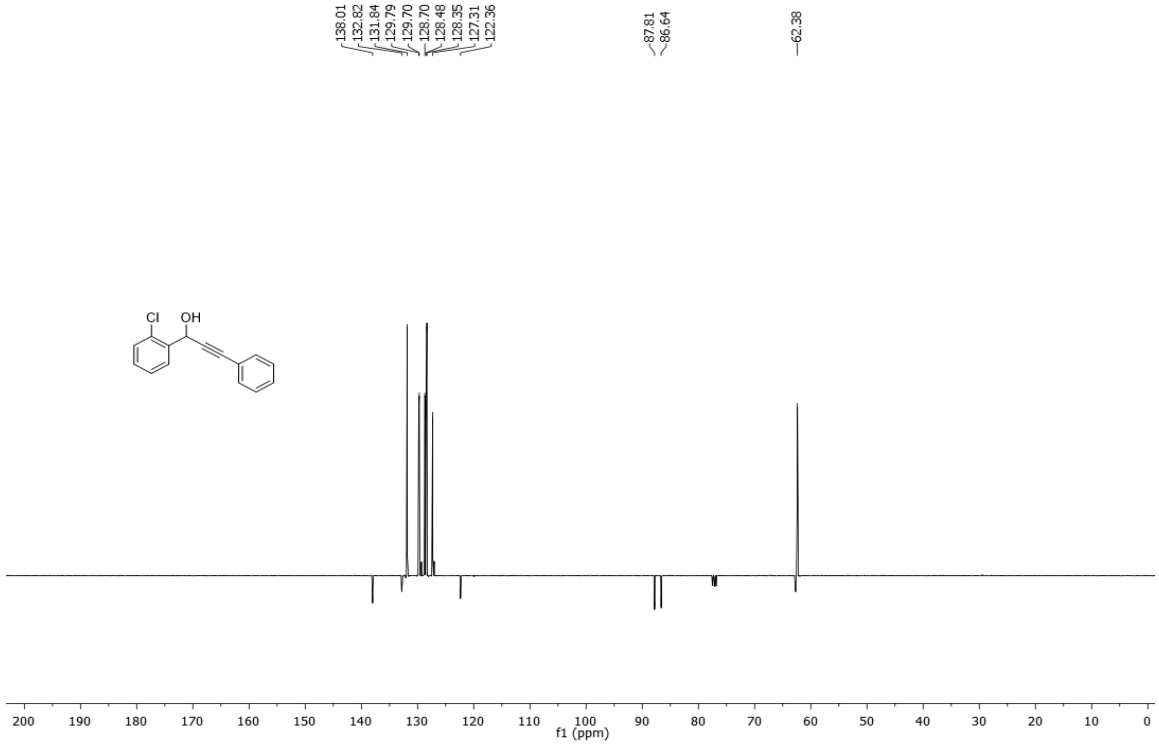
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	5.272	12810.849	982.811	100.0	100.0	0.20	
	Total	12810.849	982.811	100.0	100.0		

1-(2-Chlororophenyl)-3-phenylprop-2-yn-1-ol (13).

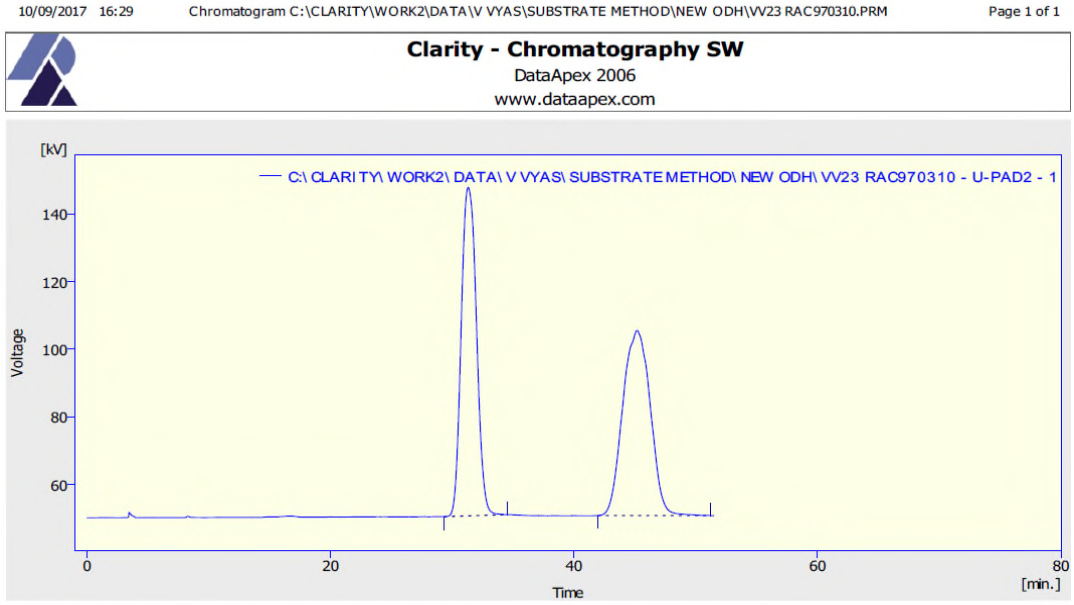
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



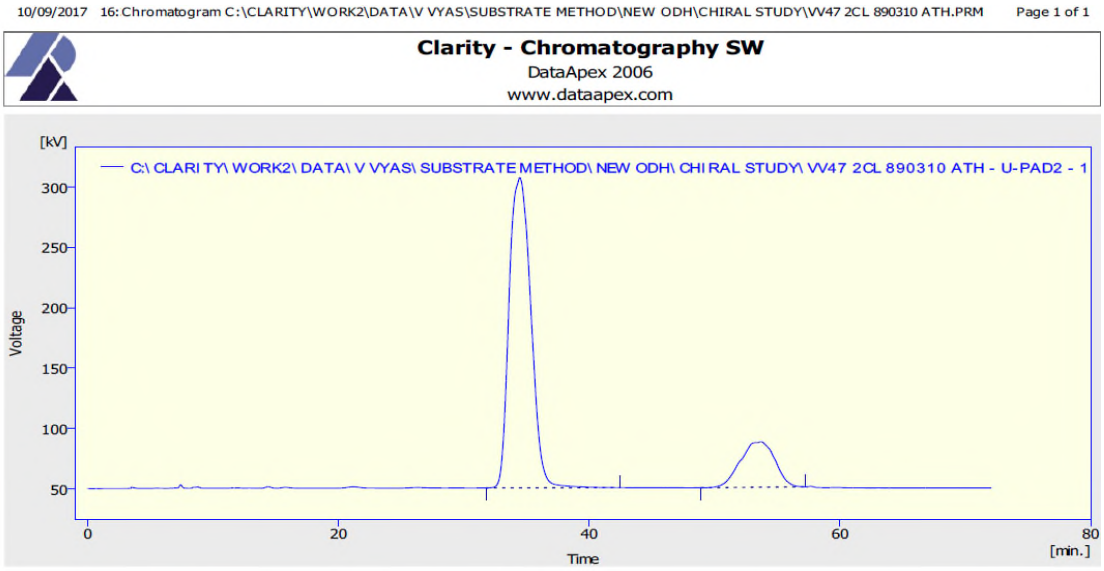
Racemic HPLC of 1-(2-chlororophenyl)-3-phenylprop-2-yn-1-ol (**13**).



Result Table (Uncal - C:\CLARITY\WORK2\DATA\V VYAS\SUBSTRATE METHOD\NEW ODH\VV23 RAC970310 - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	31.316	8450.227	97.141	49.5	64.0	1.39	
2	45.172	8604.438	54.743	50.5	36.0	2.56	
	Total	17054.665	151.884	100.0	100.0		

HPLC after ATH of 1-(2-chlororophenyl)-3-phenylprop-2-yn-1-ol (**13**) (100% conversion, 62.2% ee).

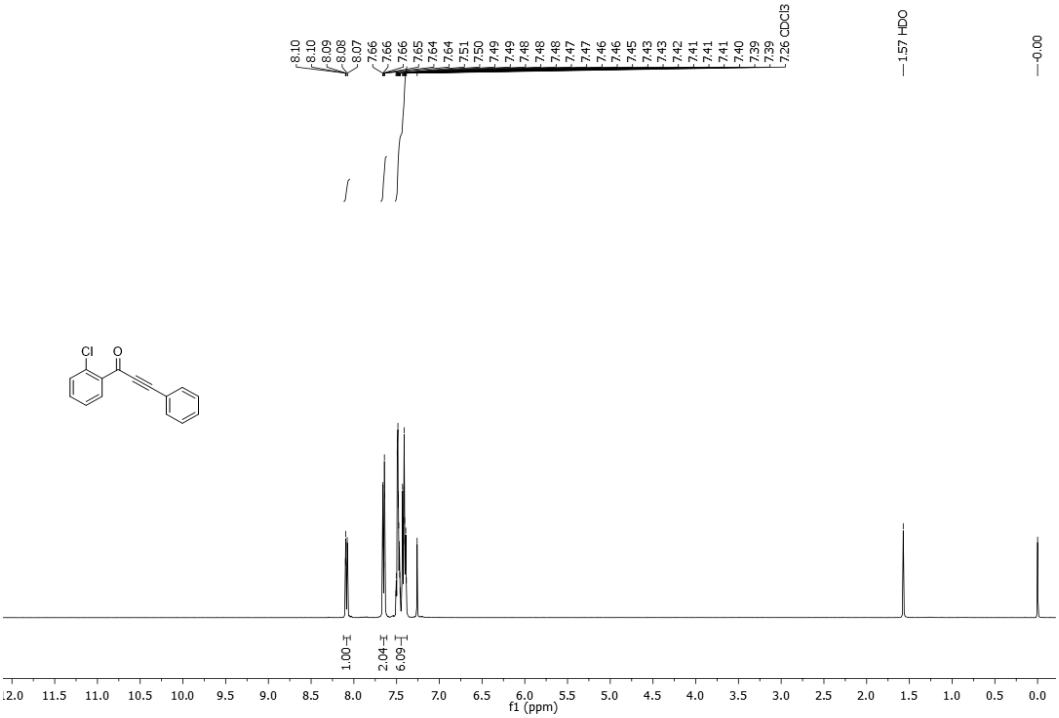


Result Table (Uncal - C:\CLARITY\WORK2\DATA\V VYAS\SUBSTRATE METHOD\NEW ODH\CHIRAL STUDY\VV47 2CL 890310 ATH - U-PAD2 - 1)

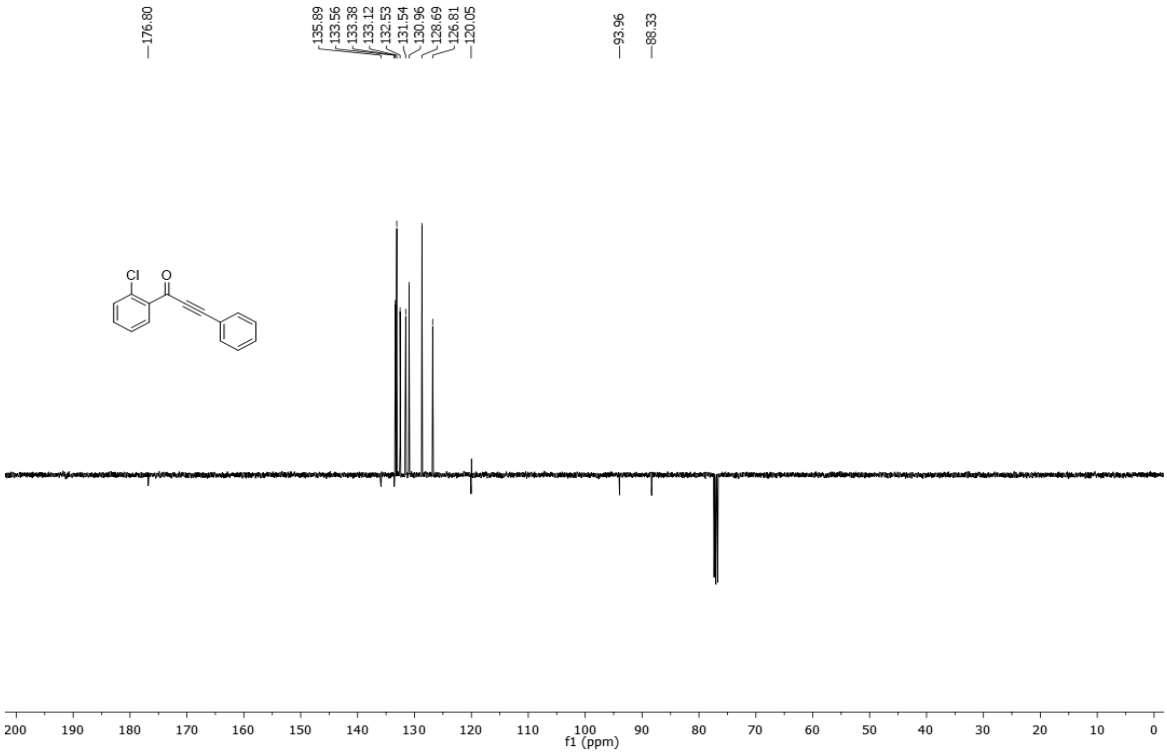
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	34.464	30975.782	256.967	81.1	87.2	1.94	
2	53.716	7224.882	37.725	18.9	12.8	3.17	
	Total	38200.664	294.692	100.0	100.0		

1-(2-Chlorophenyl)-3-phenylprop-2-yn-1-one.

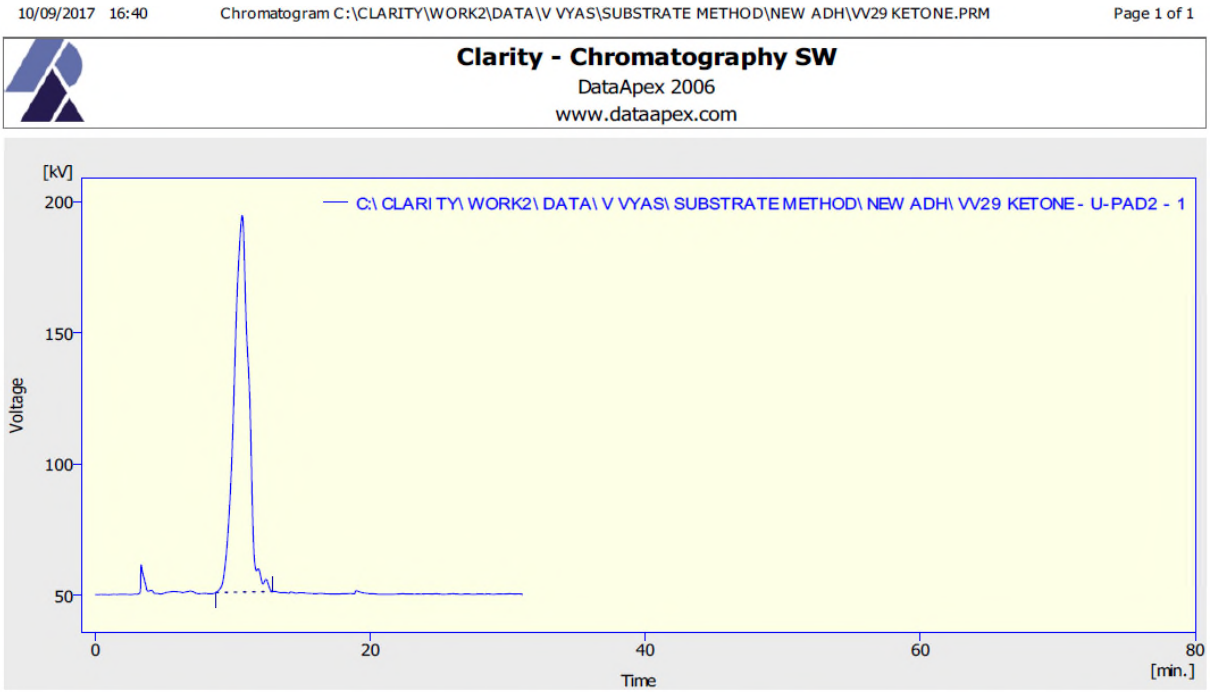
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



Ketone HPLC of 1-(2-chlorophenyl)-3-phenylprop-2-yn-1-one.

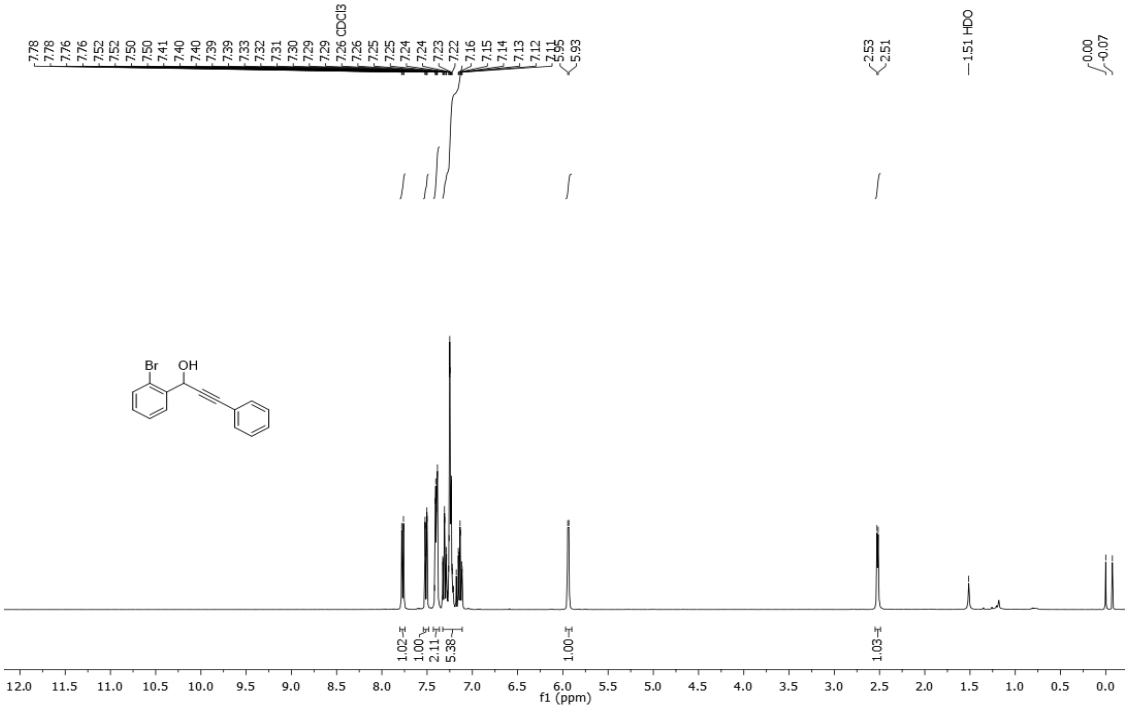


Result Table (Uncal - C:\|CLARITY\|WORK2\|DATA\|V VYAS\|SUBSTRATE METHOD\|NEW ADH\|VV29 KETONE - U-PAD2 - 1)

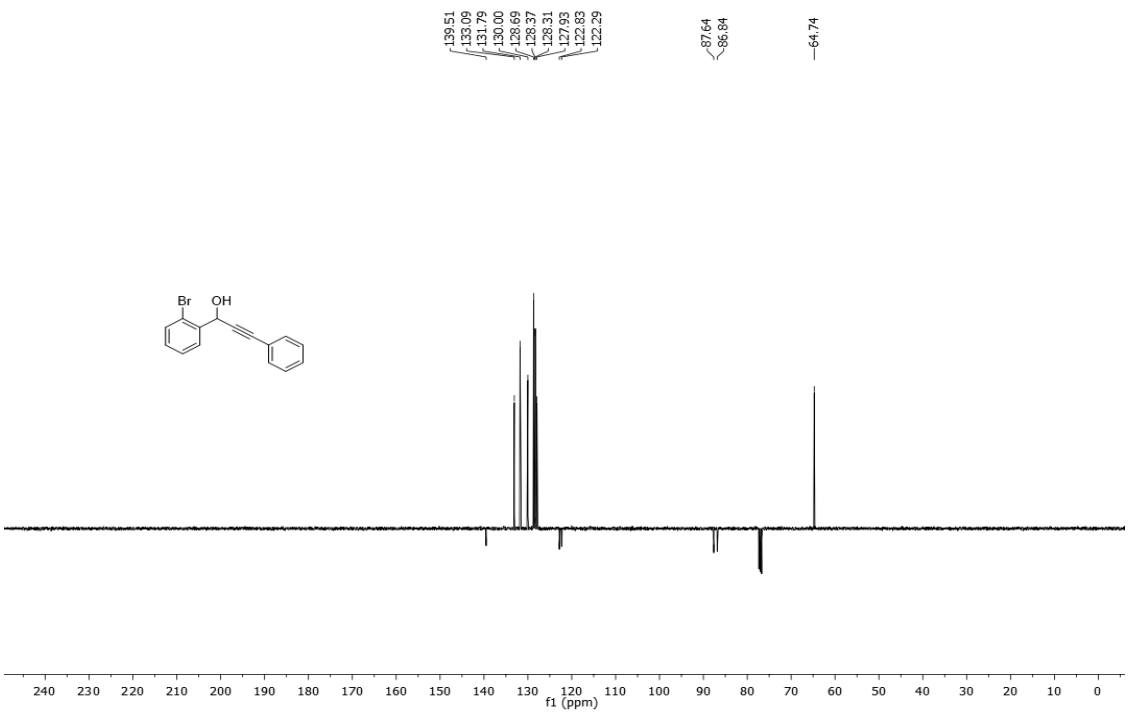
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	10.684	10477.930	143.377	100.0	100.0	1.18	
	Total	10477.930	143.377	100.0	100.0		

1-(2-Bromophenyl)-3-phenylprop-2-yn-1-ol (14).

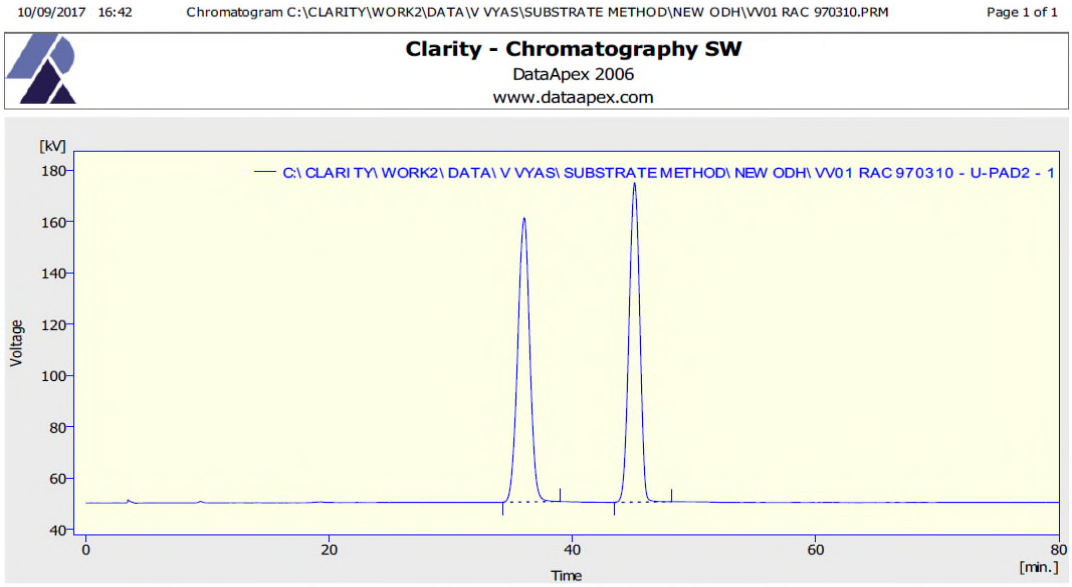
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



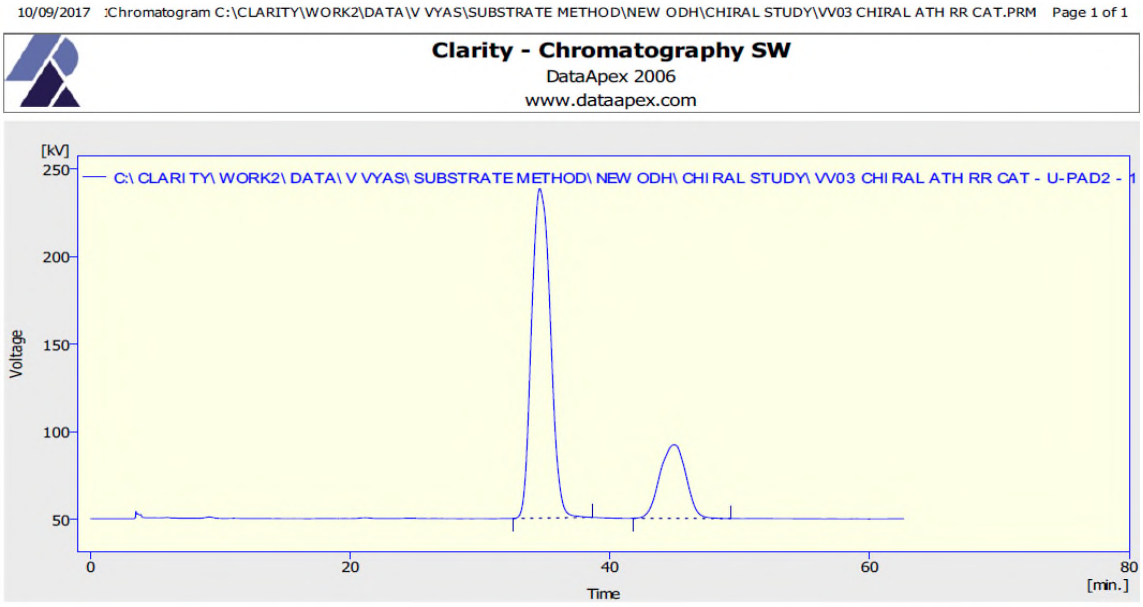
Racemic HPLC of 1-(2-bromophenyl)-3-phenylprop-2-yn-1-ol (**14**).



Result Table (Uncal - C:\|CLARITY\|WORK2\|DATA\|V VYAS\|SUBSTRATE METHOD\|NEW ODH\|VV01 RAC 970310 - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	36.044	7608.741	110.819	50.0	47.1	1.06	
2	45.112	7611.138	124.490	50.0	52.9	0.98	
	Total	15219.879	235.309	100.0	100.0		

HPLC after ATH of 1-(2-Bromophenyl)-3-phenylprop-2-yn-1-ol (**14**) (100% conversion, 52.8% ee).

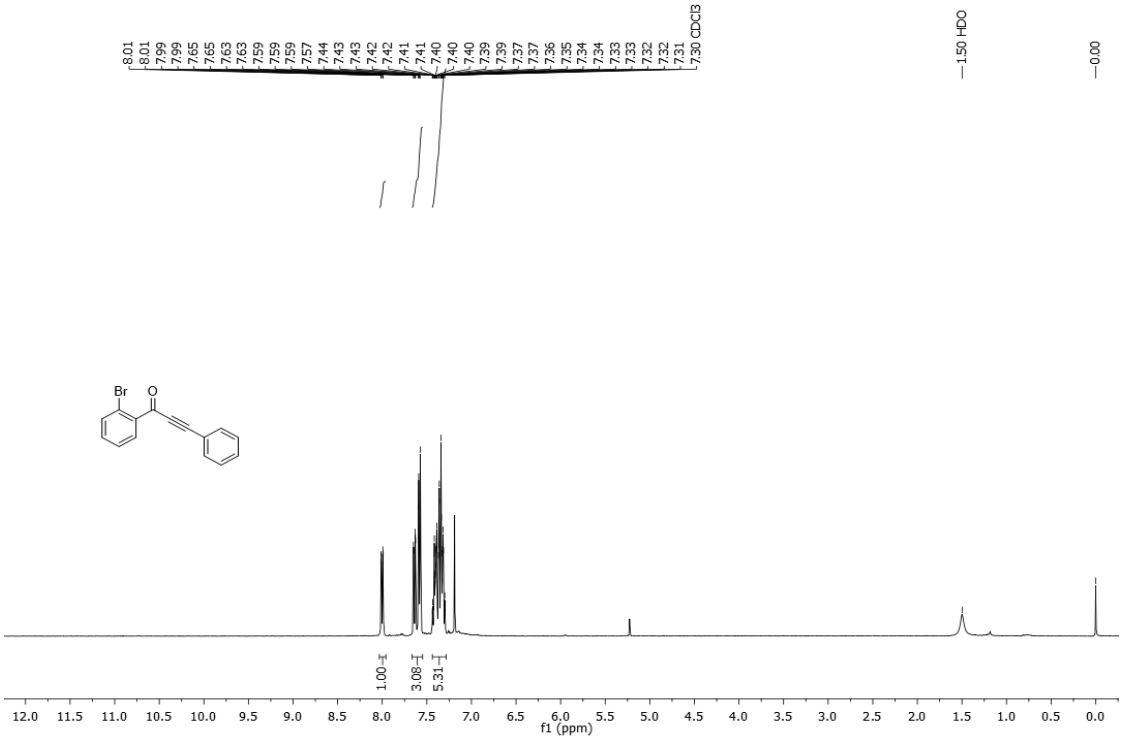


Result Table (Uncal - C:\|CLARITY\|WORK2\|DATA\|V VYAS\|SUBSTRATE METHOD\|NEW ODH\|CHIRAL STUDY\|VV03 CHIRAL ATH RR CAT - U-PAD2 - 1)

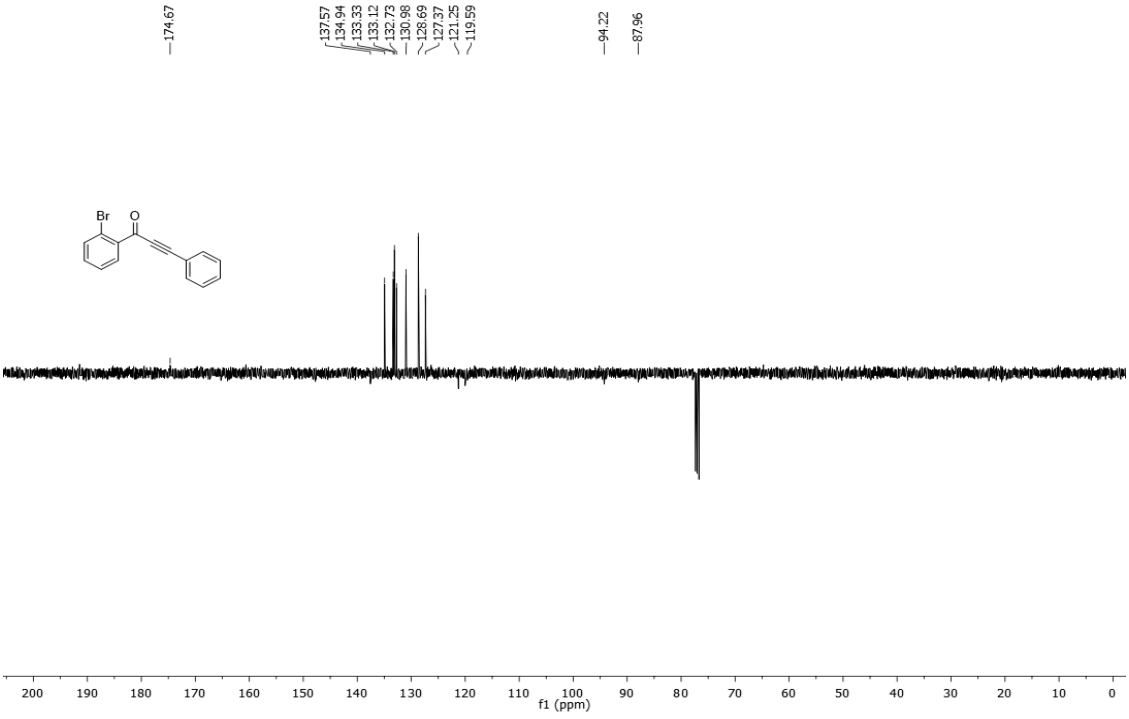
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	34.596	19027.778	188.148	76.4	81.7	1.64	
2	44.964	5874.544	42.077	23.6	18.3	2.27	
	Total	24902.322	230.225	100.0	100.0		

1-(2-Bromophenyl)-3-phenylprop-2-yn-1-one.

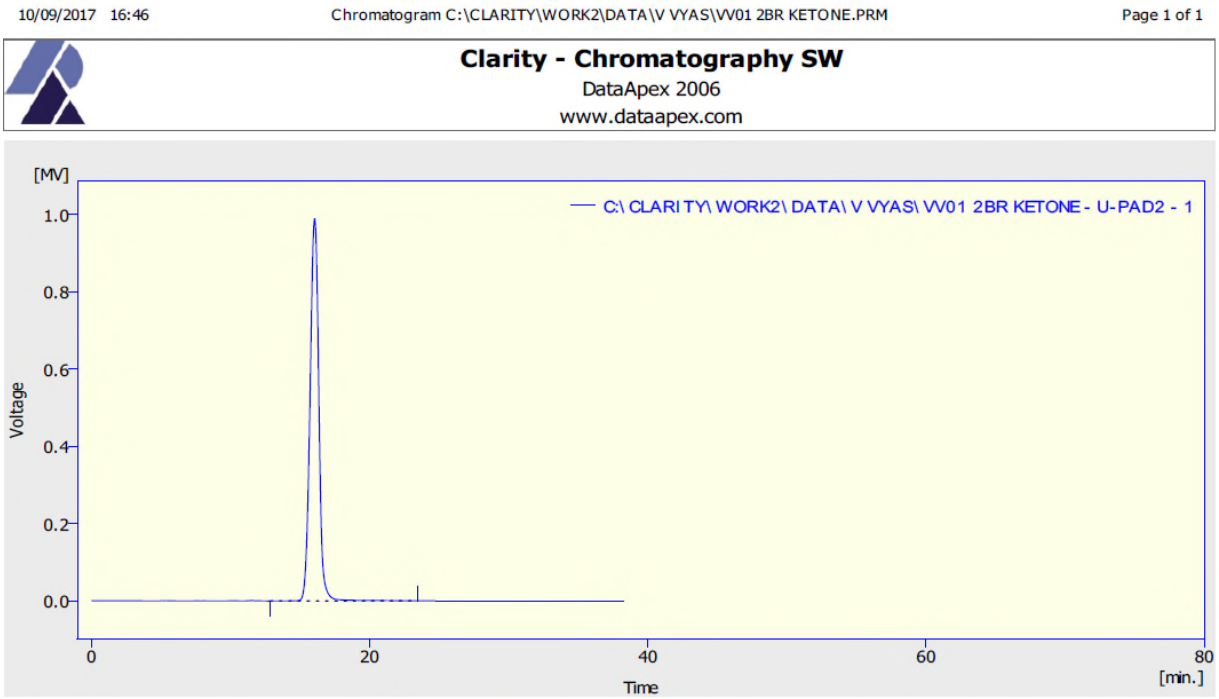
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



Ketone HPLC of 1-(2-bromophenyl)-3-phenylprop-2-yn-1-one.

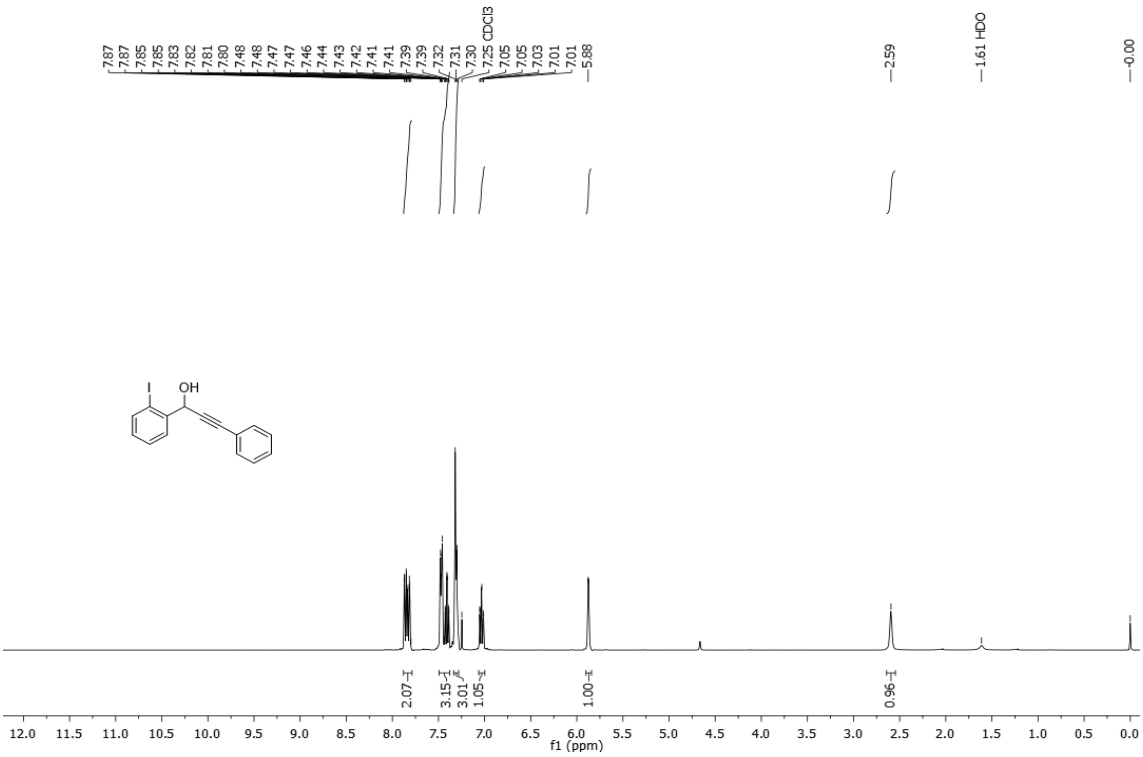


Result Table (Uncal - C:\CLARITY\WORK2\DATA\V VYAS\VV01 2BR KETONE - U-PAD2 - 1)

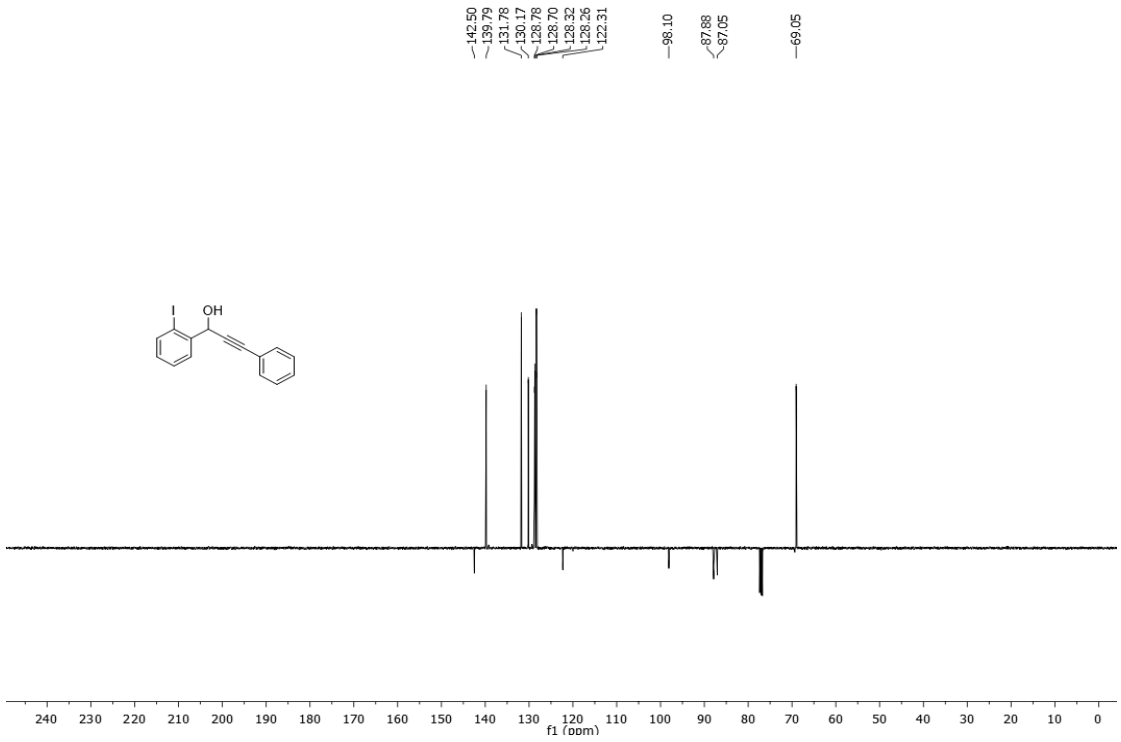
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	16.048	43373.991	989.601	100.0	100.0	0.67	
	Total	43373.991	989.601	100.0	100.0		

1-(2-Iodorophenyl)-3-phenylprop-2-yn-1-ol (15).

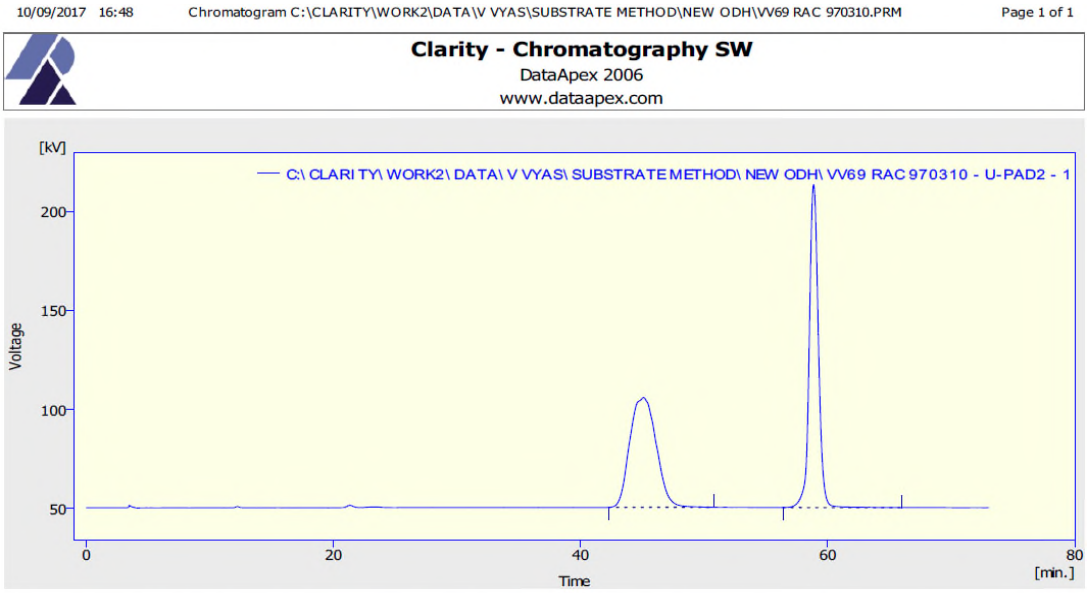
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



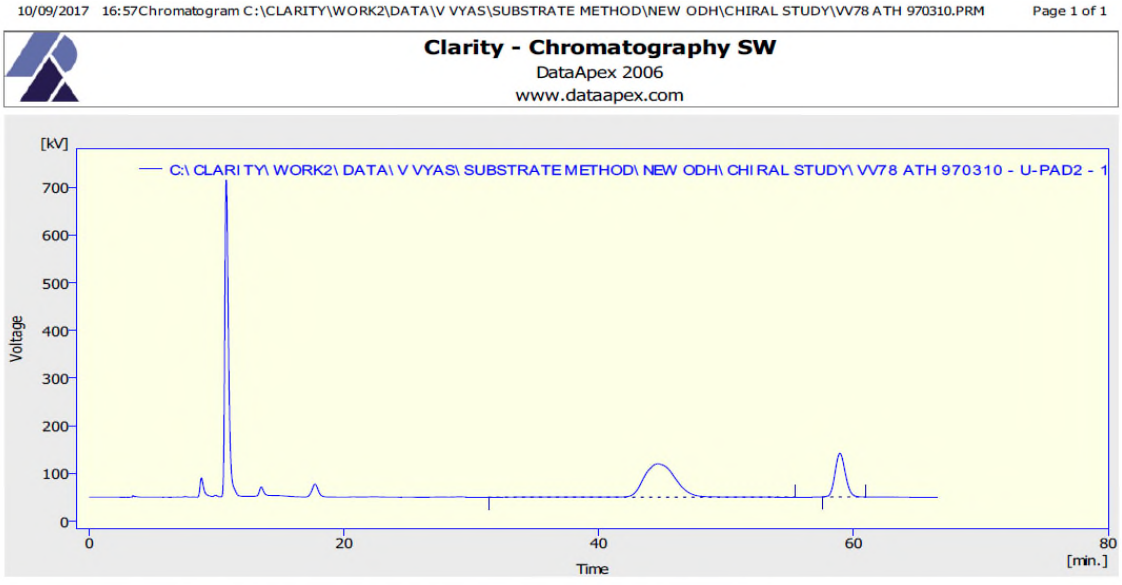
Racemic HPLC of 1-(2-iodorophenyl)-3-phenylprop-2-yn-1-ol (**15**).



Result Table (Uncal - C:\|CLARITY\|WORK2\|DATA\|V VYAS\|SUBSTRATE METHOD\|NEW ODH\|VV69 RAC 970310 - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	45.108	8256.824	55.494	49.7	25.4	2.43	
2	58.864	8361.999	163.251	50.3	74.6	0.77	
	Total	16618.823	218.745	100.0	100.0		

HPLC after ATH of 1-(2-Iodorophenyl)-3-phenylprop-2-yn-1-ol (**15**) (56% conversion, 40.0% ee).

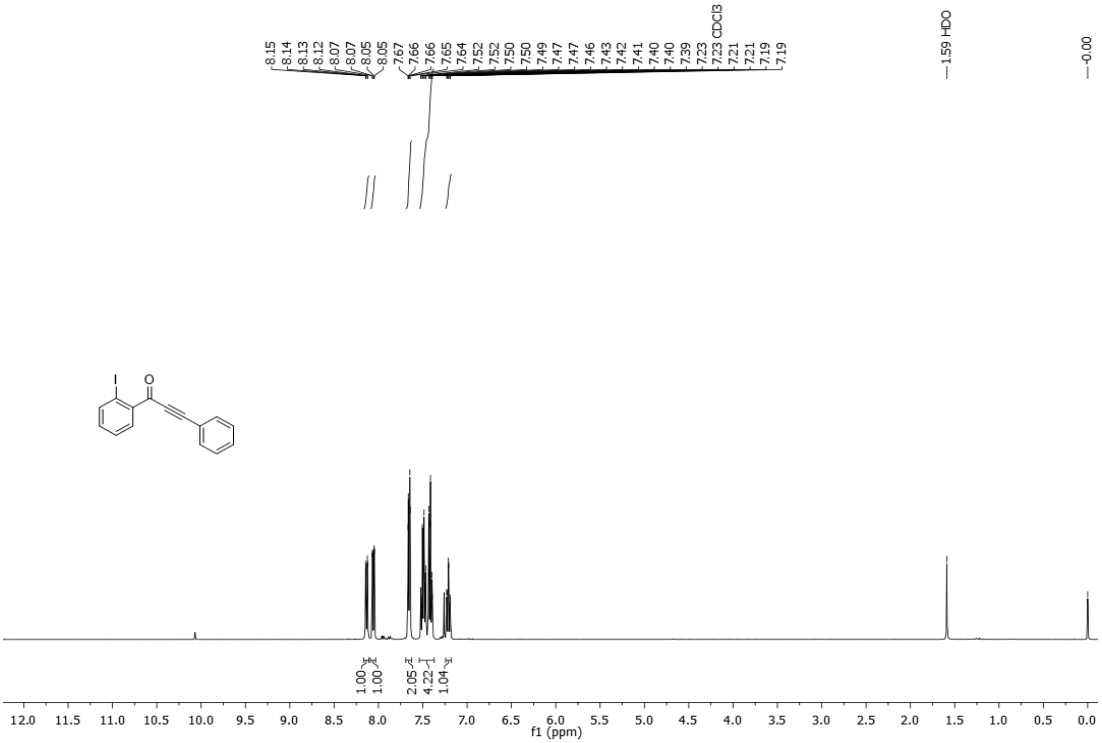


Result Table (Uncal - C:\|CLARITY\|WORK2\|DATA\|V VYAS\|SUBSTRATE METHOD\|NEW ODH\|CHIRAL STUDY\|VV78 ATH 970310 - U-PAD2 - 1)

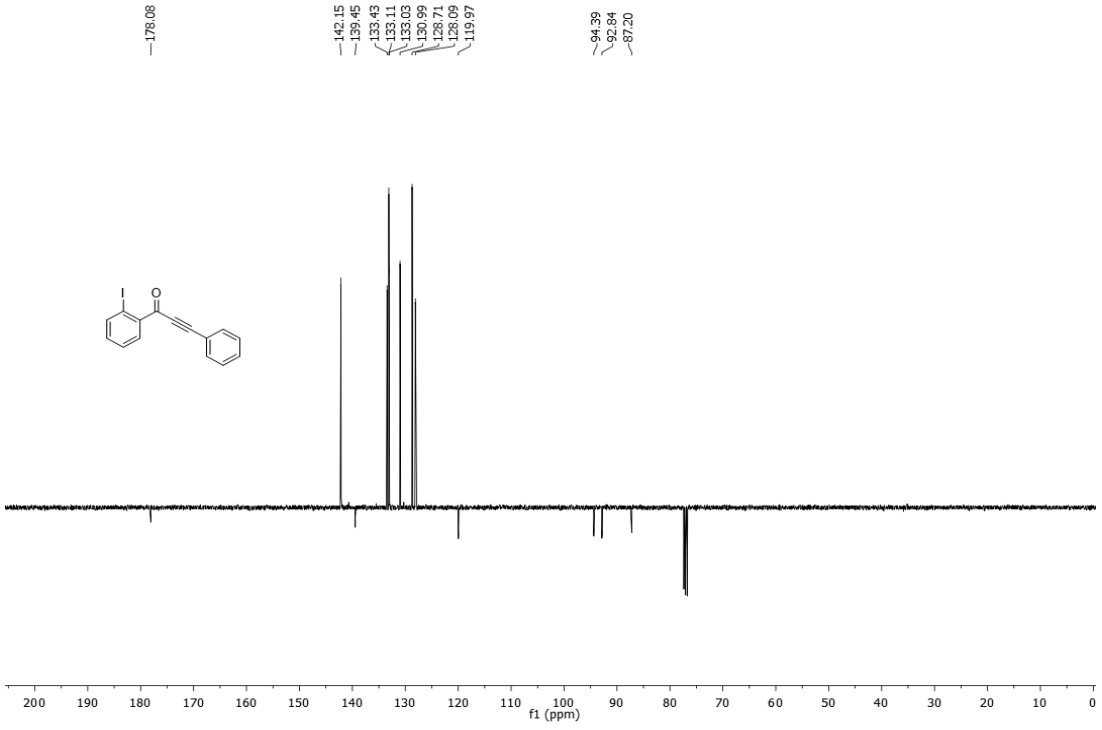
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	44.664	11928.145	70.043	70.0	43.4	2.71	
2	58.936	5118.389	91.300	30.0	56.6	0.88	
	Total	17046.534	161.343	100.0	100.0		

1-(2-Iodophenyl)-3-phenylprop-2-yn-1-one.

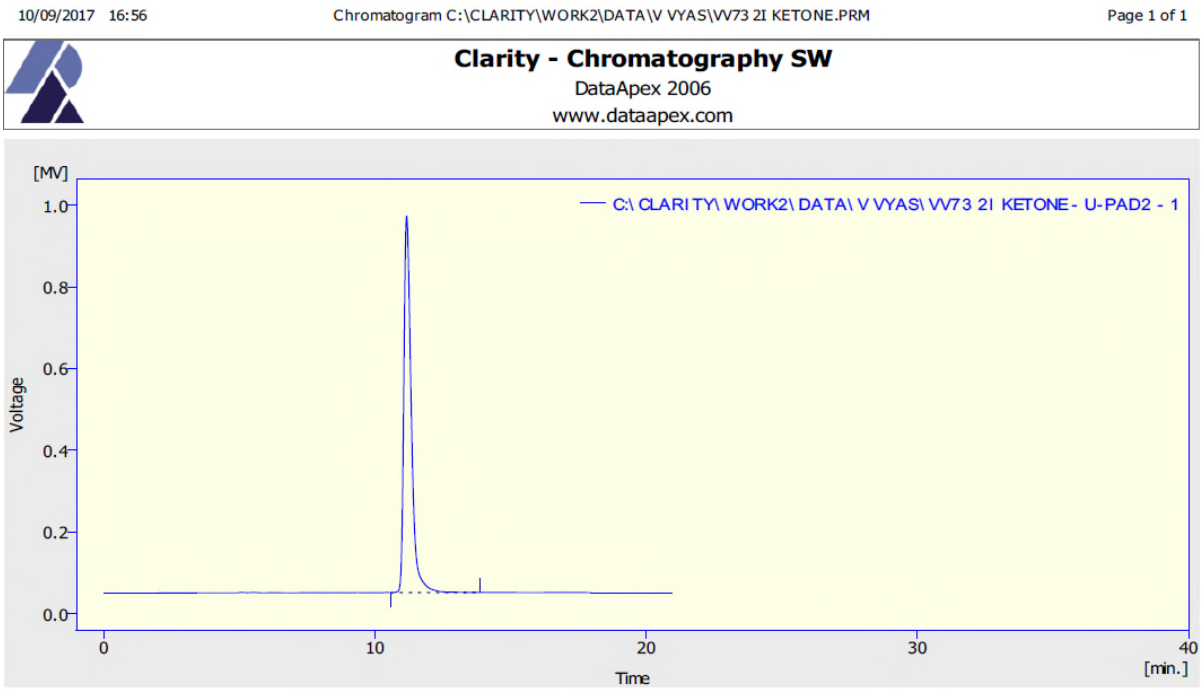
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



Ketone HPLC of 1-(2-iodophenyl)-3-phenylprop-2-yn-1-one.

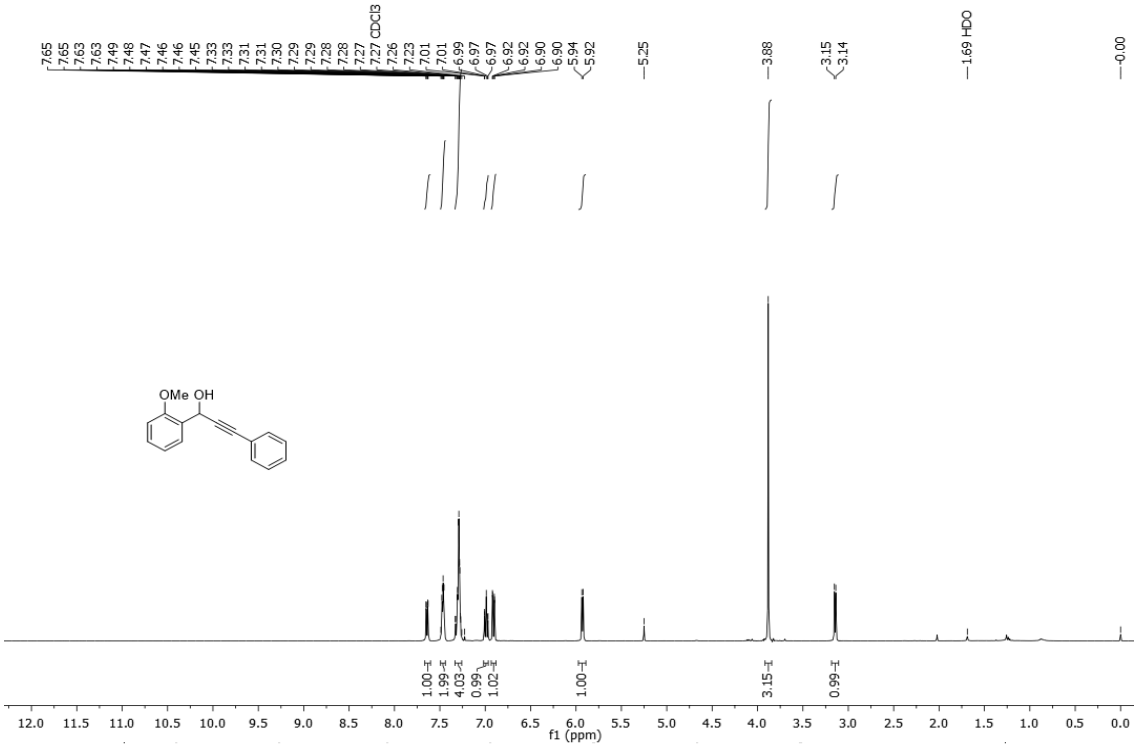


Result Table (Uncal - C:\CLARITY\WORK2\DATA\V VYAS\VV73 2I KETONE - U-PAD2 - 1)

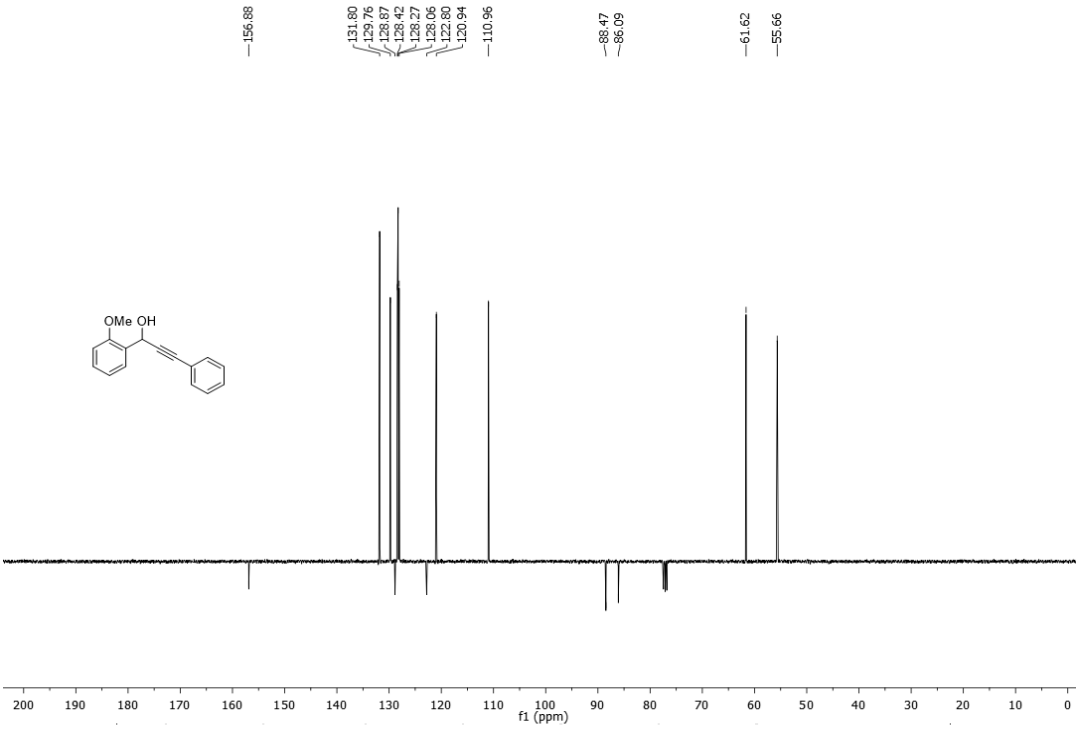
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	11.172	17543.343	921.884	100.0	100.0	0.28	
	Total	17543.343	921.884	100.0	100.0		

1-(2-Methoxyphenyl)-3-phenylprop-2-yn-1-ol (16).

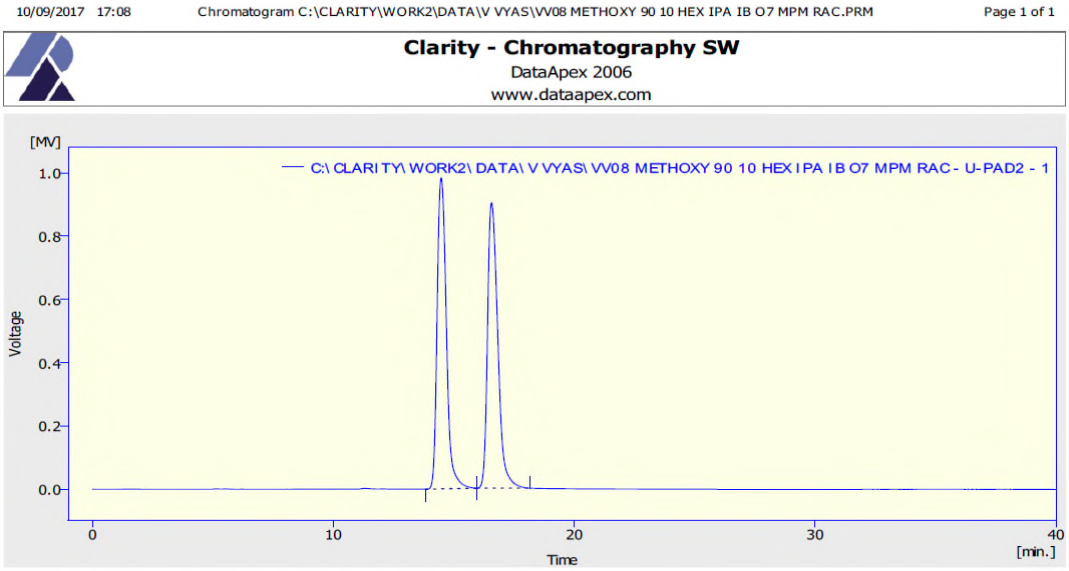
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



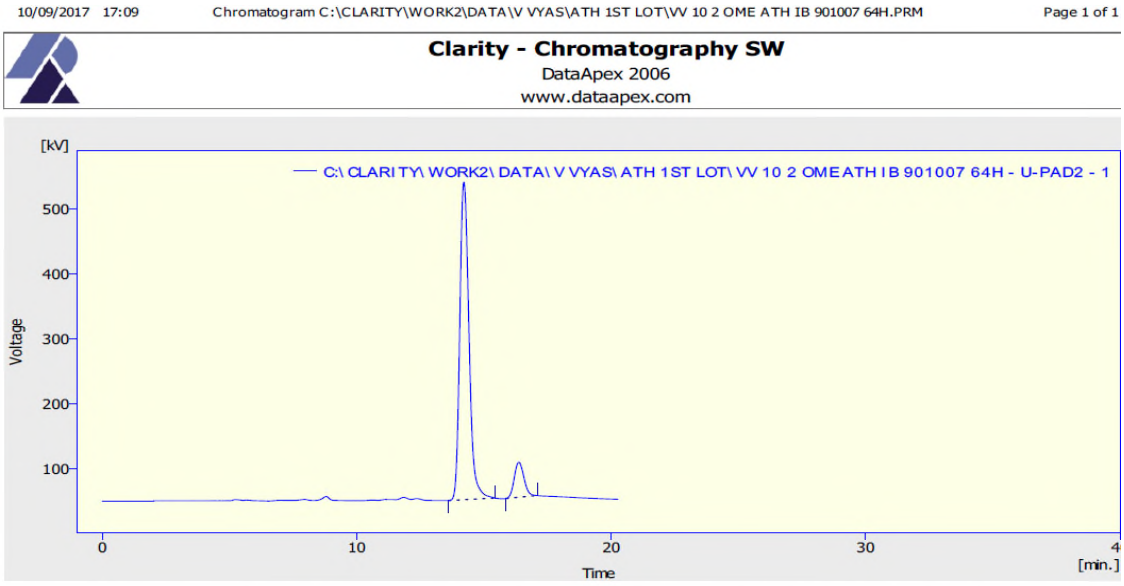
Racemic HPLC of 1-(2-methoxyphenyl)-3-phenylprop-2-yn-1-ol (**16**).



Result Table (Uncal - C:\|CLARITY\|WORK2\|DATA\|V VYAS\|VV08 METHOXY 90 10 HEX IPA IB O7 MPM RAC - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	14.480	26165.014	982.945	49.5	52.1	0.41	
2	16.568	26705.908	902.178	50.5	47.9	0.46	
	Total	52870.922	1885.123	100.0	100.0		

HPLC after ATH of 1-(2-methoxyphenyl)-3-phenylprop-2-yn-1-ol (**16**) (100% conversion, 79.2% ee).

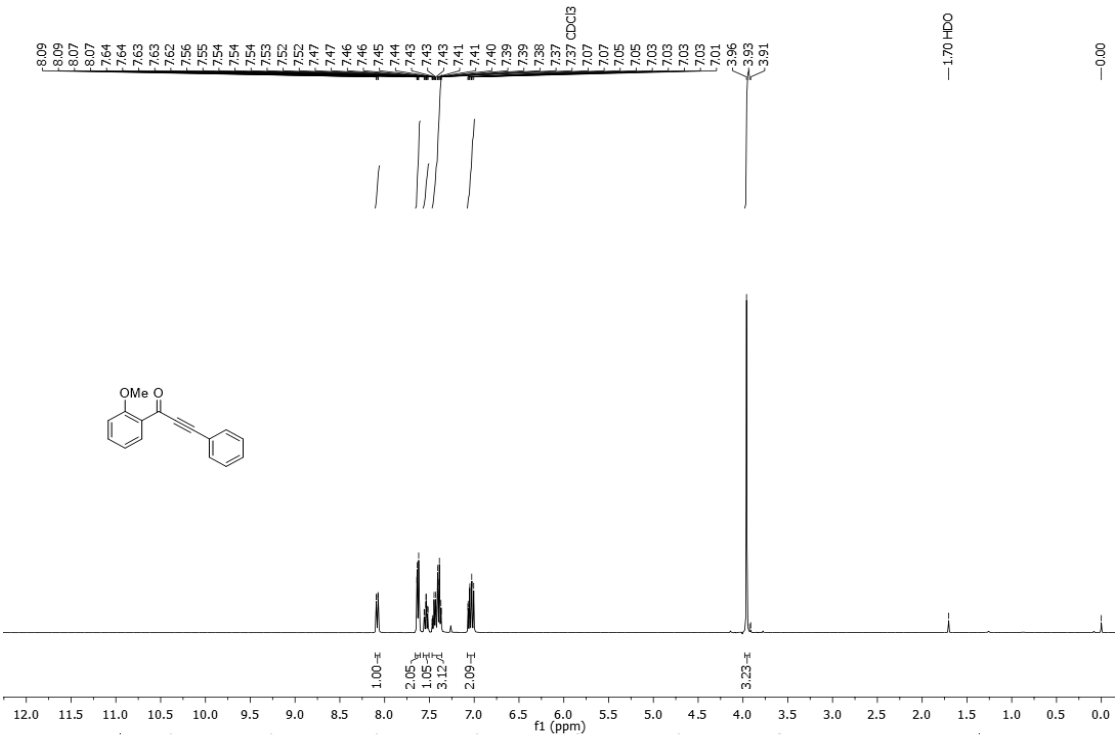


Result Table (Uncal - C:\|CLARITY\|WORK2\|DATA\|V VYAS\|ATH 1ST LOT\|VV 10 2 OME ATH IB 901007 64H - U-PAD2 - 1)

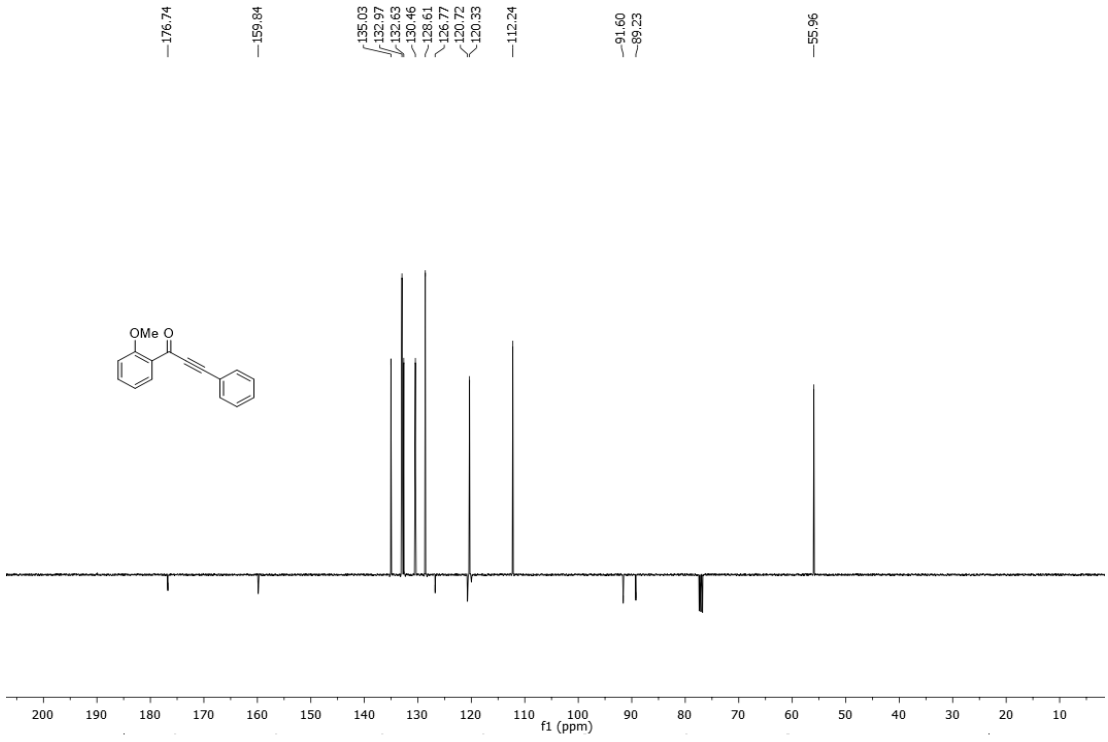
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	14.212	12321.665	488.636	89.6	90.1	0.38	
2	16.368	1425.875	53.792	10.4	9.9	0.42	
	Total	13747.539	542.427	100.0	100.0		

1-(2-Methoxyphenyl)-3-phenylprop-2-yn-1-one.

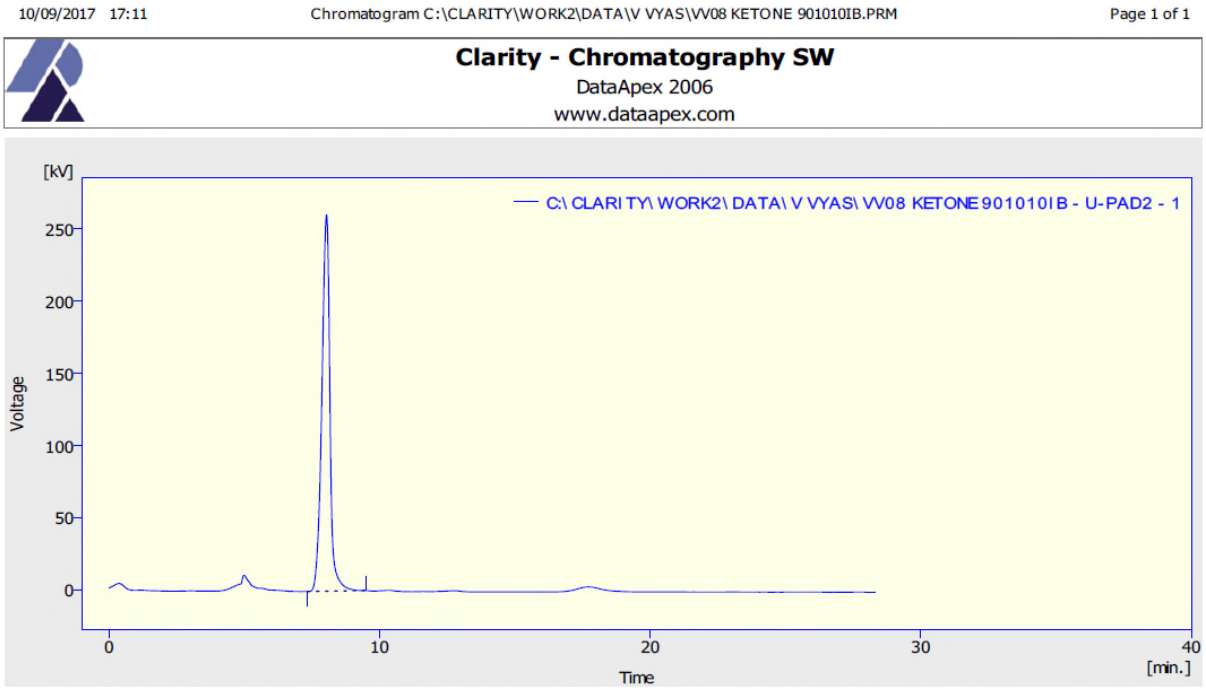
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



Ketone HPLC of 1-(2-methoxyphenyl)-3-phenylprop-2-yn-1-one.

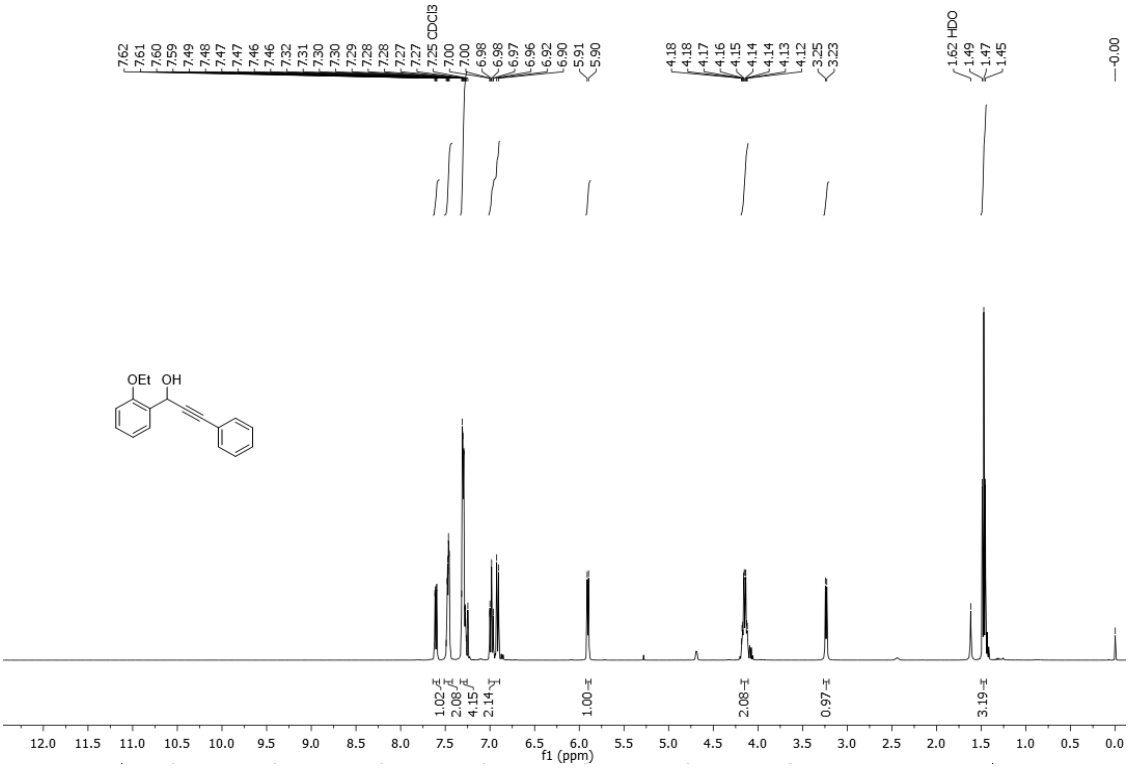


Result Table (Uncal - C:\|CLARITY\|WORK2\|DATA\|V VYAS\|VV08 KETONE 901010IB - U-PAD2 - 1)

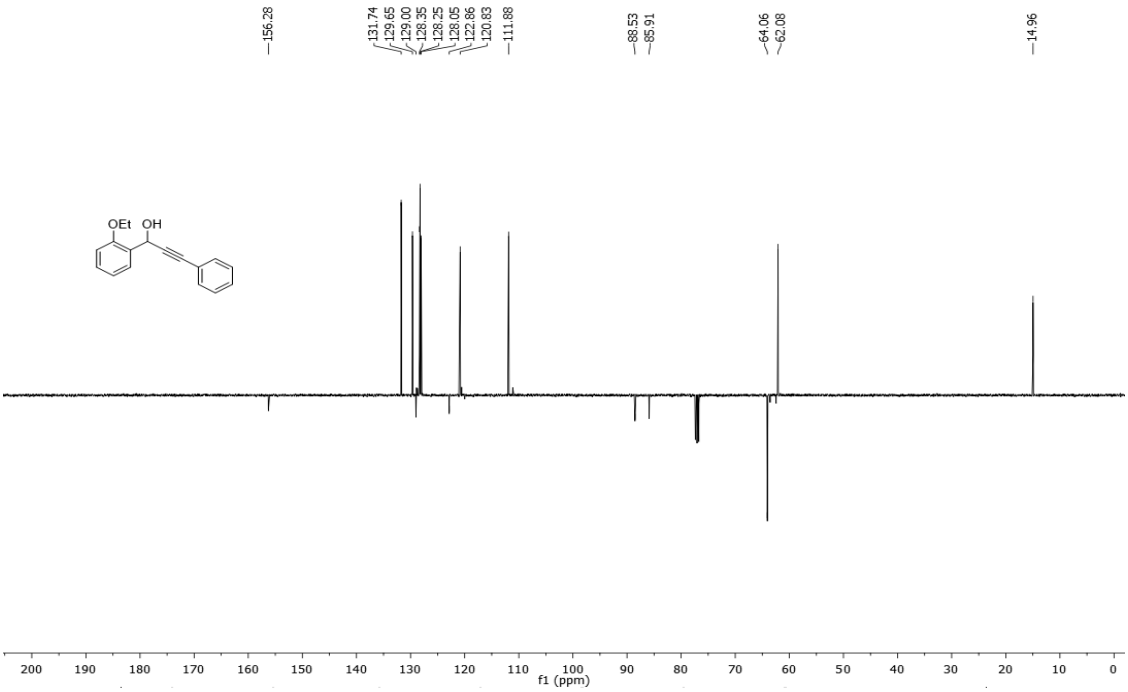
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	8.040	5438.054	260.818	100.0	100.0	0.31	
	Total	5438.054	260.818	100.0	100.0		

1-(2-Ethoxyphenyl)-3-phenylprop-2-yn-1-ol (17).

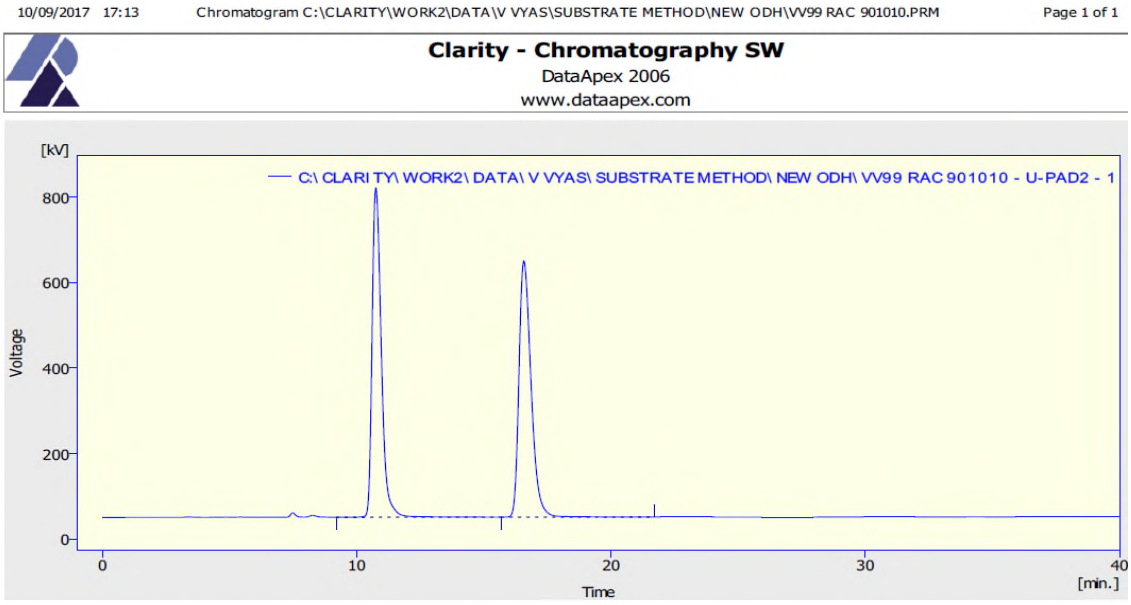
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



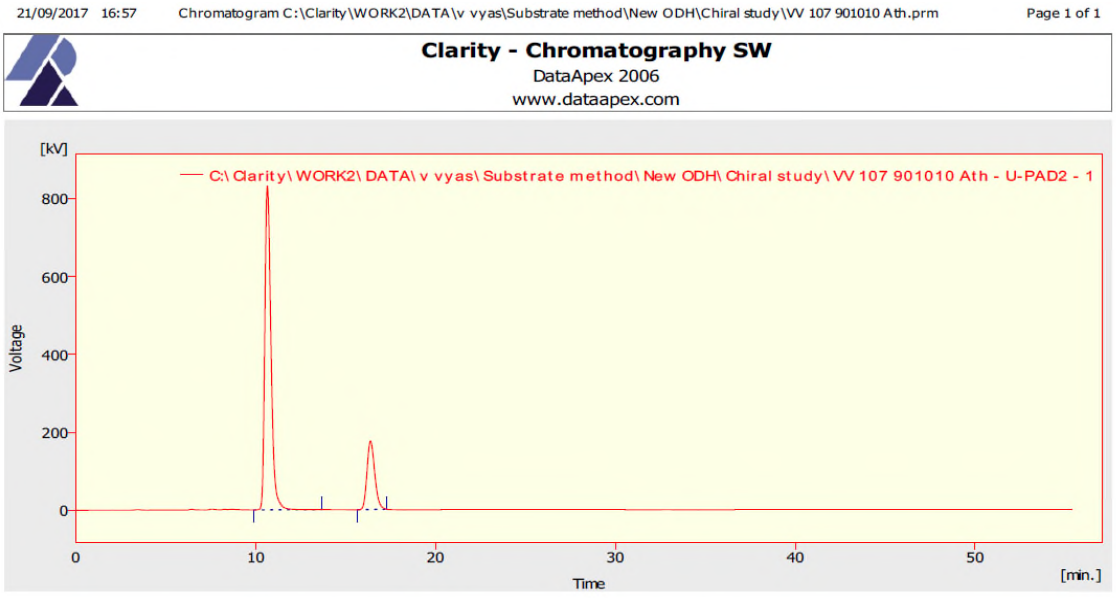
Racemic HPLC of 1-(2-ethoxyphenyl)-3-phenylprop-2-yn-1-ol (**17**).



Result Table (Uncal - C:\|CLARITY\|WORK2\|DATA\|V VYAS\|SUBSTRATE METHOD\|NEW ODH\|VV99 RAC 901010 - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	10.752	19364.557	770.526	49.4	56.2	0.38	
2	16.572	19813.123	599.502	50.6	43.8	0.51	
	Total	39177.681	1370.028	100.0	100.0		

HPLC after ATH of 1-(2-ethoxyphenyl)-3-phenylprop-2-yn-1-ol (**17**) (100% conversion, 58.4% ee).

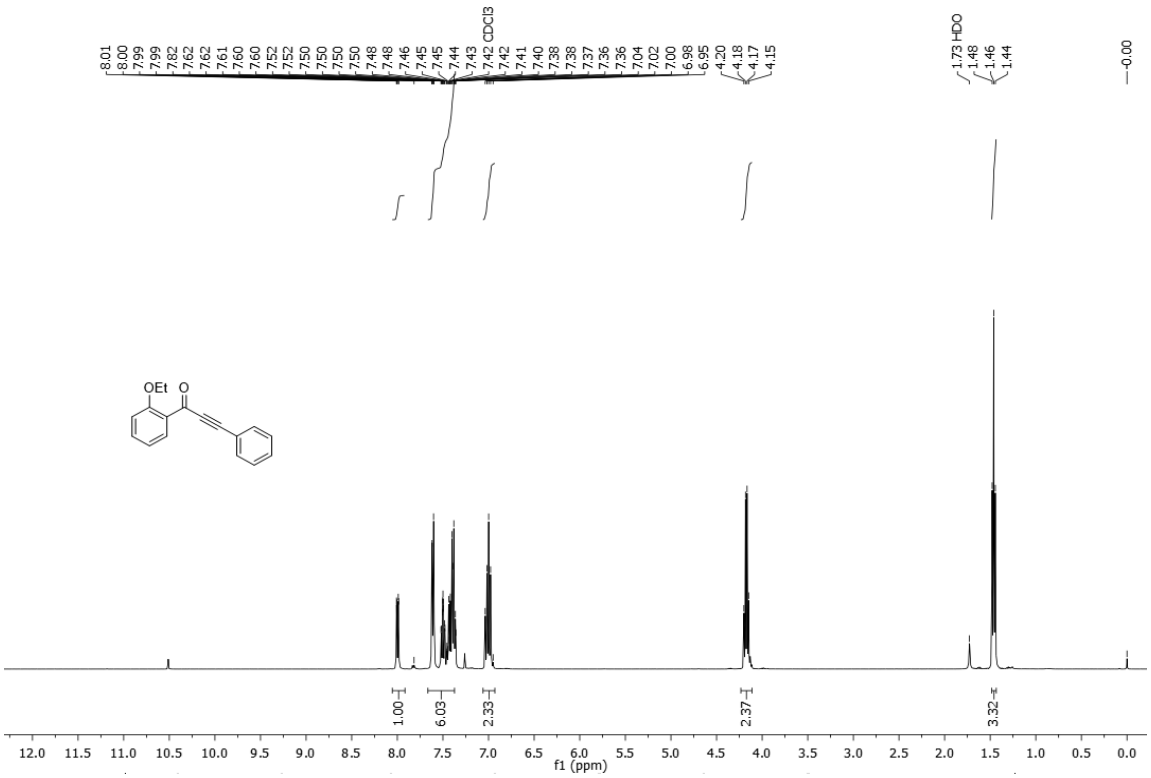


Result Table (Uncal - C:\|Clarity\|WORK2\|DATA\|v vyas\|Substrate method\|New ODH\|Chiral study\|VV 107 901010 Ath - U-PAD2 - 1)

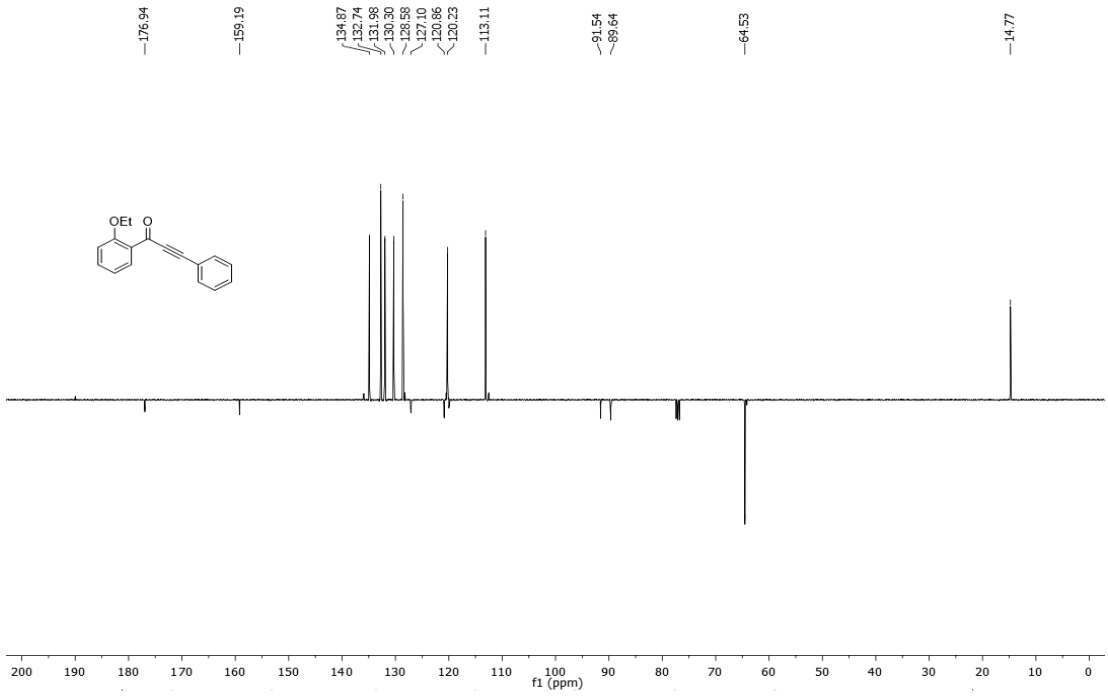
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	10.656	19936.617	830.695	79.2	82.6	0.36	
2	16.392	5225.875	175.582	20.8	17.4	0.46	
	Total	25162.492	1006.276	100.0	100.0		

1-(2-Ethoxyphenyl)-3-phenylprop-2-yn-1-one.

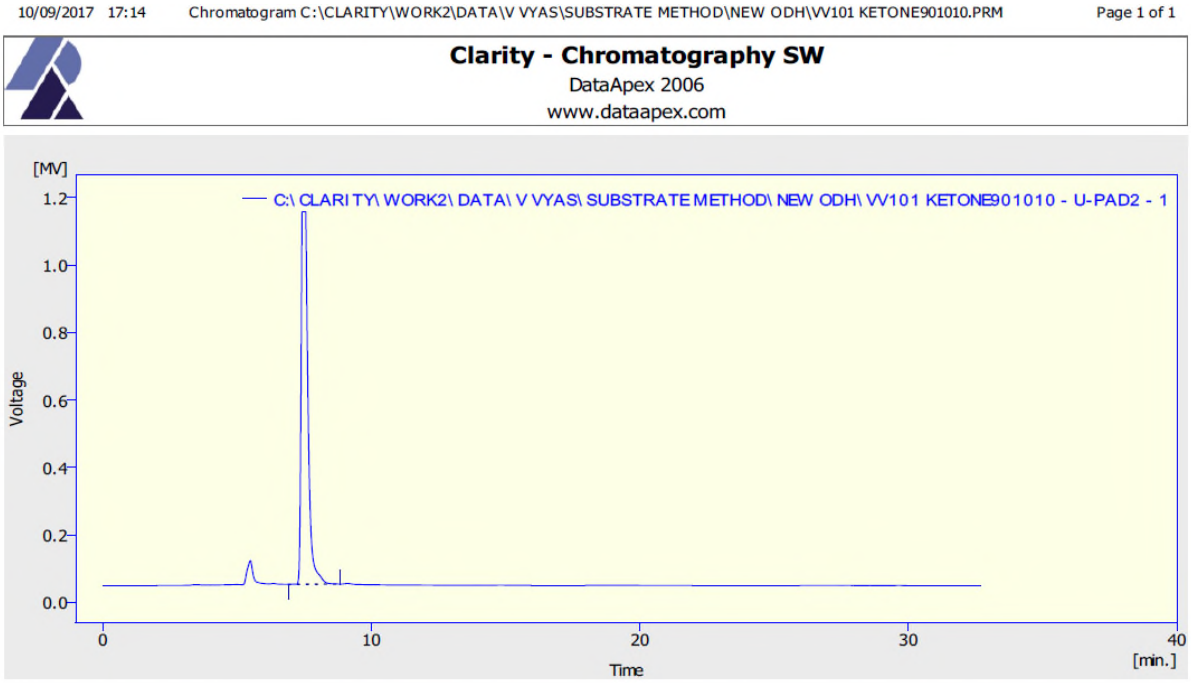
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



Ketone HPLC of 1-(2-ethoxyphenyl)-3-phenylprop-2-yn-1-one.

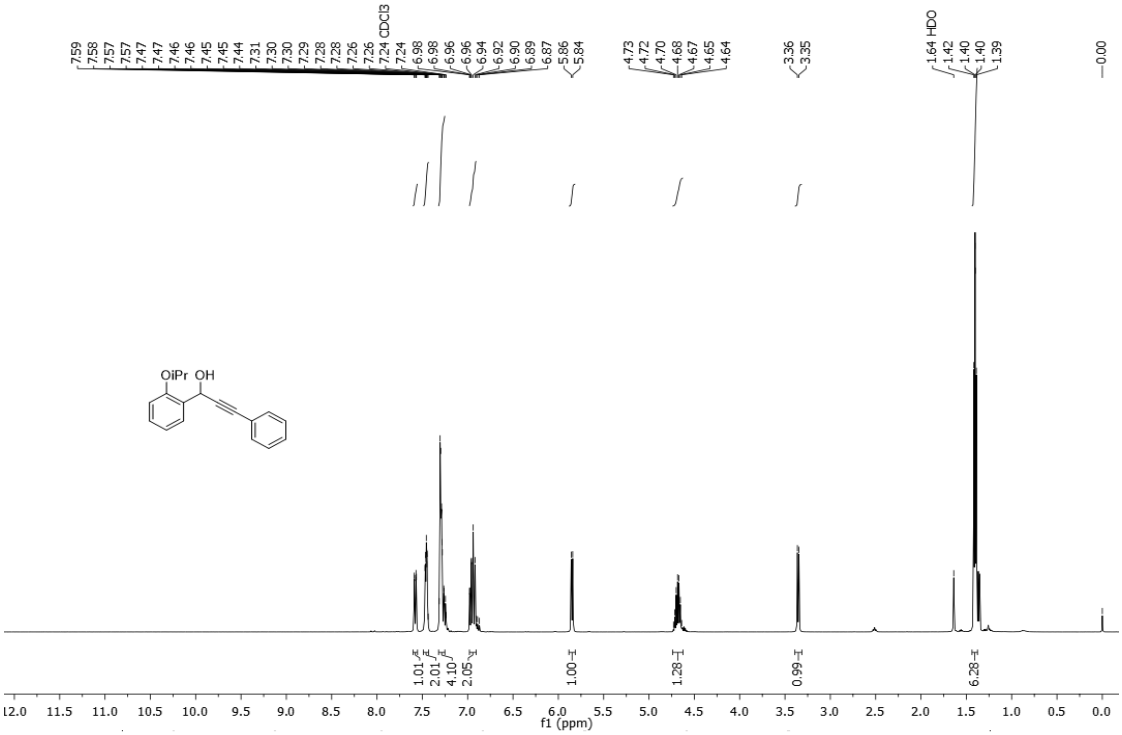


Result Table (Uncal - C:\CLARITY\WORK2\DATA\V VYAS\SUBSTRATE METHOD\NEW ODH\VV101 KETONE901010 - U-PAD2 - 1)

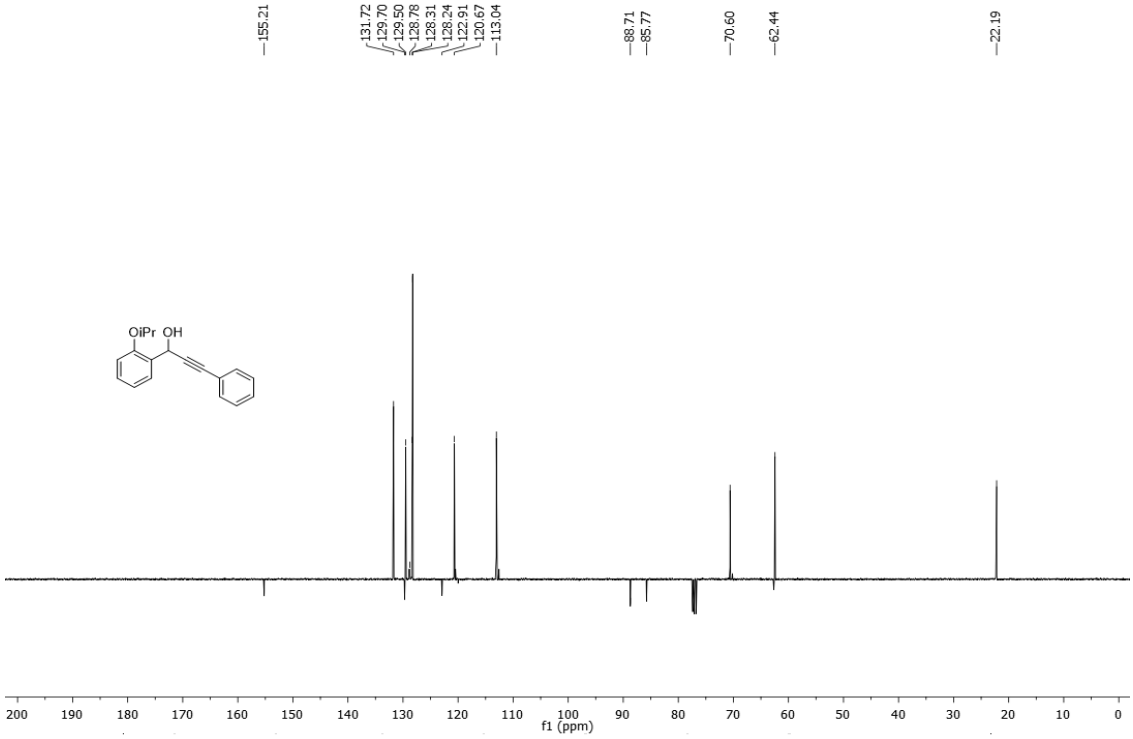
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	7.552	19878.334	1104.314	100.0	100.0	0.27	
	Total	19878.334	1104.314	100.0	100.0		

1-(2-Isoprooxyphenyl)-3-phenylprop-2-yn-1-ol (18).

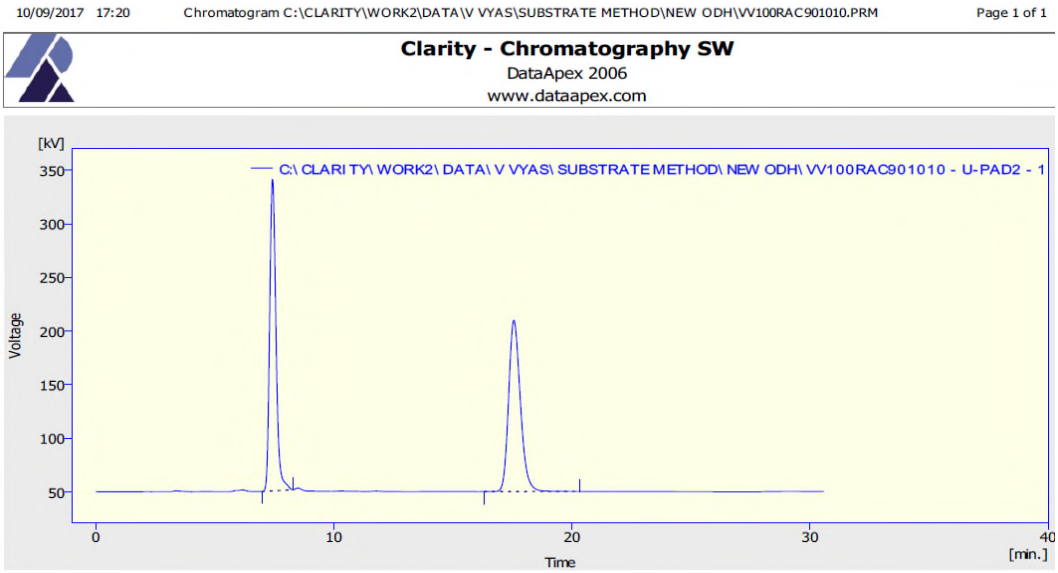
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



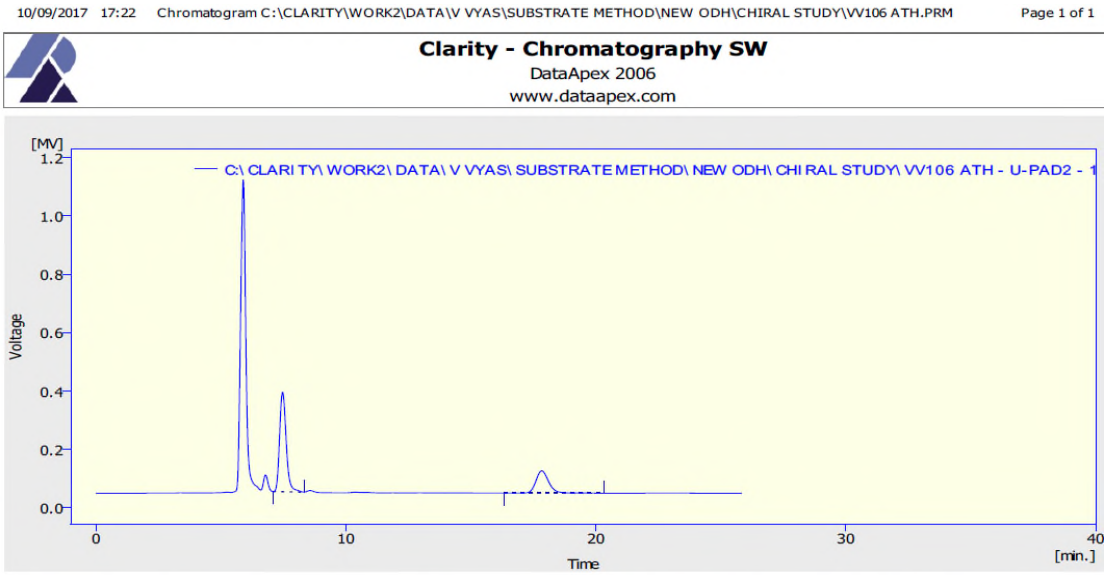
Racemic HPLC of 1-(2-isoprooxyphenyl)-3-phenylprop-2-yn-1-ol (**18**).



Result Table (Uncal - C:\|CLARITY\|WORK2\|DATA\|V VYAS\|SUBSTRATE METHOD\|NEW ODH\|VV100RAC901010 - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	7.424	5347.692	290.508	49.4	64.5	0.28	
2	17.560	5480.919	159.615	50.6	35.5	0.53	
	Total	10828.611	450.123	100.0	100.0		

HPLC after ATH of 1-(2-isoprooxyphenyl)-3-phenylprop-2-yn-1-ol (**18**) (37% conversion, 40.4% ee).

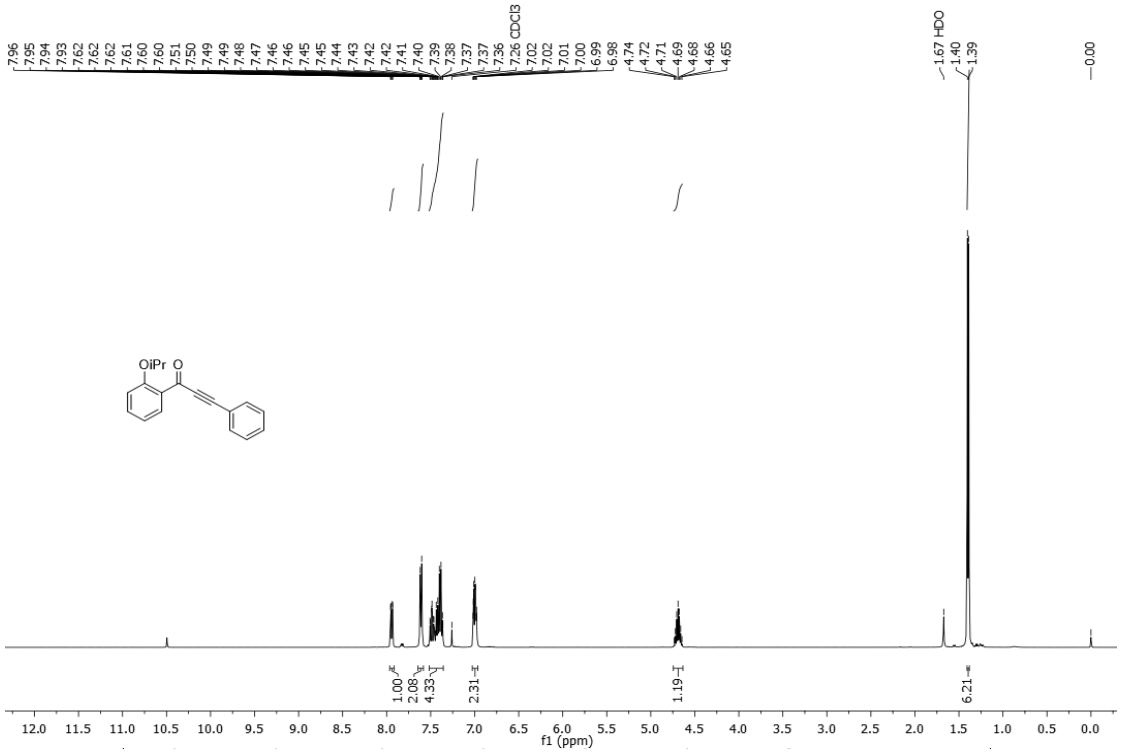


Result Table (Uncal - C:\|CLARITY\|WORK2\|DATA\|V VYAS\|SUBSTRATE METHOD\|NEW ODH\|CHIRAL STUDY\|VV106 ATH - U-PAD2 - 1)

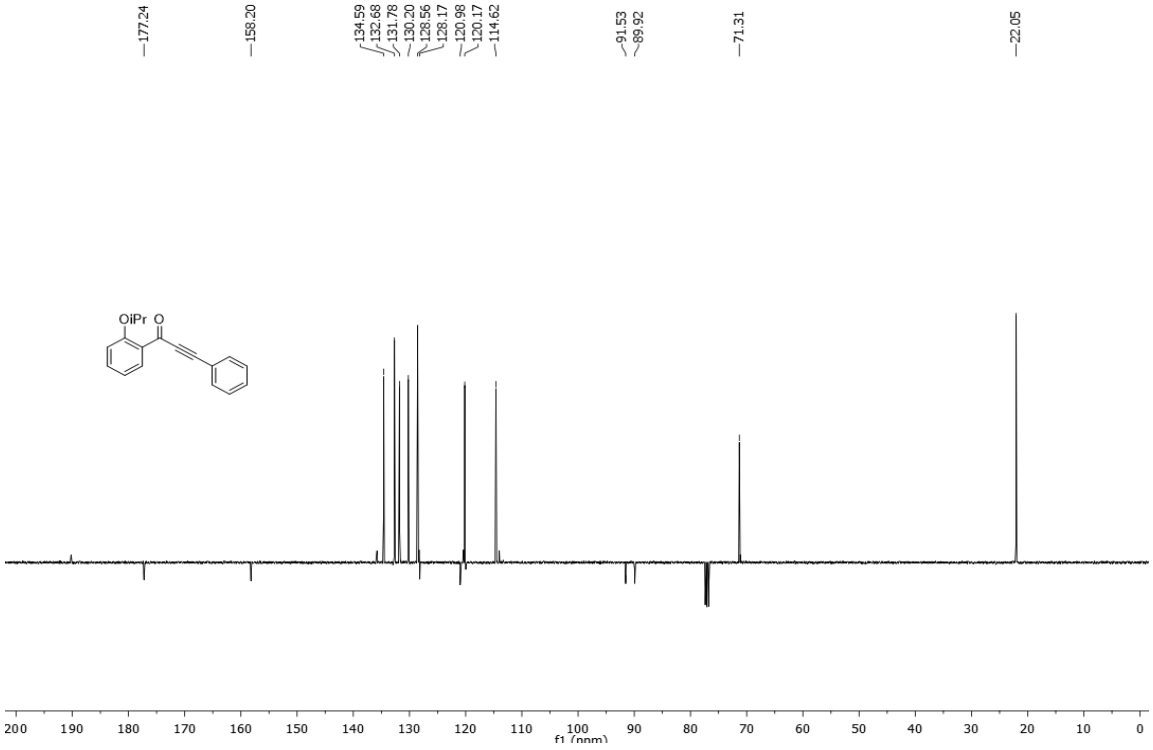
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	7.468	6279.195	341.246	70.2	81.7	0.28	
2	17.836	2659.256	76.193	29.8	18.3	0.53	
	Total	8938.451	417.439	100.0	100.0		

1-(2-Isopropoxyphenyl)-3-phenylprop-2-yn-1-one.

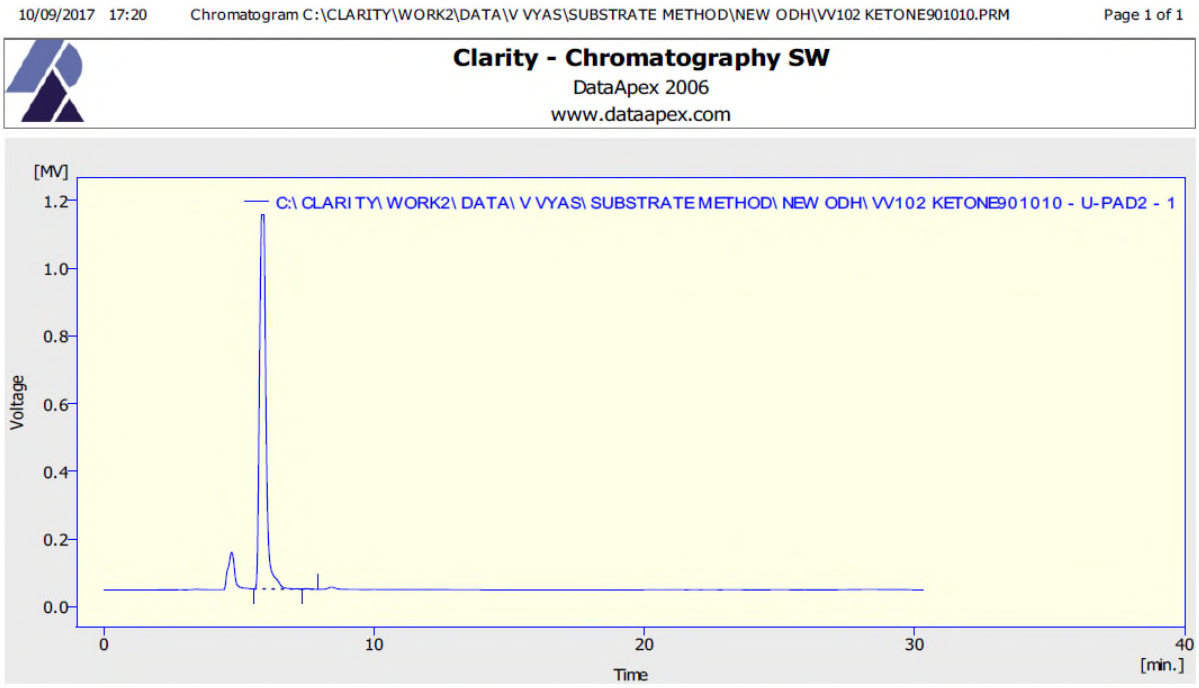
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



Ketone HPLC of 1-(2-isopropoxyphenyl)-3-phenylprop-2-yn-1-one.

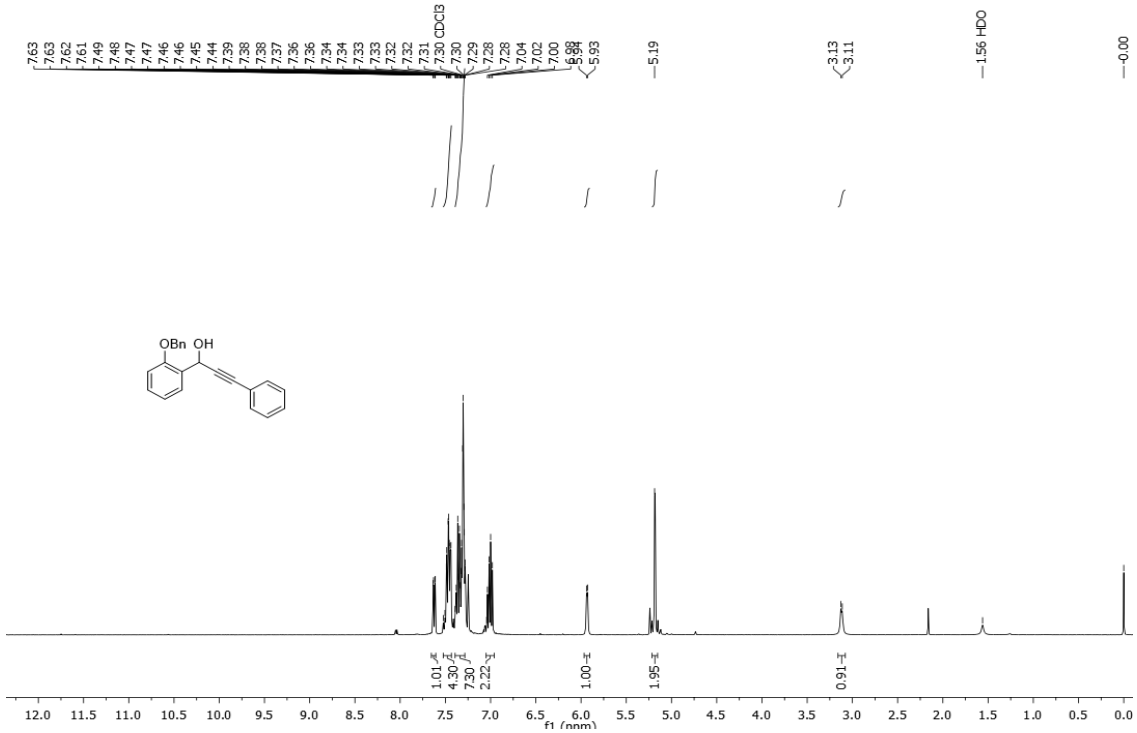


Result Table (Uncal - C:\|CLARITY\|WORK2\|DATA\|V VYAS\|SUBSTRATE METHOD\|NEW ODH\|VV102 KETONE901010 - U-PAD2 - 1)

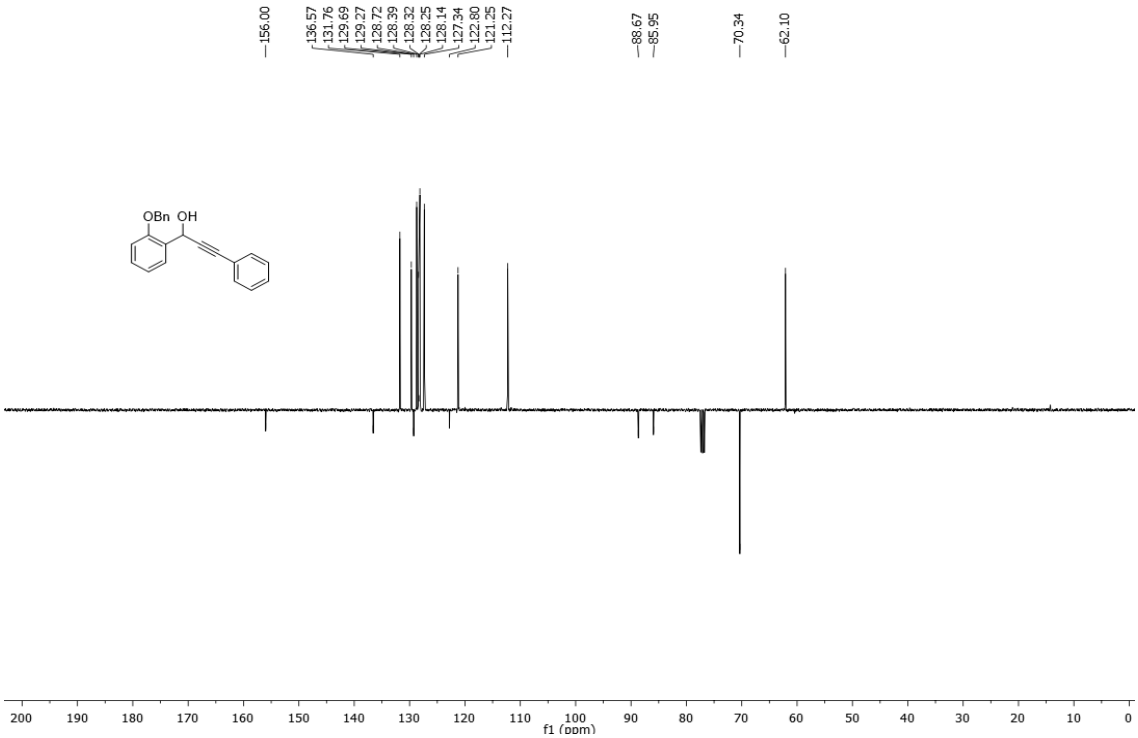
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	5.884	18544.503	1105.618	99.9	99.9	0.26	
2	7.504	23.290	1.537	0.1	0.1	0.25	
	Total	18567.794	1107.156	100.0	100.0		

1-(2- Benzyloxyphenyl)-3-phenylprop-2-yn-1-ol (19).

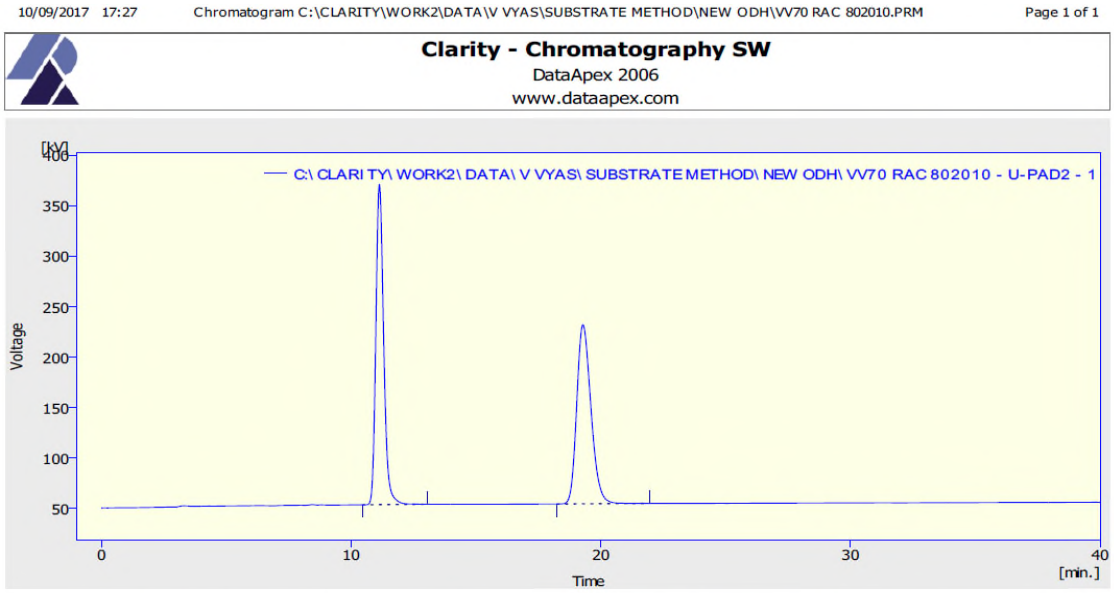
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



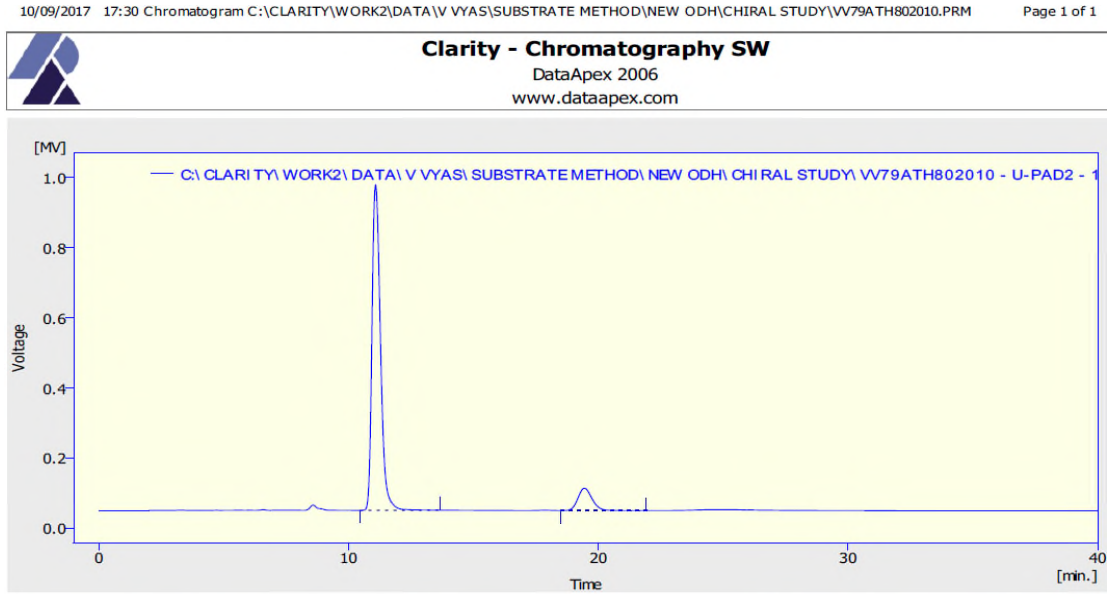
Racemic alcohol 1-(2- benzyloxyphenyl)-3-phenylprop-2-yn-1-ol (**19**).



Result Table (Uncal - C:\|CLARITY\|WORK2\|DATA\|V VYAS\|SUBSTRATE METHOD\|NEW ODH\|VV70 RAC 802010 - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	11.132	6935.421	317.195	49.7	64.1	0.33	
2	19.284	7019.431	177.456	50.3	35.9	0.61	
	Total	13954.852	494.651	100.0	100.0		

HPLC after ATH of 1-(2-benzyloxyphenyl)-3-phenylprop-2-yn-1-ol (**19**) (100% conversion, 79.4% ee).

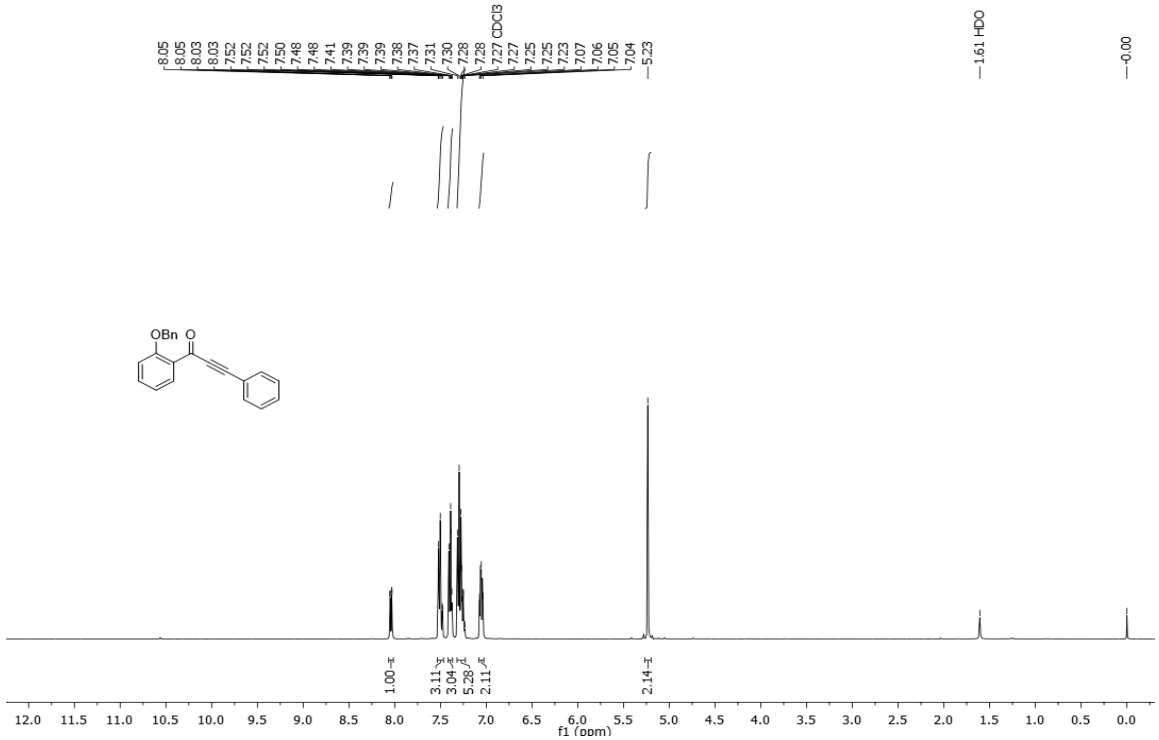


Result Table (Uncal - C:\|CLARITY\|WORK2\|DATA\|V VYAS\|SUBSTRATE METHOD\|NEW ODH\|CHIRAL STUDY\|VV79ATH802010 - U-PAD2 - 1)

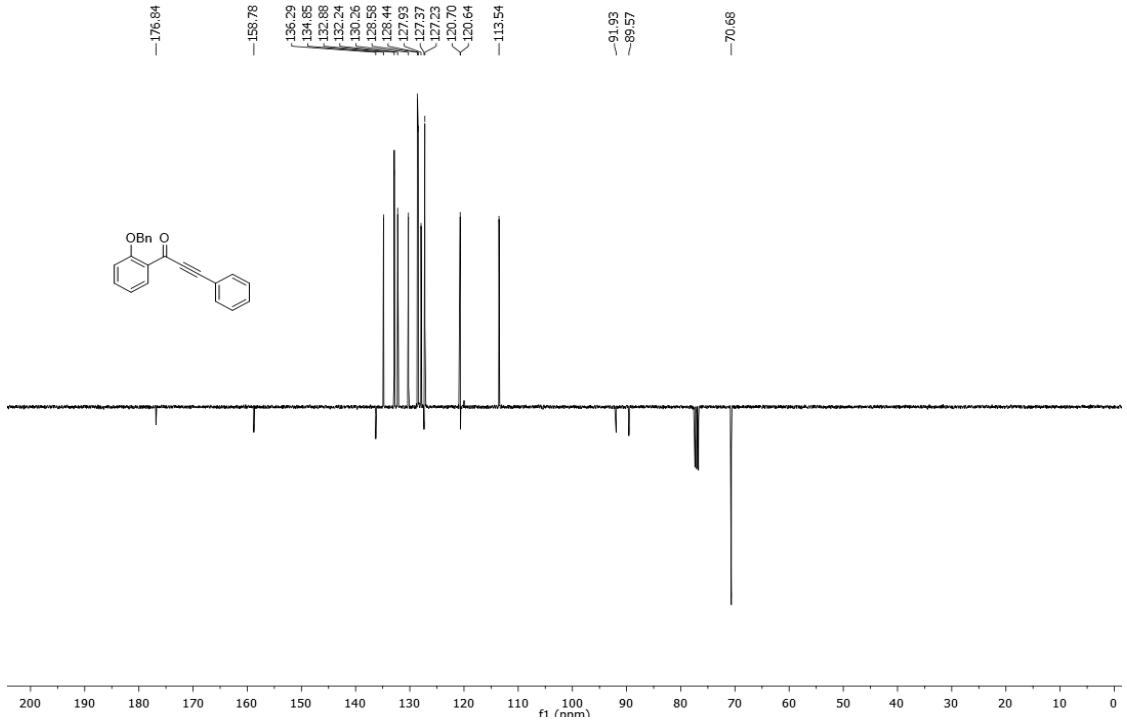
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	11.084	21967.562	927.999	89.7	93.6	0.36	
2	19.448	2514.411	63.929	10.3	6.4	0.61	
	Total	24481.973	991.928	100.0	100.0		

1-(2- Benzyloxyphenyl)-3-phenylprop-2-yn-1-one.

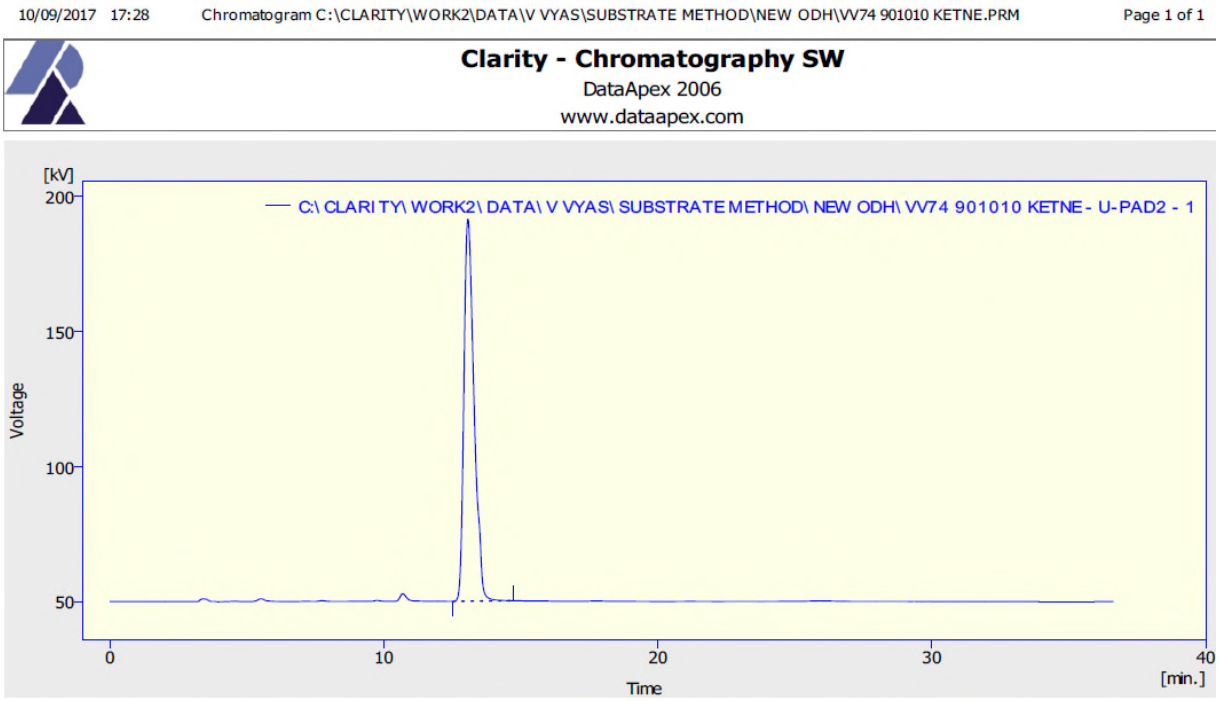
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



Ketone HPLC of 1-(2-benzyloxyphenyl)-3-phenylprop-2-yn-1-one.

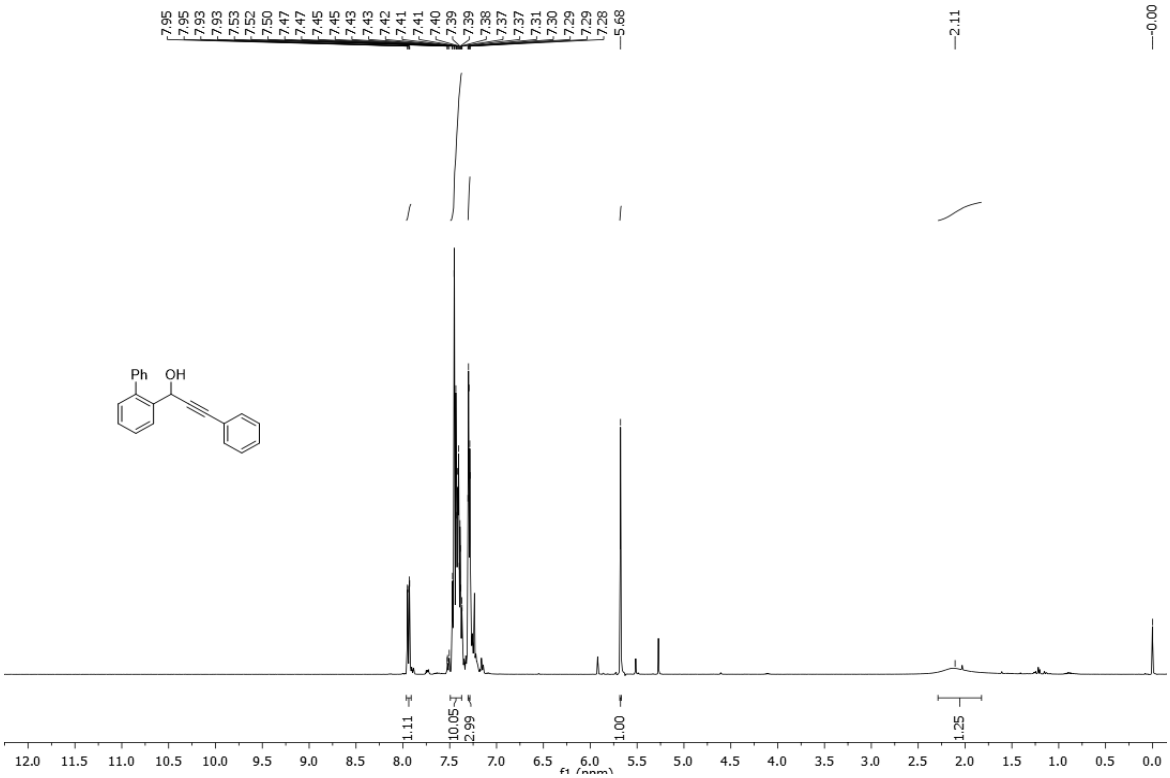


Result Table (Uncal - C:\|CLARITY\|WORK2\|DATA\|V VYAS\|SUBSTRATE METHOD\|NEW ODH\|VV74 901010 KETNE - U-PAD2 - 1)

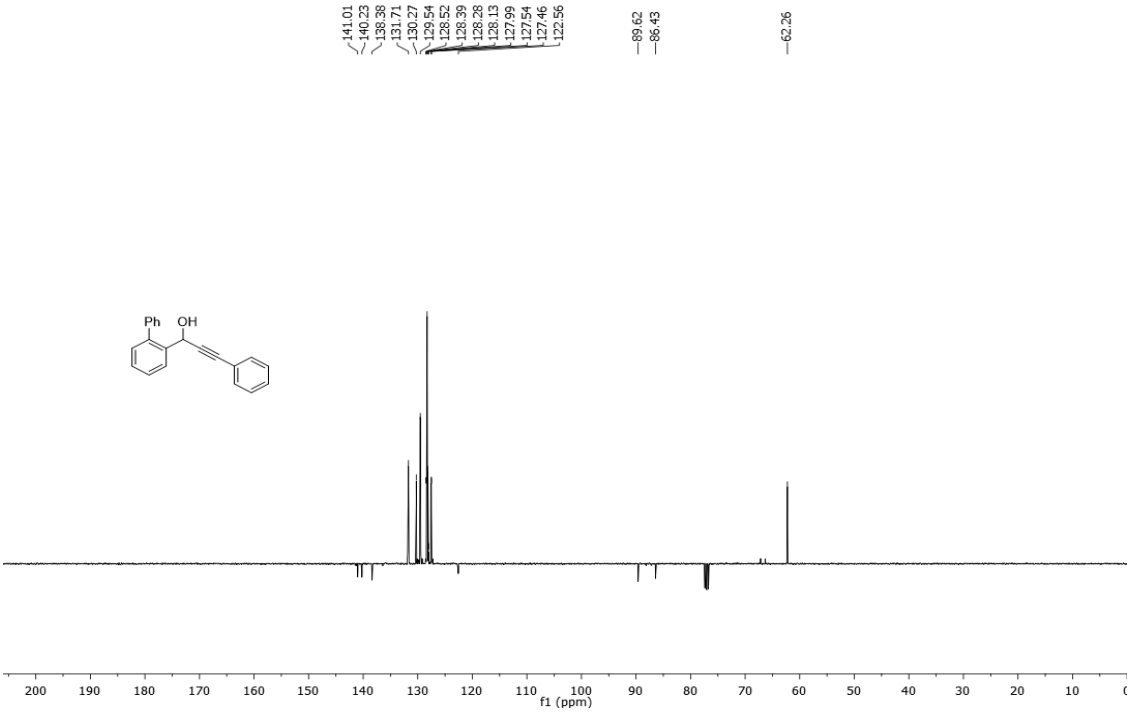
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	13.068	3636.152	141.354	100.0	100.0	0.40	
	Total	3636.152	141.354	100.0	100.0		

1-([1,1'-Biphenyl]-2-yl)-3-phenylprop-2-yn-1-ol (20).

^{1}H NMR (400 MHz, $CDCl_3$)

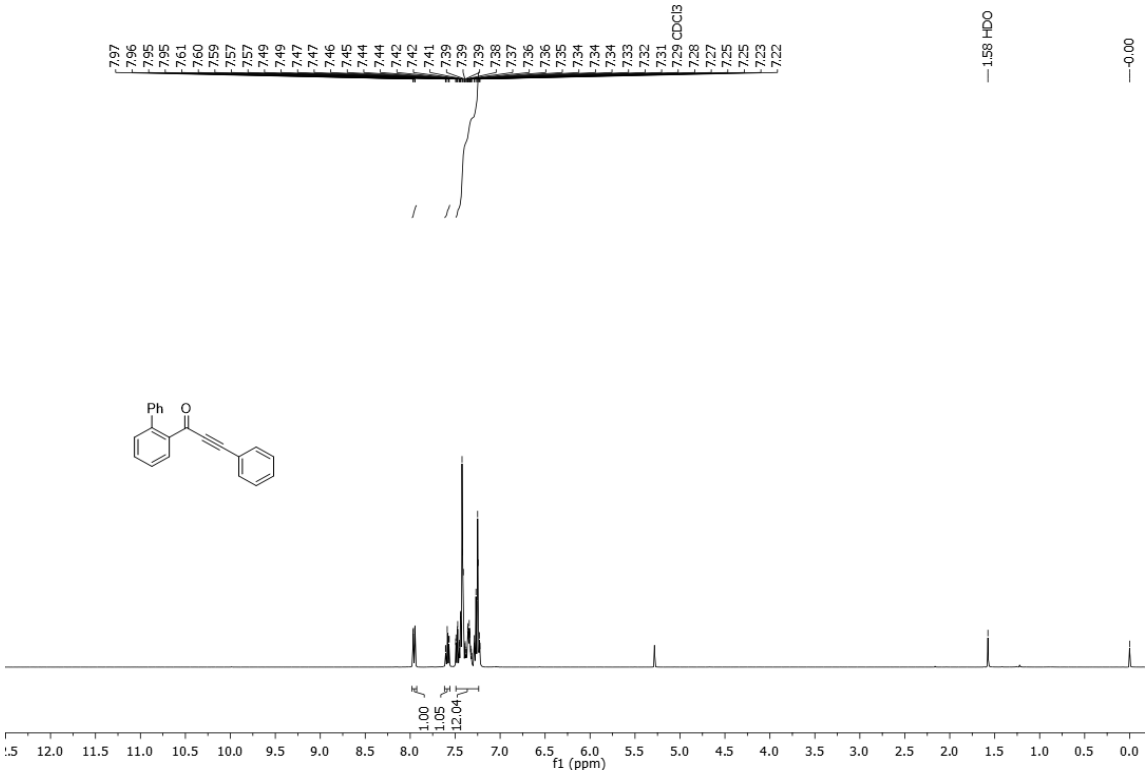


^{13}C NMR (101 MHz, $CDCl_3$)

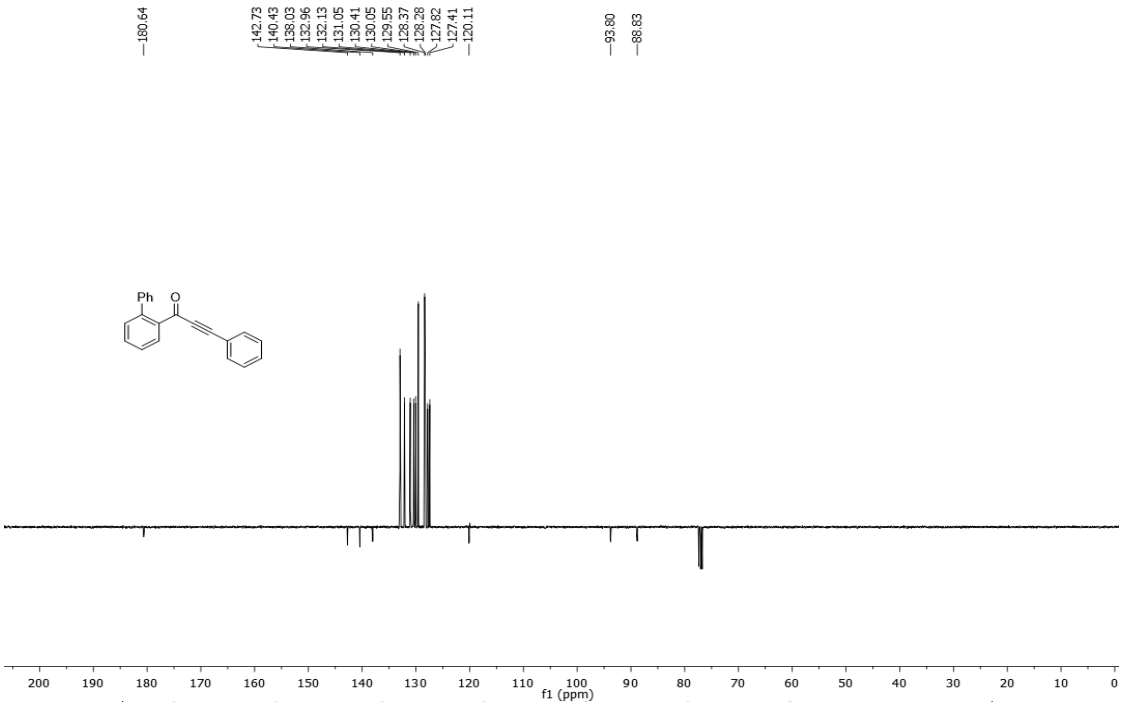


1-([1,1'-Biphenyl]-2-yl)-3-phenylprop-2-yn-1-one.

^{1}H NMR (400 MHz, $CDCl_3$)

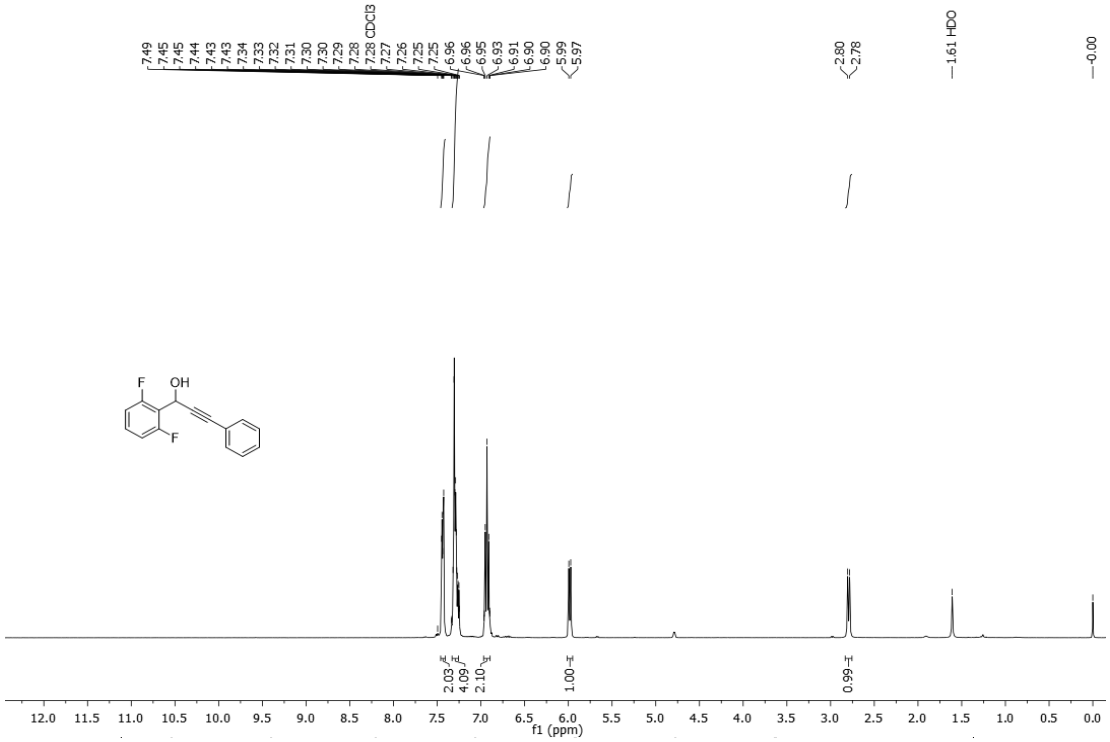


^{13}C NMR (101 MHz, $CDCl_3$)

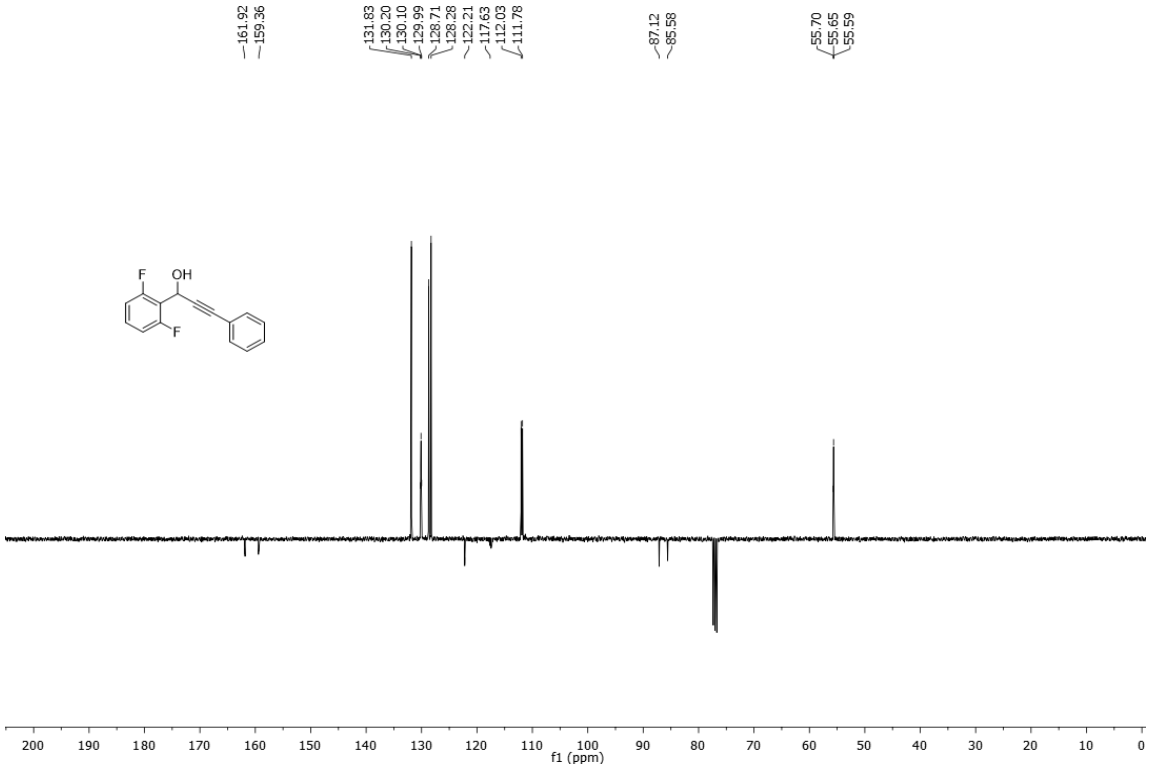


1-(2,6-Difluorophenyl)-3-phenylprop-2-yn-1-ol (21).

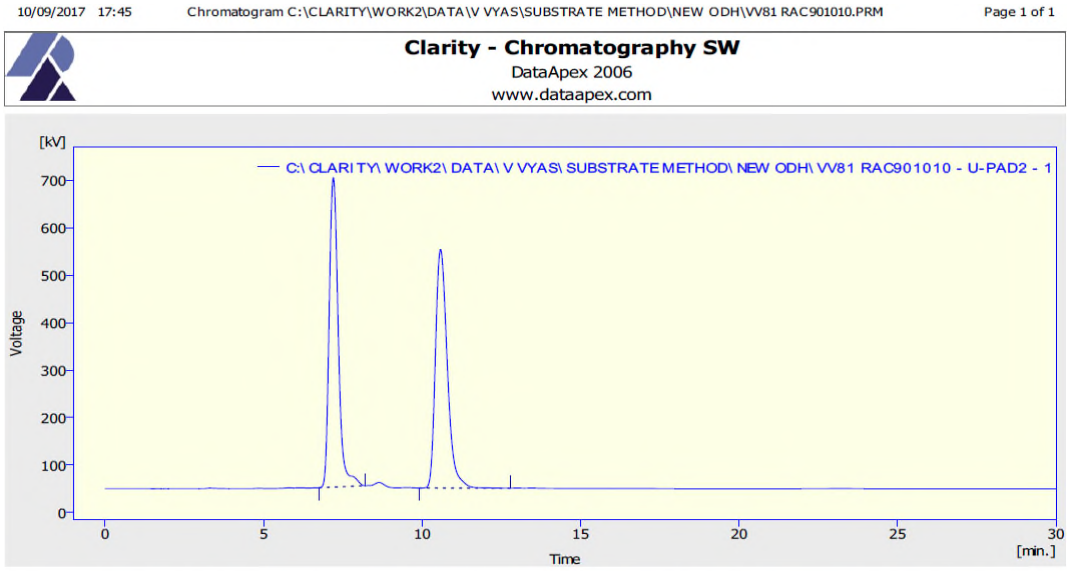
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



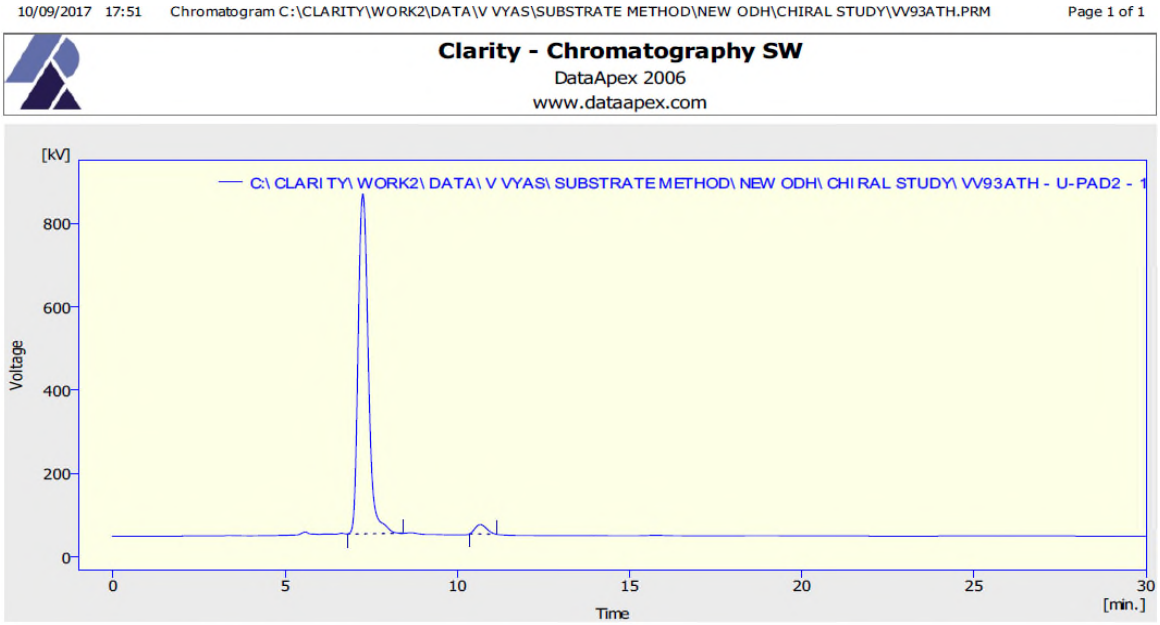
Racemic HPLC of 1-(2,6-Difluorophenyl)-3-phenylprop-2-yn-1-ol (**21**).



Result Table (Uncal - C:|CLARITY|WORK2|DATA|V VYAS|SUBSTRATE METHOD|NEW ODH|VV81 RAC901010 - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	7.200	13006.771	652.048	49.8	56.5	0.30	
2	10.580	13104.624	502.899	50.2	43.5	0.40	
	Total	26111.396	1154.947	100.0	100.0		

HPLC after ATH of 1-(2,6-difluorophenyl)-3-phenylprop-2-yn-1-ol (**21**) (100% conversion, 94.0% ee).

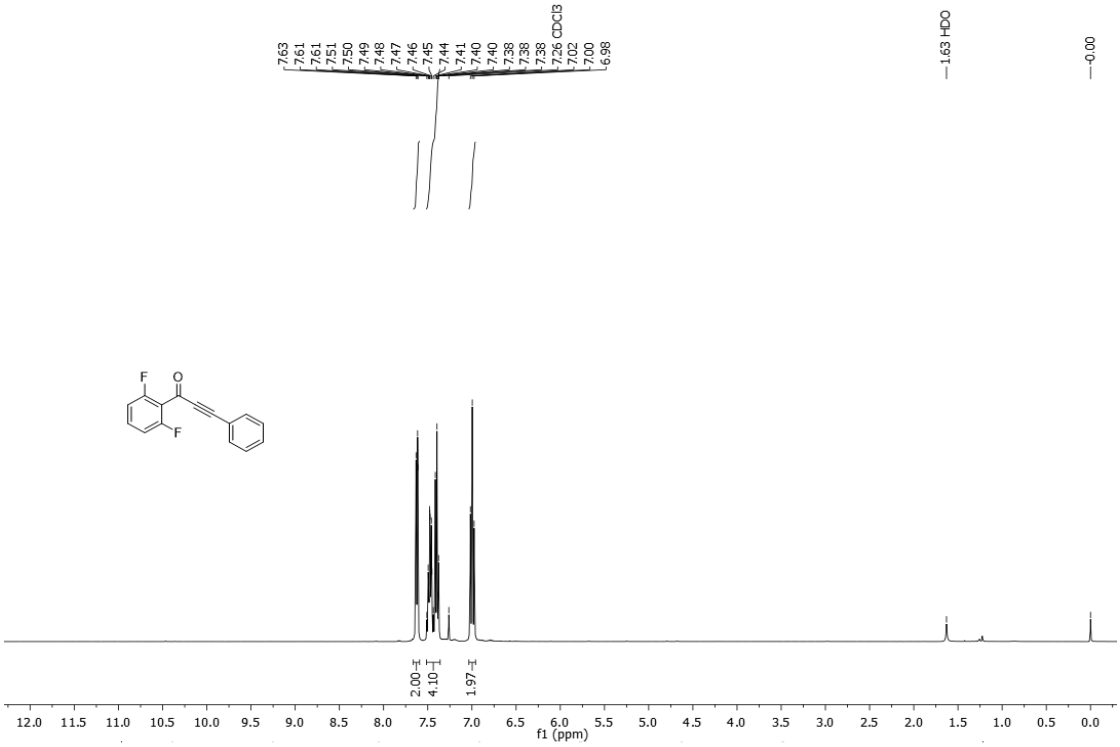


Result Table (Uncal - C:|CLARITY|WORK2|DATA|V VYAS|SUBSTRATE METHOD|NEW ODH|CHIRAL STUDY|VV93ATH - U-PAD2 - 1)

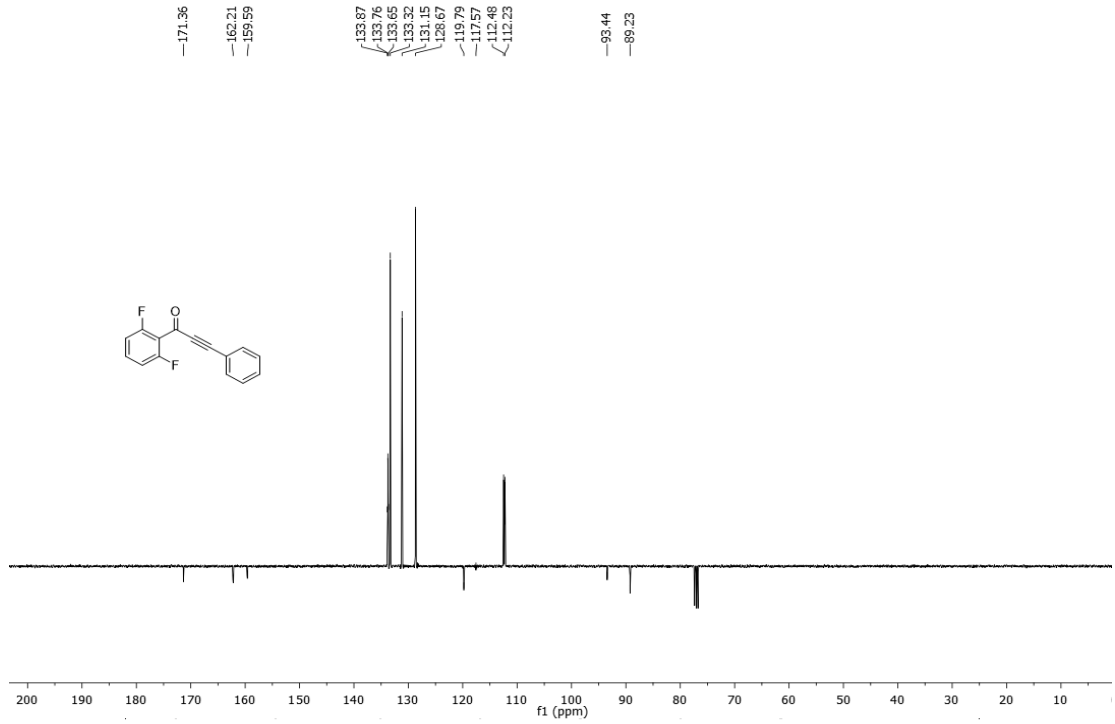
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	7.256	16757.084	815.354	97.0	97.3	0.32	
2	10.664	517.828	22.489	3.0	2.7	0.38	
	Total	17274.912	837.843	100.0	100.0		

1-(2,6-Difluorophenyl)-3-phenylprop-2-yn-1-one.

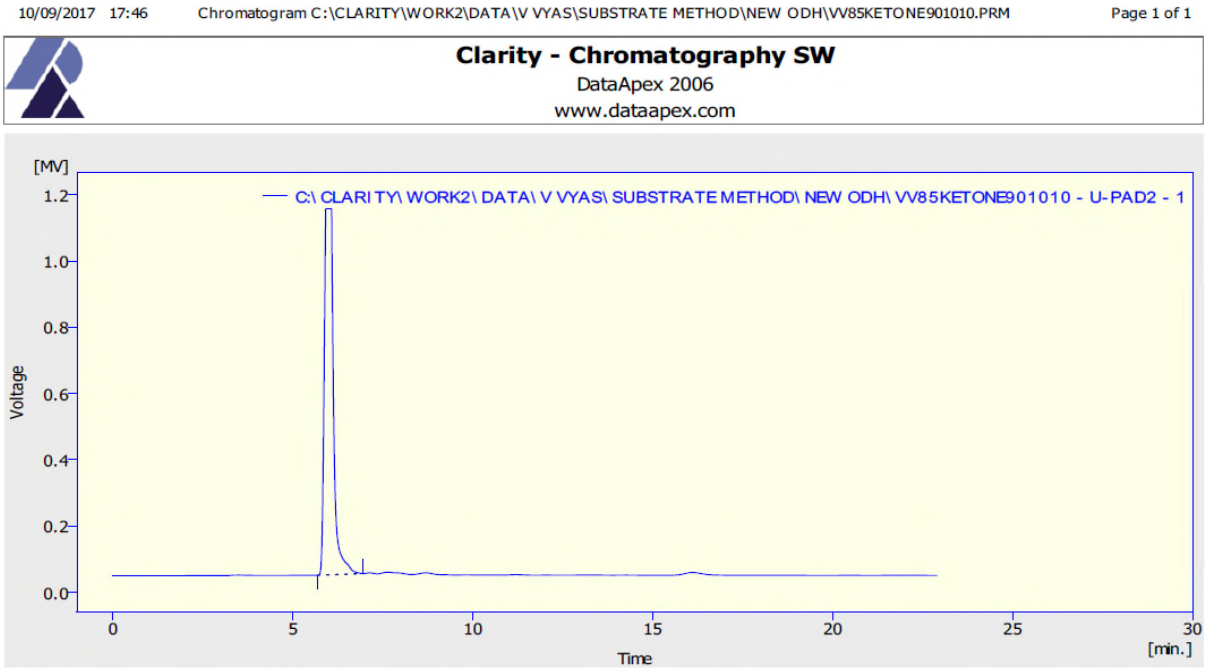
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



Ketone HPLC of 1-(2,6-difluorophenyl)-3-phenylprop-2-yn-1-one.

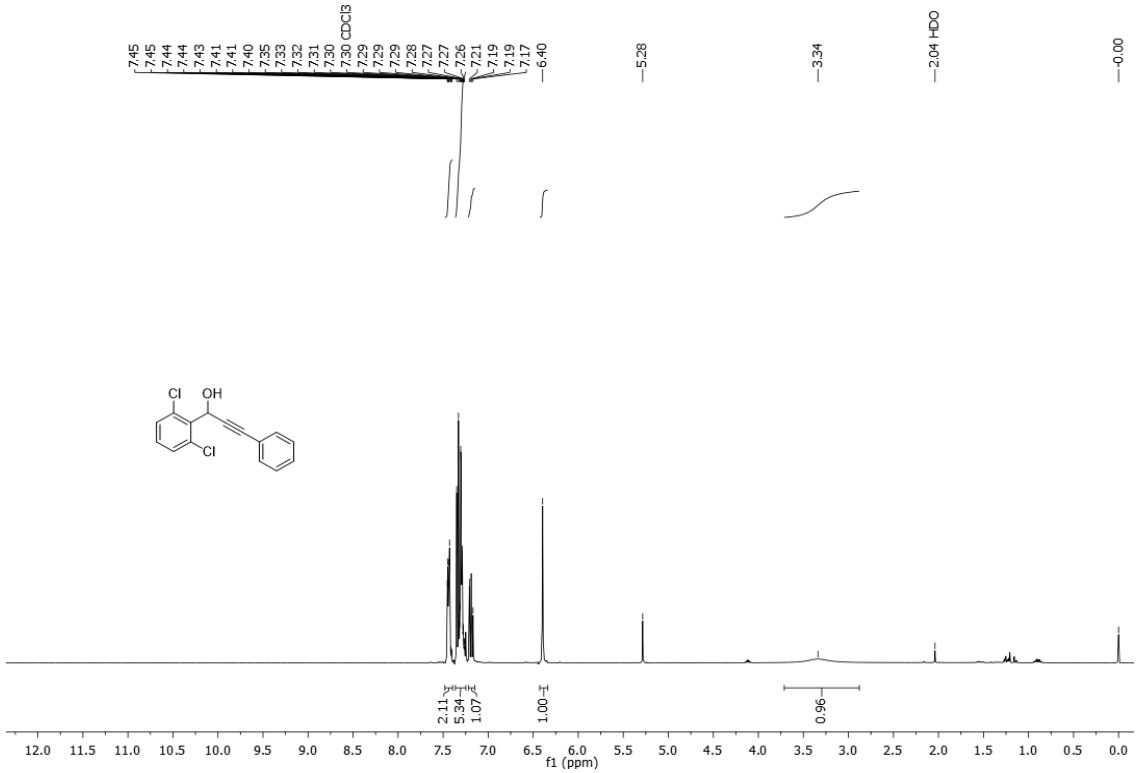


Result Table (Uncal - C:|CLARITY|WORK2|DATA|V VYAS|SUBSTRATE METHOD|NEW ODH|VV85KETONE901010 - U-PAD2 - 1)

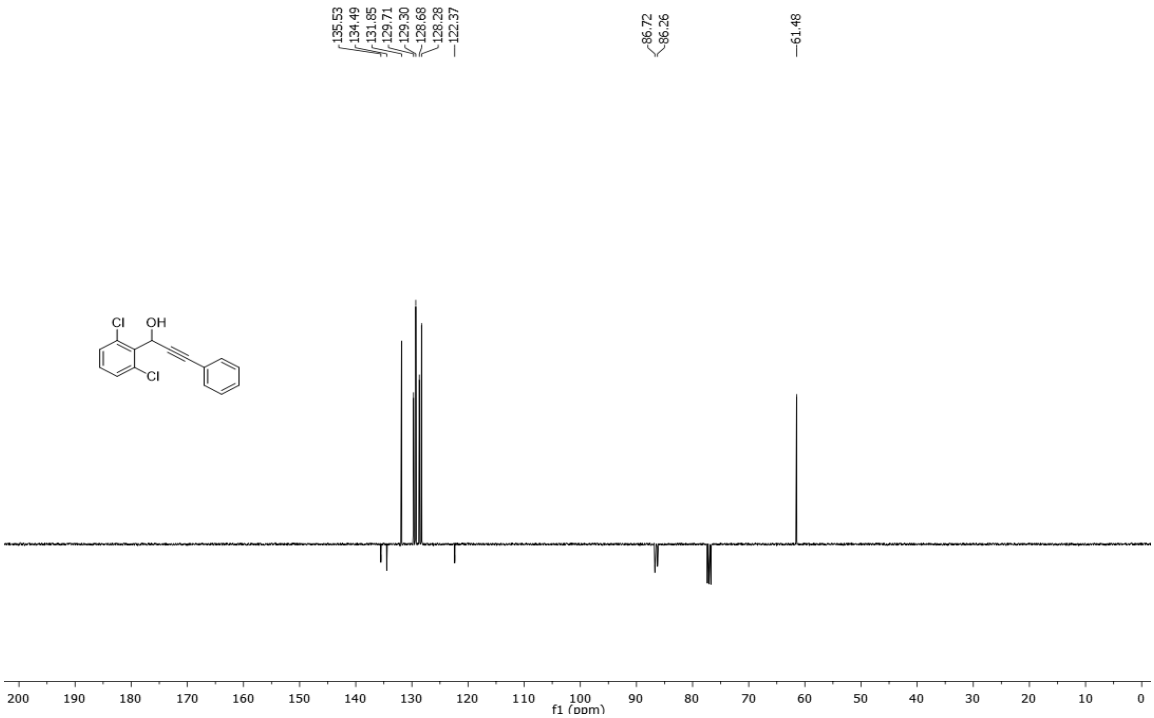
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	5.984	19731.036	1106.050	100.0	100.0	0.26	
	Total	19731.036	1106.050	100.0	100.0		

1-(2,6-Dichlorophenyl)-3-phenylprop-2-yn-1-ol (22).

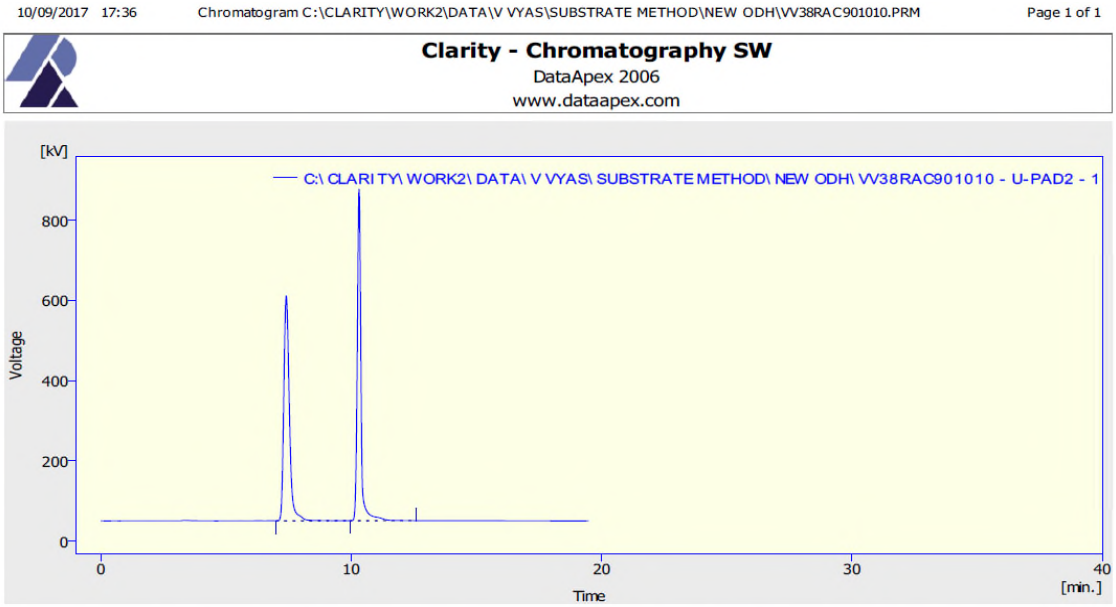
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



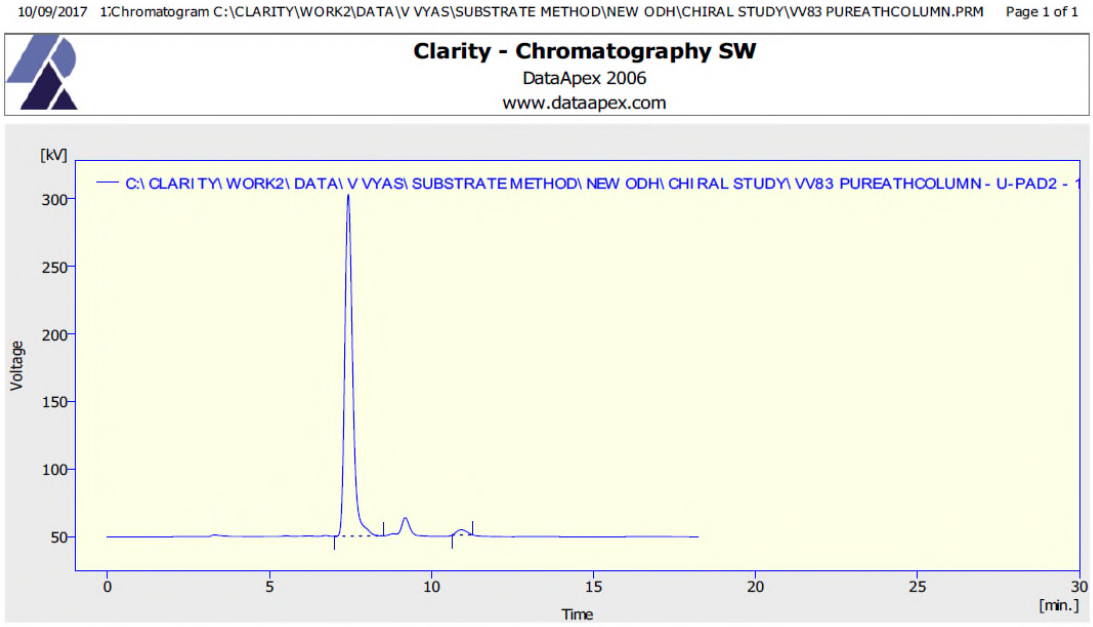
Racemic HPLC of 1-(2,6-Dichlorophenyl)-3-phenylprop-2-yn-1-ol (**22**).



Result Table (Uncal - C:\CLARITY\WORK2\DATA\V VYAS\SUBSTRATE METHOD\NEW ODH\VV38RAC901010 - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	7.404	8772.174	560.810	50.6	40.4	0.24	
2	10.316	8574.615	826.527	49.4	59.6	0.15	
	Total	17346.789	1387.337	100.0	100.0		

HPLC after ATH of 1-(2,6-Dichlorophenyl)-3-phenylprop-2-yn-1-ol (**22**) (96.0% ee).

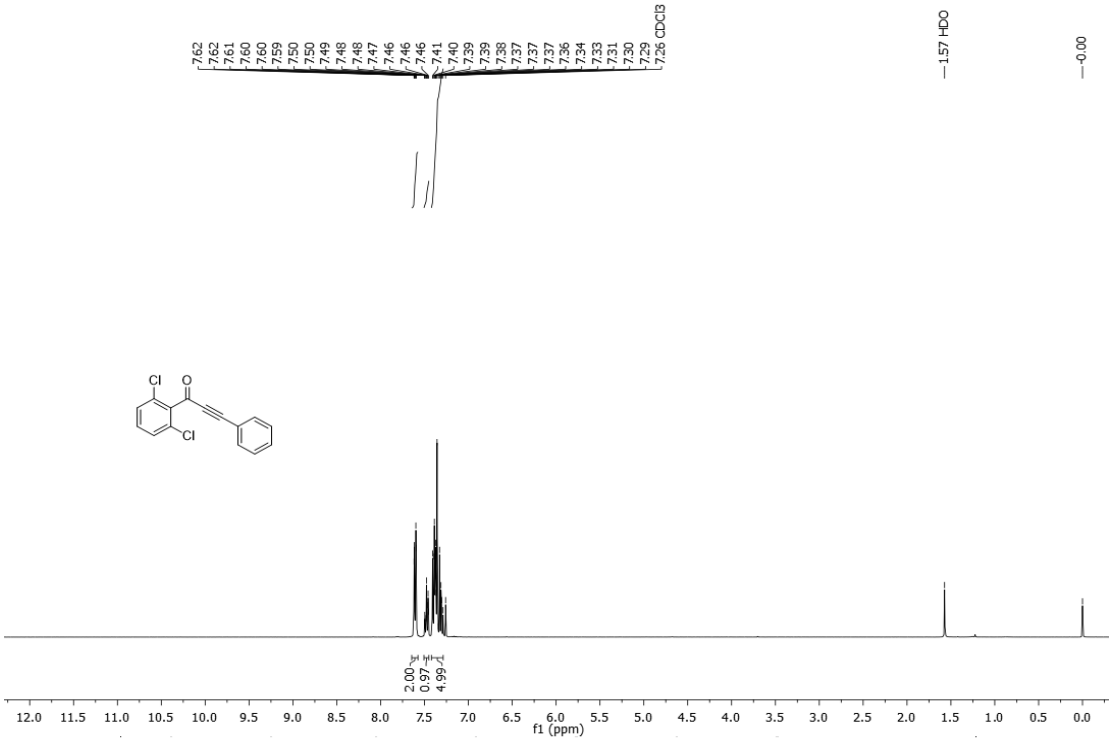


Result Table (Uncal - C:\CLARITY\WORK2\DATA\V VYAS\SUBSTRATE METHOD\NEW ODH\CHIRAL STUDY\VV83 PUREATHCOLUMN - U-PAD2 - 1)

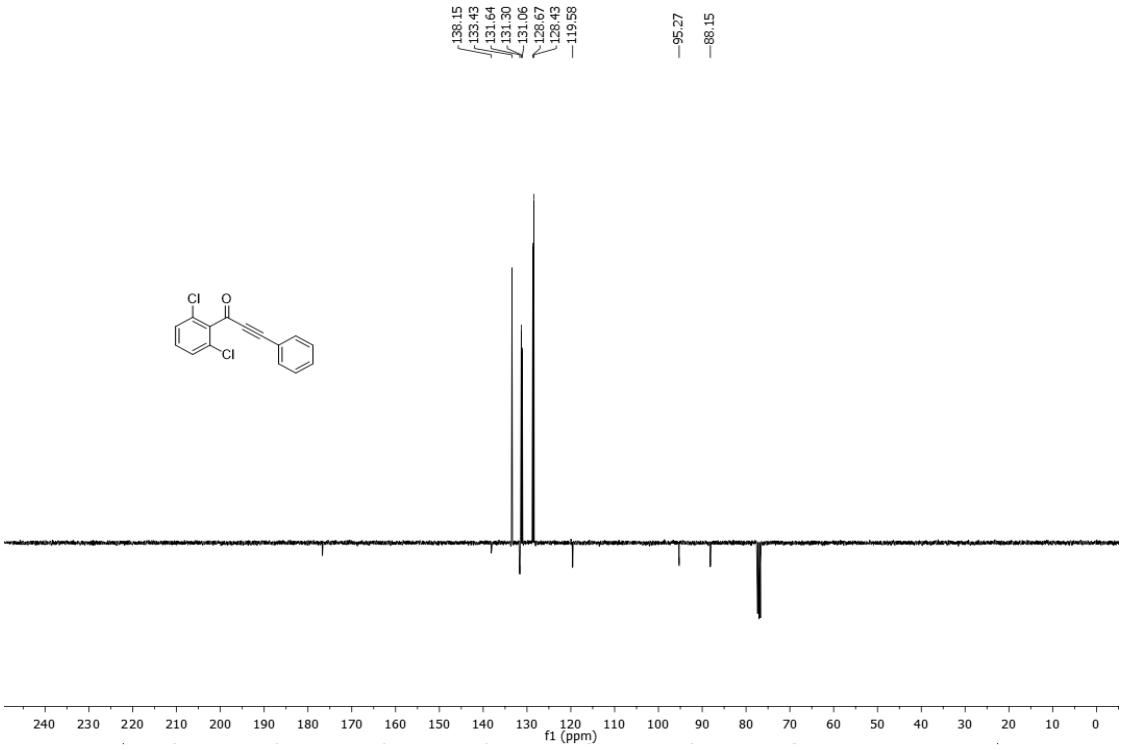
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	7.432	4233.245	252.626	98.0	98.5	0.26	
2	10.920	84.488	3.887	2.0	1.5	0.37	
	Total	4317.733	256.513	100.0	100.0		

1-(2,6-Dichlorophenyl)-3-phenylprop-2-yn-1-one.

^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



Ketone HPLC of 1-(2,6-dichlorophenyl)-3-phenylprop-2-yn-1-one.

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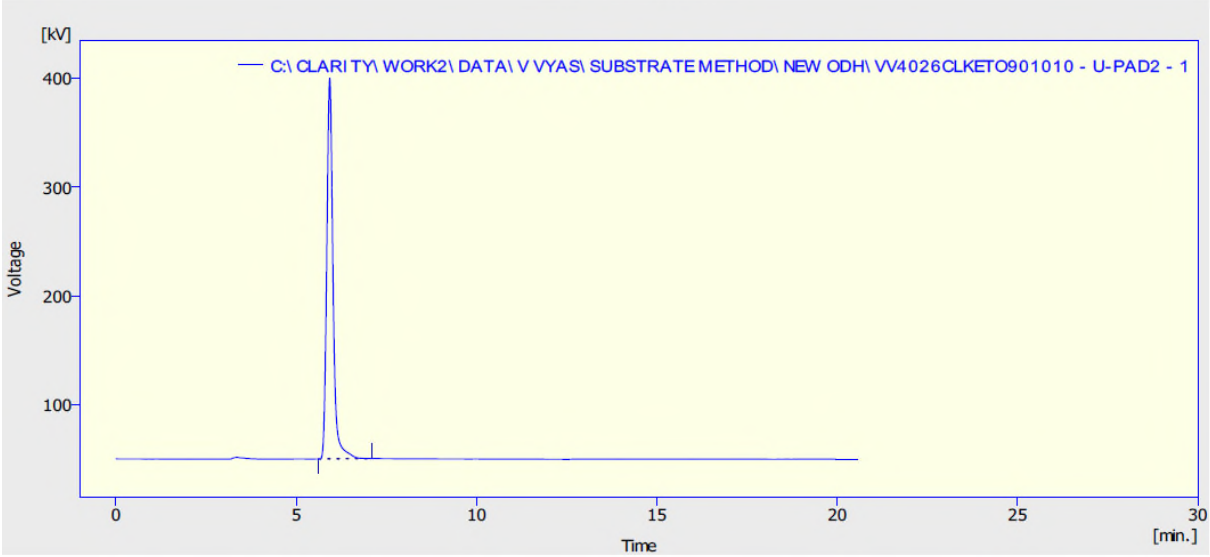
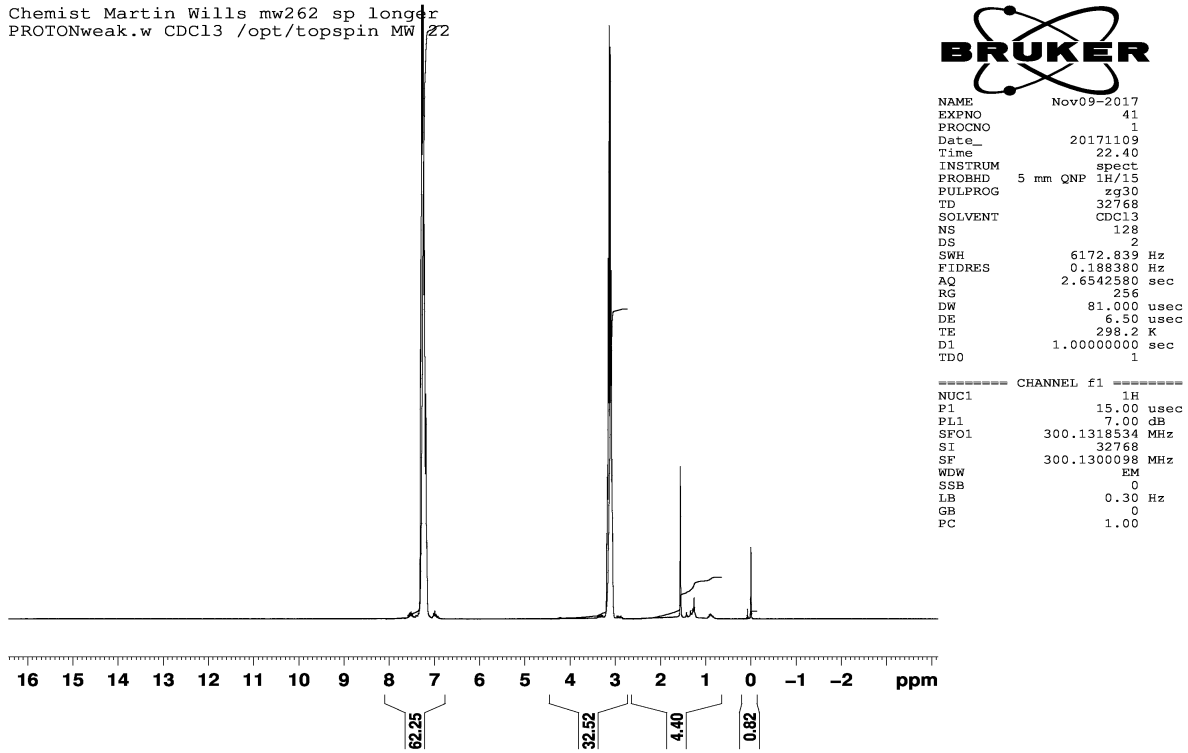


Result Table (Uncal - C:\CLARITY\WORK2\DATA\V VYAS\SUBSTRATE METHOD\NEW ODH\VV4026CLKETO901010 - U-PAD2 - 1)

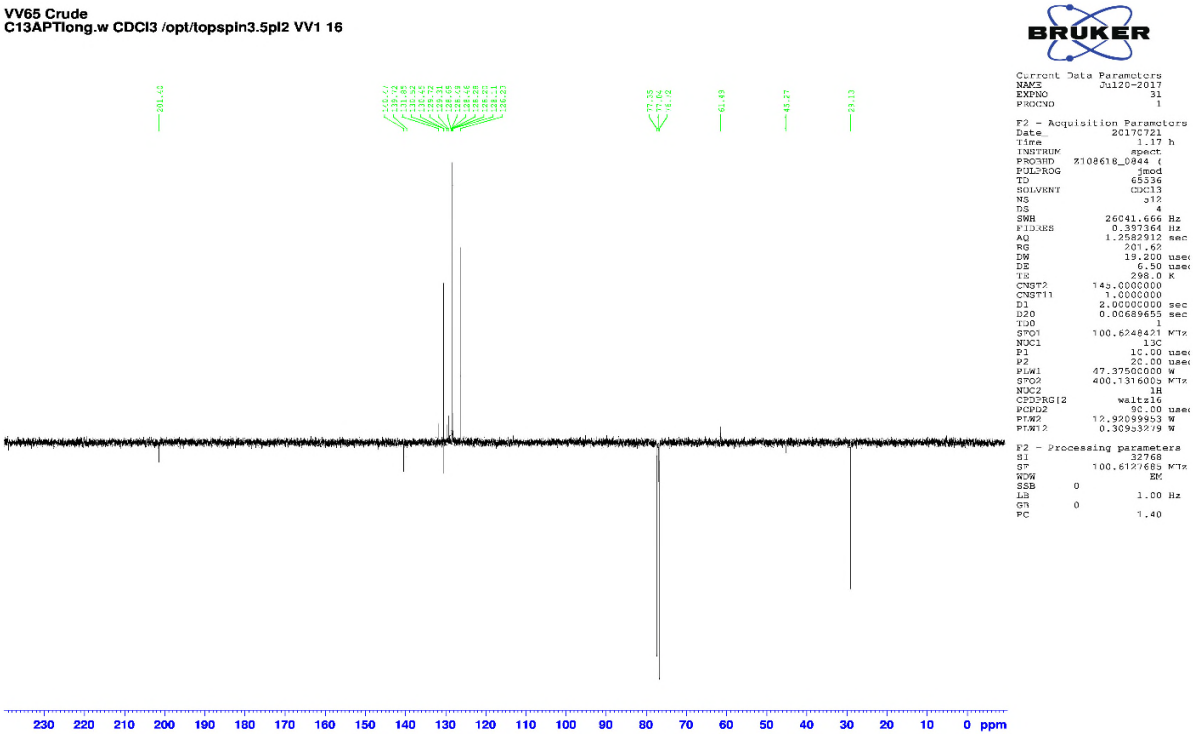
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	5.928	4228.996	349.666	100.0	100.0	0.18	
	Total	4228.996	349.666	100.0	100.0		

1-(2,6-Dichlorophenyl)-3-phenylpropanone.

^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



HPLC of 1-(2,6-dichlorophenyl)-3-phenylpropanone.

Clarity - Chromatography SW
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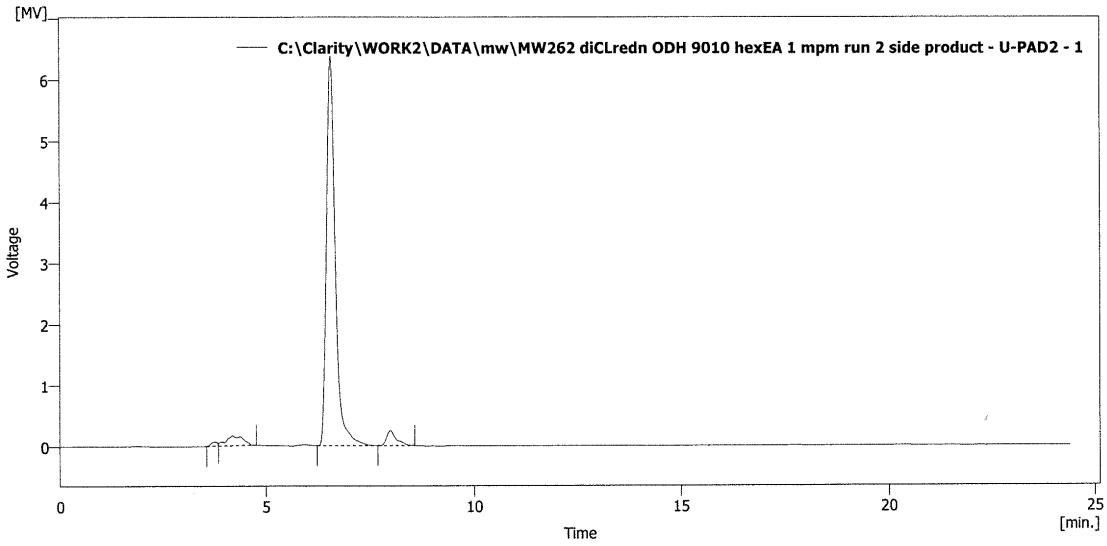
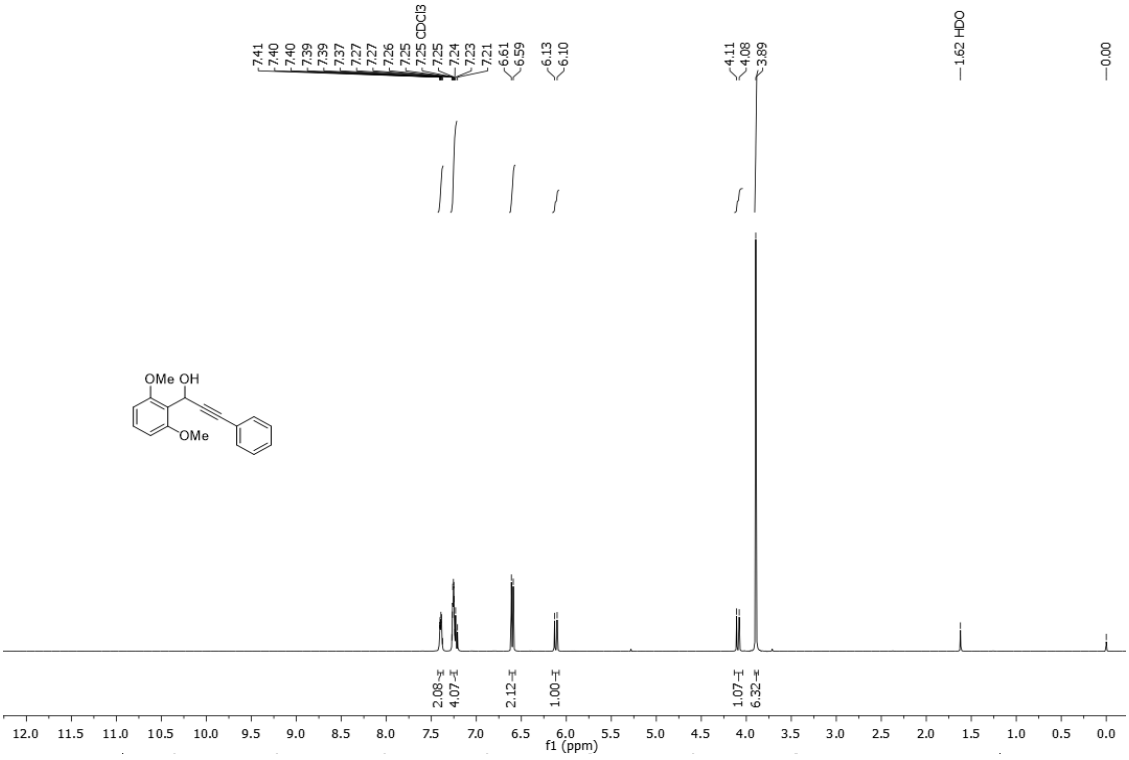


Result Table (Uncal - C:\Clarity\WORK2\DATA\mw\MW262 diCLredn ODH 9010 hexEA 1 mpm run 2 side product - U-PAD2 - 1)

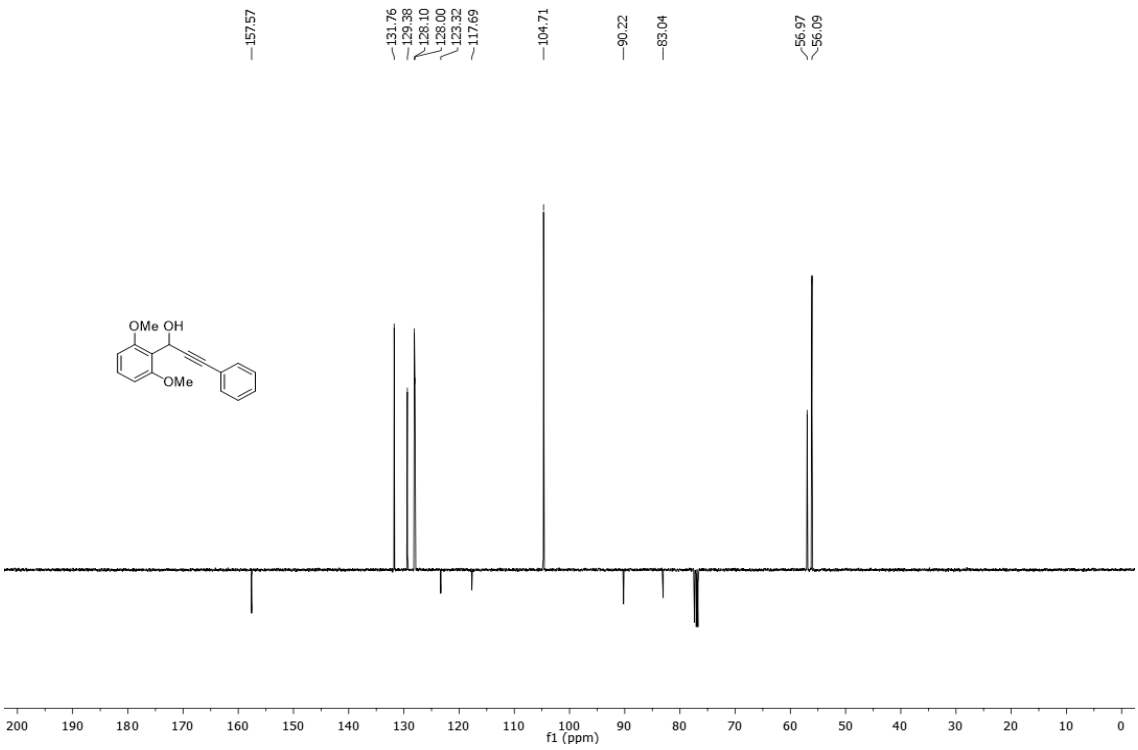
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	3.772	7.609	0.722	0.7	1.1	0.20	
2	4.188	47.245	1.639	4.6	2.4	0.45	
3	6.556	934.806	63.640	90.8	93.0	0.22	
4	7.980	39.441	2.438	3.8	3.6	0.22	
	Total	1029.101	68.438	100.0	100.0		

1-(2,6-Dimethoxyphenyl)-3-phenylprop-2-yn-1-ol (23).

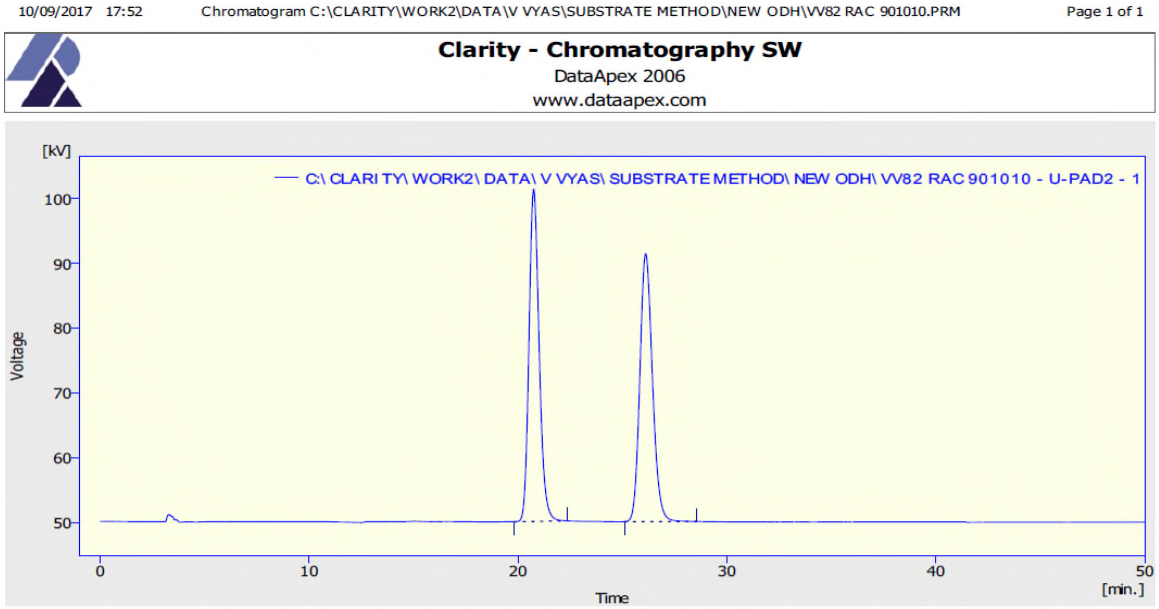
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



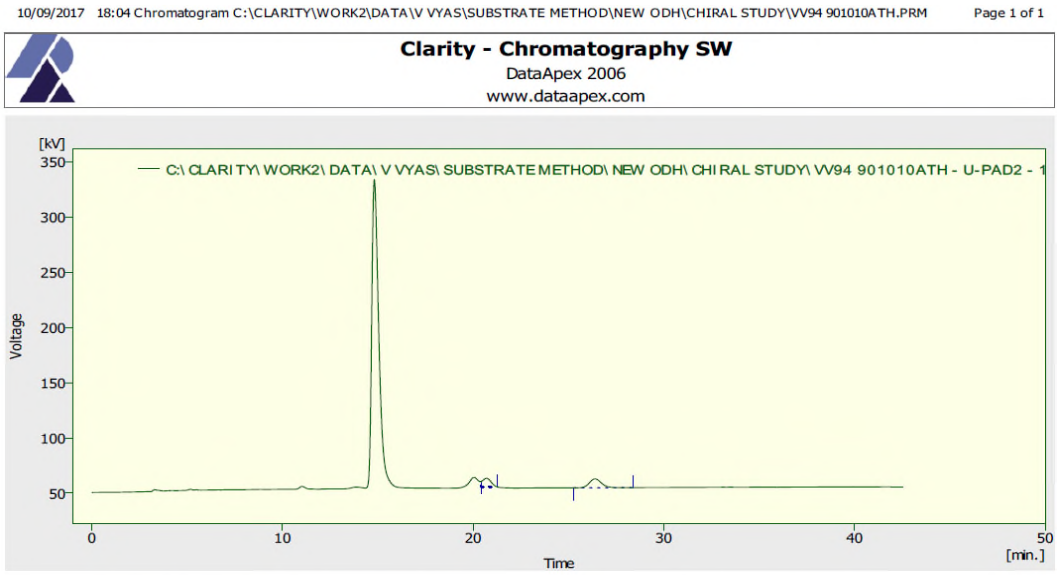
Racemic HPLC of 1-(2,6-dimethoxyphenyl)-3-phenylprop-2-yn-1-ol (**23**).



Result Table (Uncal - C:\|CLARITY\|WORK2\|DATA\|V VYAS\|SUBSTRATE METHOD\|NEW ODH\|VV82 RAC 901010 - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	20.748	1726.660	51.231	49.9	55.4	0.52	
2	26.108	1732.884	41.312	50.1	44.6	0.65	
	Total	3459.544	92.543	100.0	100.0		

HPLC after ATH of 1-(2,6-Dimethoxyphenyl)-3-phenylprop-2-yn-1-ol (**23**) (8% conversion, 20.4% ee).

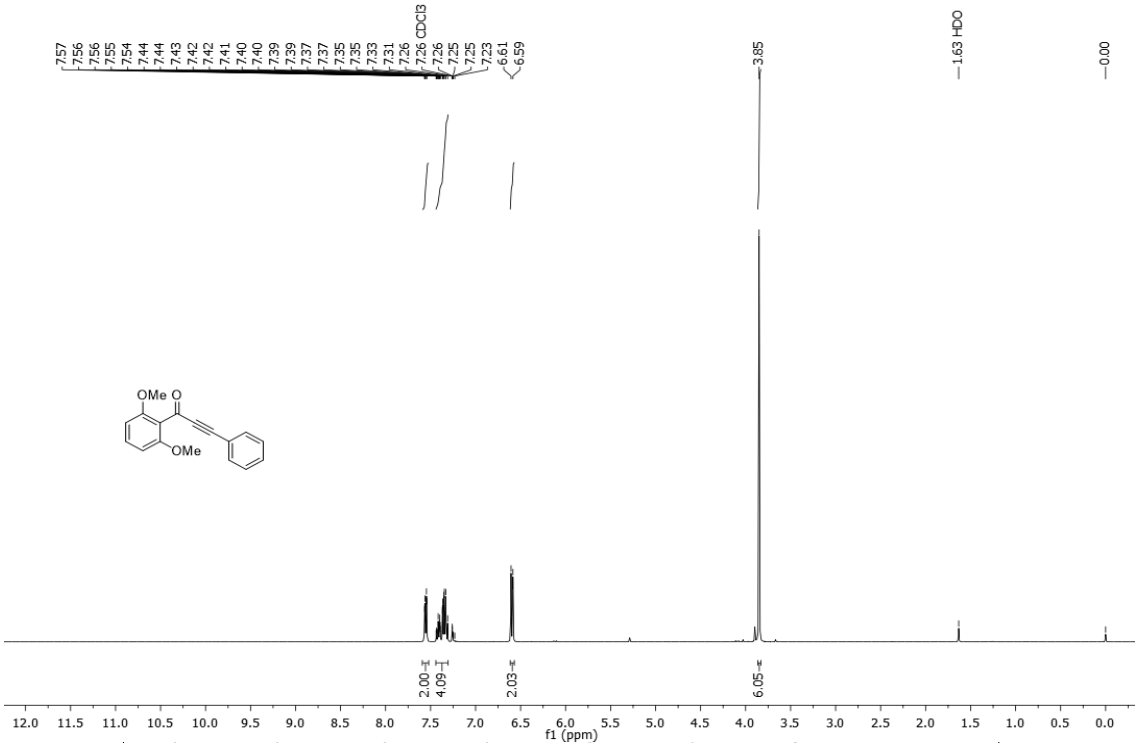


Result Table (Uncal - C:\|CLARITY\|WORK2\|DATA\|V VYAS\|SUBSTRATE METHOD\|NEW ODH\|CHIRAL STUDY\|VV94 901010ATH - U-PAD2 - 1)

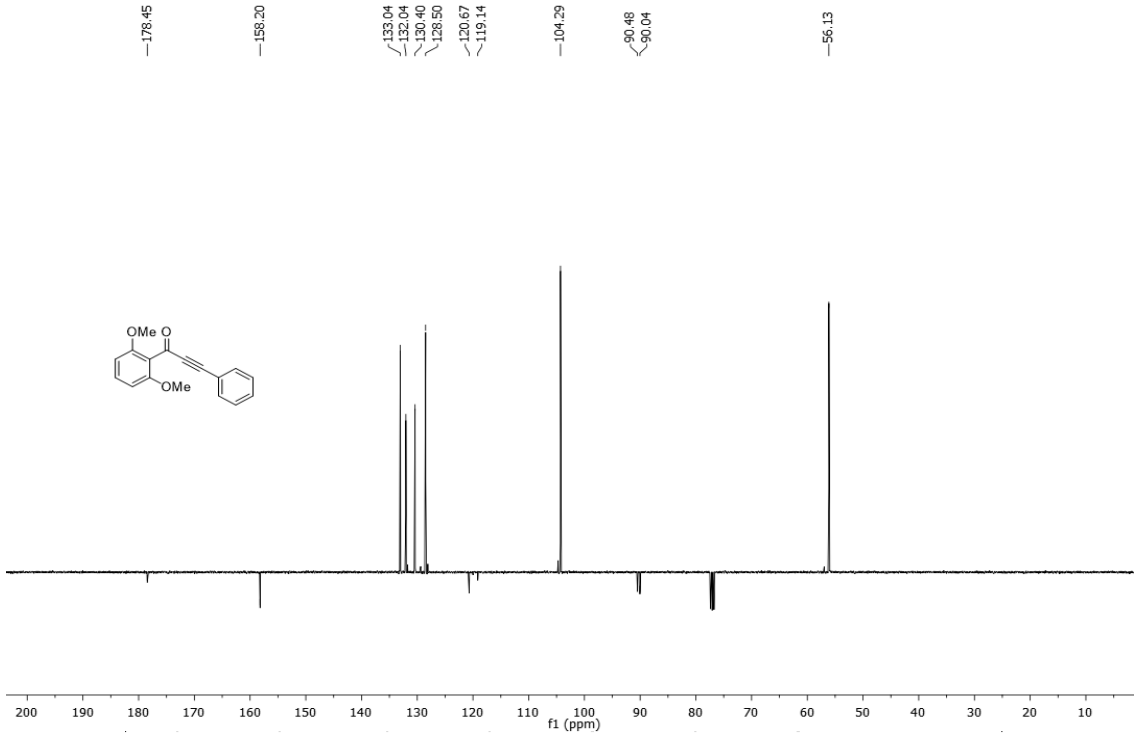
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	20.696	236.161	7.791	39.8	49.1	0.54	
2	26.396	357.263	8.086	60.2	50.9	0.68	
	Total	593.425	15.877	100.0	100.0		

1-(2,6-Dimethoxyphenyl)-3-phenylprop-2-yn-1-one.

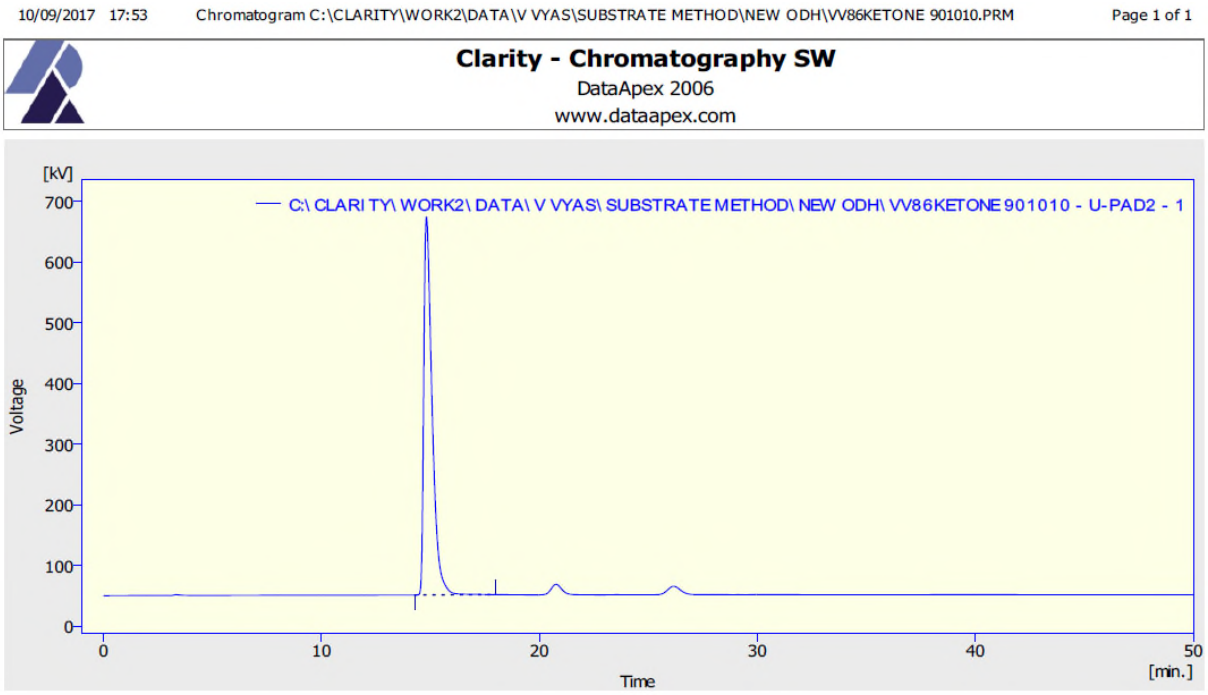
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



Ketone HPLC of 1-(2,6-dDimethoxyphenyl)-3-phenylprop-2-yn-1-one.

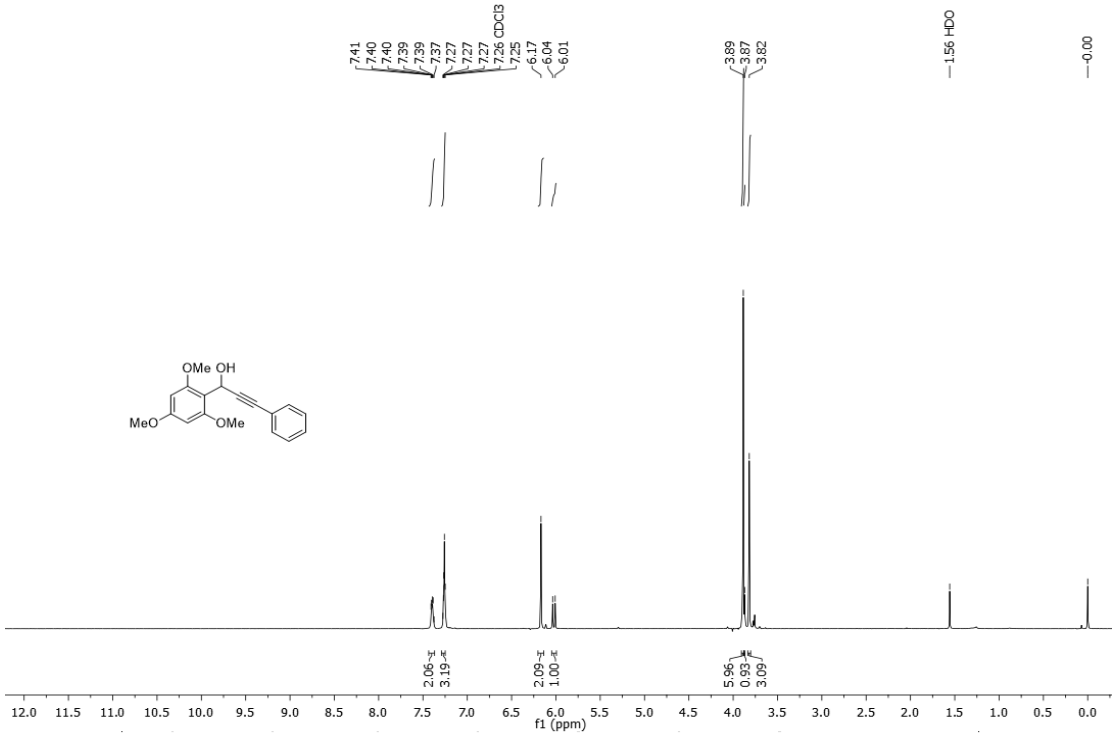


Result Table (Uncal - C:|CLARITY|WORK2|DATA|V VYAS|SUBSTRATE METHOD|NEW ODH|VV86KETONE 901010 - U-PAD2 - 1)

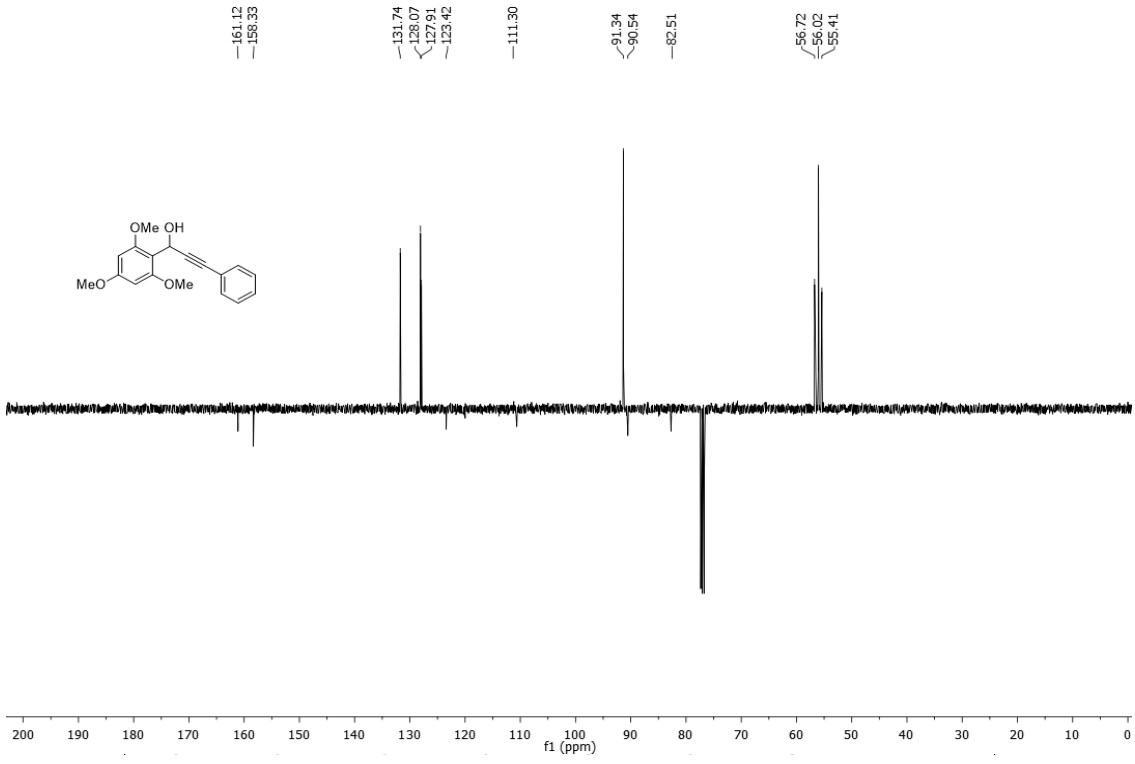
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	14.820	16539.702	622.902	100.0	100.0	0.40	
	Total	16539.702	622.902	100.0	100.0		

3-Phenyl-1-(2,4,6-trimethoxyphenyl)prop-2-yn-1-ol (24).

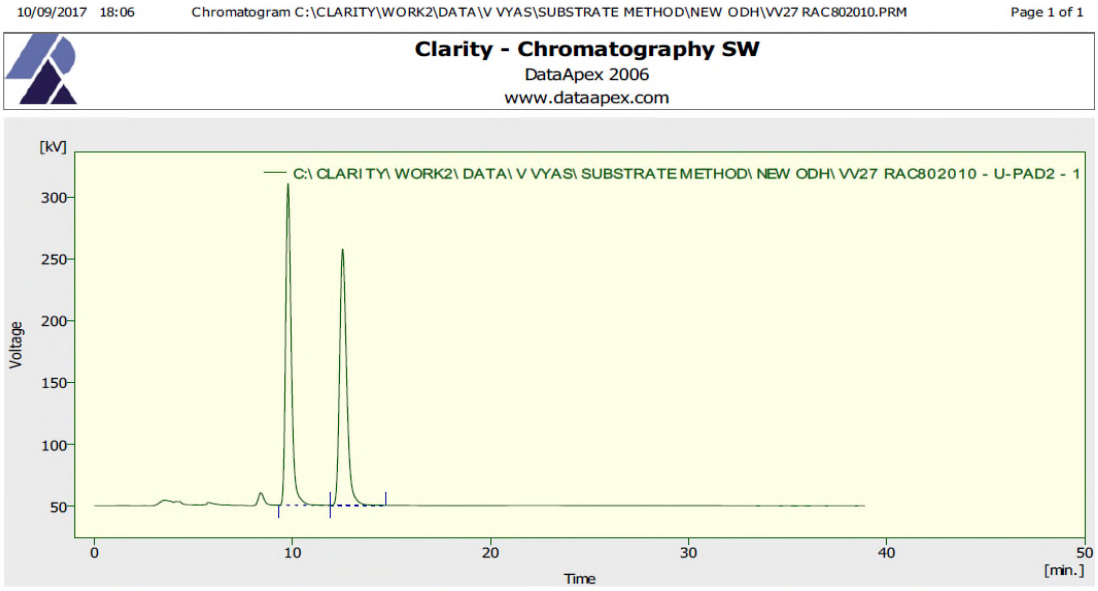
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



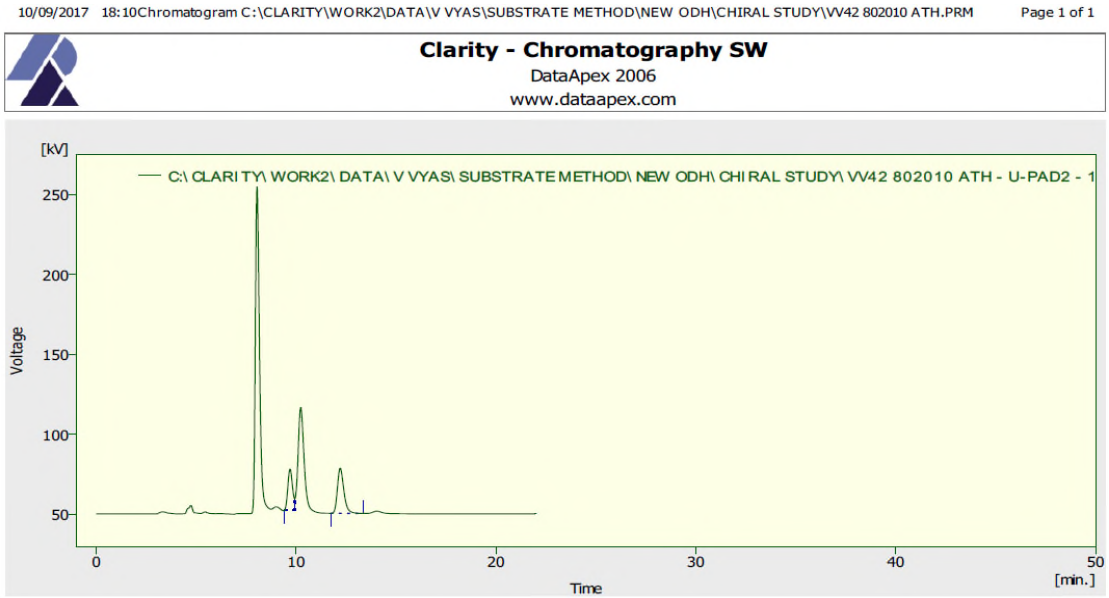
Racemic HPLC of 3-phenyl-1-(2,4,6-trimethoxyphenyl)prop-2-yn-1-ol (**24**).



Result Table (Uncal - C:|CLARITY|WORK2|DATA|V VYAS|SUBSTRATE METHOD|NEW ODH|VV27 RAC802010 - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	9.776	5126.736	260.130	50.0	55.7	0.30	
2	12.536	5135.054	207.290	50.0	44.3	0.38	
	Total	10261.789	467.420	100.0	100.0		

HPLC after ATH of 3-phenyl-1-(2,4,6-trimethoxyphenyl)prop-2-yn-1-ol (**24**) (20% conversion, 20% ee).

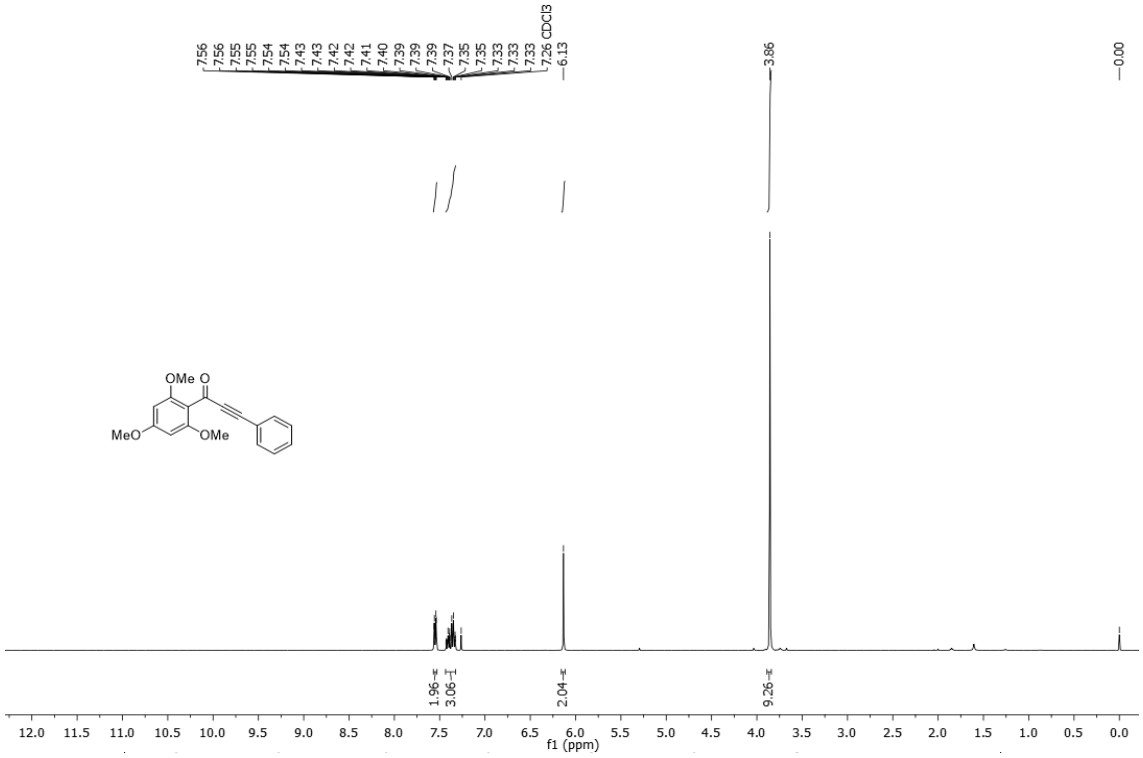


Result Table (Uncal - C:|CLARITY|WORK2|DATA|V VYAS|SUBSTRATE METHOD|NEW ODH|CHIRAL STUDY|VV42 802010 ATH - U-PAD2 - 1)

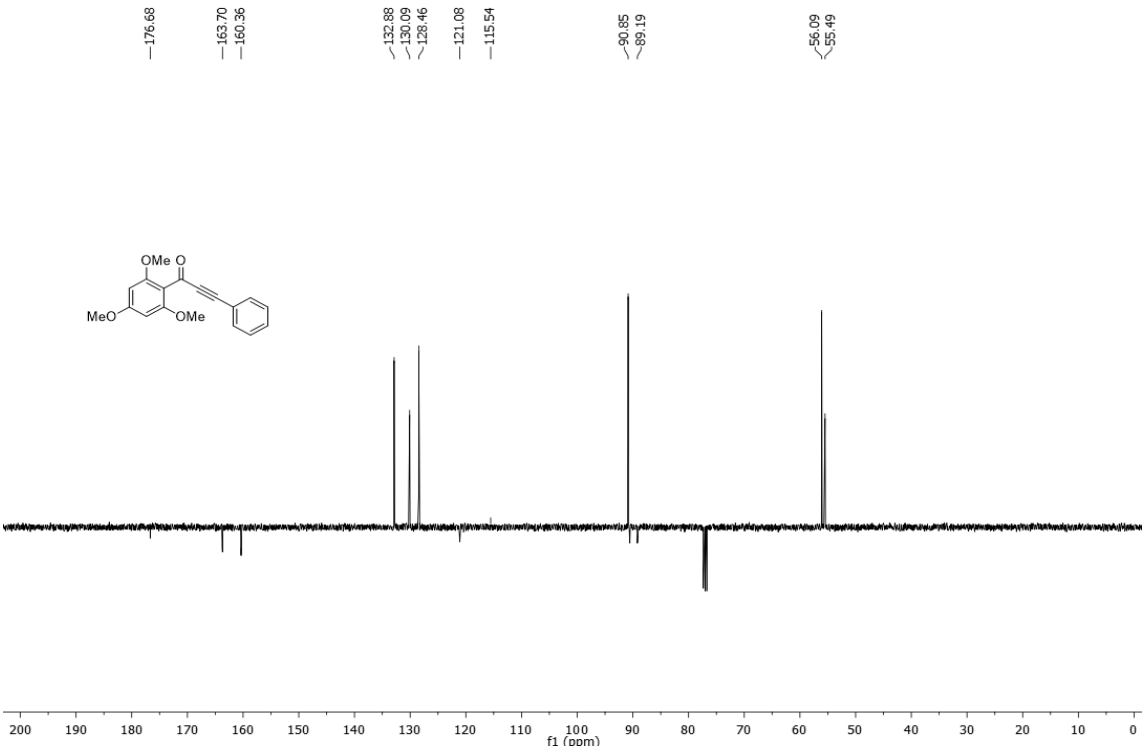
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	9.696	422.717	25.704	40.0	47.6	0.27	
2	12.204	634.104	28.261	60.0	52.4	0.34	
	Total	1056.821	53.965	100.0	100.0		

3-Phenyl-1-(2,4,6-trimethoxyphenyl)prop-2-yn-1-one.

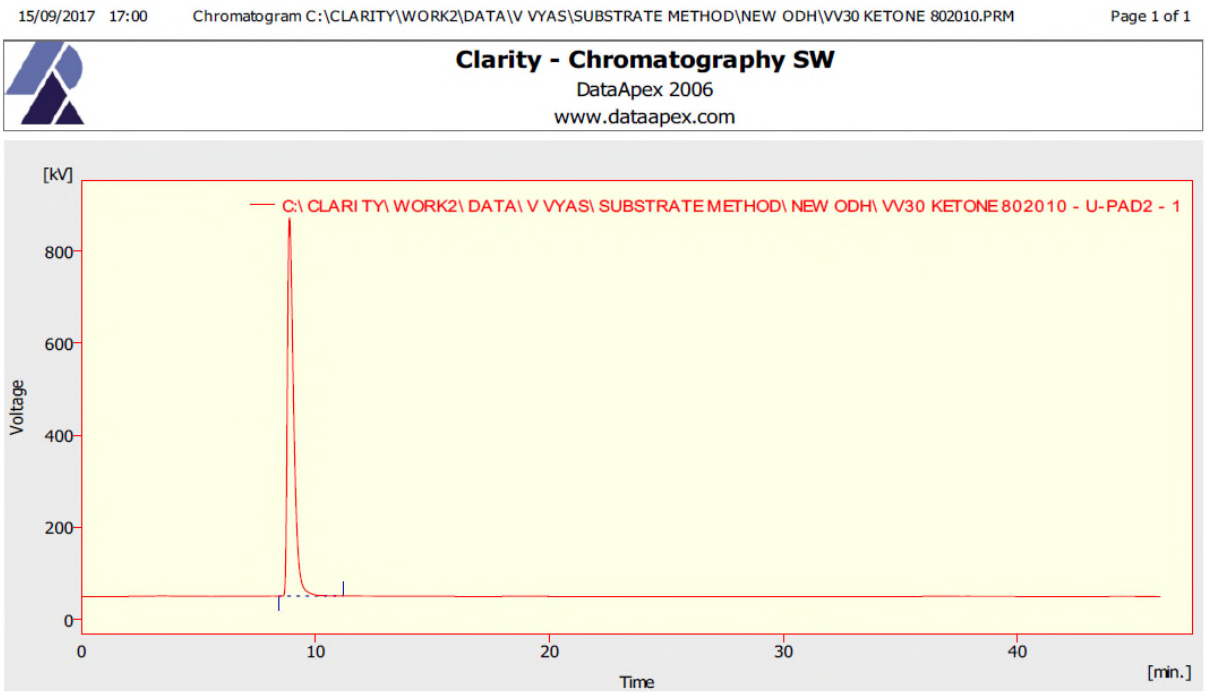
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



Ketone HPLC of 3-phenyl-1-(2,4,6-trimethoxyphenyl)prop-2-yn-1-one.

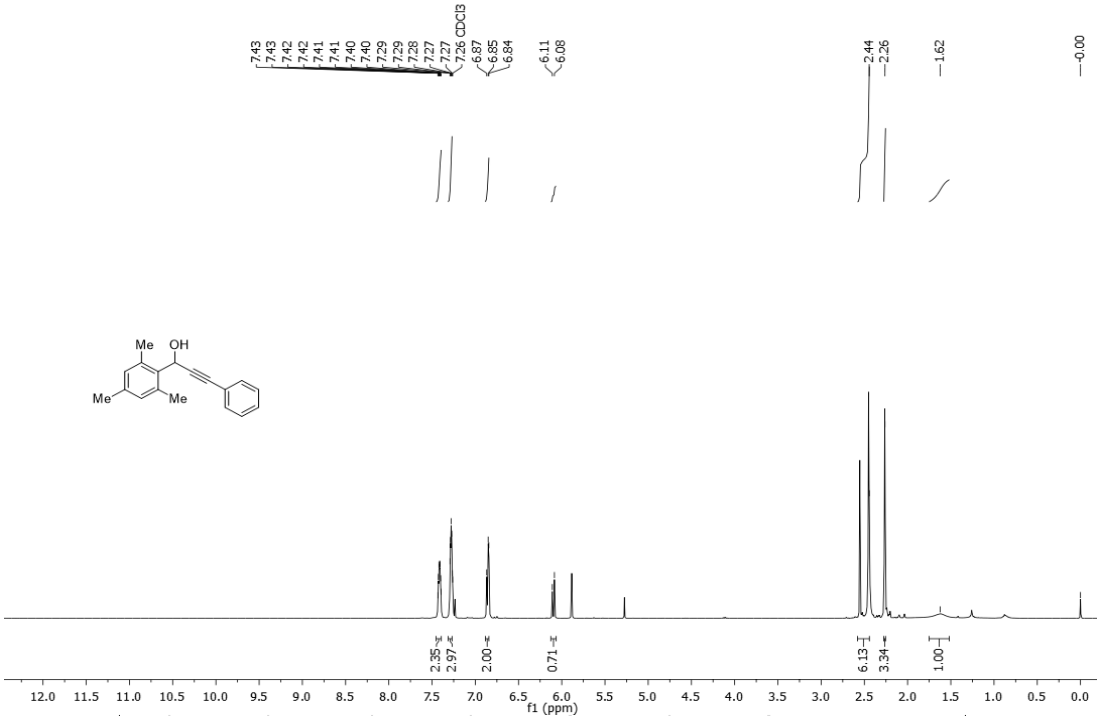


Result Table (Uncal - C:\CLARITY\WORK2\DATA\V VYAS\SUBSTRATE METHOD\NEW ODH\VV30 KETONE 802010 - U-PAD2 - 1)

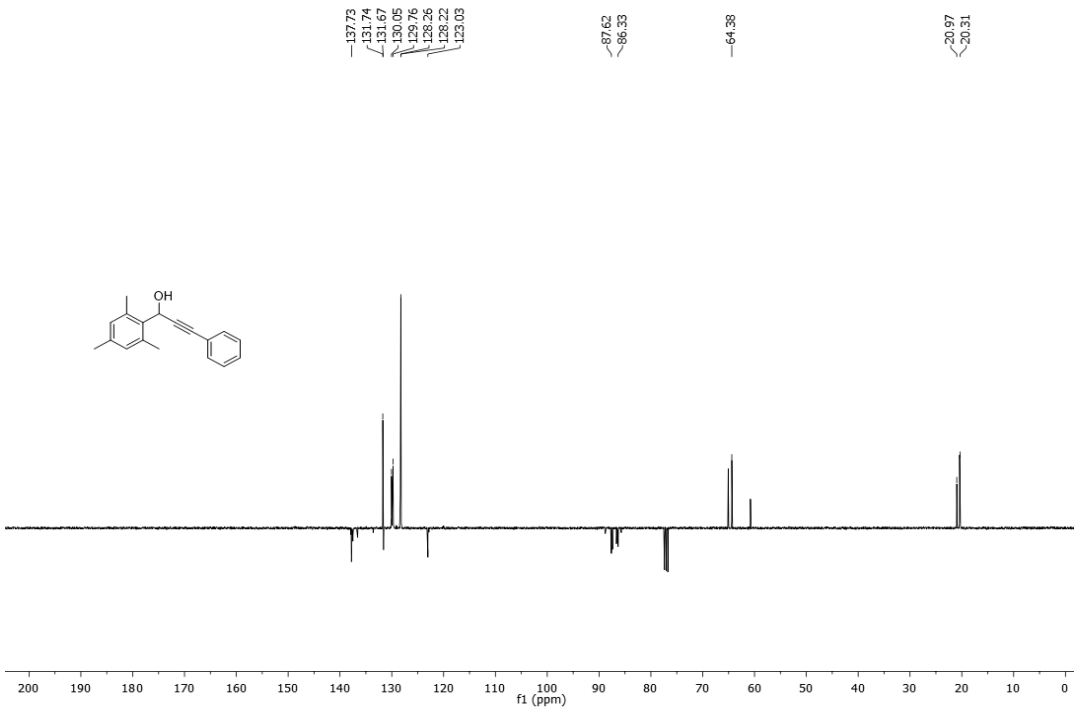
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	8.888	15387.919	821.568	100.0	100.0	0.28	
	Total	15387.919	821.568	100.0	100.0		

1-Mesityl-3-phenylprop-2-yn-1-ol (25).

^{1}H NMR (400 MHz, $CDCl_3$)

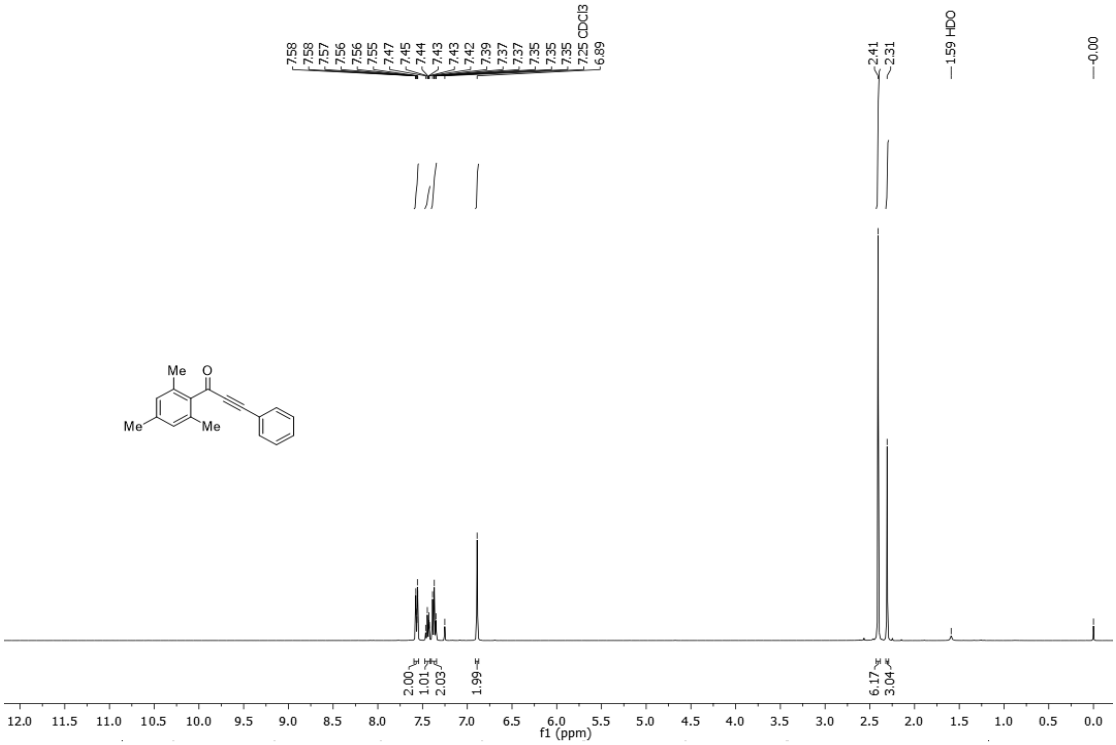


^{13}C NMR (101 MHz, $CDCl_3$)

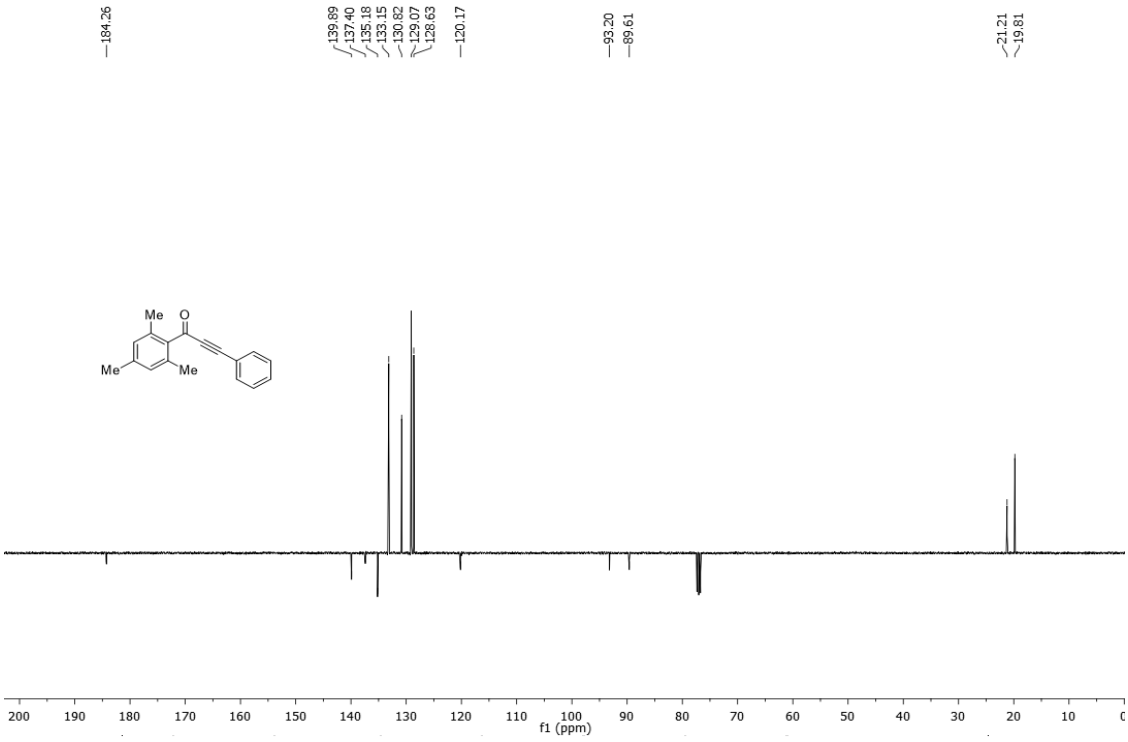


1-Mesityl-3-phenylprop-2-yn-1-one.

^{1}H NMR (400 MHz, $CDCl_3$)

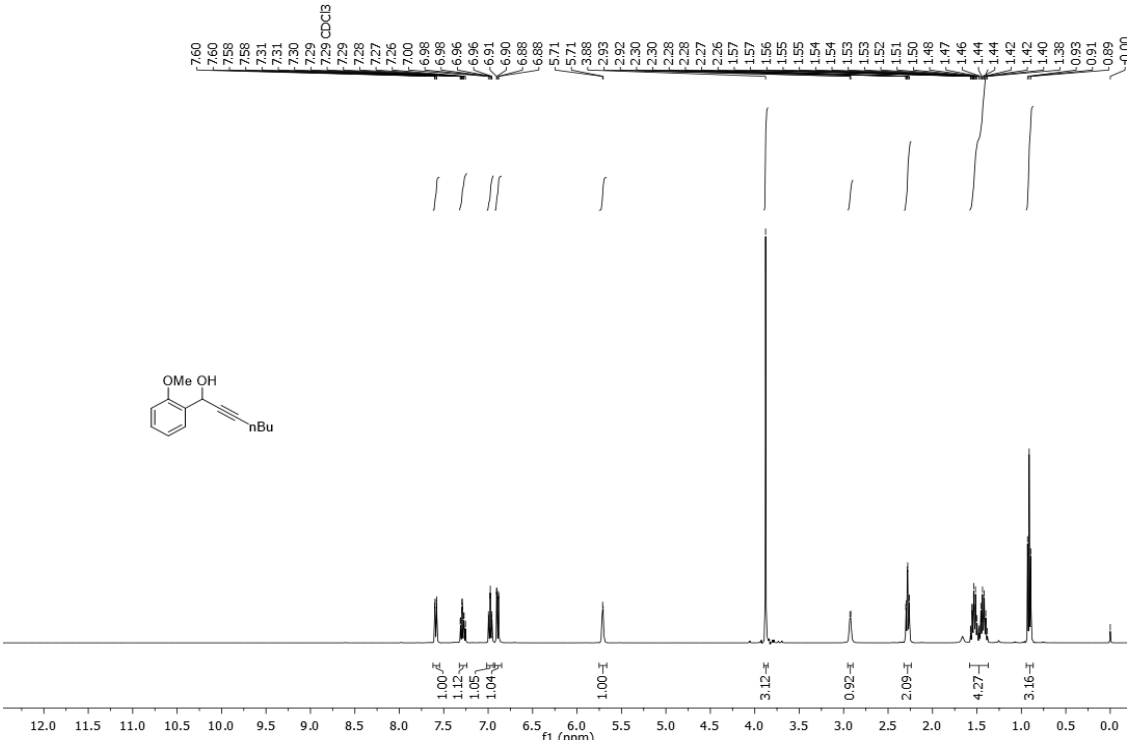


^{13}C NMR (101 MHz, $CDCl_3$)

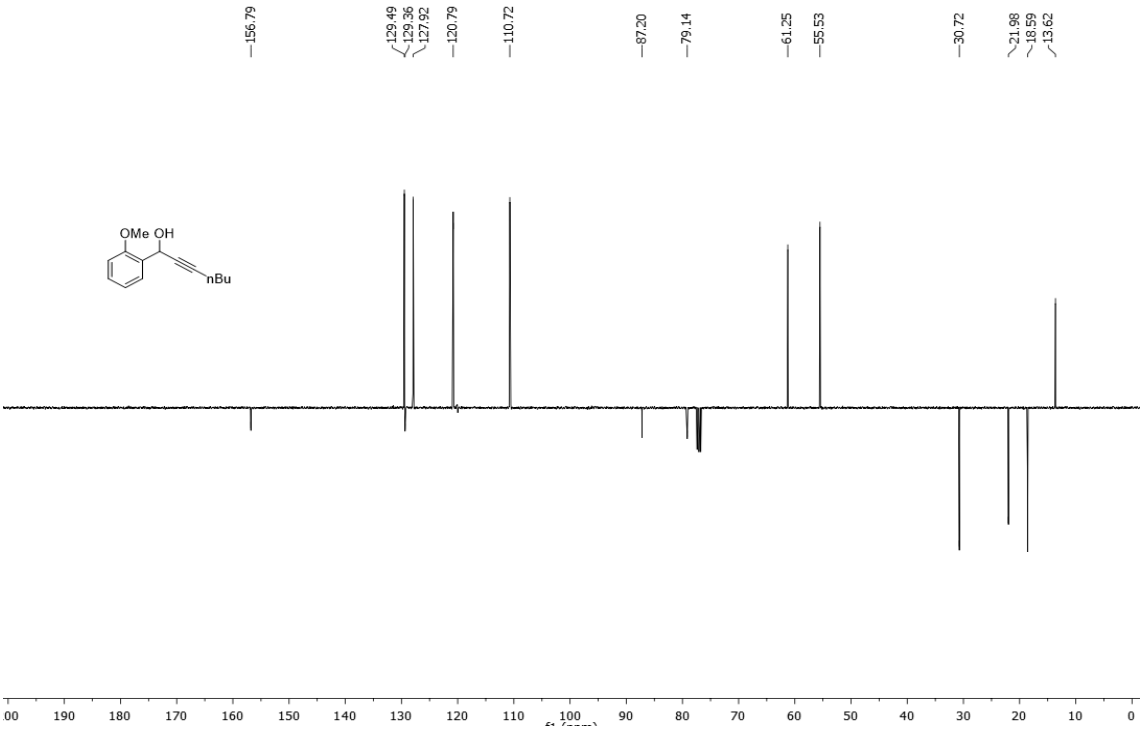


1-(2-methoxyphenyl)hept-2-yn-1-ol (27).

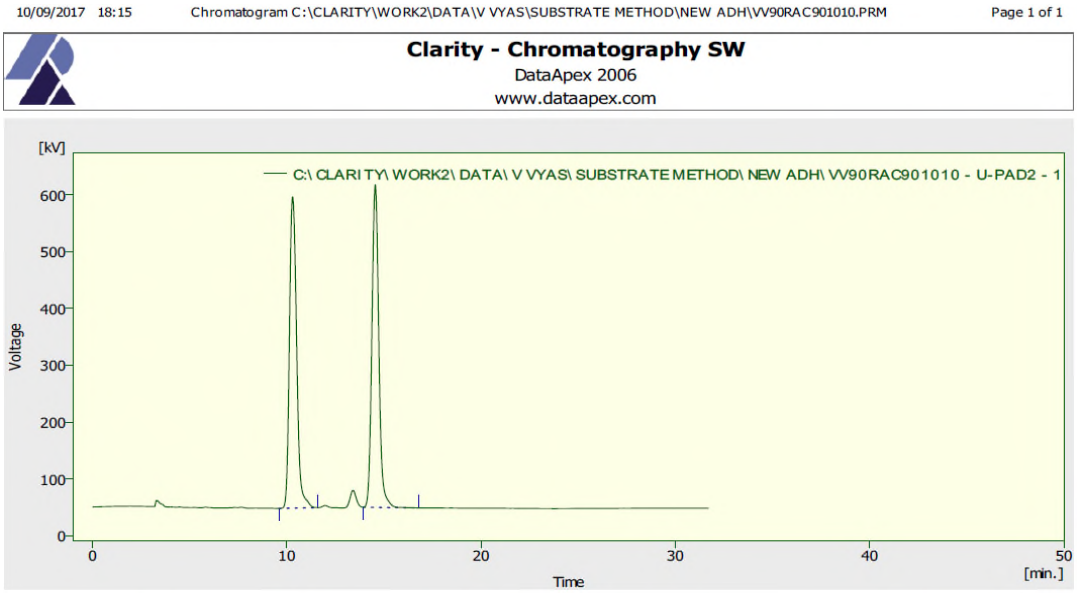
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



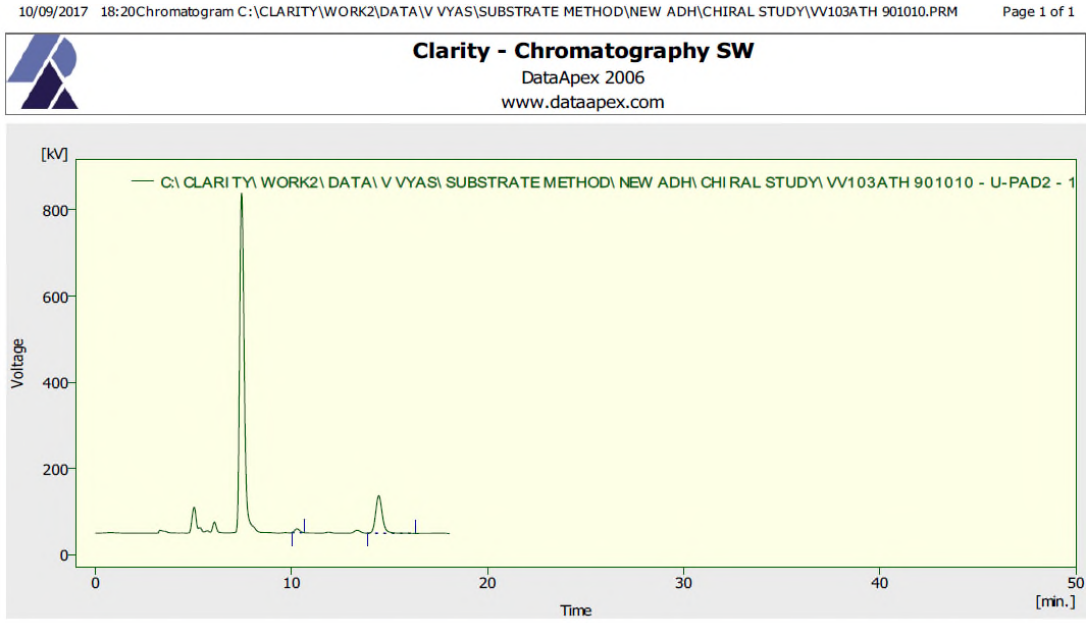
Racemic HPLC of 1-(2-methoxyphenyl)hept-2-yn-1-ol (**27**).



Result Table (Uncal - C:\|CLARITY\|WORK2\|DATA\|V VYAS\|SUBSTRATE METHOD\|NEW ADH\|VV90RAC901010 - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	10.300	14090.603	547.240	50.1	49.1	0.40	
2	14.556	14030.866	567.136	49.9	50.9	0.38	
	Total	28121.469	1114.376	100.0	100.0		

HPLC after ATH of 1-(2-methoxyphenyl)hept-2-yn-1-ol (**27**) (15% conversion, 86% ee).

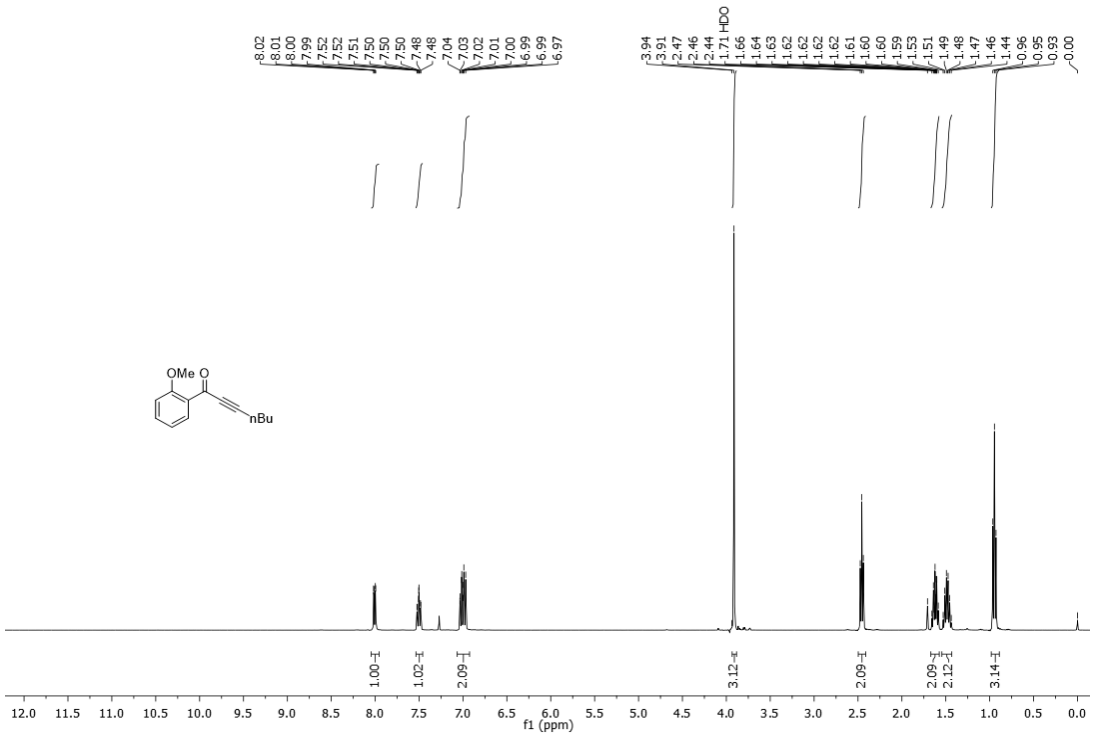


Result Table (Uncal - C:\|CLARITY\|WORK2\|DATA\|V VYAS\|SUBSTRATE METHOD\|NEW ADH\|CHIRAL STUDY\|VV103ATH 901010 - U-PAD2 - 1)

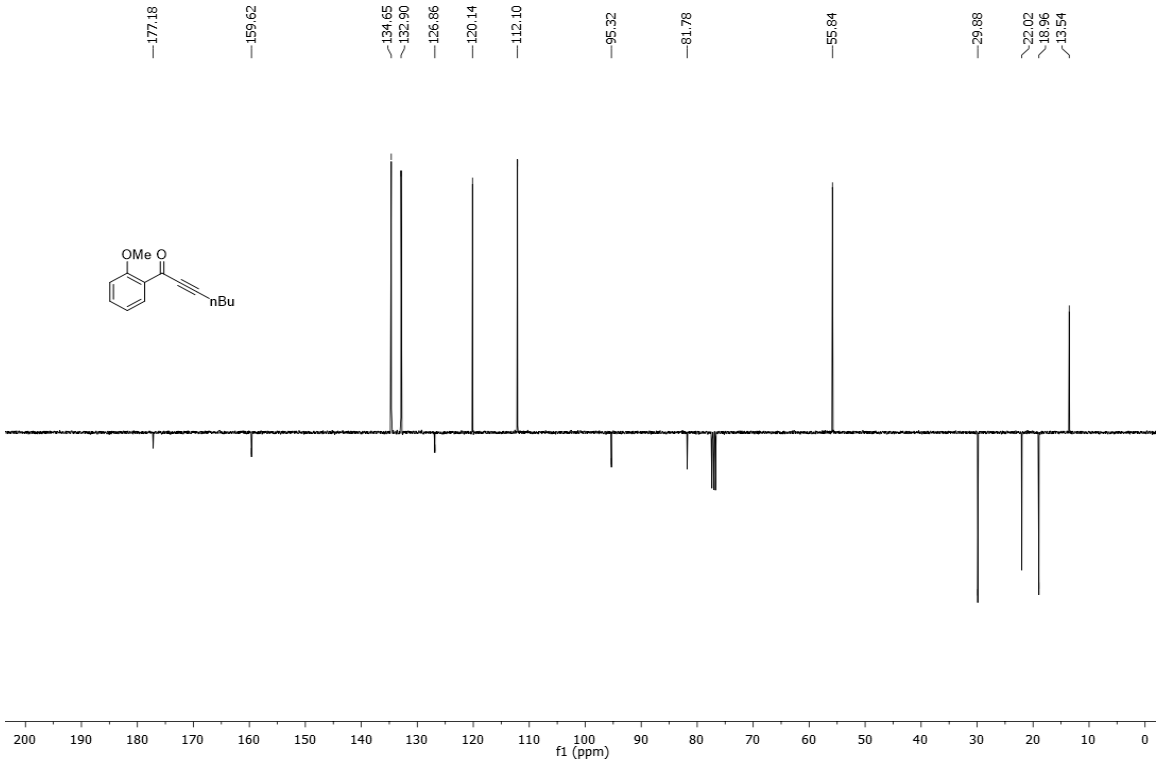
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	10.280	154.689	8.842	7.0	9.2	0.28	
2	14.452	2042.913	87.109	93.0	90.8	0.35	
	Total	2197.601	95.951	100.0	100.0		

1-(2-Methoxyphenyl)hept-2-yn-1-one.

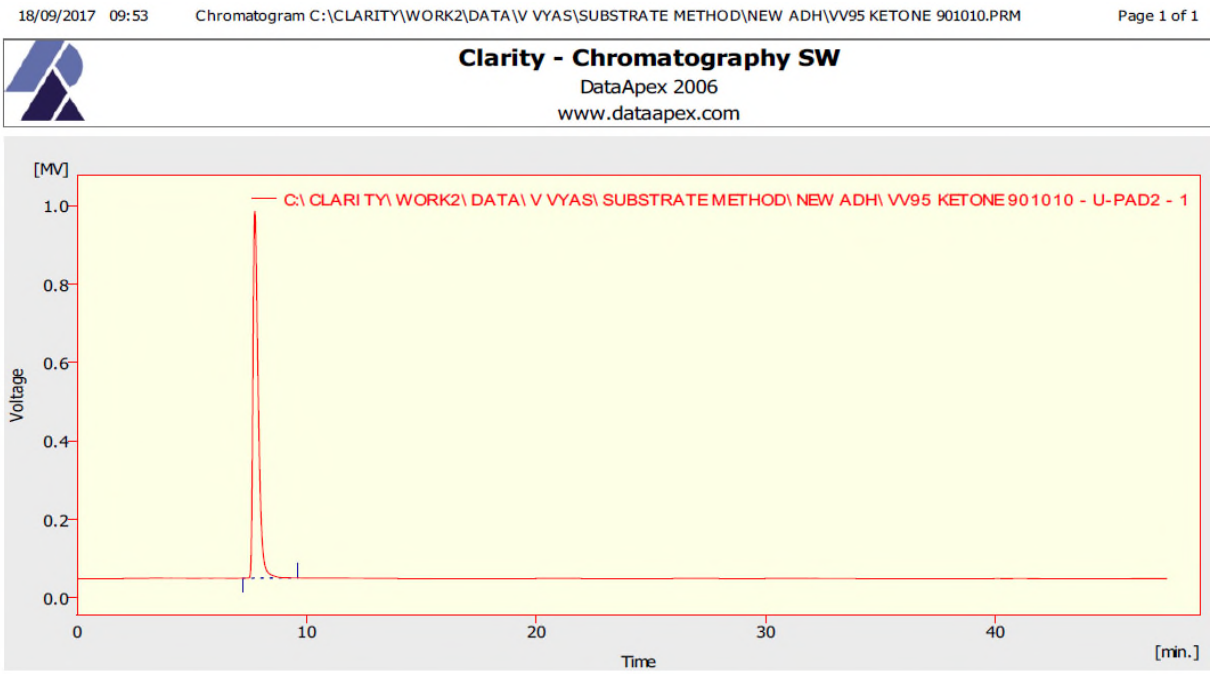
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



Ketone HPLC of 1-(2-Methoxyphenyl)hept-2-yn-1-one.

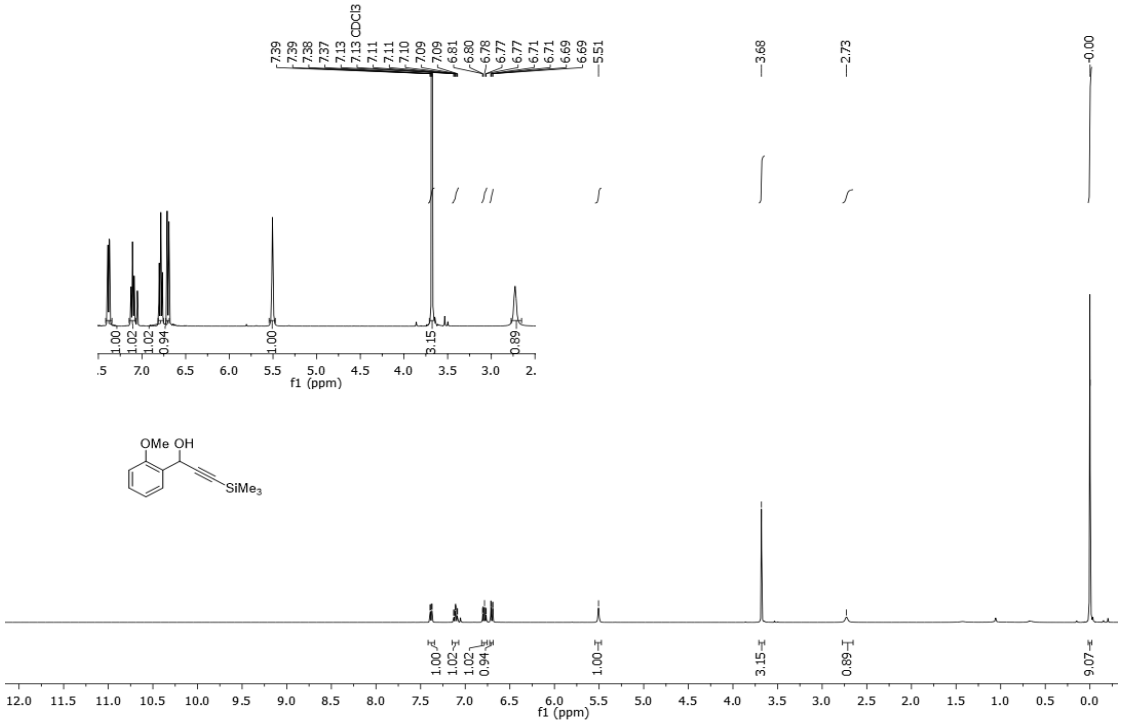


Result Table (Uncal - C:\CLARITY\WORK2\DATA\V VYAS\SUBSTRATE METHOD\NEW ADH\VV95 KETONE 901010 - U-PAD2 - 1)

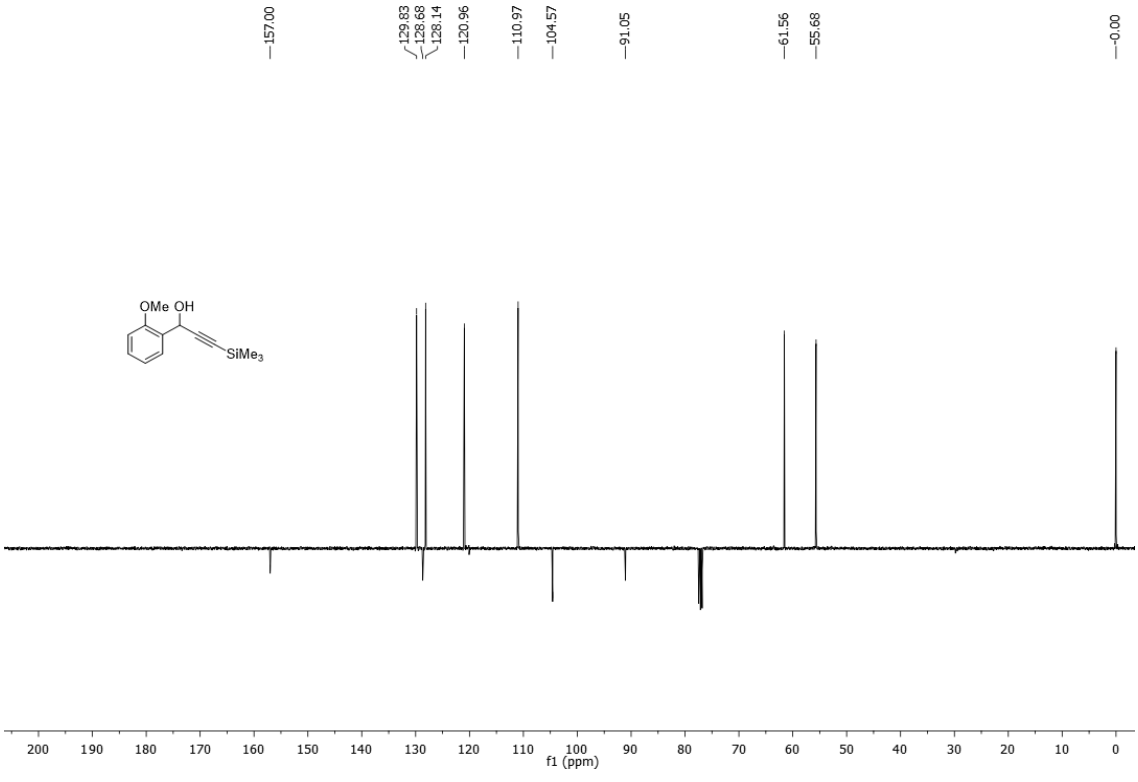
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	7.740	15186.493	934.443	100.0	100.0	0.24	
	Total	15186.493	934.443	100.0	100.0		

1-(2-Methoxyphenyl)-3-(trimethylsilyl)prop-2-yn-1-ol (28).

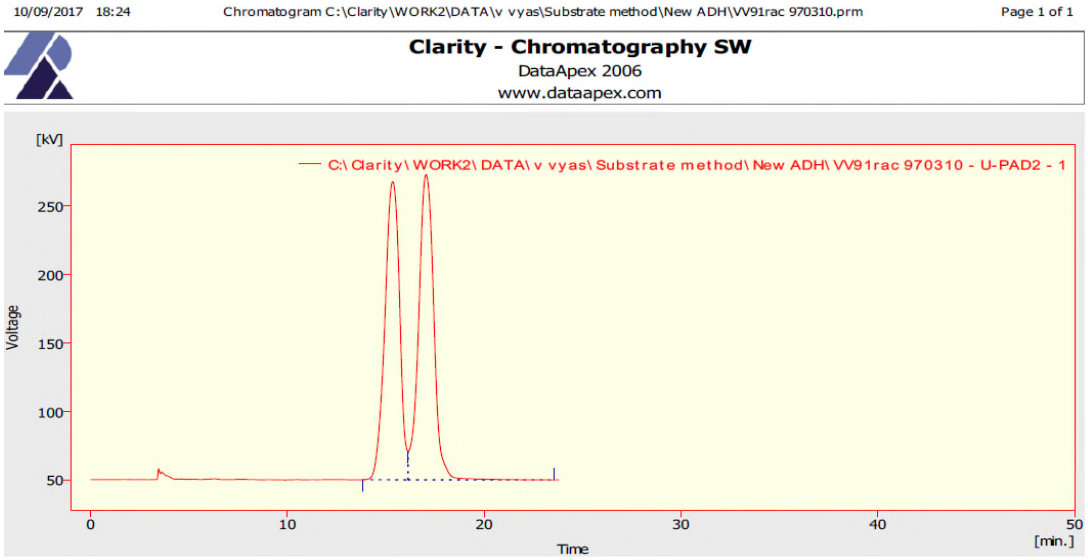
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



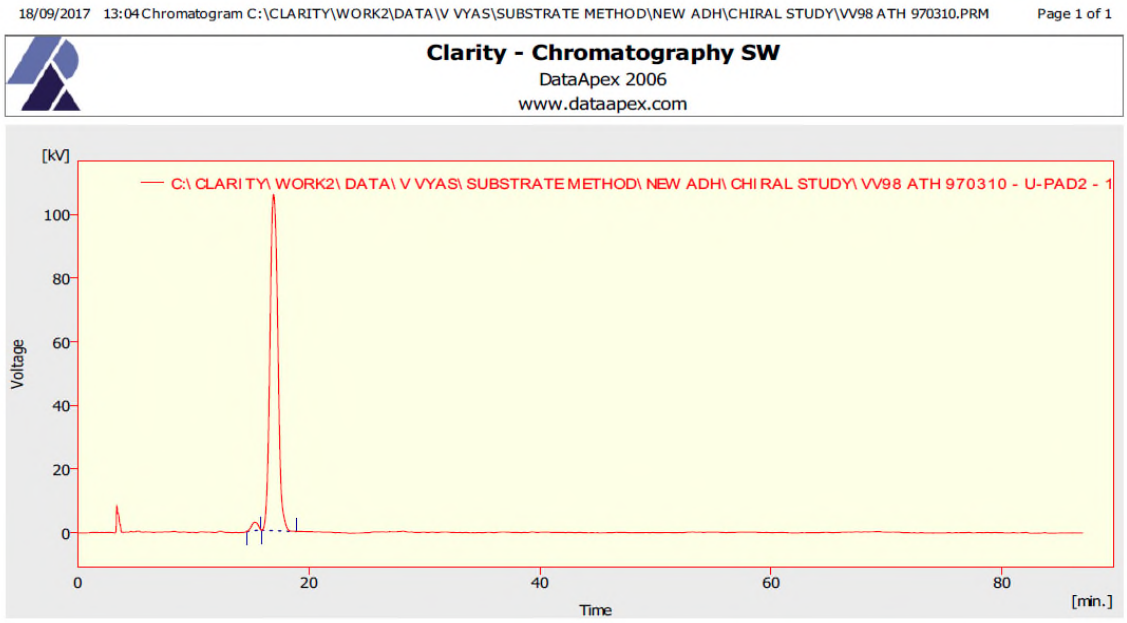
Racemic HPLC of 1-(2-methoxyphenyl)-3-(trimethylsilyl)prop-2-yn-1-ol (28).



Result Table (Uncal - C:\Clarity\WORK2\DATA\v vyas\Substrate method\New ADH\VV91rac 970310 - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	15.352	11374.008	217.704	48.8	49.4	0.82	
2	17.048	11940.672	222.894	51.2	50.6	0.81	
	Total	23314.681	440.598	100.0	100.0		

HPLC after ATH of 1-(2-methoxyphenyl)-3-(trimethylsilyl)prop-2-yn-1-ol (**28**) (100% conversion,96% ee).

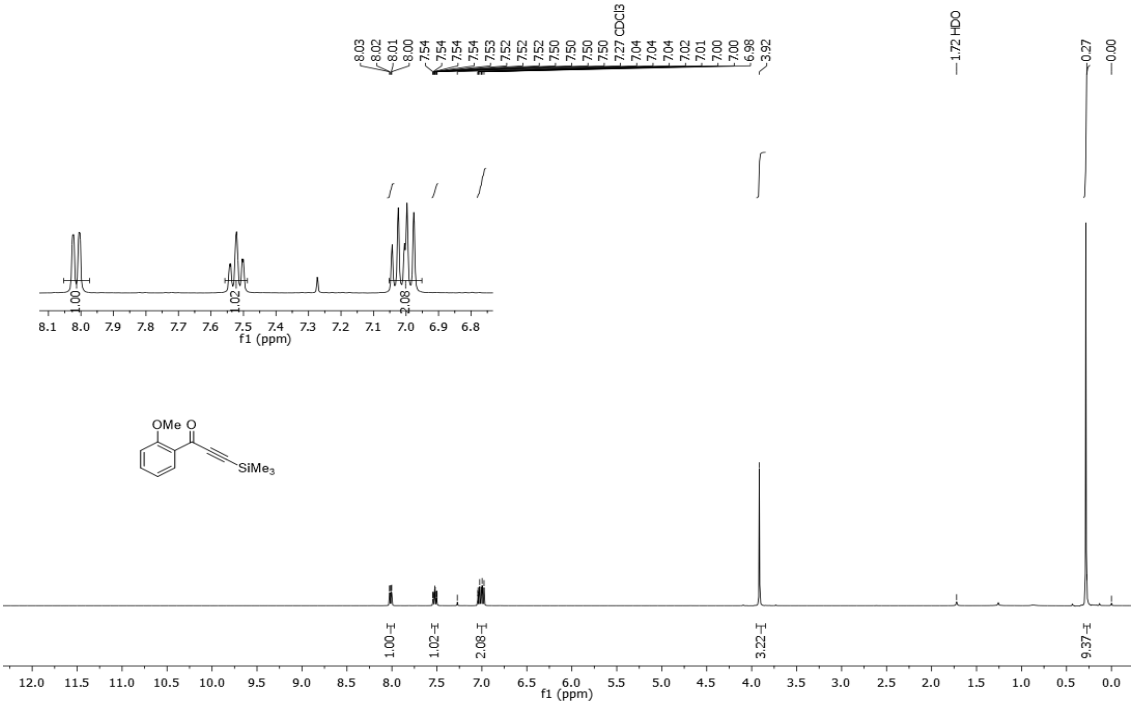


Result Table (Uncal - C:\CLARITY\WORK2\DATA\V VYAS\SUBSTRATE METHOD\NEW ADH\CHIRAL STUDY\VV98 ATH 970310 - U-PAD2 - 1)

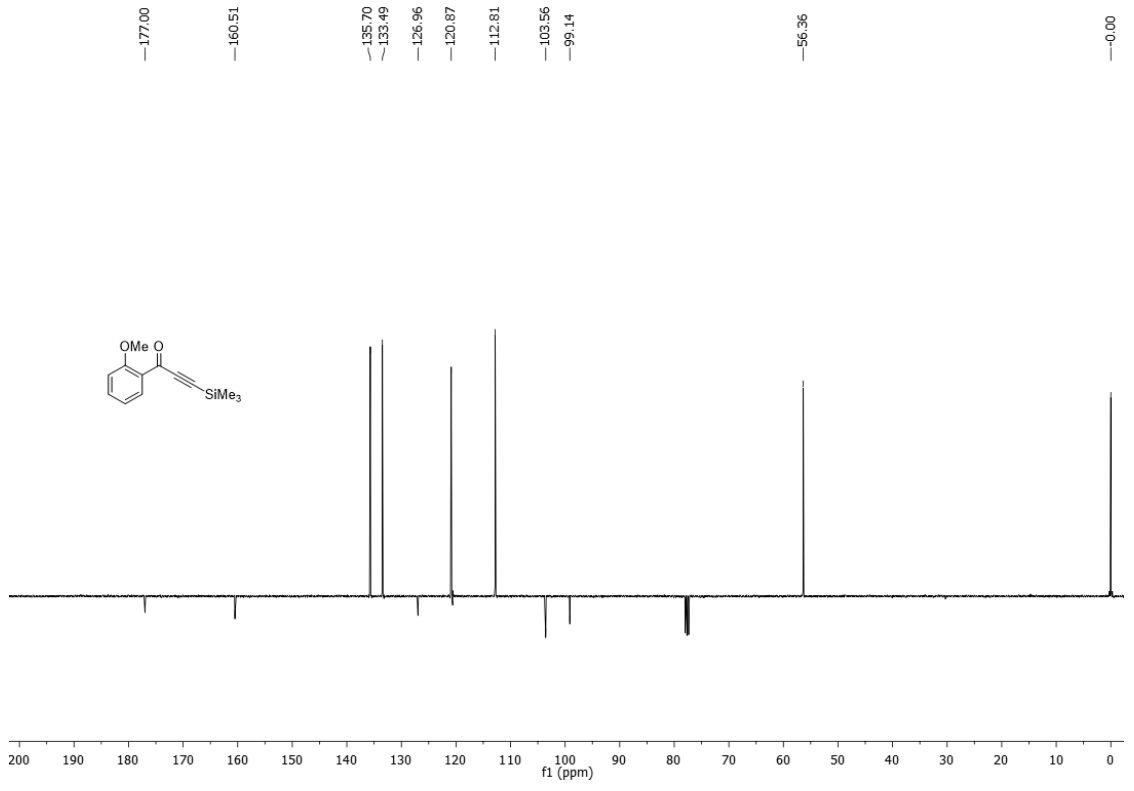
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	15.328	104.426	2.625	2.0	2.4	0.66	
2	16.944	5035.301	105.648	98.0	97.6	0.75	
	Total	5139.727	108.274	100.0	100.0		

1-(2-Methoxyphenyl)-3-(trimethylsilyl)prop-2-yn-1-one.

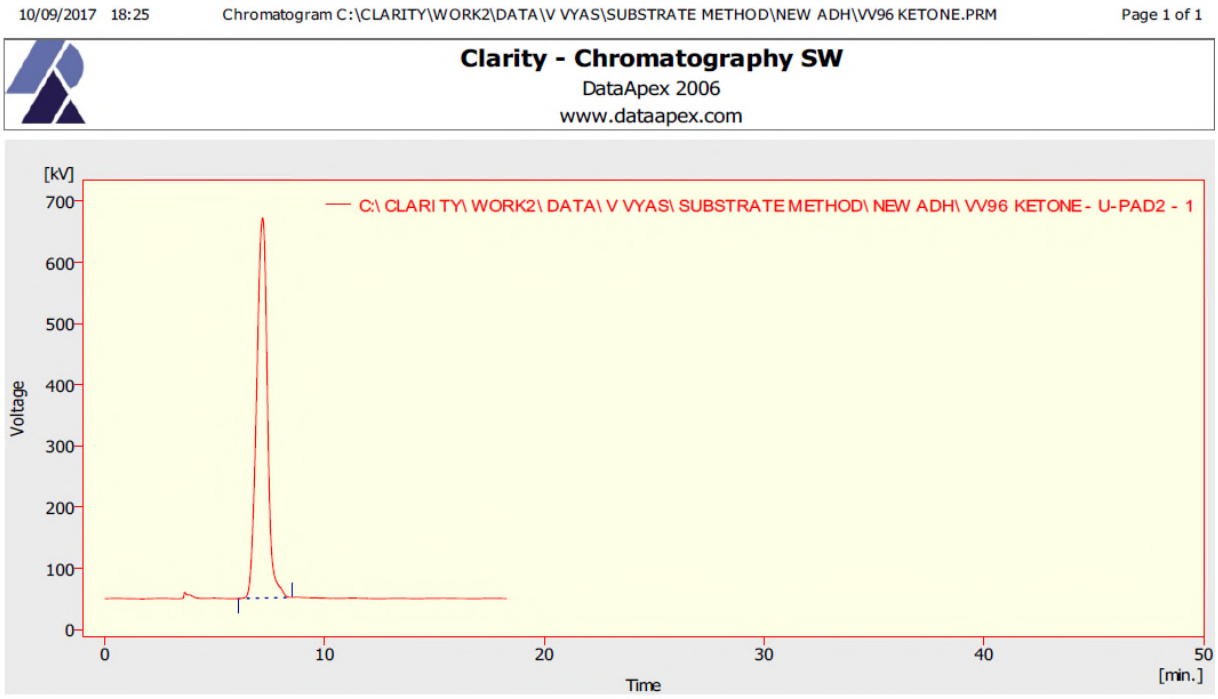
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



Ketone HPLC of 1-(2-methoxyphenyl)-3-(trimethylsilyl)prop-2-yn-1-one.

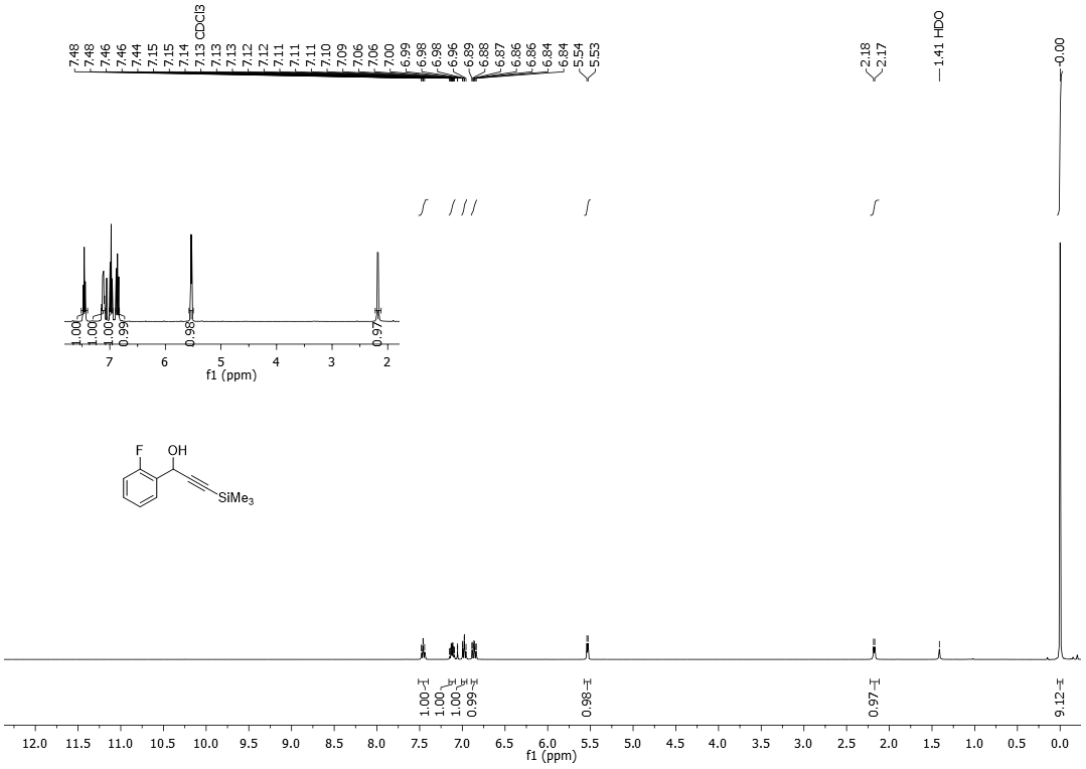


Result Table (Uncal - C:|CLARITY|WORK2|DATA|V VYAS|SUBSTRATE METHOD|NEW ADH|VV96 KETONE - U-PAD2 - 1)

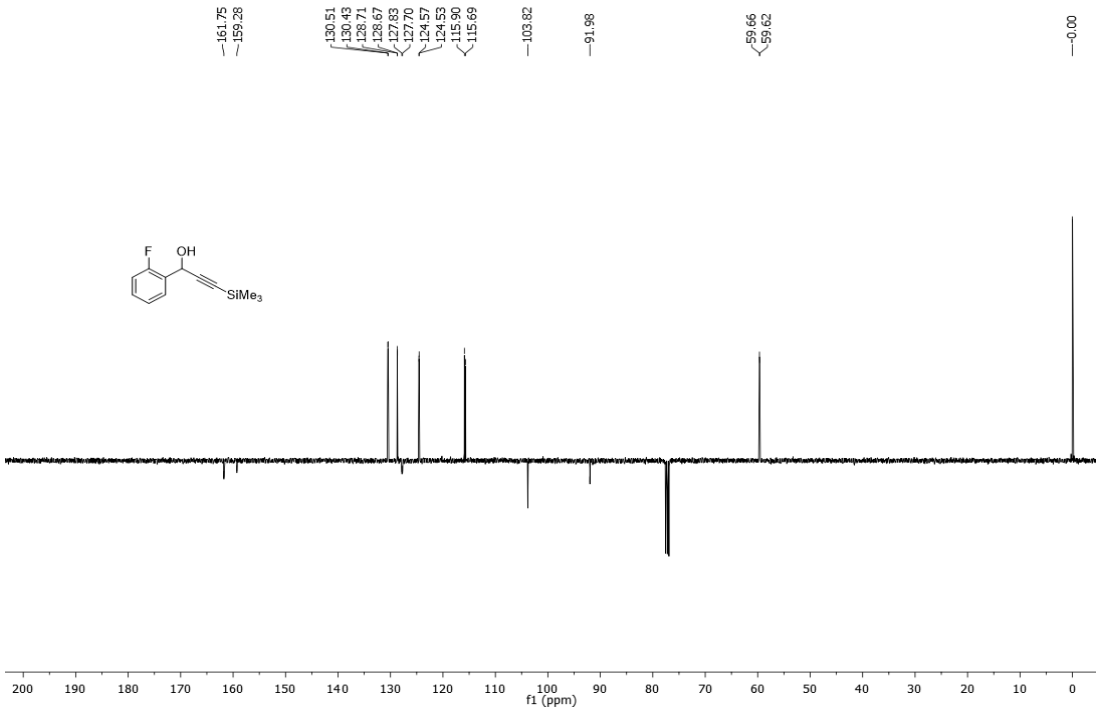
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	7.184	21282.589	621.535	100.0	100.0	0.52	
	Total	21282.589	621.535	100.0	100.0		

1-(2-Fluorophenyl)-3-(trimethylsilyl)prop-2-yn-1-ol (29).

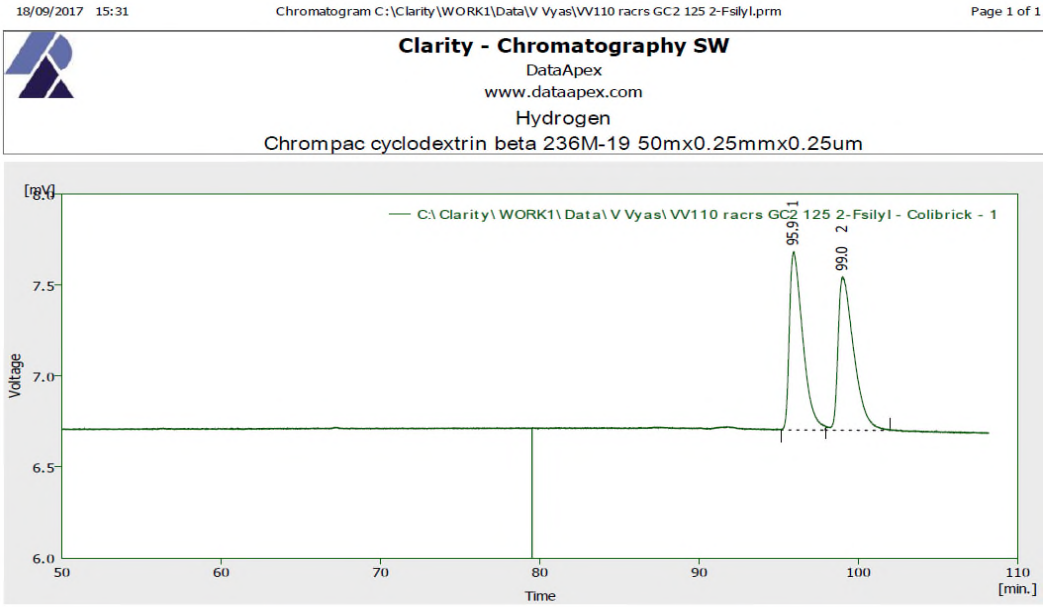
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



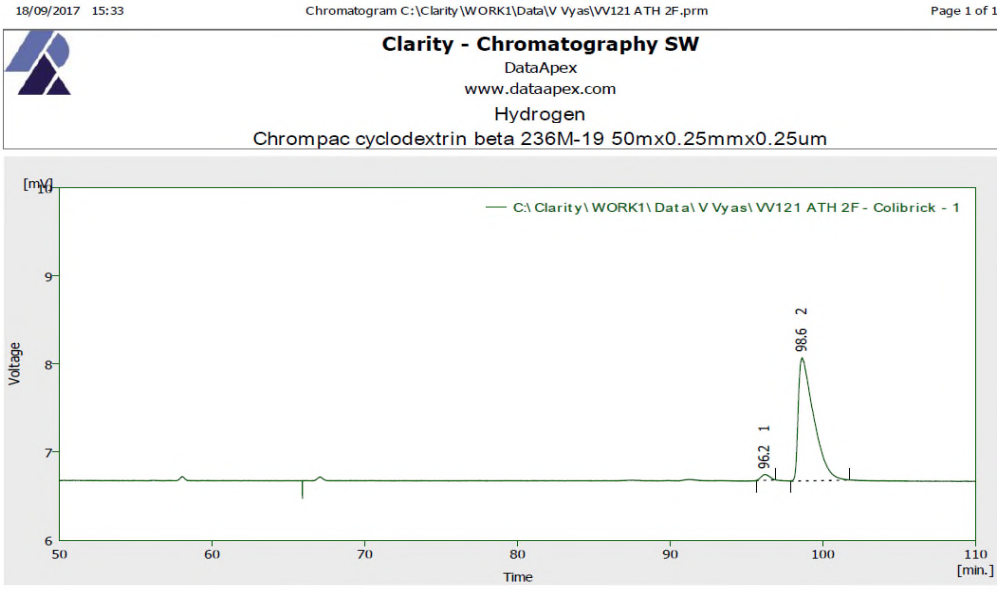
Racemic GC of 1-(2-fluorophenyl)-3-(trimethylsilyl)prop-2-yn-1-ol (**29**).



Result Table (Uncal - C:\|Clarity\|WORK1\|Data\|V Vyas\|VV110 racrs GC2 125 2-Fsilyl - Colibrick - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	95.928	57.111	0.981	49.5	53.8	0.89	
2	99.008	58.170	0.844	50.5	46.2	1.04	
	Total	115.280	1.825	100.0	100.0		

GC after ATH of 1-(2-Fluorophenyl)-3-(trimethylsilyl)prop-2-yn-1-ol (**29**) (100% conversion, 94.8% ee).

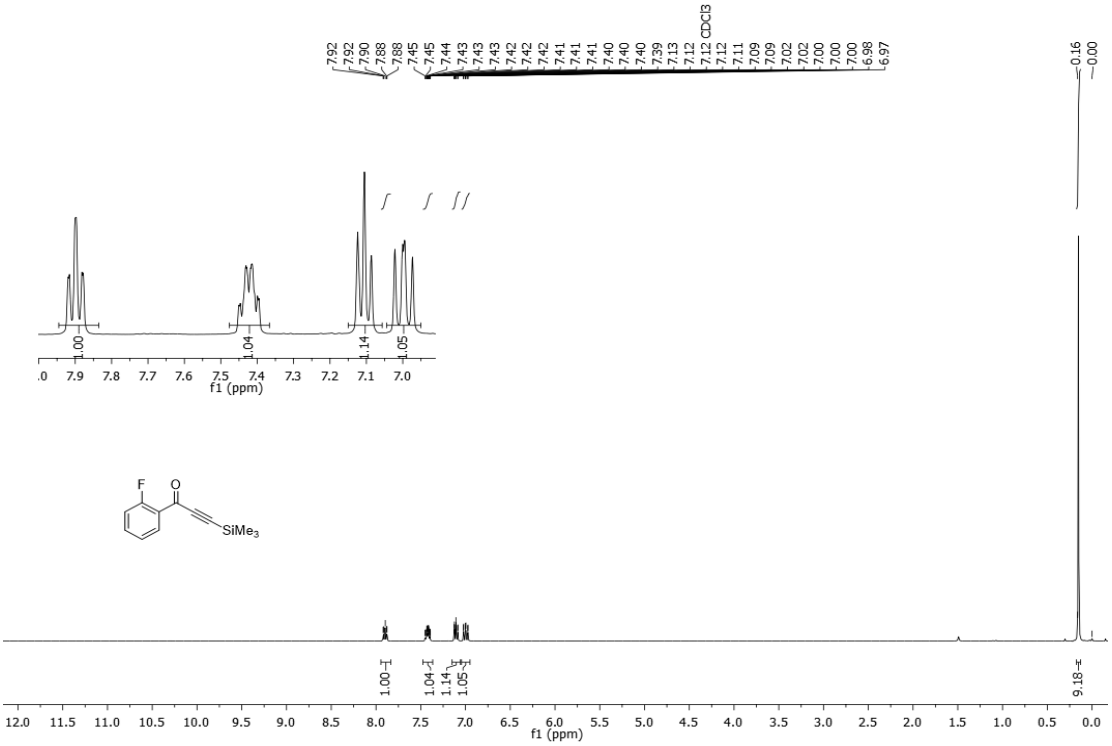


Result Table (Uncal - C:\|Clarity\|WORK1\|Data\|V Vyas\|VV121 ATH 2F - Colibrick - 1)

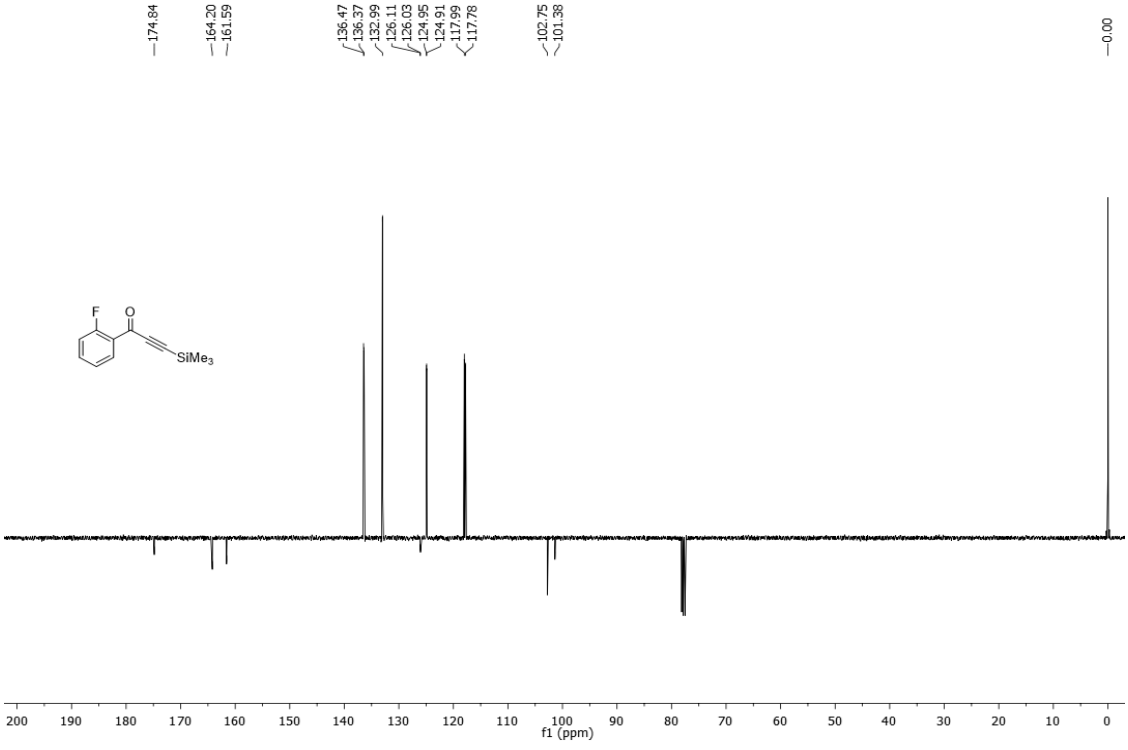
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	96.196	2.587	0.067	2.6	4.5	0.65	
2	98.640	98.441	1.401	97.4	95.5	1.08	
	Total	101.028	1.468	100.0	100.0		

1-(2-Fluorophenyl)-3-(trimethylsilyl)prop-2-yn-1-one.

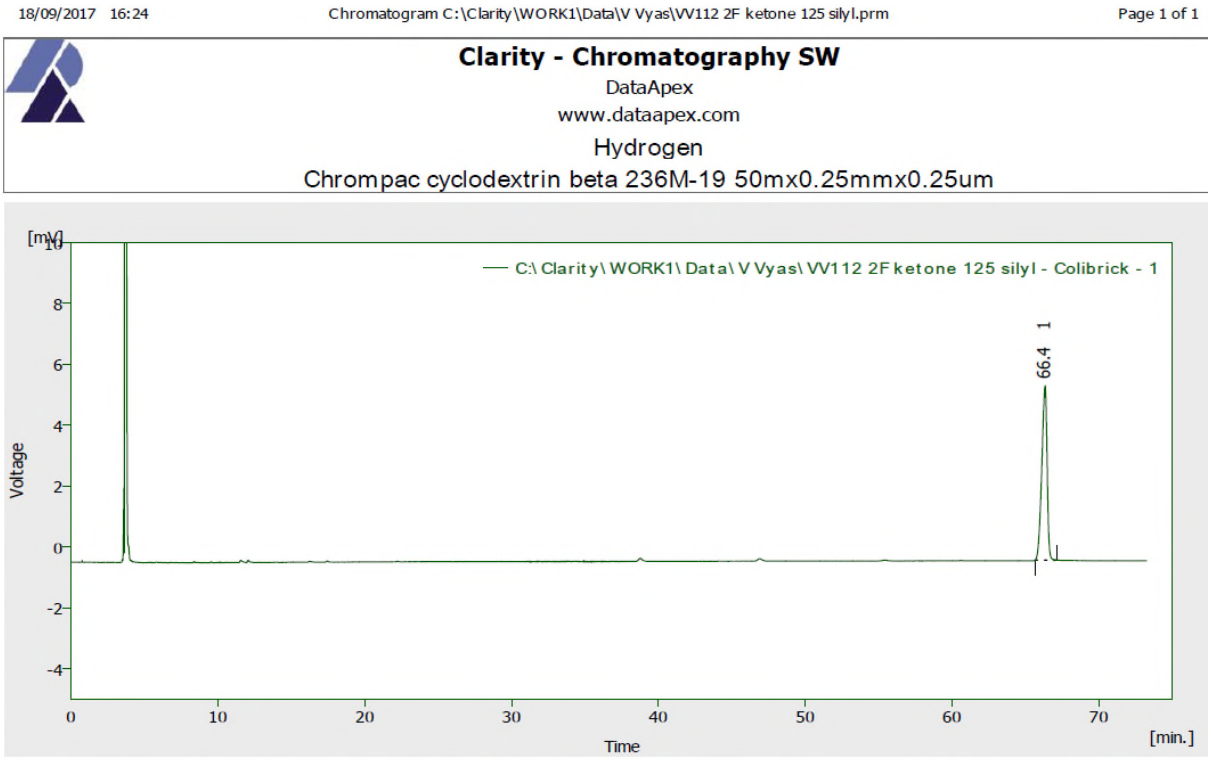
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



Ketone GC of 1-(2-fluorophenyl)-3-(trimethylsilyl)prop-2-yn-1-one.

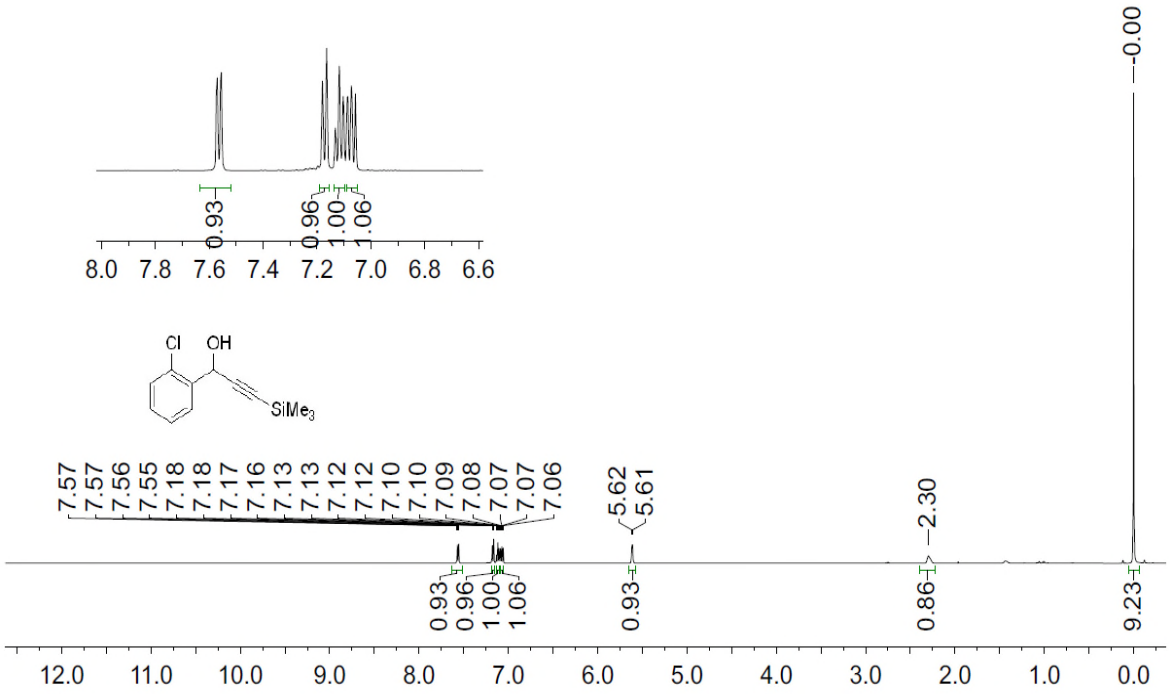


Result Table (Uncal - C:|Clarity|WORK1|Data|V Vyas|VV112 2F ketone 125 silyl - Colibrick - 1)

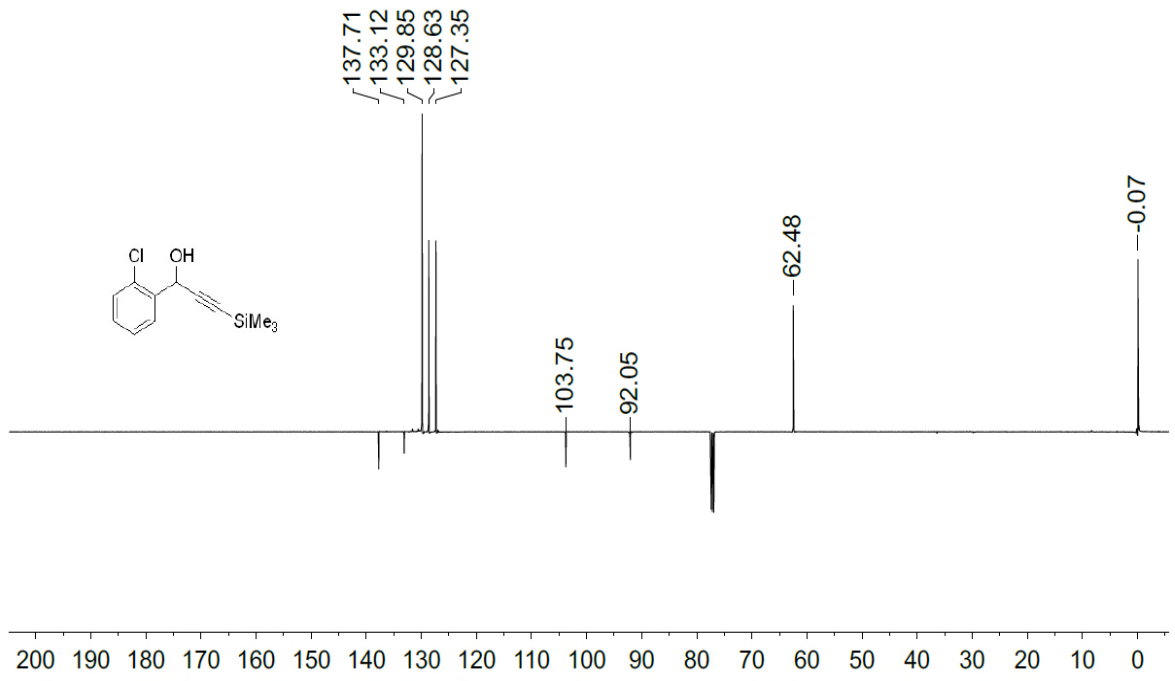
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	66.352	143.759	5.739	100.0	100.0	0.40	
	Total	143.759	5.739	100.0	100.0		

1-(2-Chlororophenyl)-3-(trimethylsilyl)prop-2-yn-1-ol (30).

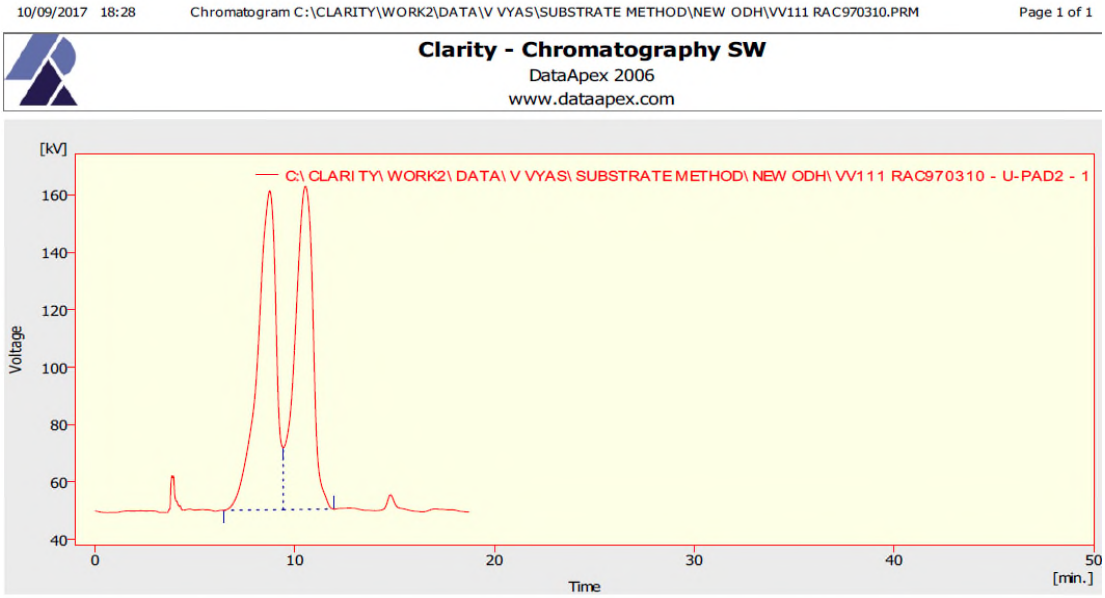
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)



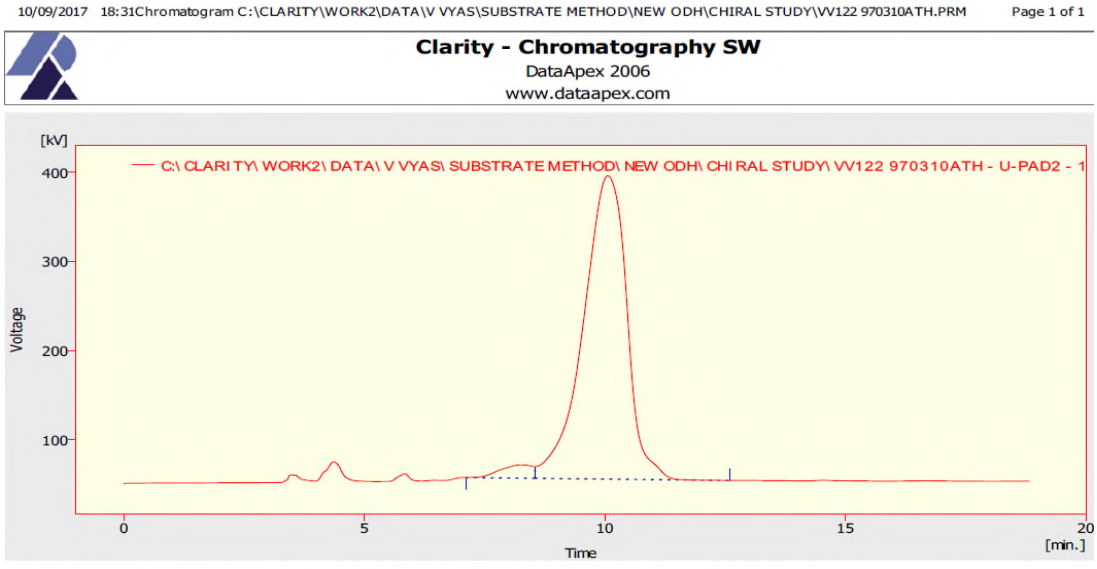
Racemic HPLC of 1-(2-chlororophenyl)-3-(trimethylsilyl)prop-2-yn-1-ol (**30**).



Result Table (Uncal - C:\CLARITY\WORK2\DATA\V VYAS\SUBSTRATE METHOD\NEW ODH\VV111 RAC970310 - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	8.748	7291.329	111.151	50.6	49.7	0.95	
2	10.536	7114.422	112.603	49.4	50.3	0.97	
	Total	14405.751	223.755	100.0	100.0		

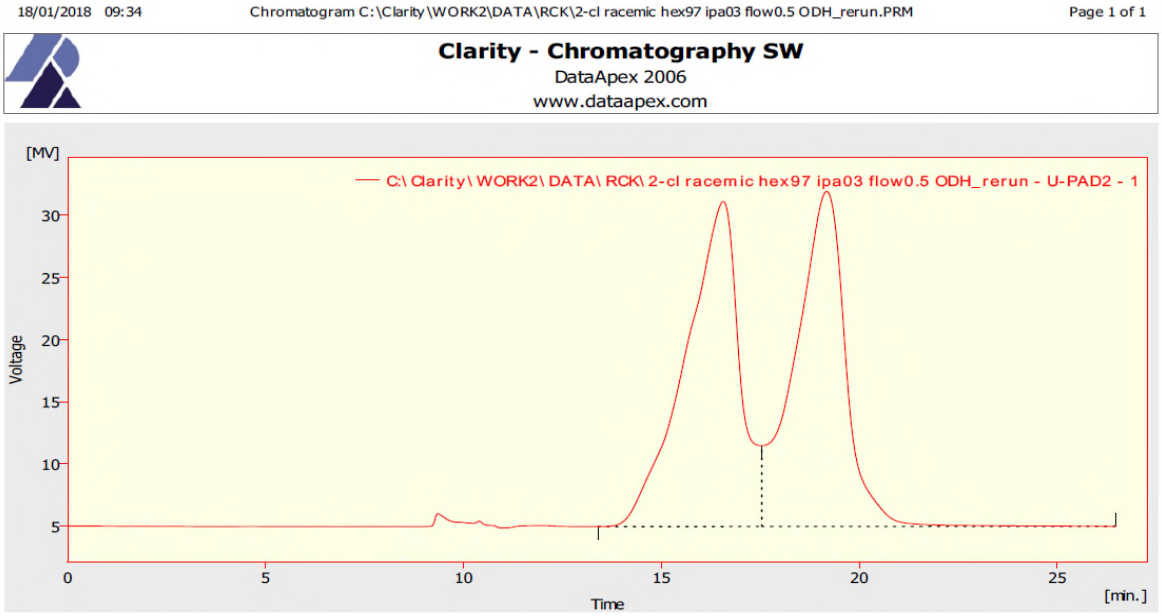
HPLC after ATH of 1-(2-chlororophenyl)-3-(trimethylsilyl)prop-2-yn-1-ol (**30**) (100% conversion, 93.8% ee).



Result Table (Uncal - C:\CLARITY\WORK2\DATA\V VYAS\SUBSTRATE METHOD\NEW ODH\CHIRAL STUDY\VV122 970310ATH - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	8.264	691.022	14.881	3.1	4.2	0.81	
2	10.064	21412.354	340.296	96.9	95.8	0.96	
	Total	22103.377	355.177	100.0	100.0		

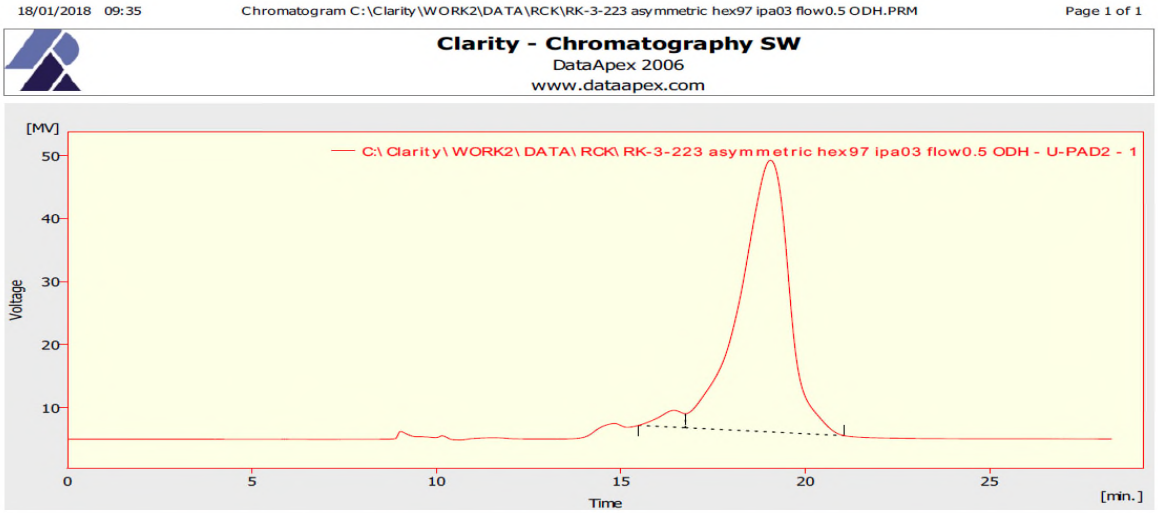
Racemic HPLC of 1-(2-chlororophenyl)-3-(trimethylsilyl)prop-2-yn-1-ol (**30**) from larger scale reaction under different HPLC conditions:



Result Table (Uncal - C:\Clarity\WORK2\DATA\RCK\2-cl racemic hex97 ipa03 flow0.5 ODH_rerun - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	16.564	24954.666	261.013	51.1	49.2	1.42	
2	19.176	23899.796	269.051	48.9	50.8	1.31	
	Total	48854.462	530.064	100.0	100.0		

HPLC after ATH of 1-(2-chlororophenyl)-3-(trimethylsilyl)prop-2-yn-1-ol (**30**) from larger scale reaction under different HPLC conditions (100% conversion, 94.2% ee).

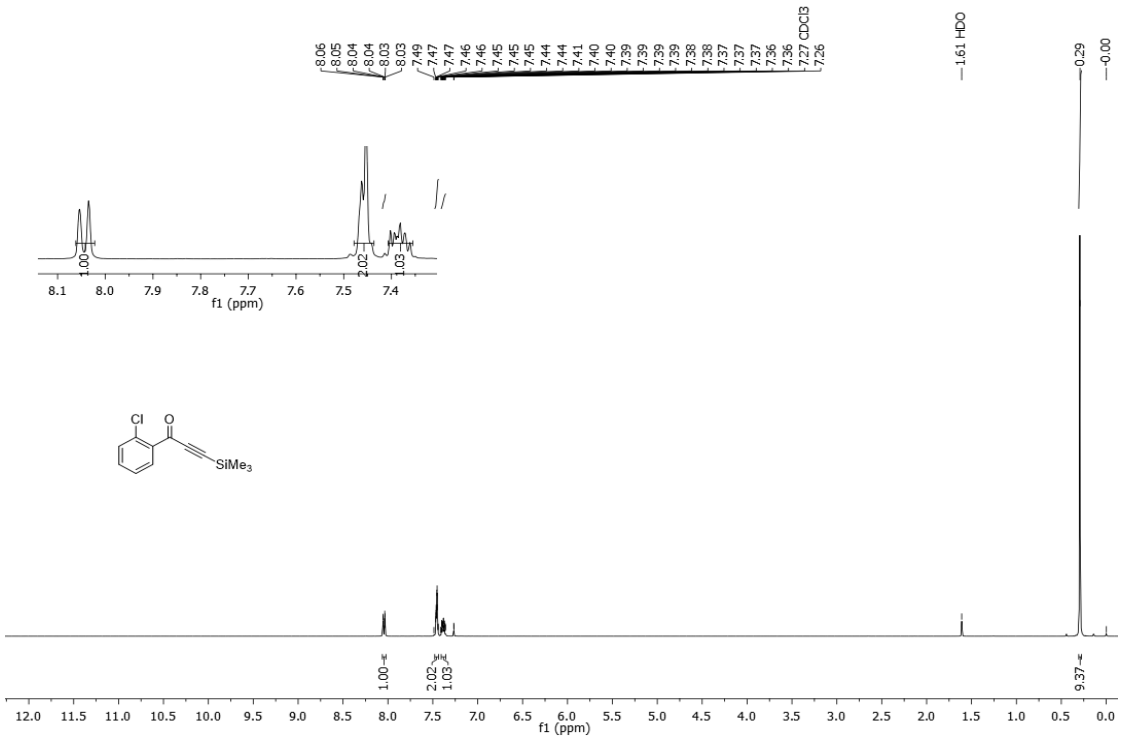


Result Table (Uncal - C:\Clarity\WORK2\DATA\RCK\RK-3-223 asymmetric hex97 ipa03 flow0.5 ODH - U-PAD2 - 1)

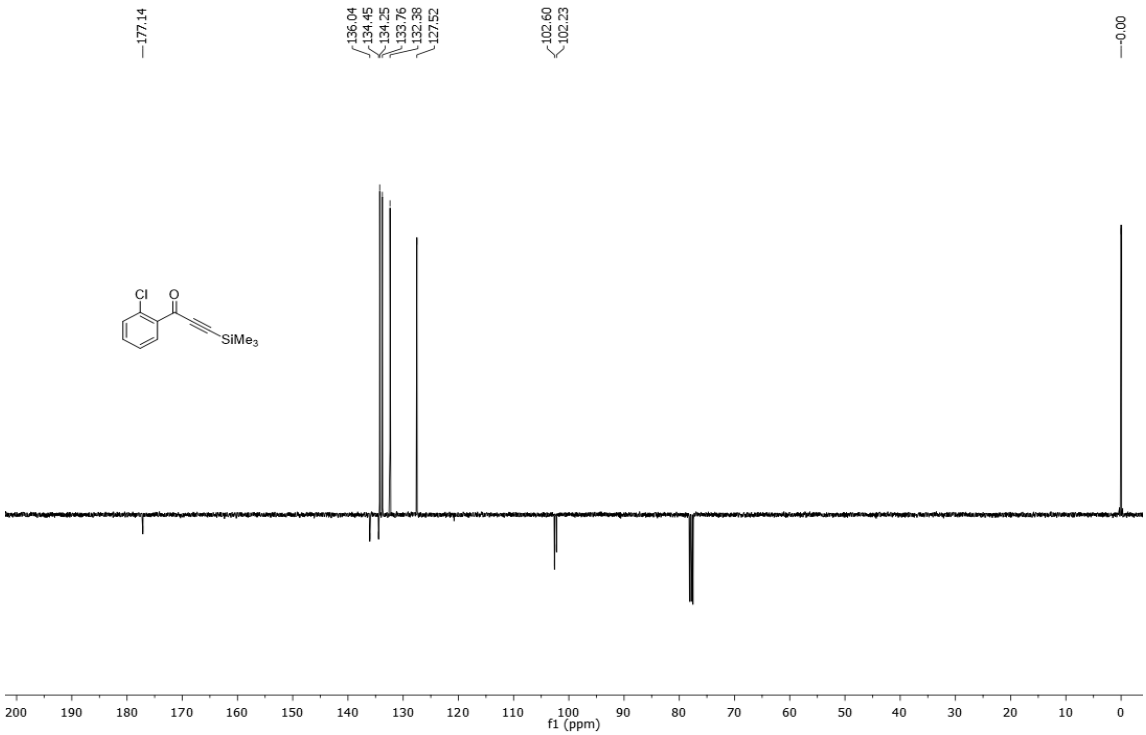
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	16.436	1205.934	26.635	2.9	5.8	0.80	
2	19.056	40101.423	430.816	97.1	94.2	1.35	
	Total	41307.357	457.451	100.0	100.0		

1-(2-Chlorophenyl)-3-(trimethylsilyl)prop-2-yn-1-one.

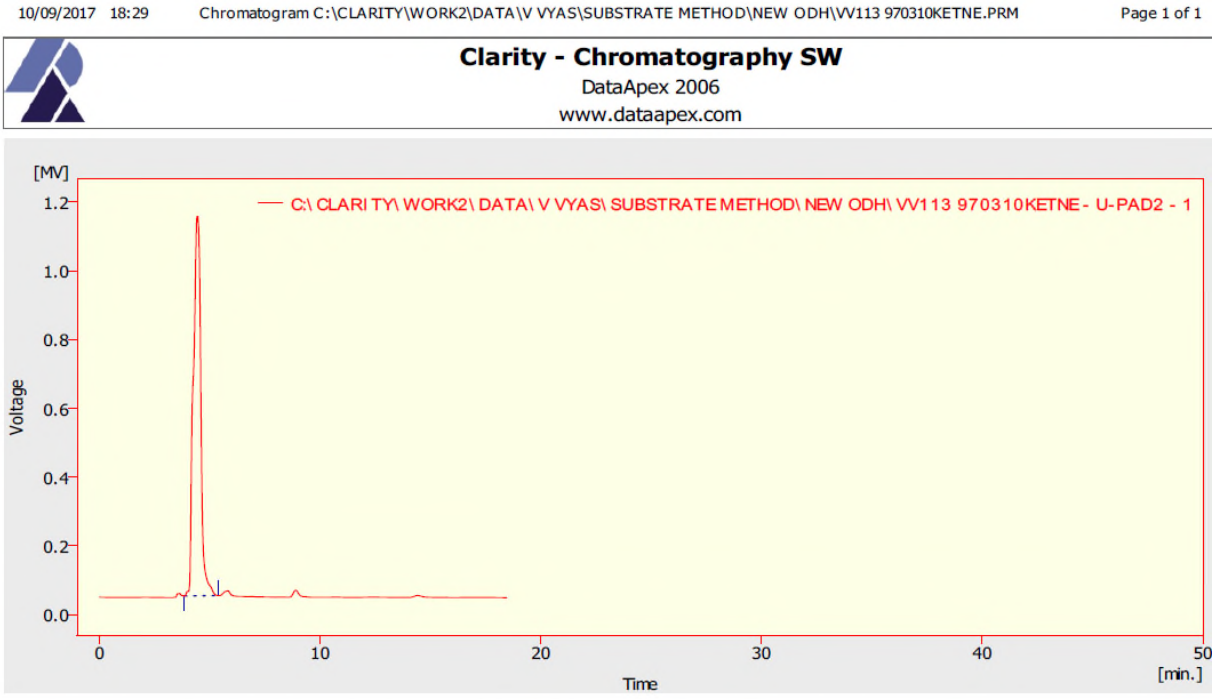
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



Ketone HPLC of 1-(2-chlorophenyl)-3-(trimethylsilyl)prop-2-yn-1-one.

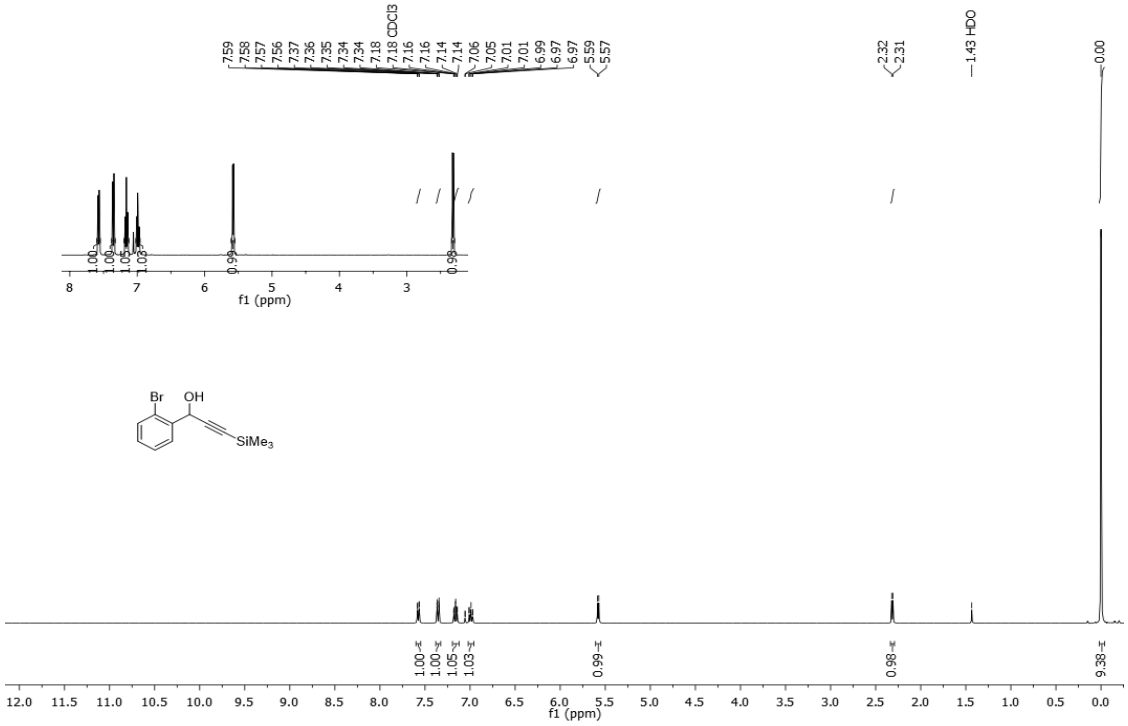


Result Table (Uncal - C:\|CLARITY\|WORK2\|DATA\|V VYAS\|SUBSTRATE METHOD\|NEW ODH\|VV113 970310KETNE - U-PAD2 - 1)

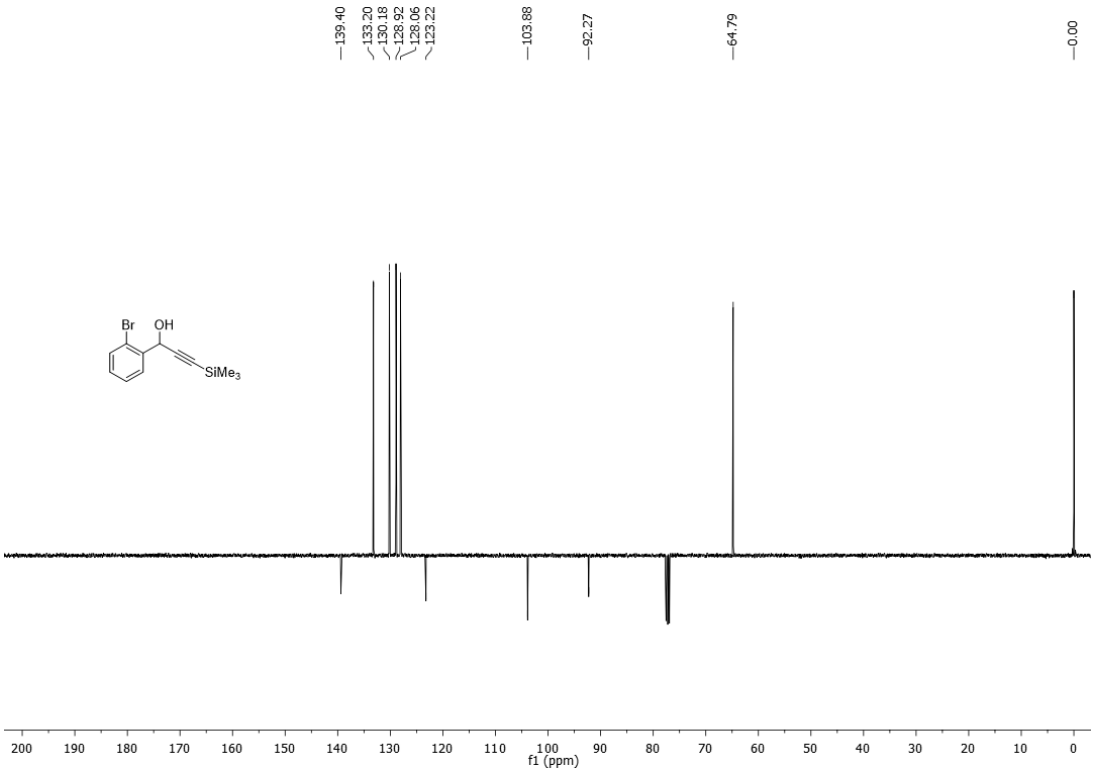
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	4.432	26176.433	1104.027	100.0	100.0	0.40	
	Total	26176.433	1104.027	100.0	100.0		

1-(2-Bromophenyl)-3-(trimethylsilyl)prop-2-yn-1-ol (31).

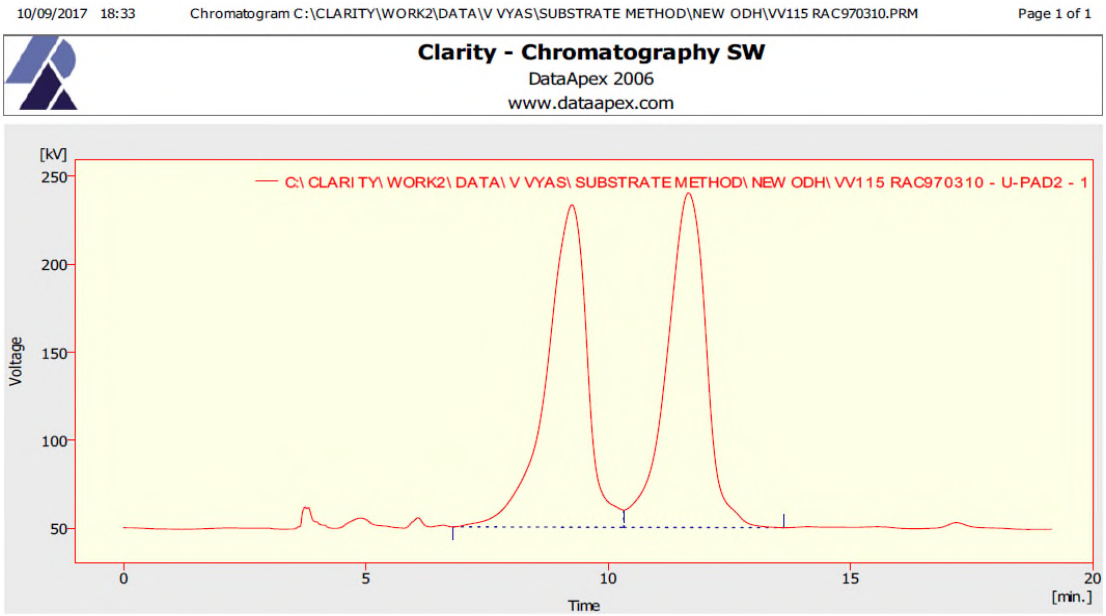
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



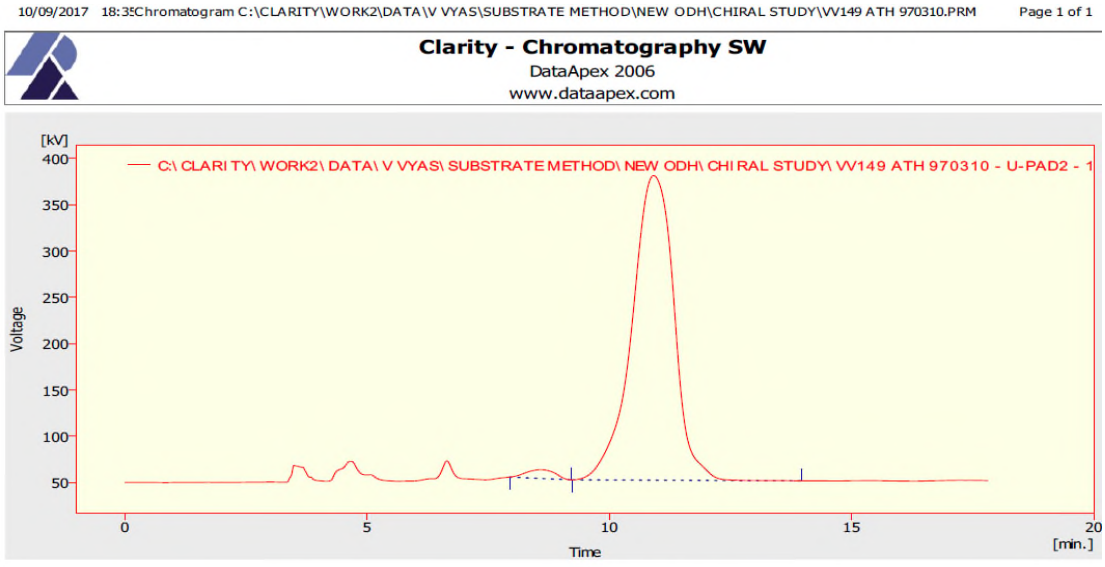
Racemic HPLC of 1-(2-bromophenyl)-3-(trimethylsilyl)prop-2-yn-1-ol (31).



Result Table (Uncal - C:\CLARITY\WORK2\DATA\V VYAS\SUBSTRATE METHOD\NEW ODH\VV115 RAC970310 - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	9.252	10790.481	183.178	50.1	49.1	0.84	
2	11.660	10765.291	190.125	49.9	50.9	0.85	
	Total	21555.772	373.303	100.0	100.0		

HPLC after ATH of 1-(2-bromophenyl)-3-(trimethylsilyl)prop-2-yn-1-ol (**31**) (100% conversion, 96.2% ee).

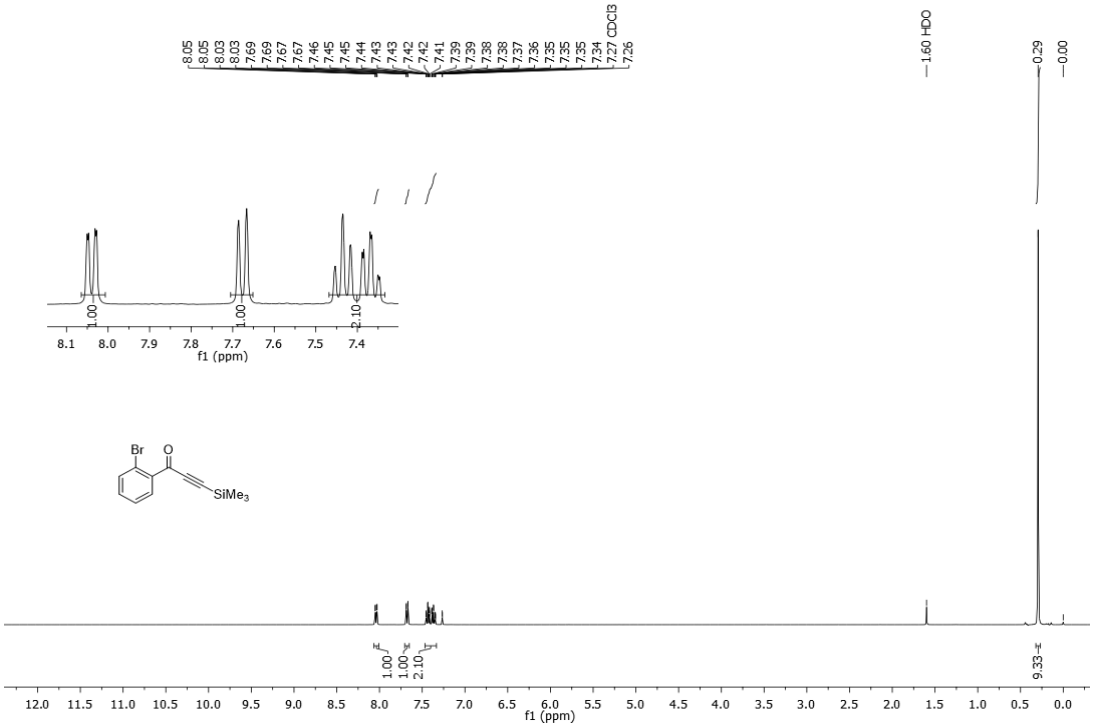


Result Table (Uncal - C:\CLARITY\WORK2\DATA\V VYAS\SUBSTRATE METHOD\NEW ODH\CHIRAL STUDY\VV149 ATH 970310 - U-PAD2 - 1)

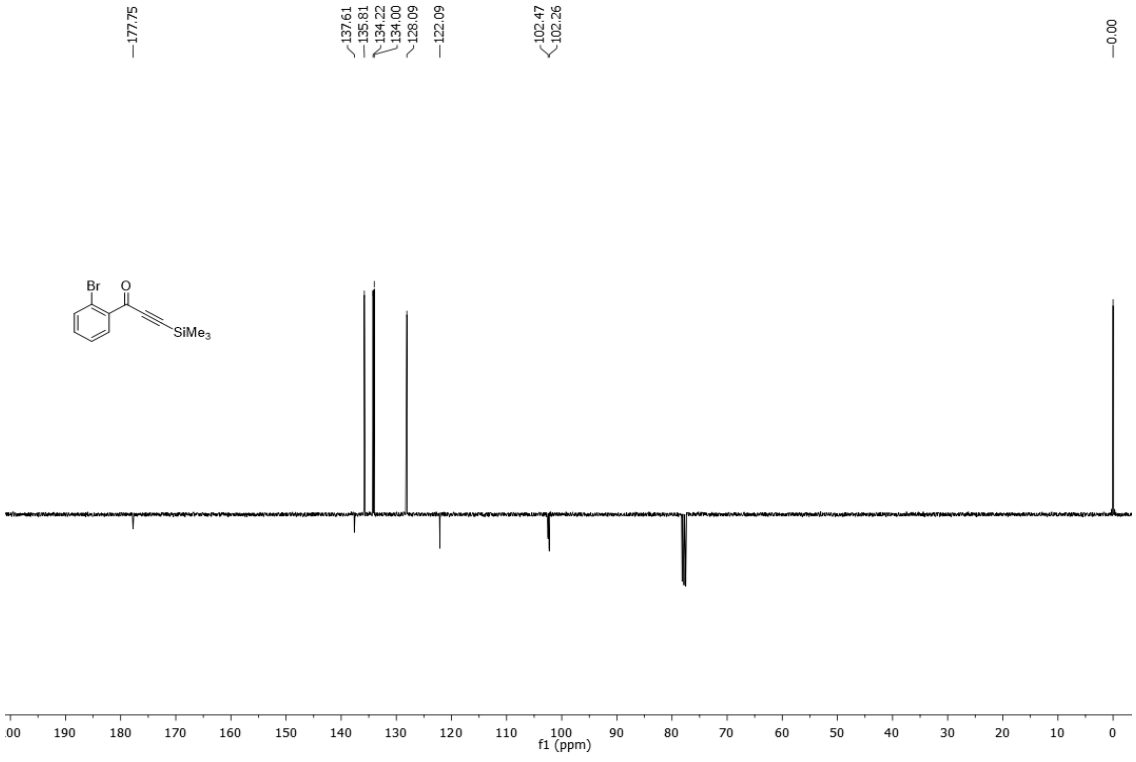
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	8.584	391.733	9.557	1.9	2.8	0.71	
2	10.920	19883.167	328.834	98.1	97.2	0.91	
	Total	20274.900	338.391	100.0	100.0		

1-(2-Bromophenyl)-3-(trimethylsilyl)prop-2-yn-1-one.

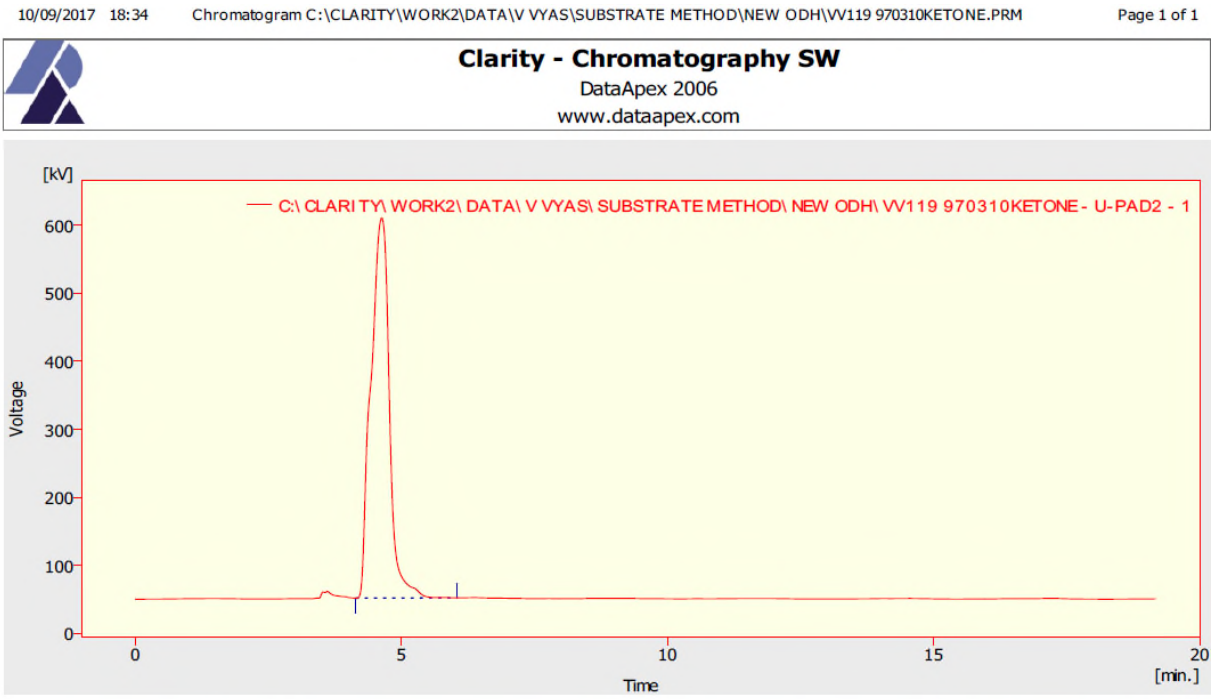
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



Ketone HPLC of 1-(2-Bromophenyl)-3-(trimethylsilyl)prop-2-yn-1-one.

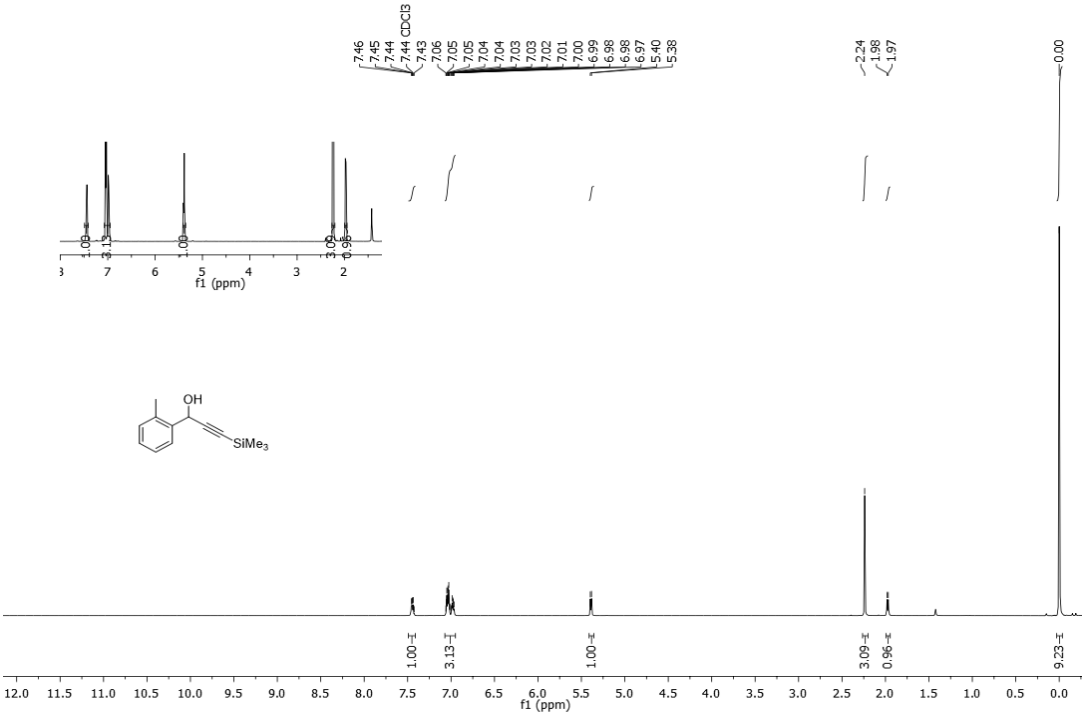


Result Table (Uncal - C:\|CLARITY\|WORK2\|DATA\|V VYAS\|SUBSTRATE METHOD\|NEW ODH\|VV119 970310KETONE - U-PAD2 - 1)

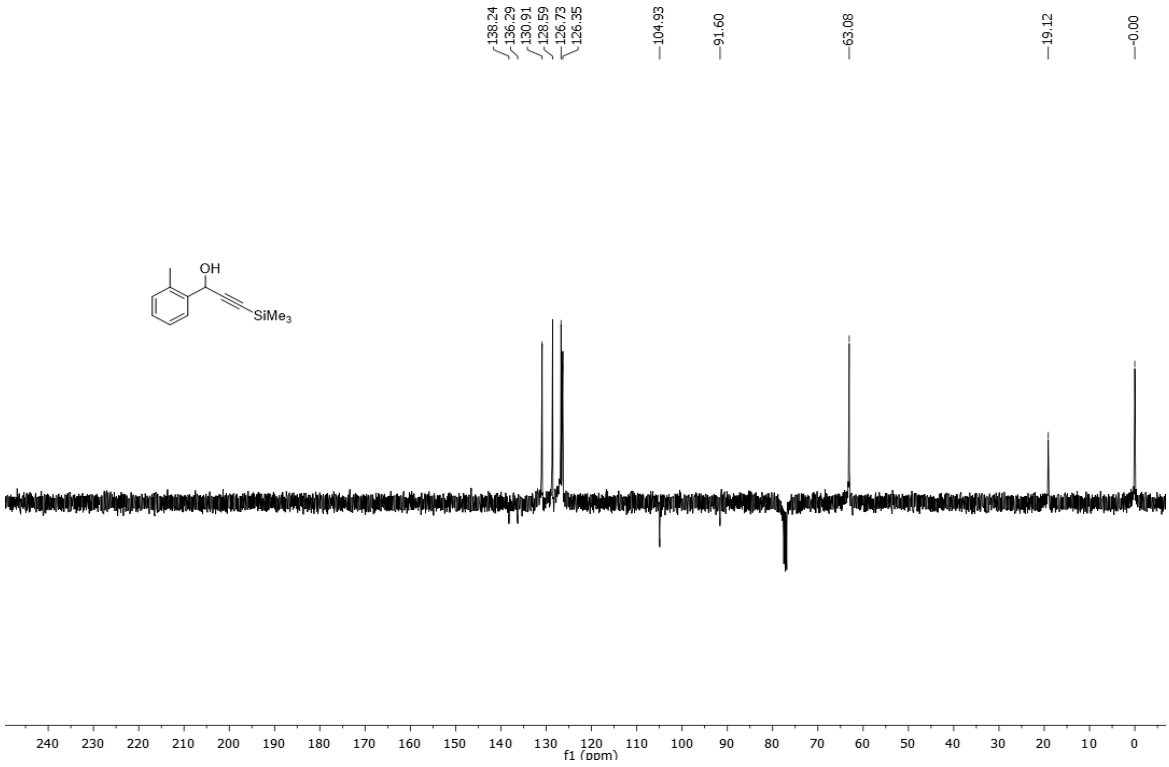
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	4.636	13481.216	558.700	100.0	100.0	0.40	
	Total	13481.216	558.700	100.0	100.0		

1-(o-Tolyl)-3-(trimethylsilyl)prop-2-yn-1-ol (32).

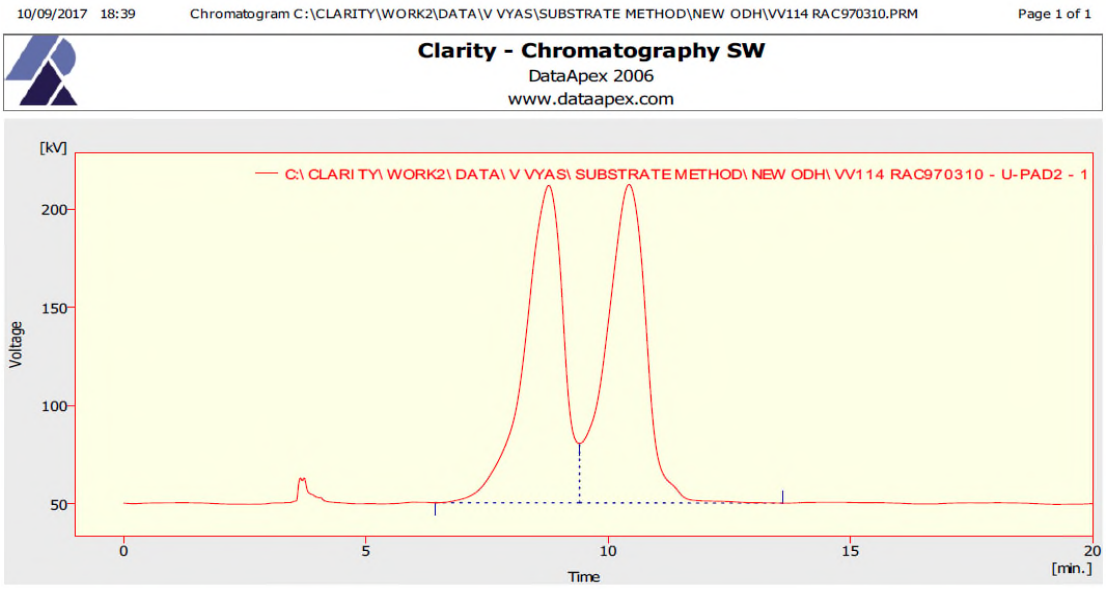
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



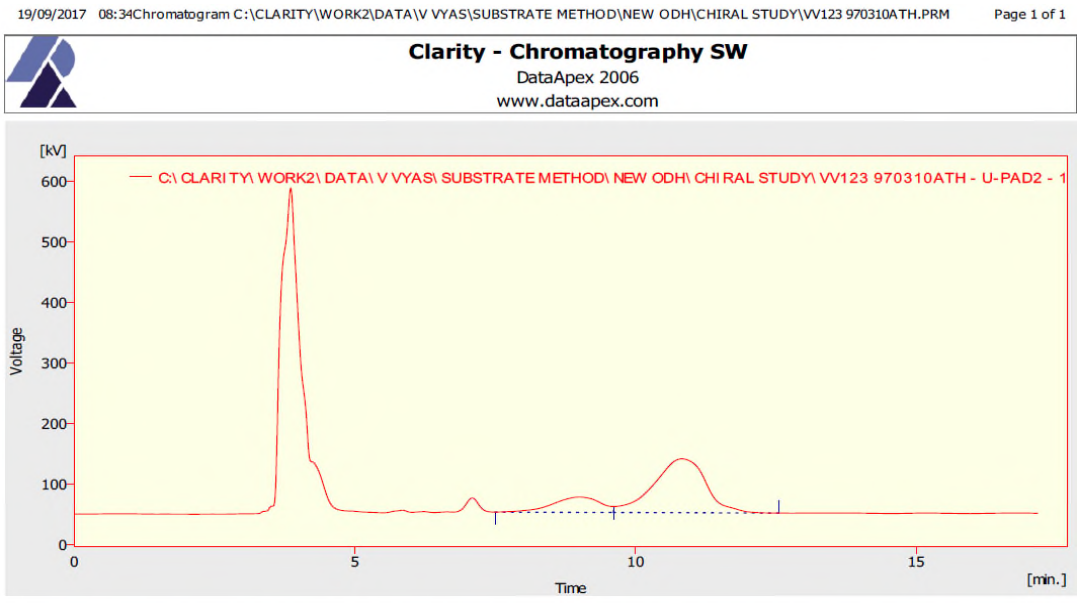
Racemic HPLC of 1-(o-tolyl)-3-(trimethylsilyl)prop-2-yn-1-ol (**32**).



Result Table (Uncal - C:\|CLARITY\|WORK2\|DATA\|V VYAS\|SUBSTRATE METHOD\|NEW ODH\|VV114 RAC970310 - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	8.776	9095.631	161.520	49.5	49.9	0.82	
2	10.436	9296.526	162.070	50.5	50.1	0.86	
	Total	18392.157	323.590	100.0	100.0		

HPLC after ATH of 1-(o-tolyl)-3-(trimethylsilyl)prop-2-yn-1-ol (**32**) (36% conversion, 58.8% ee).

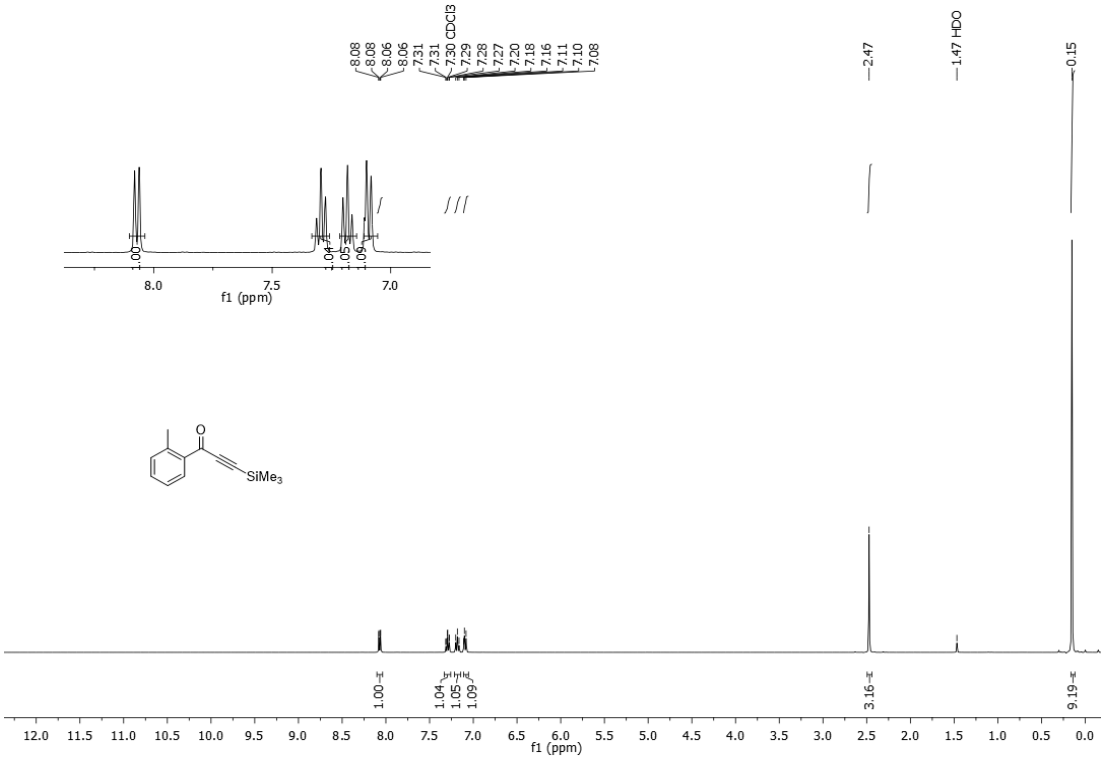


Result Table (Uncal - C:\|CLARITY\|WORK2\|DATA\|V VYAS\|SUBSTRATE METHOD\|NEW ODH\|CHIRAL STUDY\|VV123 970310ATH - U-PAD2 - 1)

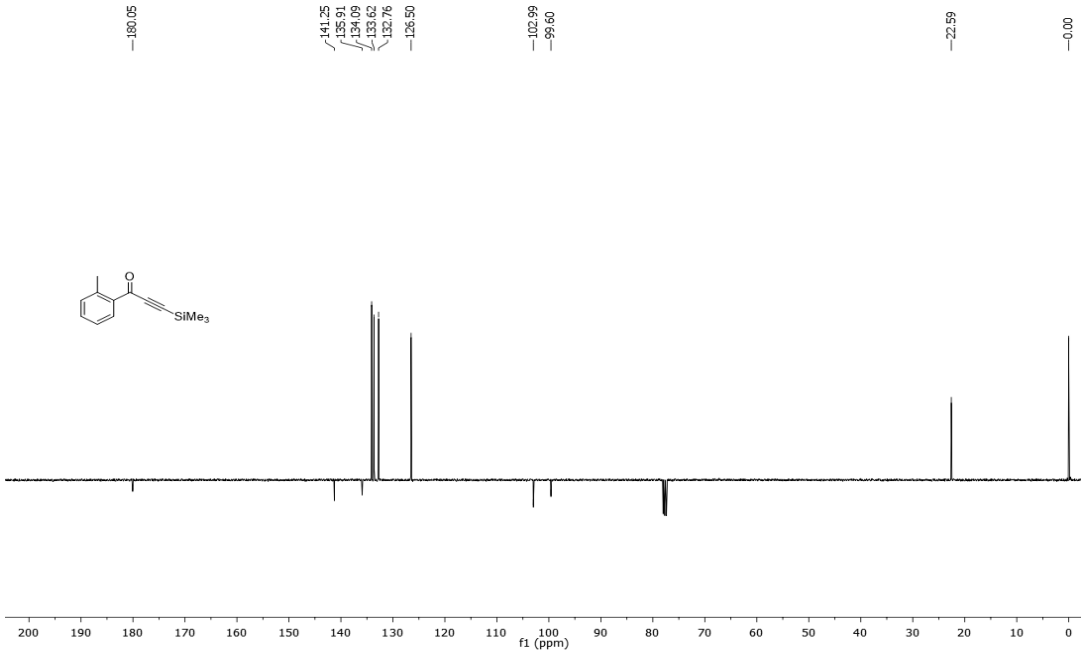
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	9.000	1499.994	25.302	20.6	22.1	0.96	
2	10.824	5773.849	88.955	79.4	77.9	0.98	
	Total	7273.843	114.257	100.0	100.0		

1-(o-Tolyl)-3-(trimethylsilyl)prop-2-yn-1-one.

^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



Ketone HPLC of 1-(o-tolyl)-3-(trimethylsilyl)prop-2-yn-1-one.

Clarity - Chromatography SW
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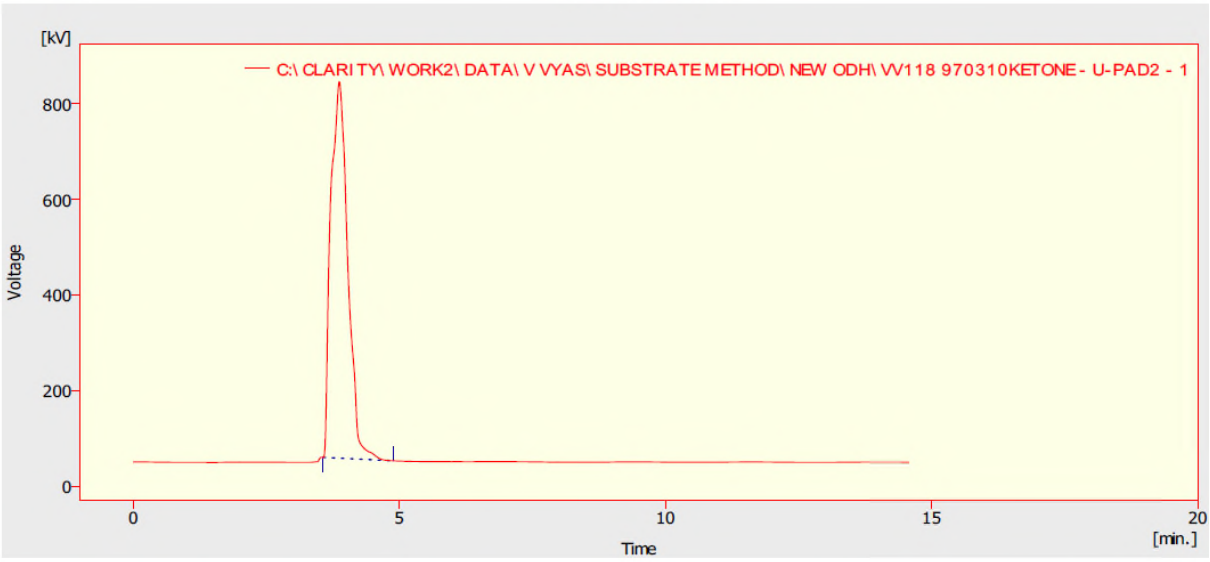
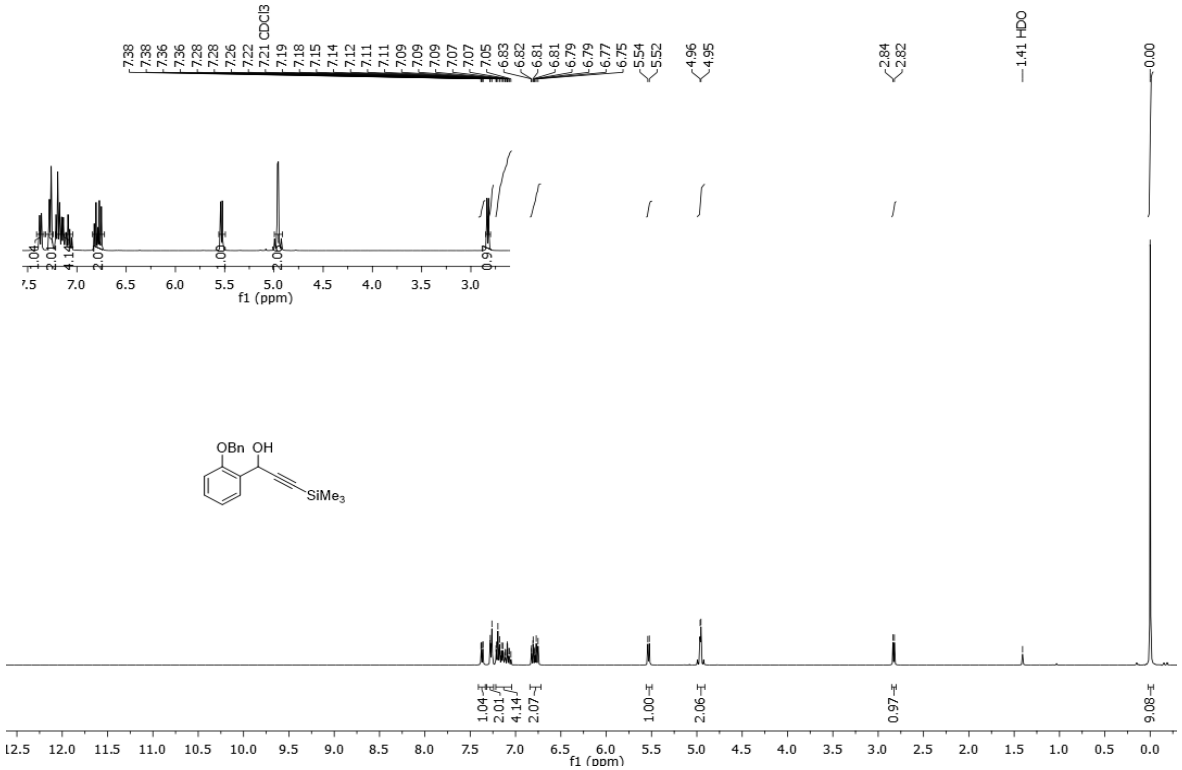


Result Table (Uncal - C:\CLARITY\WORK2\DATA\V VYAS\SUBSTRATE METHOD\NEW ODH\VV118 970310KETONE - U-PAD2 - 1)

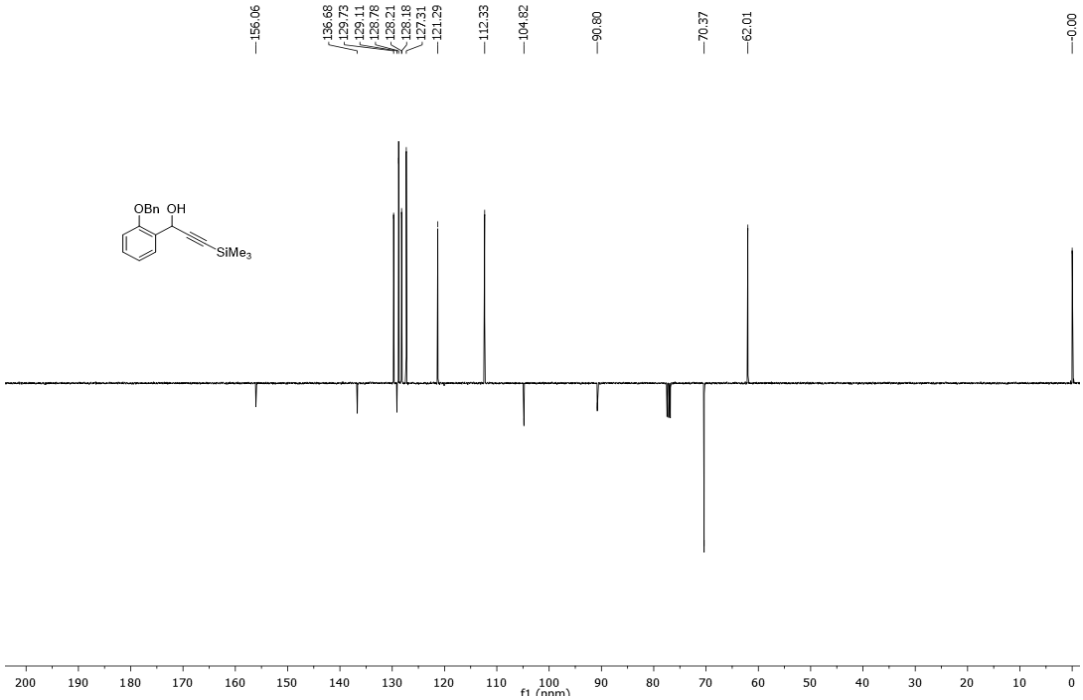
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	3.876	17476.257	786.713	100.0	100.0	0.37	
	Total	17476.257	786.713	100.0	100.0		

1-(2-Benzyloxyphenyl)-3-(trimethylsilyl)prop-2-yn-1-ol (33).

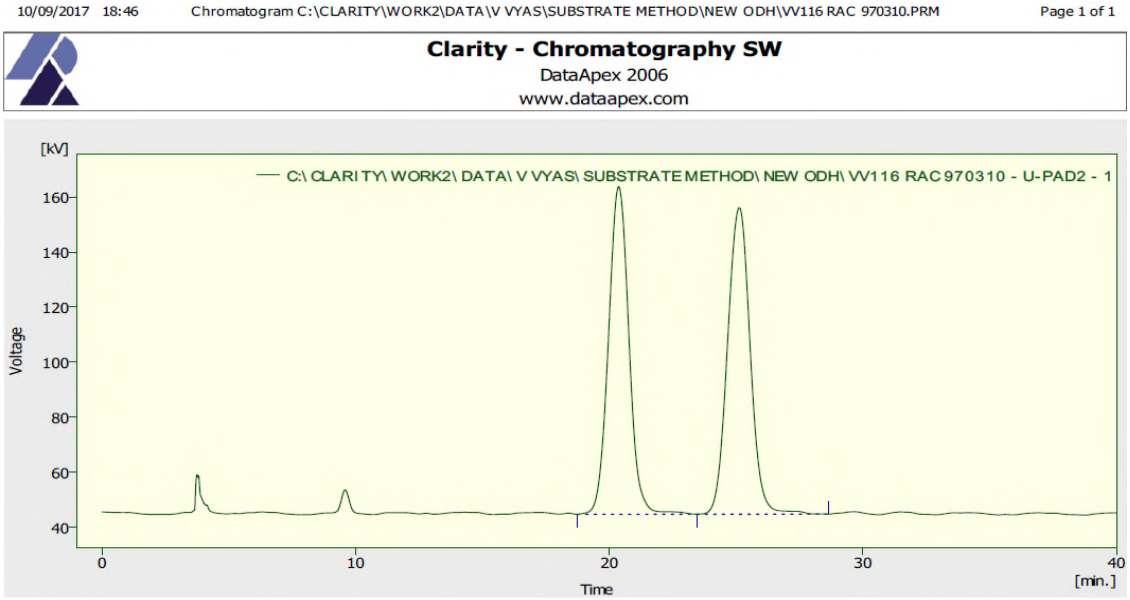
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



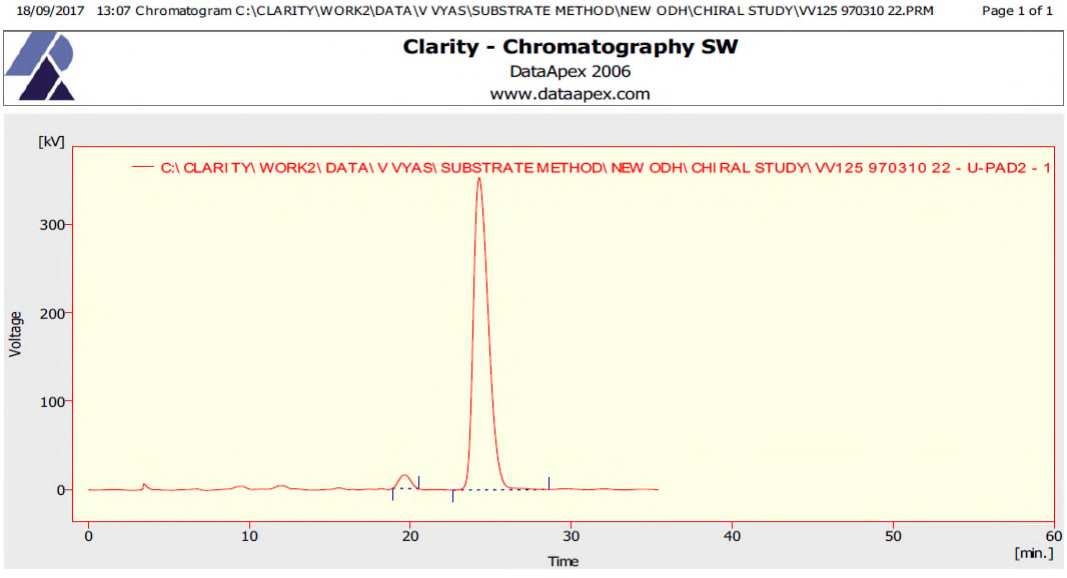
Racemic HPLC of 1-(2-benzyloxyphenyl)-3-(trimethylsilyl)prop-2-yn-1-ol (**33**).



Result Table (Uncal - C:\|CLARITY\|WORK2\|DATA\|V VYAS\|SUBSTRATE METHOD\|NEW ODH\|VV116 RAC 970310 - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	20.372	6696.959	119.213	49.1	51.7	0.86	
2	25.128	6936.188	111.494	50.9	48.3	0.96	
	Total	13633.147	230.707	100.0	100.0		

HPLC after ATH of 1-(2-benzyloxyphenyl)-3-(trimethylsilyl)prop-2-yn-1-ol (**33**) (100% conversion, 93.4% ee).

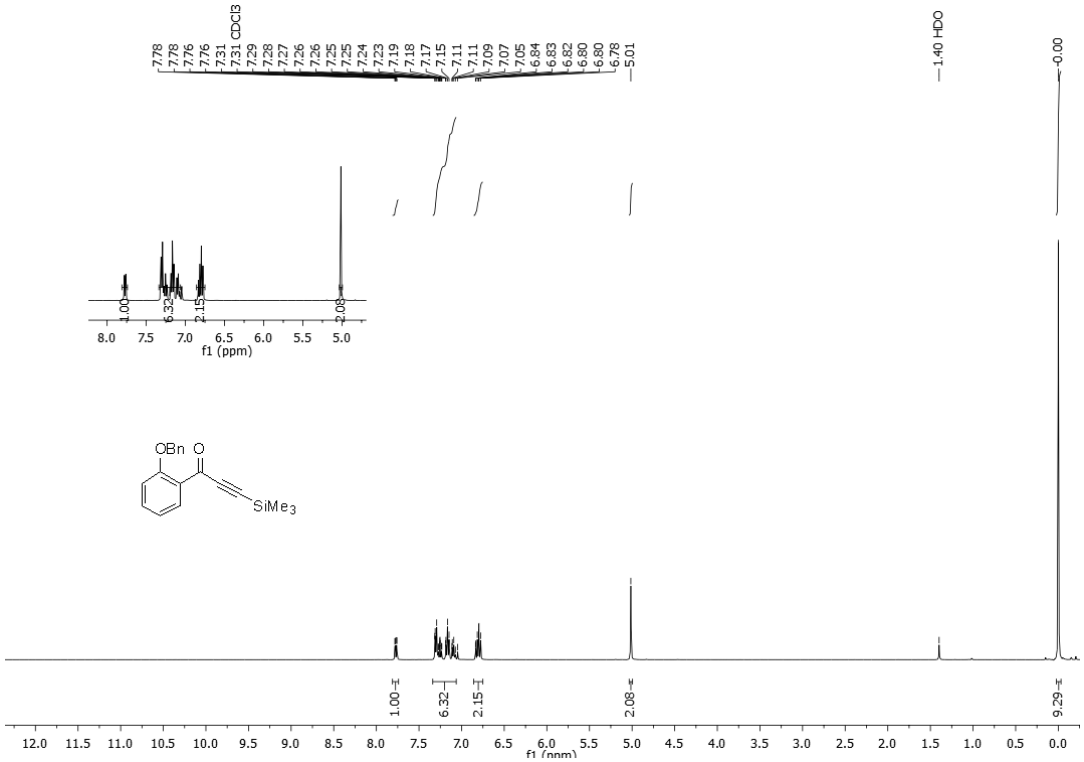


Result Table (Uncal - C:\|CLARITY\|WORK2\|DATA\|V VYAS\|SUBSTRATE METHOD\|NEW ODH\|CHIRAL STUDY\|VV125 970310 22 - U-PAD2 - 1)

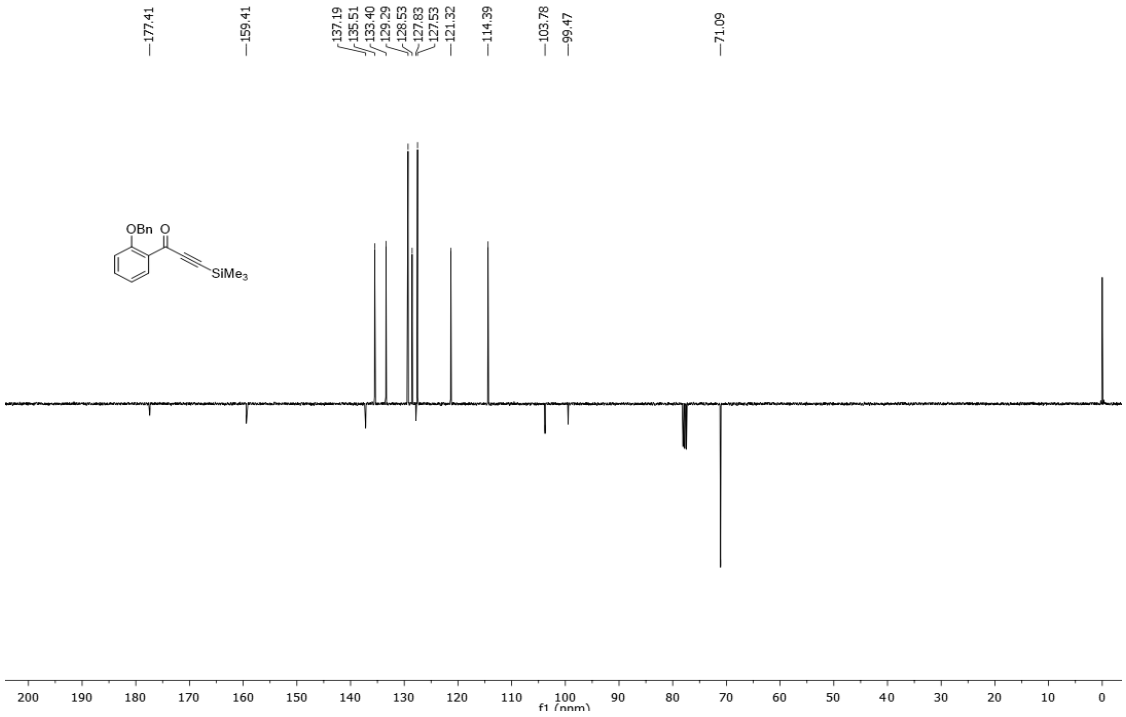
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	19.636	779.760	15.434	3.3	4.2	0.84	
2	24.276	22920.030	353.393	96.7	95.8	1.02	
	Total	23699.790	368.827	100.0	100.0		

1-(2-Benzyloxyphenyl)-3-(trimethylsilyl)prop-2-yn-1-one.

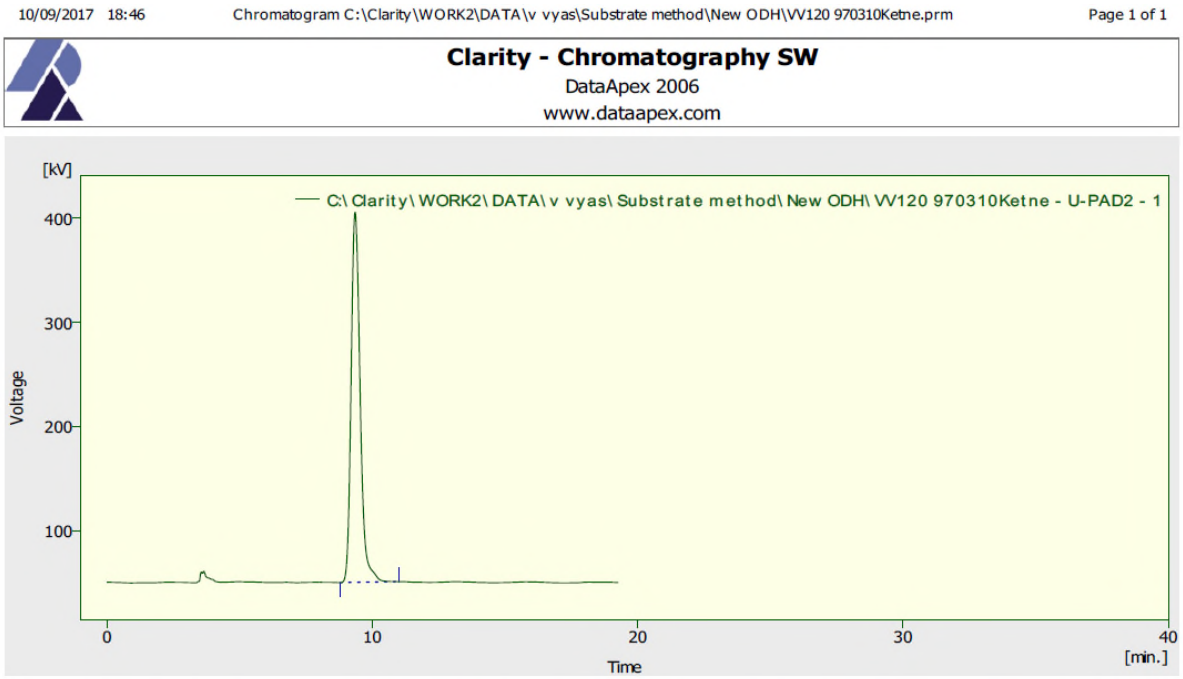
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



Ketone HPLC of 1-(2-benzyloxyphenyl)-3-(trimethylsilyl)prop-2-yn-1-one.

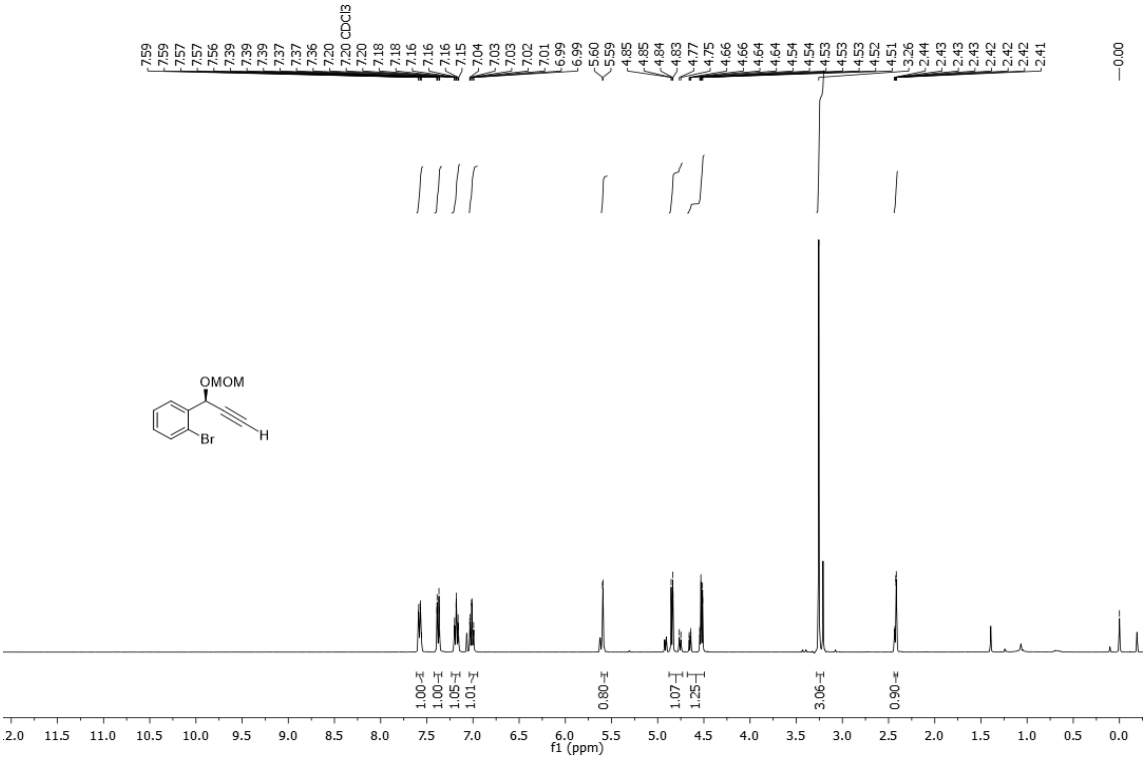


Result Table (Uncal - C:|Clarity|WORK2|DATA|v vyas|Substrate method|New ODH|VV120 970310Ketne - U-PAD2 - 1)

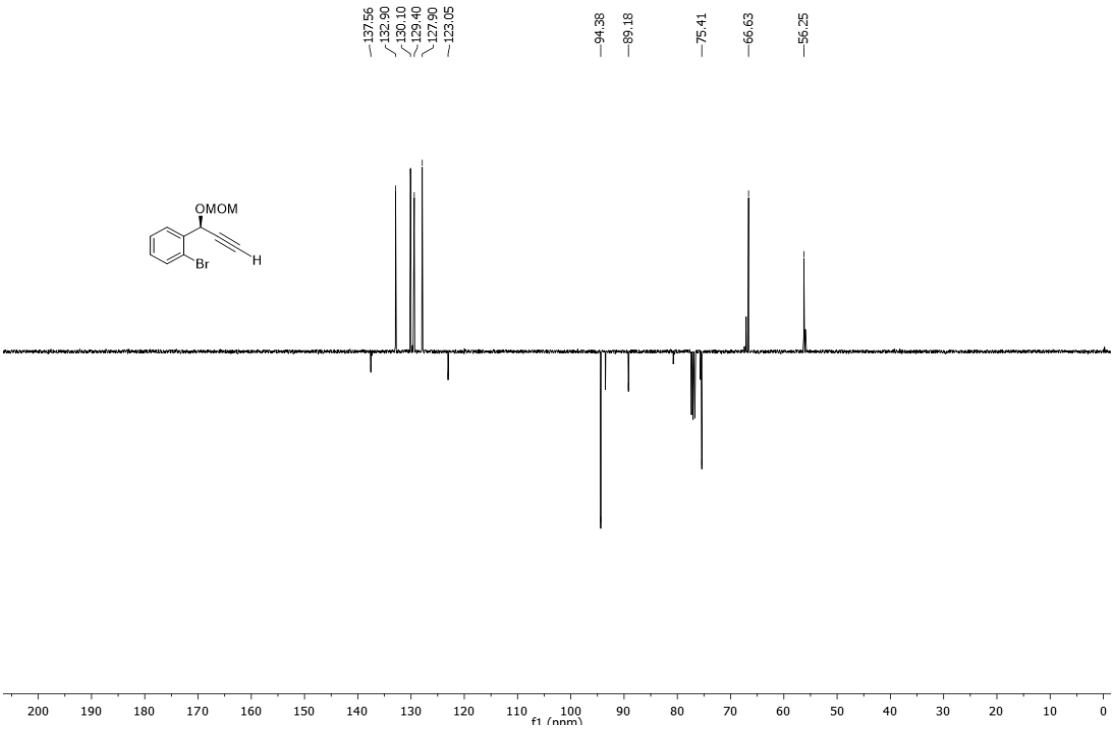
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	9.352	8428.498	355.730	100.0	100.0	0.36	
	Total	8428.498	355.730	100.0	100.0		

1-Bromo-2-(1-(methoxymethoxy)prop-2-yn-1-yl)benzene (34).

^{1}H NMR (400 MHz, $CDCl_3$)

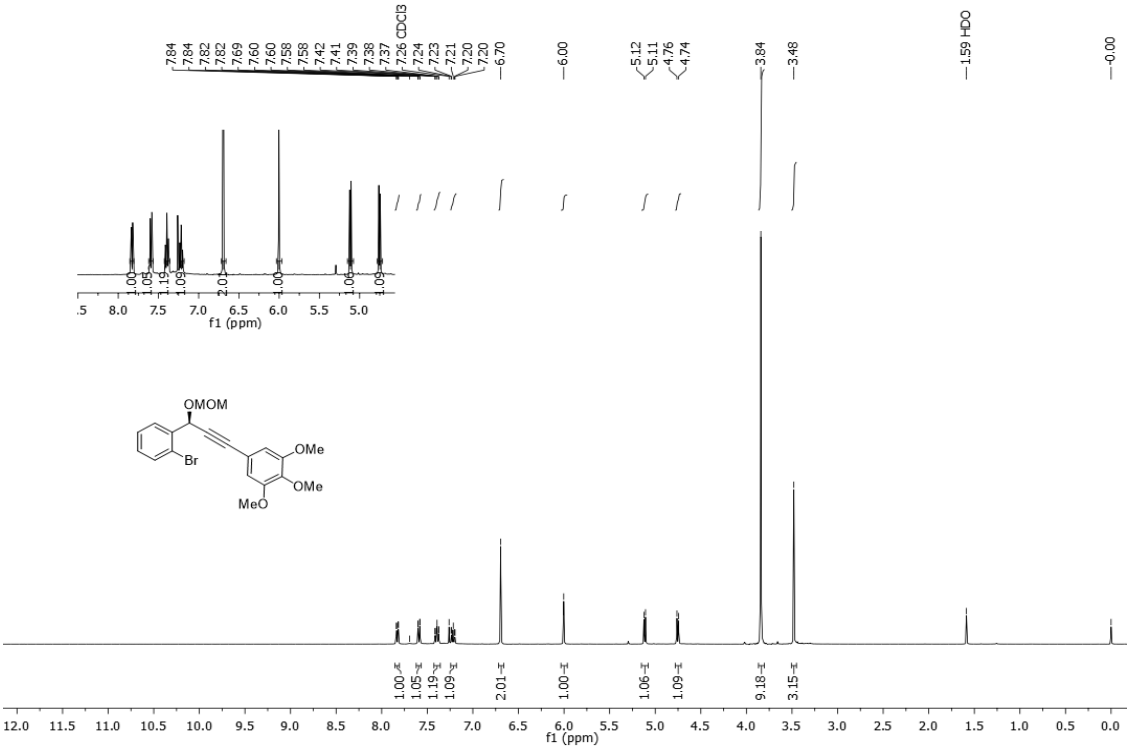


^{13}C NMR (101 MHz, $CDCl_3$)

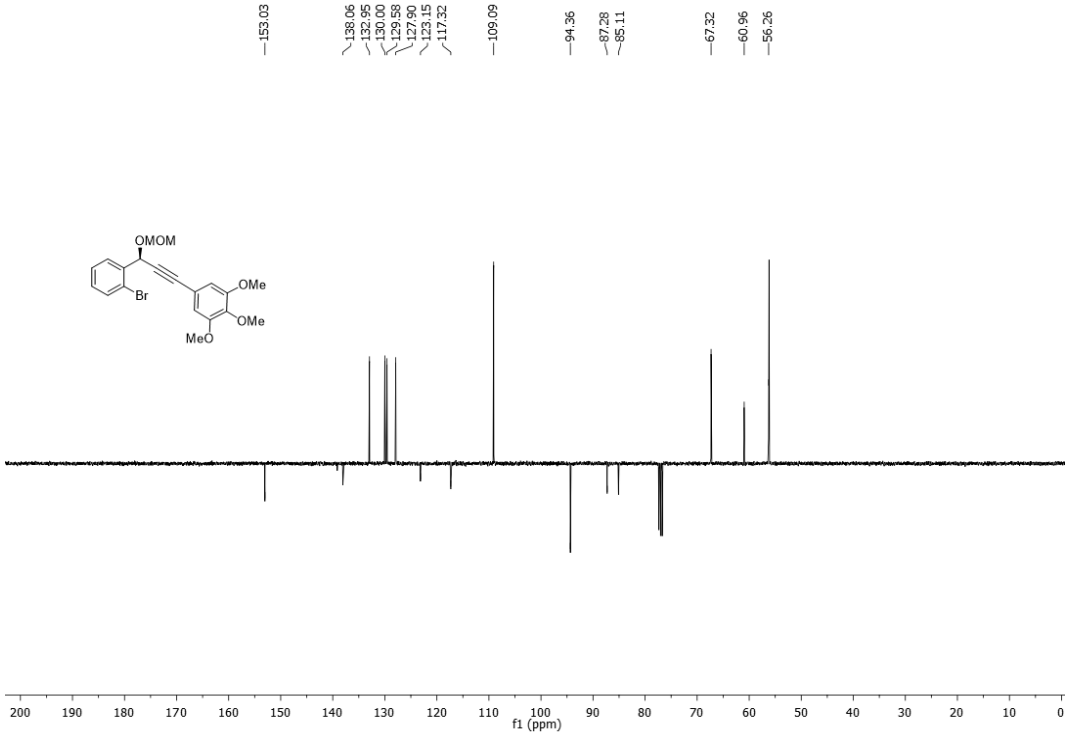


5-(3-(2-Bromophenyl)-3-(methoxymethoxy)prop-1-yn-1-yl)-1,2,3-trimethoxybenzene (35).

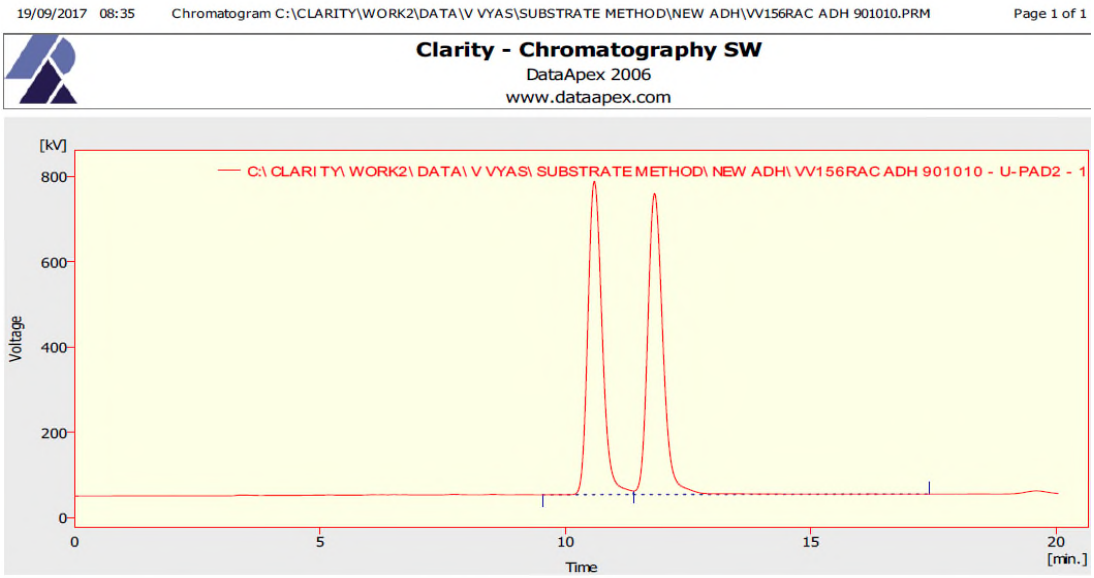
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



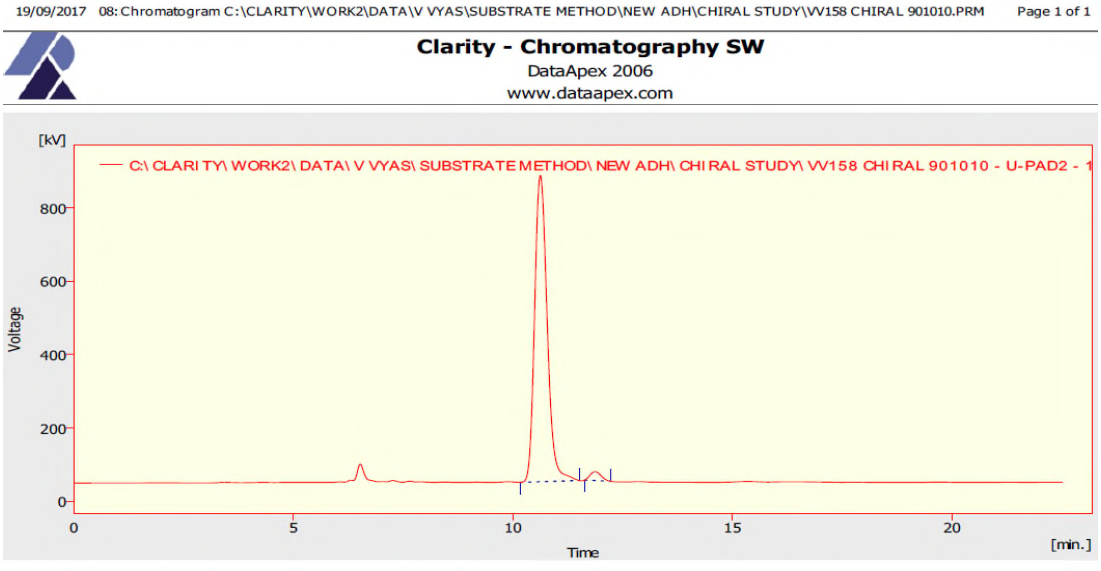
Racemic HPLC of 5-(3-(2-bromophenyl)-3-(methoxymethoxy)prop-1-yn-1-yl)-1,2,3-trimethoxybenzene (**35**).



Result Table (Uncal - C:\CLARITY\WORK2\DATA\V VYAS\SUBSTRATE METHOD\NEW ADH\VV156RAC ADH 901010 - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	10.588	14904.511	734.510	49.2	51.0	0.31	
2	11.816	15371.889	705.857	50.8	49.0	0.33	
	Total	30276.401	1440.367	100.0	100.0		

HPLC of 5-(3-(2-bromophenyl)-3-(methoxymethoxy)prop-1-yn-1-yl)-1,2,3-trimethoxybenzene (**35**) after catalytic synthesis (95.0% ee).

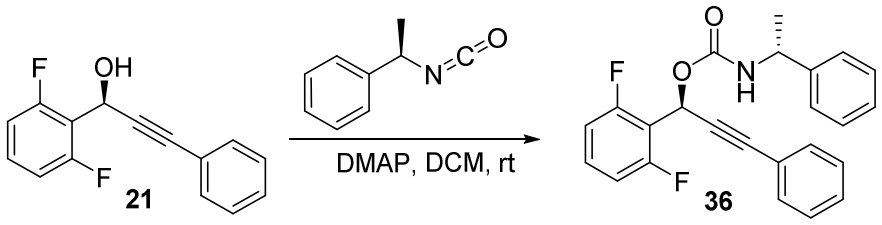


Result Table (Uncal - C:\CLARITY\WORK2\DATA\V VYAS\SUBSTRATE METHOD\NEW ADH\CHIRAL STUDY\VV158 CHIRAL 901010 - U-PAD2 - 1)

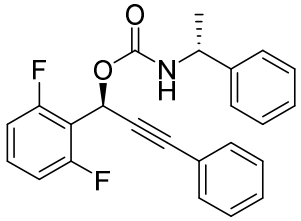
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	10.624	16572.533	835.024	97.5	97.2	0.31	
2	11.868	419.062	24.380	2.5	2.8	0.28	
	Total	16991.595	859.404	100.0	100.0		

Determination of absolute configuration of 26 (CCDC 1574558).

(*R*)-1-(2,6-Difluorophenyl)-3-phenylprop-2-yn-1-ol **21** (93 mg, 0.38 mmol, 1 equiv) was dissolved in DCM (2 mL) at rt in a dry schlenk tube under a nitrogen atmosphere. DMAP (a few crystals) and (*R*)-(+)-α-Methylbenzyl isocyanate (60 μL, 0.38 mmol, 1 equiv) were added. The reaction mixture was stirred overnight. At the end of this time the isocyanate adduct was purified by column chromatography on silica gel (n-hexane:EtOAc 85/15) as a white solid (75 mg, 0.19 mmol, 50%). VV144. Procedure adapted from Simpson, A.F.; Bodkin, C. D.; Butts, C. P.; Armitage, M. A.; Gallagher, T. *J. Chem. Soc., Perkin Trans. 1*, **2000**, 3047-3054



(*R*)-1-(2,6-difluorophenyl)-3-phenylprop-2-yn-1-yl ((R)-1-phenylethyl)carbamate (36).



This compound is novel.

(found (ESI) [M+Na]+, 414.1282. $C_{24}H_{19}F_2NNaO_2$ requires 414.1276).

ν_{max}: 3387(sharp), 1689, 1514, 1472, 1236, 1050, 1010, 789, 703, 548 cm^{-1}.

mp: 139-141 ºC

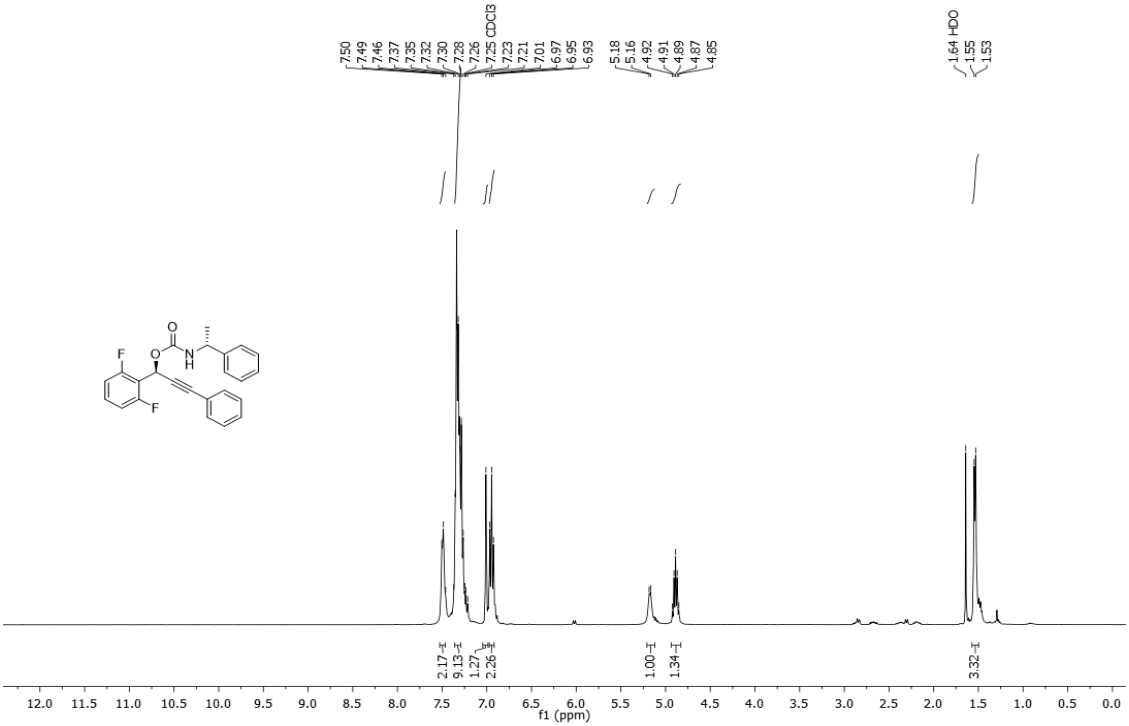
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (2H, d, *J* = 7.3 Hz, ArH), 7.38 – 7.27 (9H, m, ArH), 7.01 (1H, s, CH), 6.95 (2H, t, *J* = 8.2 Hz, ArH), 5.17 (1H, d, *J* = 7.7 Hz, NH), 4.89 (1H, p, *J* = 7.2 Hz, CH), 1.54 (3H, d, *J* = 6.9 Hz, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.91 (d, J = 260.3 Hz) 153.95, 132.05, 130.75 (t, J = 10.5 Hz), 128.80, 128.66, 128.22, 127.43, 126.00, 122.09, 114.46 (t, J = 16.4 Hz), 111.85 (d, J = 25.3 Hz), 85.94, 84.39, 56.92, 51.03, 22.47.

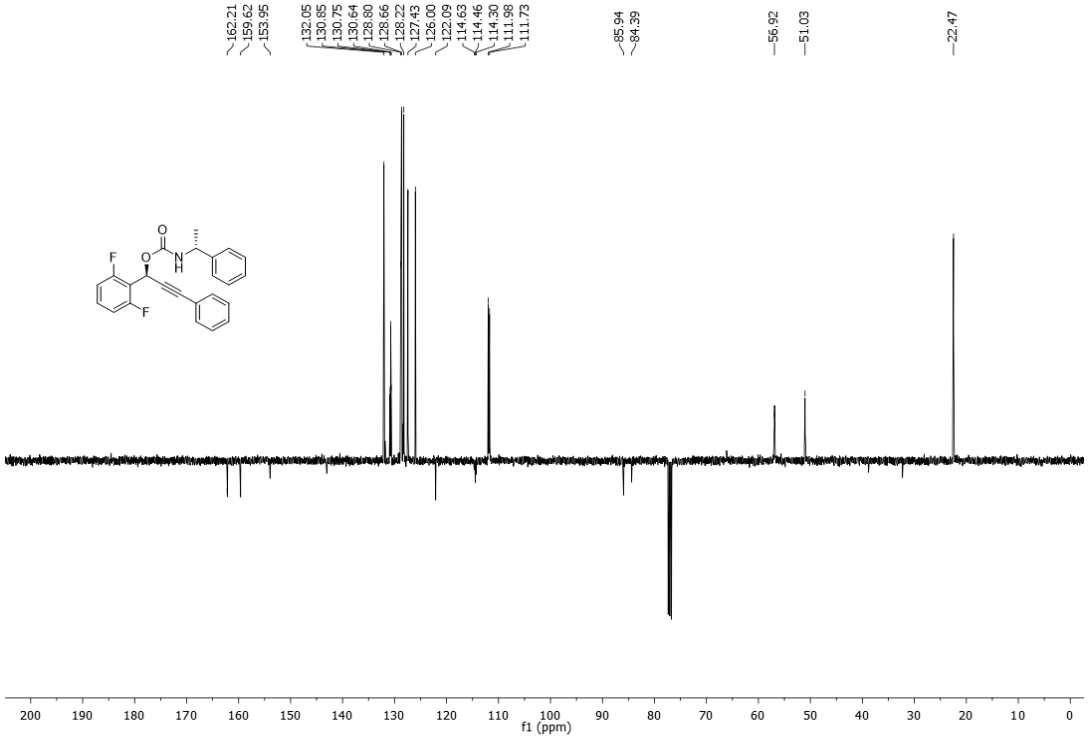
m/z (ESI) 413.9 ([M + Na]+, 100 %).

(*R*)-1-(2,6-difluorophenyl)-3-phenylprop-2-yn-1-yl ((*R*)-1-phenylethyl)carbamate (26).

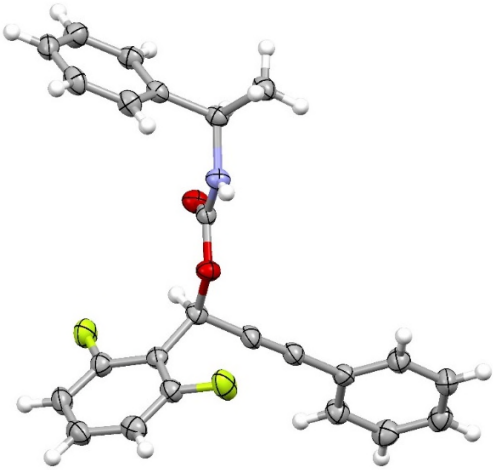
^{1}H NMR (400 MHz, $CDCl_3$)



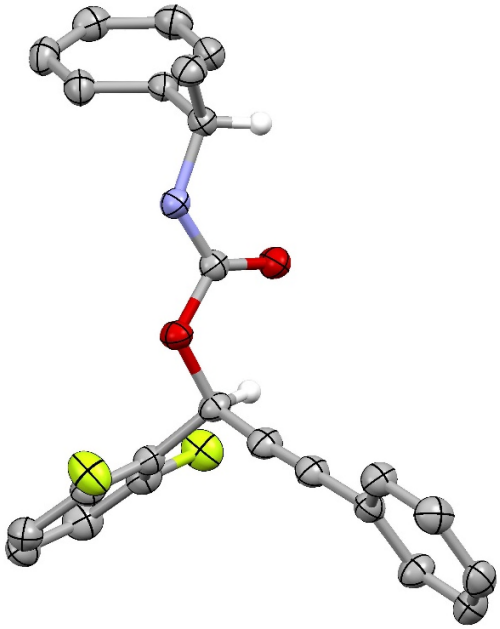
^{13}C NMR (101 MHz, $CDCl_3$)



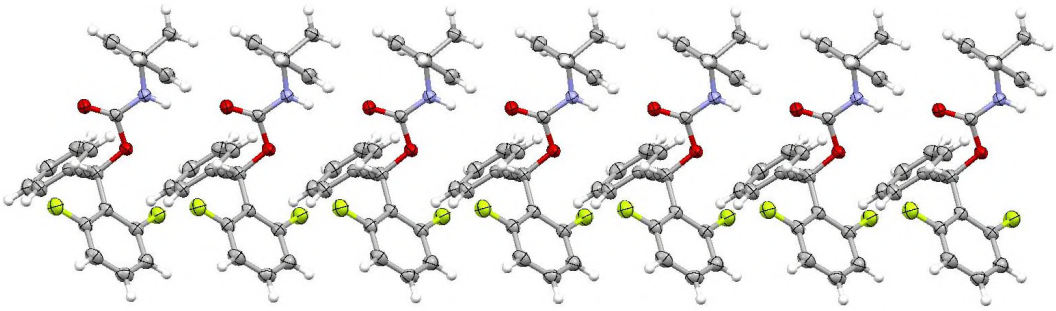
Compound 26; CCDC 1574558



Single crystal x-ray structure of **26** (ellipsoids are plotted at the 50% probability level)

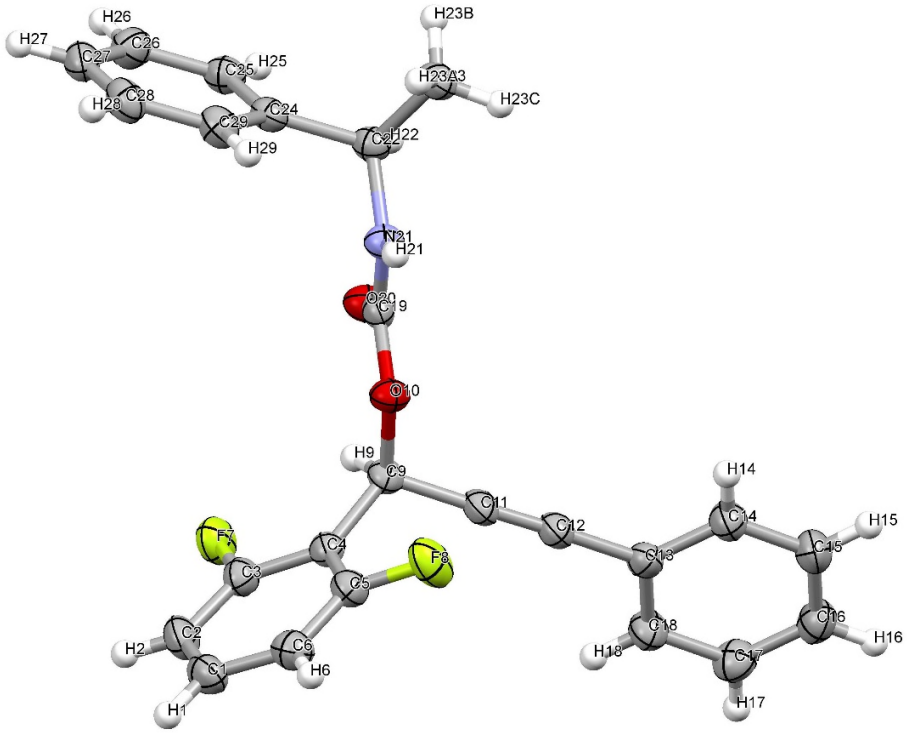


Single crystal x-ray structure of **26** (ellipsoids are plotted at the 50% probability level, non-chiral H-atoms omitted for clarity)



One-dimensional solid-state packing of **26** (ellipsoids are plotted at the 50% probability level)

X-ray crystallographic structure of **26** with atom labelling (CCDC 1574558). See the .cif file for full crystallographic details.



CCDC 1574558 contains the supplementary crystallographic data for this paper. These can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Single crystals of **26** were grown from vapour diffusion of *n*-hexane into a chloroform solution of the compound over several days. A suitable crystal was mounted on a Mitegen head with Fomblin oil and collected on an Xcalibur Gemini diffractometer with a Ruby CCD area detector at 150(2) K. The structure was solved using Olex2[1] and the ShelXT[2] structure solution program using Direct Methods and refined with the ShelXL[3] refinement package using Least Squares refinement.

The asymmetric unit contains the diastereomerically pure carbamate. There are two molecules within the unit cell. The molecule adopts a layered structure in the solid state with offset aromatic donor-acceptor (π-π) interactions of the difluorophenyl moieties.

The molecule displayed an absolute configuration of R,R which was deduced through the use of an enantiopure chiral axillary which allowed assignment of the remaining chiral centre. Additionally Flack and Hooft parameters were obtained and found to be 0.15(14) and 0.07(7) respectively.

Compound Reference	**Compound 26**
Chemical Formula	$C_{24}H_{19}F_2NO_2$
Formula Mass	391.40
Crystal system	Monoclinic
a/ Å	5.3070(1)
b/ Å	11.1814(1)
c/ Å	16.4228(2)
α/ °	90
β/ °	96.202(1)
γ/ °	90
Unit cell volume/ Å	968.82(2)
Temperature/ K	150(2)

Space group	P 2yb
Crystal size/ mm	0.2 × 0.12 × 0.05
Radiation	CuKα (λ = 1.54178)
Goodness-of-fit on F^2	0.9683
No. of formula units per unit cell, Z	2
No. of reflections measured	20164
No. of independent reflections	9300
Final R_1 vaules (I > 2σ(*I*))	0.0375
Final *wR*(F^2) values (I > 2σ(*I*))	0.1092
Final R_1 values (all data)	0.0427
Final *wR*(F^2) (all data)	0.1231

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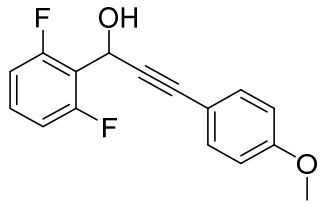
1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.

2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.

3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8

Synthesis and X-ray crystallographic data for 1-(2,6-Difluorophenyl)-3-(4-methoxyphenyl)prop-2-yn-1-one 37.

1-(2,6-Difluorophenyl)-3-(4-methoxyphenyl)prop-2-yn-1-ol.



This compound was prepared in racemic form following procedure A using: 4-methoxyphenyl acetylene (0.80 mL, 6.0 mmol, 1.2 equiv), 2,6-difluoro benzaldehyde (0.53 mL, 5.0 mmol, 1.0 equiv), nBuLi, 2.5 M in hexane (2.0 mL, 5.0 mmol, 1.0 equiv) and dry THF (25 mL). 1-(2,6-difluorophenyl)-3-(4-methoxyphenyl)prop-2-yn-1-ol was isolated by flash chromatography (hexane/ EtOAc: 80:20) as a colourless oil (710 mg, 2.58 mmol, 51.8%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.34 (2H, m, ArH), 7.33 – 7.23 (1H, m, ArH), 6.93 (2H, t, *J* = 8.2 Hz, ArH), 6.86 – 6.79 (2H, m, ArH), 5.97 (1H, dt, *J* = 9.0, 1.4 Hz, HCO), 3.80 (1H, s, OCH_3), 2.74 (1H, dt, *J* = 8.9, 1.7 Hz, OH).

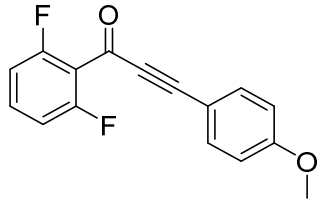
^{13}C NMR (126 MHz, $CDCl_3$) δ 161.8 (d, *J* = 7.9 Hz), 160.0, 159.8 (d, *J* = 7.9 Hz), 133.5, 130.1 (t, *J* = 10.6 Hz), 114.4, 114.0, 112.2 – 119.9, 86.0, 85.7, 55.8 (t, *J* = 5.4 Hz), 55.4.

HRMS (found (ESI) [M+Na]+, 297.0698. $C_{16}H_{12}F_2NaO_2$ requires 297.0698)

ν_{max}: 3392, 1625, 1603, 1508, 1466, 1286, 1232, 1175, 1026, 992, 827, 787, 736, 556, 533 cm^{-1}.

mp: 72-75 ^{o}C.

1-(2,6-Difluorophenyl)-3-(4-methoxyphenyl)prop-2-yn-1-one 37.



This compound was prepared following procedure B using 1-(2,6-difluorophenyl)-3-(4-methoxyphenyl)prop-2-yn-1-ol (127 mg, 0.463 mmol, 1.0 equiv), MnO_2 (402 mg, 4.6 mmol, 10.0

equiv), DCM (10 mL). 1-(4-Fluorophenyl)-3-phenylprop-2-yn-1-one was isolated by flash chromatography (pet ether/ EtOAc: 90:10) as a white solid (126 mg, 0.46 mmol, 85.7%)

mp: 72-75 ^{o}C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.55 (2H, m, ArH), 7.49 – 7.42 (m, 1H, ArH), 6.99 (2H, t, *J* = 8.4 Hz, ArH), 6.94 – 6.88 (2H, m, ArH), 3.85 (s, 3H, OCH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.4, 162.2, 161.0 (d, *J* = 5.8 Hz), 159.9 (d, *J* = 5.5 Hz), 135.6, 133.6 (t, *J* = 10.8 Hz), 114.6, 112.6 – 112.3 (m), 111.7, 95.1 (d, *J* = 1.9 Hz), 89.6, 55.6.

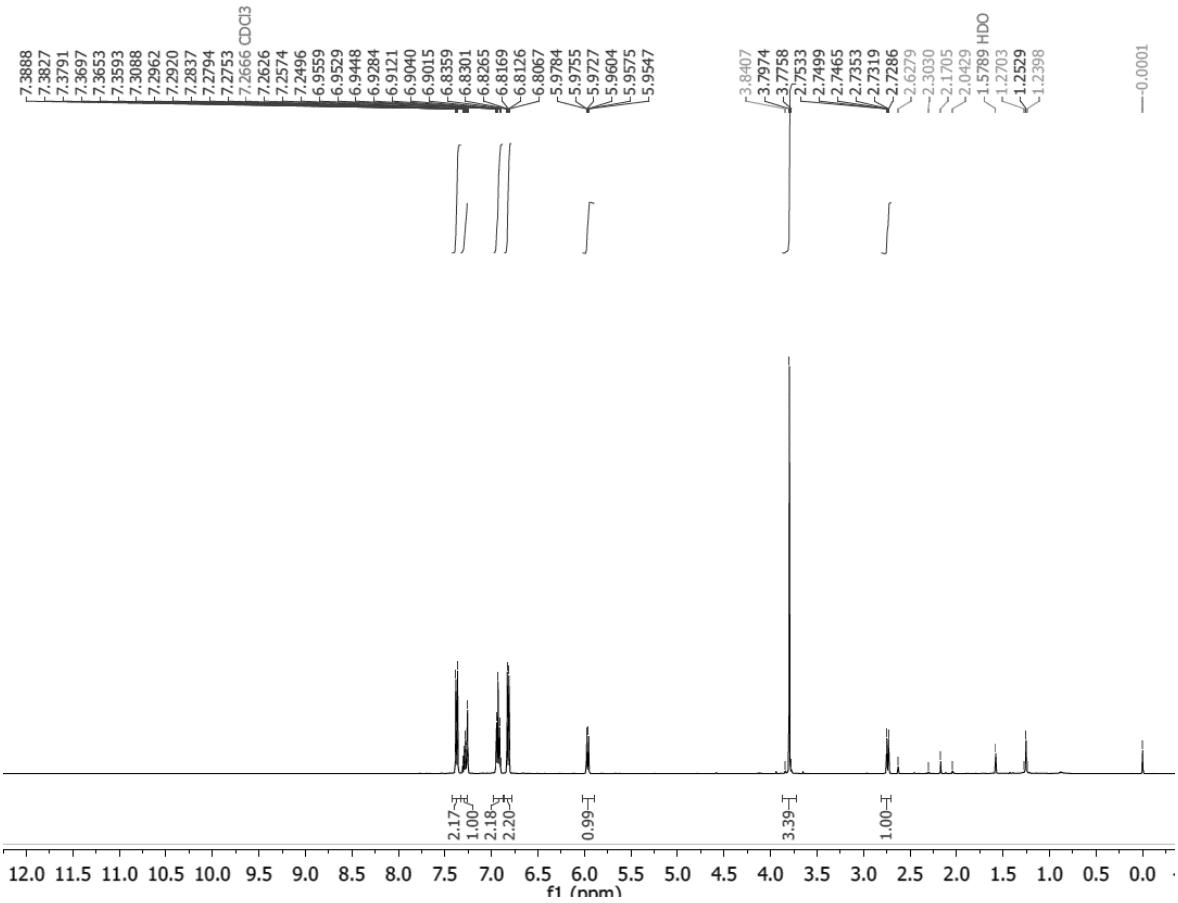
HRMS (found (ESI) [M+Na]+, 295.0543. $C_{16}H_{10}F_2NaO_2$ requires 295.0541)

ν_{max}: 2185, 1621,1597, 1507, 1461, 1319, 1237, 1171, 1068, 1031, 995, 827, 789, 749, 685, 624, 589, 562, 540 cm^{-1}.

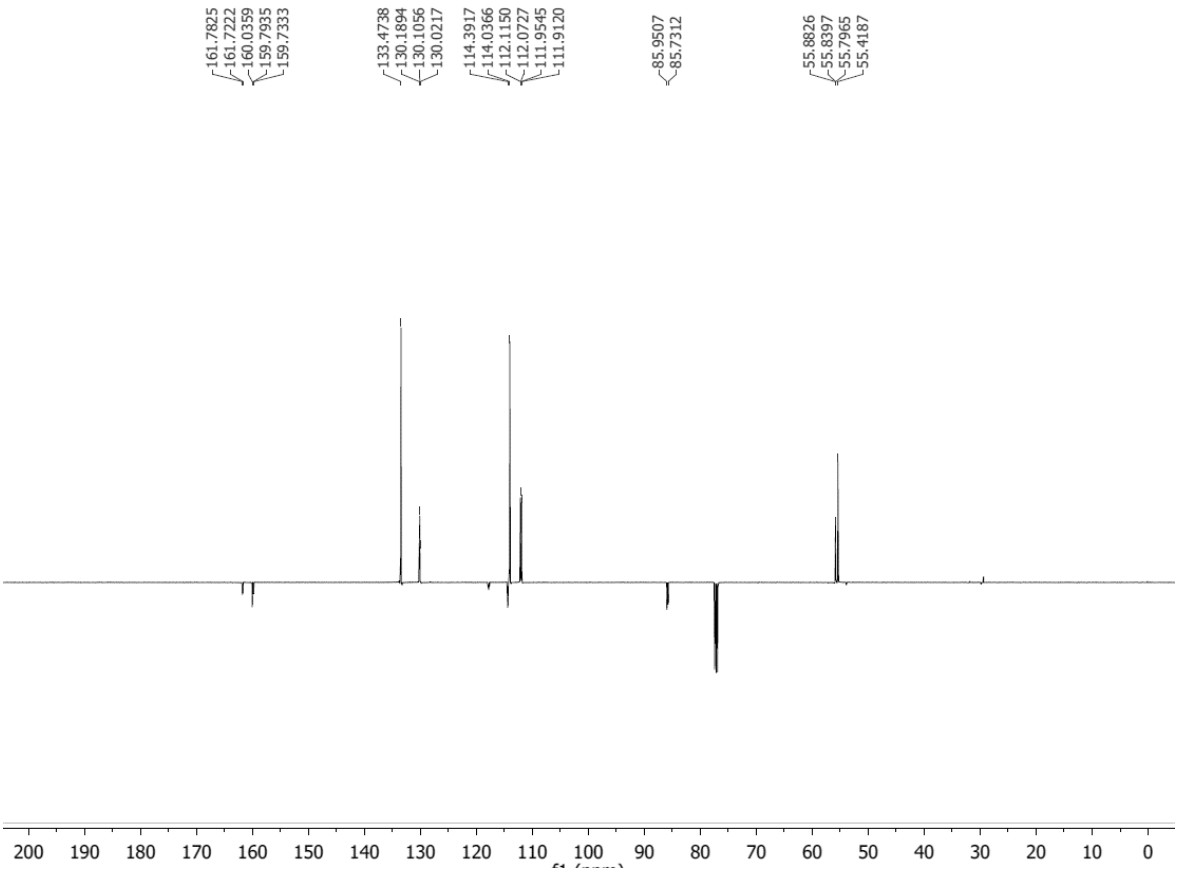
mp: 78-81 ^{o}C

1-(2,6-Difluorophenyl)-3-(4-methoxyphenyl)prop-2-yn-1-ol.

^{1}H NMR (500 MHz, $CDCl_3$)

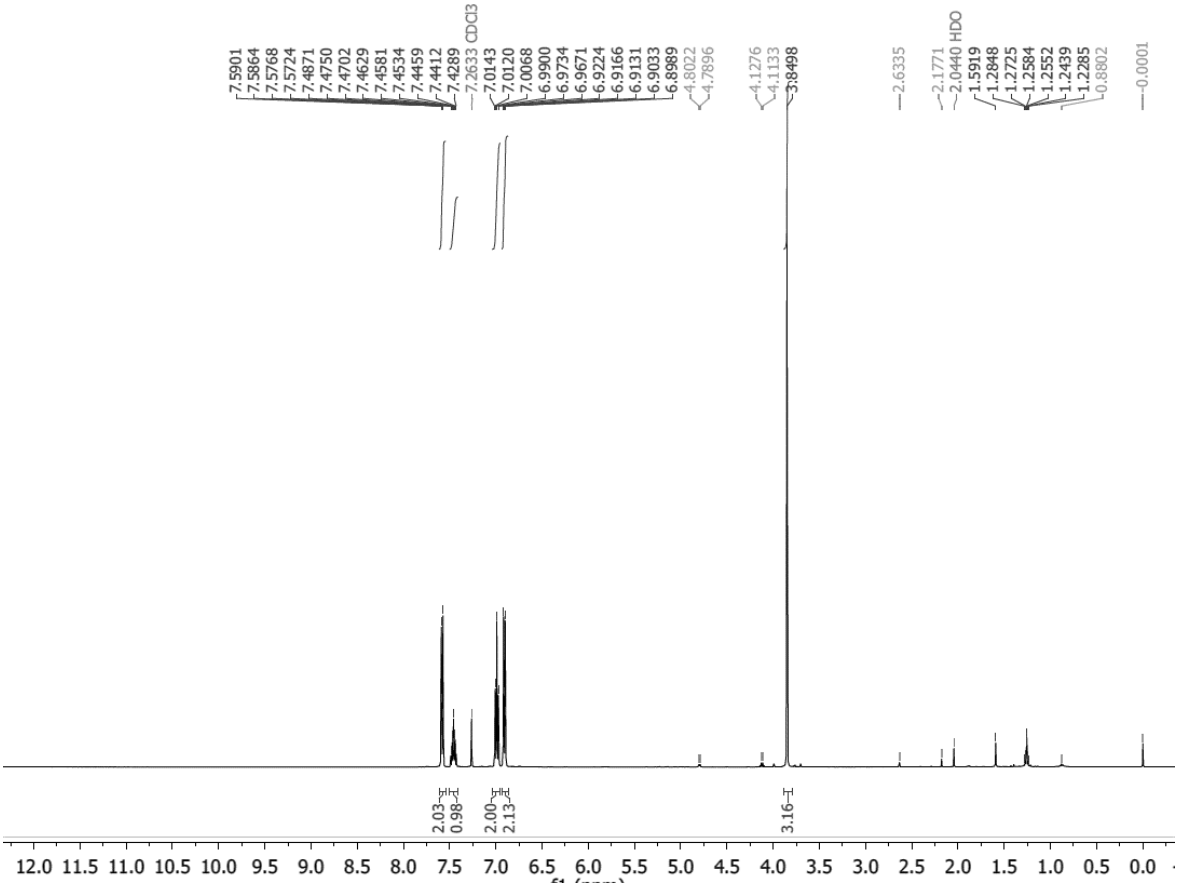


^{13}C NMR (126 MHz, $CDCl_3$)

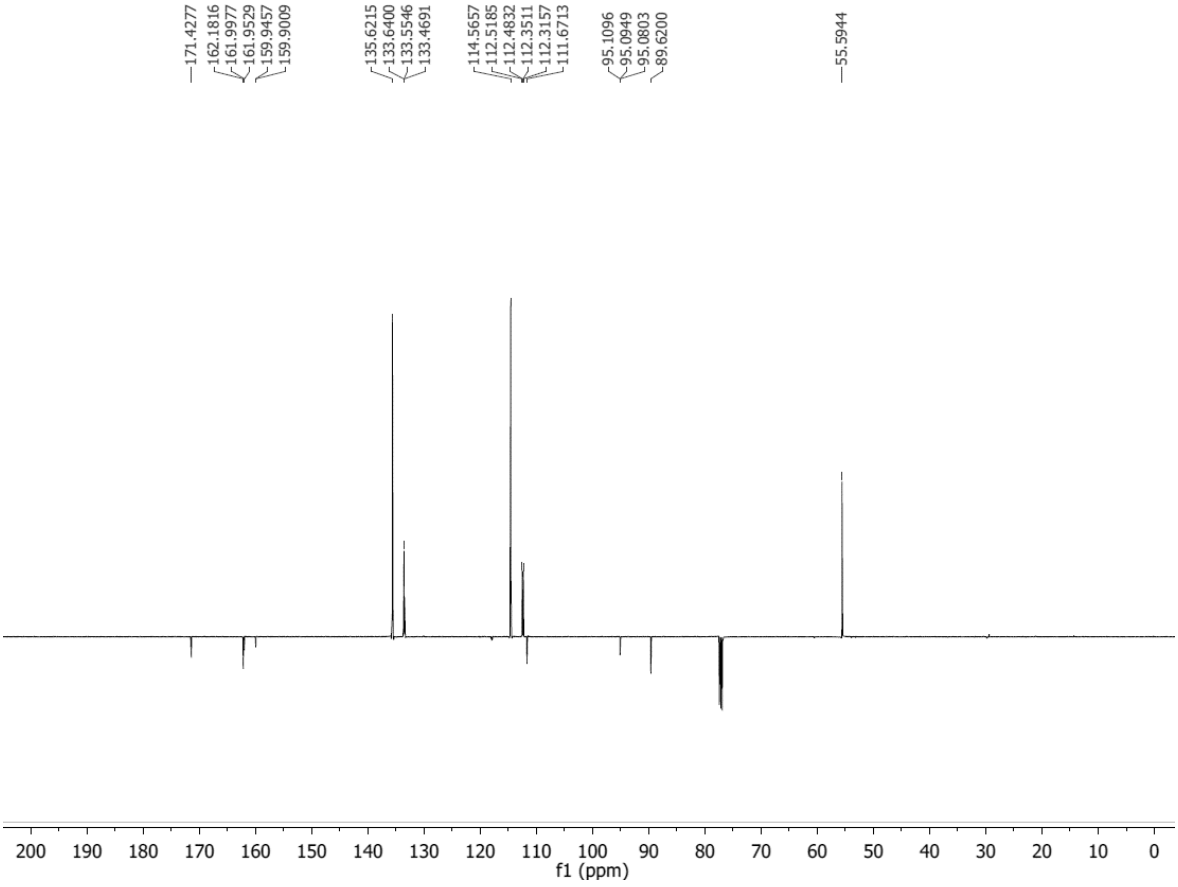


1-(2,6-Difluorophenyl)-3-(4-methoxyphenyl)prop-2-yn-1-one 37.

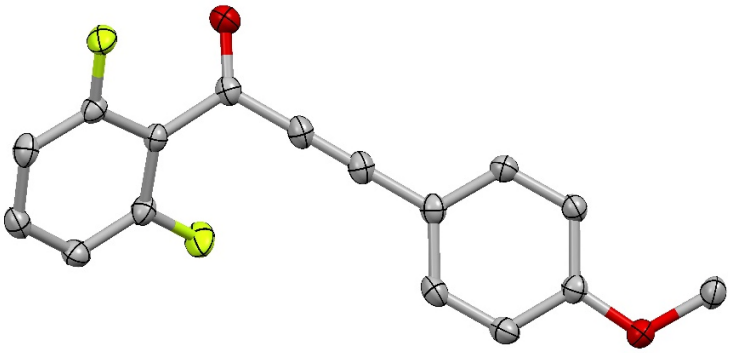
^{1}H NMR (500 MHz, $CDCl_3$)



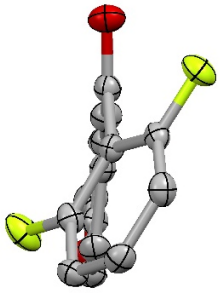
^{13}C NMR (126 MHz, $CDCl_3$).



Compound 37. CCDC 1582072

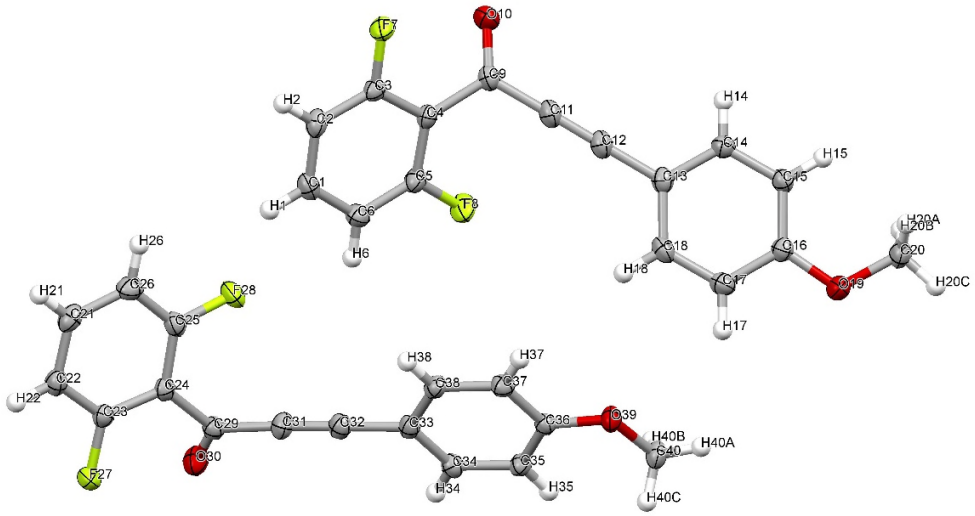


Single crystal x-ray structure of **37** (ellipsoids are plotted at the 50% probability level)



Single crystal X-ray structure of **37** (ellipsoids are plotted at the 50% probability level).

X-ray crystallographic structure of **37** with atom labelling (CCDC 1582072). See the .cif file for full crystallographic details



CCDC 1582072 contains the supplementary crystallographic data for this compound. These can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Single crystals of **37** were grown from slow evaporation of a n-hexane/EtOAc (1:1) solution of the compound over several days. A suitable crystal was mounted on a glass fibre with Fomblin oil and collected on a Rigaku Oxford Diffraction SuperNova diffractometer with a duel source (Cu at zero) equipped with an AtlasS2 CCD area detector at 150(2) K. The structure was solved using Olex2[1] and the ShelXT[2] structure solution program using Direct Methods and refined with the ShelXL[3] refinement package using Least Squares refinement.

The asymmetric unit contains two distinct molecules. The crystal exhibits a layered structure with significant donor-acceptor (π-π) interactions of the difluorophenyl moieties. The molecules display significant non-planarity arising from the steric requirements of the 2,6-difluoro functionalised phenyl ring and the adjacent carbonyl moiety. The dihedral angles between the difluorobenzene and ketone are 41.9° and -37.8° for the two independent molecules.

Compound Reference	**Compound 37**
Chemical Formula	$C_{20}H_{16}F_2O_2$
Formula Mass	272.24
Crystal system	triclinic
a/ Å	3.83441(11)
b/ Å	15.5277(4)
c/ Å	22.1954(5)
α/ °	108.682(2)
β/ °	91.293(2)
γ/ °	96.764(2)
Unit cell volume/ Å	1240.60(6)
Temperature/ K	150(2)
Space group	P-1
Crystal size/ mm	0.3 × 0.08 × 0.02
Radiation	CuKα (λ = 1.54178)
Goodness-of-fit on F^2	1.029
No. of formula units per unit cell, Z	4
No. of reflections measured	4965
No. of independent reflections	4179
Final R_1 vaules (I > 2σ(*I*))	0.0373
Final *wR*(F^2) values (I > 2σ(*I*))	0.0908
Final R_1 values (all data)	0.0468
Final *wR*(F^2) (all data)	0.0971

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.

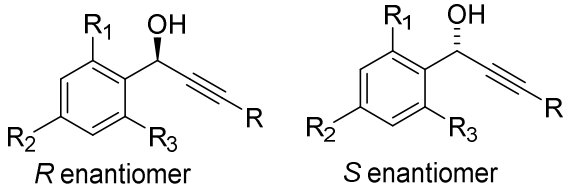
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.

3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8

Summary of literature survey on aryl/propargylic ketone reduction products.

In this report we follow the convention in the literature for assignment of *R/S* used throughout the preceding literature, i.e.

Irrespective of substituents on the aromatic ring:



The product configurations were confirmed as follows:

i) The p-substituted/Ph product configurations were confirmed by literature comparisons where possible, and others were then related to them.

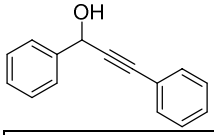
ii) The o-substituted/Ph product configurations were confirmed by literature comparisons where possible and others were then related to them.

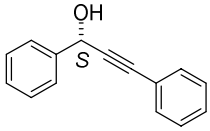
iii) The 2,6-disubstituted/Ph were confirmed by the X-ray analysis of the difluoro derivative, and others were related to that compound.

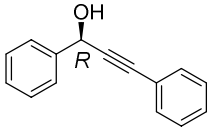
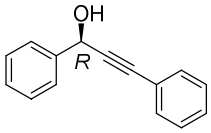
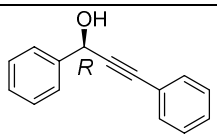
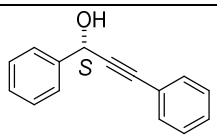
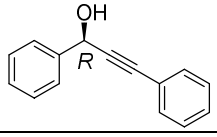
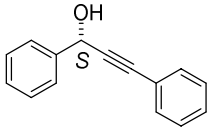
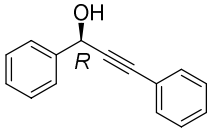
iv) The o-substituted/TMS product configurations were confirmed by comparison of the rotation and HPLC data for the reported derivative of the o-Br alcohol used in the formal synthesis.

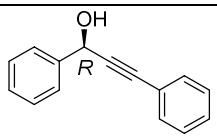
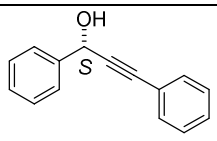
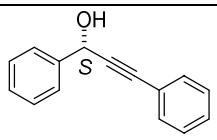
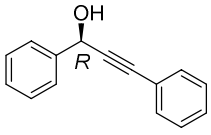
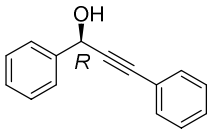
The Table below summarises literature comparisons that we have made between configuration, sign of optical rotation and HPLC data where available. The list is not fully comprehensive and for reasons of space not all reports for commonly-prepared compounds are included.

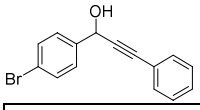
Tables of literature precedent for each reduction product which were used to aid our assignments of configurations; The result in our study is given in first row of each Table. Literature references are given at the end of the Tables.

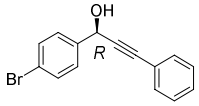
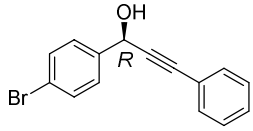
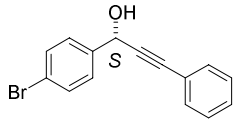


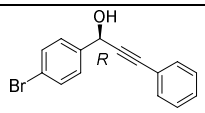
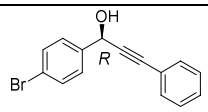
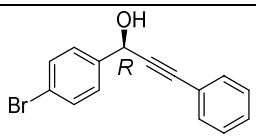
Reference	**Major enantiomer illustrated**	**HPLC conditions**	**Retention times.**
This work.	 17% conv. Not isolated.	OD-H Hex:IPA 90:10 0.7 mpm.	12.1 (minor) R 17.7 (major) S

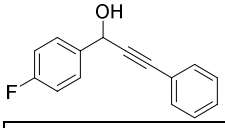
19. Ramos Tombo 1990	*S*	correlation with reduction product	
22. Soai 1990	R-(+)		
21. Corey 1994	R-(+)		
11. Carreira 2000	R-(+)	OD-H hexane:IPA 90:10	13.1 (major) R 23.0 (minor) S
4. Wang 2004.		OD-H Hex/IPA 10:1	18.14 (major) R 35.49 (minor) S
15. Pu 2004.		OD Hex/IPA 90:10 1 mpm	13.6 (major) R 24.2 (minor) S
6. Shibasaki 2005.		OD-H Hex/IPA 9:1 1 mpm	12.3 (major) R 19.0 (minor) S
16. Xu 2005		OD Hex/IPA 90:10 1 mpm	13.89 (minor) R 26.31 (major) S
23. Campagne 2005.	R.	OD Hex:IPA 90:10 1 mpm	11.5 (major) R 19.39 (minor) S
18. Pu 2007	R.	OD hex/IPA 90:10 1 mpm	9.5 (major) R 16.8 (minor) S
1. Zhang. 2008		ODH Hex/IPA 80:20	7.63 (major), 11.69 (minor)
9. Wang 2009.		OD Hex/IPA 80:20	5.74 (minor) R 7.08 (major) S
5. Nishiyama 2010.		OD Hex:IPA 80:20 1 mpm	8.2 (major) R 12.1 (minor) S

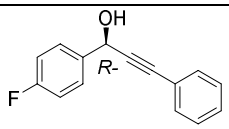
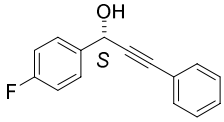
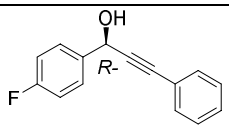
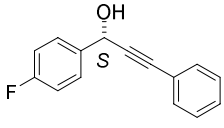
3. Chen 2012.		OD-H Hex/IPA 90:10 1 mpm	11.25 (major) R 20.54 (minor) S
8. Bian/Hou 2013.		OD-H Hex:IPA 80:20 1 mpm	8.13 (minor) R 10.27 (major) S
7. Xu 2014.		OD-H Hex:IPA 90:10 1 mpm	14.3 (minor) R 22.6 (major) S
12. Pu 2015		OD Hex/IPA 90:10 1 mpm	14.3 (major) R 22.8 (minor) S
14. Wang 2017		OD Hex/IPA 90:10 1 mpm	11.34 (major) R 21.20 (minor) S

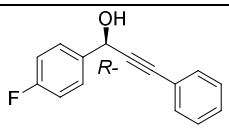


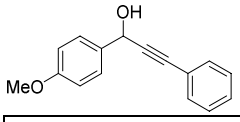
Reference	**Major enantiomer illustrated)**	**HPLC conditions**	**Retention times**
This work	Not isolated in our work.	OD-H Hex:IPA 80:20 1 mpm	6.6 (minor) R 15.7 (major) S
4. Wang 2004.		OD-H Hex/IPA 10:1	10.64 (major) R 39.58 (minor) S
15. Pu 2004	 .	OD Hex/IPA 90:10 1 mpm	12.2 (major) R 40.7 (minor) S
9. Wang 2009.	 .	OD Hex/IPA 95:5 1 mpm	6.14 (minor) R 13.08 (major) S

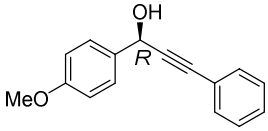
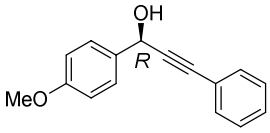
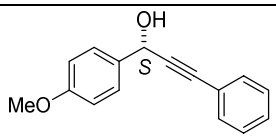
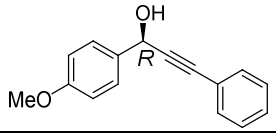
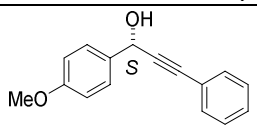
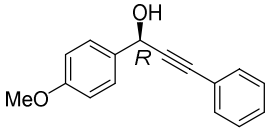
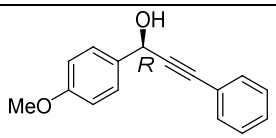
5. Nishiyama 2010.		OD-H Hex/IPA 80:20 1 mpm	6.7 (major) R 21.2 (minor) S
12. Pu 2015.		OD Hex/IPA 90:10 1 mpm	10.4 (major) R 34.1 (minor) S
14. Wang 2017		OD Hex/IPA 90:10 1 mpm	9.07 R 25.05 S

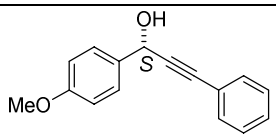
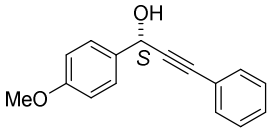
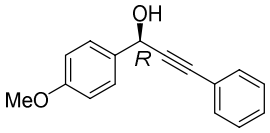
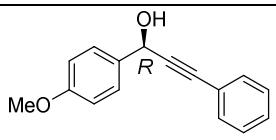


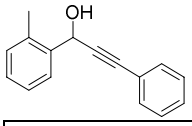
Reference	**Major enantiomer illustrated**	**HPLC conditions**	**Retention times**
This work	Not isolated, 15% Conv.	OD-H Hex/IPA 80:20 1 mpm	6.1 (minor) R. 13.5 (major) S.
4. Wang 2004.		OD-H Hex/IPA 10:1	7.72 (major) R 29.46 (minor) S
6. Shibasaki 2005.	R- (+)	OJ-H Hex/IPA 9:1 1 mpm	18.7 (major) 26.8 (minor)
9. Wang 2009.	 .	OD Hex/IPA 80:20 1 mpm	5.77 (minor)R 11.09 (major) S
3. Chen. 2012.		OD-H Hex/IPA 90:10 1 mpm	8.92 (major) R 24.97 (minor) S
8. Bian/Hou 2013.		OD-H Hex/IPA 80:20 1 mpm	6.45 (minor) R 12.47 (major) S

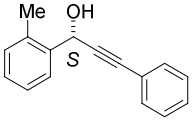
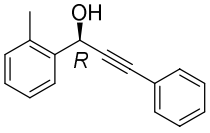
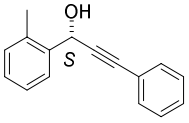
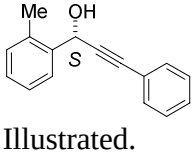
12. Pu 2015.		OD Hex/IPA 90:10. 1 mpm.	10.5 (major) R 33.4 (minor) S

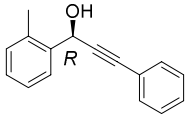
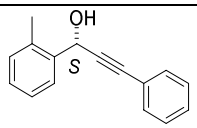
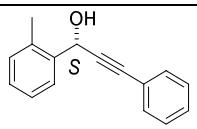
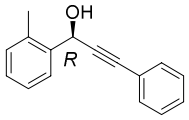


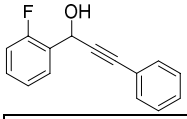
Reference	**Major enantiomer illustrated.**	**HPLC conditions**	**Retention times**
This work.	Low conv, not isolated. S.	OD-H Hex/IPA 90:10 1 mpm	15.3 (minor) R 32.3 (major) S
4. Wang 2004.		OD-H Hex/IPA 10:1	49.79 (major) R 71.37 (minor) S
15. Pu 2004	 .	OD Hex/IPA 90:10 1 mpm	16.7 (major) R 37.9 (minor) S
16. Xu 2005		OD Hex:IPA 90:10 1 mpm	15.17 (minor) R 33.24 (major) S
1. Zhang. 2008.		OD-H Hex/IPA 80:20	7.20 (major) 11.83 (minor)
9. Wang 2009.	 .	OD Hex/IPA 80:20 1 mpm	8.57 (minor) R 13.18 (major) S
5. Nishiyama 2010.		OD Hex/IPA 90:10 1 mpm	14.8 (major) R 36.3 (minor) S
3. Chen. 2012.		OD-H Hex/IPA 90:10 1 mpm	13.56 (major) R 30.01 (minor) S

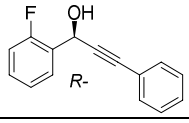
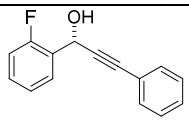
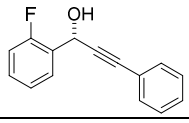
8. Bian/Hou 2013.		OD-H Hex:IPA 80:20 1 mpm	10.05 (minor) R 14.41 (major) S
7. Xu 2014.		OD-H Hex:IPA 80:20 1mpm	8.7 (minor) R 14.4 (major) S
12. Pu 2015		OD Hex/IPA 90:10 1 mpm	15.5 (major) R 30.0 (minor) S
14. Wang 2017		OD Hex/IPA 90:10 1 mpm.	14.42 R 31.71 S

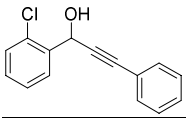


Reference	**Major enantiomer illustrated**	**HPLC conditions**	**Retention times.**
This work.	 Low conv, not isolated.	OD-H Hex/IPA 80:20 1 mpm	6.4 (minor) R 11.1 (major) S
15. Pu 2004		OD Hex/IPA 90:10 1 mpm	12.0 (major) R 27.1 (minor) S
16. Xu 2005		OD Hex/IPA 90:10 1 mpm	11.45 (minor) R 23.98 (major) S
9. Wang 2009.	 Illustrated.	OD Hex/IPA 80:20 1 mpm	6.16 (minor) R 10.40 (major) S

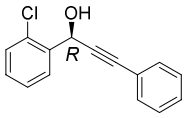
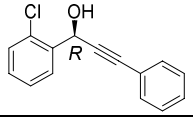
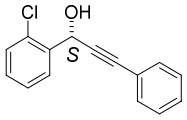
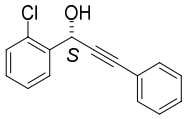
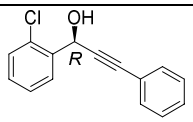
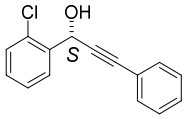
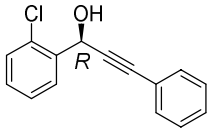
3. Chen 2012.		OD Hex/IPA 90:10 1 mpm	9.58 (major) R 20.52 (minor) S
8. Bian/Hou 2013.		OD-H Hex:IPA 80:20 1 mpm	6.29 (minor) R 9.72 (major) S
7. Xu 2014.		OD-H Hex:IPA 80:20 1 mpm	6.0 (minor) R 11.1 (major) S
12. Pu 2015		OD Hex/IPA 90:10 1 mpm	10.6 (major) R 22.5 (minor) S

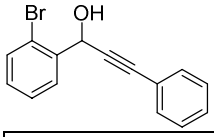


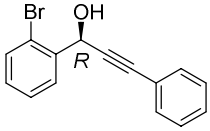
Reference	**Major enantiomer illustrated**	**Configuration assigned by rotn.**	**HPLC conditions**	**Retention times**
This work.	Isolated, 94% 	R $[\alpha]_D^{25}$ -28.3° (c 0.21 in $CHCl_3$)	OD-Hex/IPA. 80:20 1 mpm	6.0 (major) R 7.4 (minor) S
16. Xu 2005		S $[\alpha]_D^{20}$ = +5.68 (C=0.6, $CHCl_3$).	OD Hex/IPA 90:10 1 mpm	10.22 (minor) R 14.76 (major) S
9. Wang 2009.	S 	S $[\alpha]_D^{25}$ = +6.5 (c=0.71, $CHCl_3$)	OD Hex:IPA 80:20 1 mpm	5.74 (minor) R 7.08 (major) S

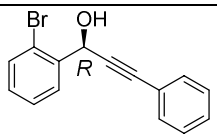
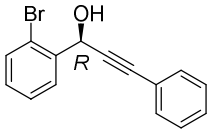
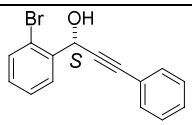


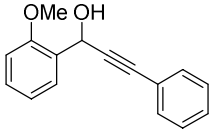
Reference	**Major enantiomer illustrated**	**Configur-ation assigned by rotn.**	**HPLC conditions**	**Retention times**

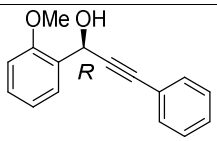
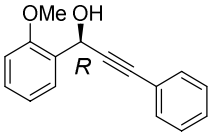
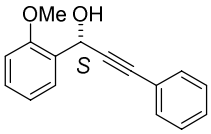
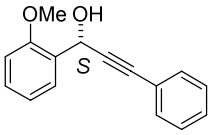
This work.	97% isolated 	R $[\alpha]_D^{25}$ -26.8º (c 0.14 in $CHCl_3$)	OD-H Hex/IPA 97:3 1 mpm	34.5 (major) R 53.7 (minor) S
1. Zhang. 2008.			OD-H hex:IPA 90:10	8.25 (major) 9.51 (minor)
16. Xu 2005		S $[\alpha]_D^{20}$ = +11.3 (c=0.6, $CHCl_3$)	OD Hex/IPA 90:10 1 mpm	11.71 (minor) R 13.15 (major) S
9. Wang 2009.		S $[\alpha]_D$ = +12.2 (c=1.17, $CHCl_3$)	OD Hex/IPA 80:20 1 mpm	9.55 (minor)R 10.66 (major)S
3. Chen. 2012.		R $[\alpha]^{22}_D$ = −49.3 (c 0.50, $CHCl_3$)	OD-H hex:IPA 90:10 1 mpm	9.07 (major) R 10.74 (minor) S
8. Bian/Hou 2013.		S $[\alpha]_D^{20}$ = +12.1 (c=1.20, $CHCl_3$)	OD-H Hex/IPA 97:3 1 mpm	29.93 (minor) R 34.49 (major) S
14. Wang 2017.	 .		OD Hex/IPA 90:10 0.5 mpm	10.46 (R) 11.56 (S)

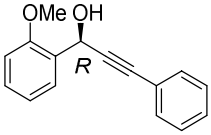
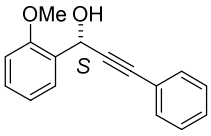
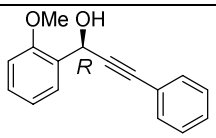


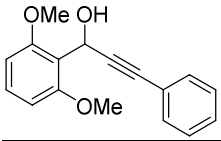
Reference	**Major enantiomer illustrated**	**Configur-ation assigned by rotn**	**HPLC conditions**	**Retention times**
This work.	 Isolated, 99%.	R $[\alpha]_D^{25}$ -22.6º (c 0.23 in $CHCl_3$)	OD-H Hex:IPA 97:3 1 mpm	34.6 (major) R 44.9 (minor) S

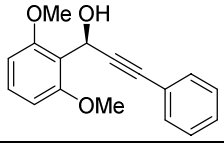
5. Nishiyama 2010.		R $[\alpha]^{23}_D$ = −55.7 (c 1.47, $CHCl_3$)	OD hex:IPA 98:2 1 mpm	56.4 (major) R 74.8 (minor) S
3. Chen 2012.		R $[\alpha]^{22.1}_D$ = −53.9 (c 1.05, $CHCl_3$)	OD-H hex:IPA 90:10 0.25 mpm	41.27 (major) R 44.53 (minor) S
8. Bian/Hou 2013.		S $[\alpha]_D^{20}$ = +71.9 (c=1.01, $CHCl_3$)	OD-H Hex/IPA 80:20 1 mpm	6.44 (major) R 6.92 (minor) S

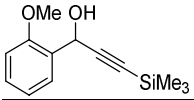


Reference	**Major enantiomer illustrated**	**Configur-ation assigned by rotn**	**HPLC conditions**	**Retention times**
This work.	 95% isolated	R $[\alpha]_D^{25}$ - 7.6º (c 0.15 in $CHCl_3$)	OD-H Hex:IPA 90;10 1 mpm	14.2 (major) R 16.3 (minor) S
4. Wang 2004.		R $[\alpha]^{18}_D$ = −8 (c 1.20, $CHCl_3$)	OD Hex:IPA 10:1	16.28 (major) R 22.23 (minor) S
16. Xu 2005.		S $[\alpha]_D^{20}$ = +9.83 (c=0.6, $CHCl_3$)	OD Hex/IPA 90:10 1 mpm	17.31 (minor) R 20.96 (major) S
9. Wang, 2009.		S $[\alpha]_D^{25}$ = +9.36 (c=0.53, $CHCl_3$)	OD hex/IPA 80:20 1 mpm	8.17 (minor) R 9.36 (major) S

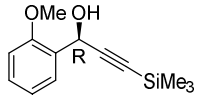
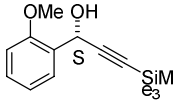
3. Chen 2012.		R $[\alpha]^{20.7}_D$ = −10.5 (c 1.20, $CHCl_3$)	OD-H hex:IPA 90:10 1 mpm	13.54 (major) R 17.12 (minor) S
8. Bian/Hou 2013.		S $[\alpha]_D^{20}$ = +12.3 C=2.03, $CHCl_3$)	OD-H Hex/IPA 80:20 1 mpm	9.19 (minor) R 10.16 (major) S
14. Wang 2017.			OD Hex/IPA 90:10 0.5 mpm	13.91 (R) 17.02 (S)

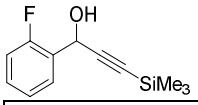


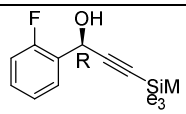
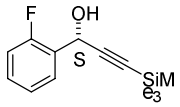
Reference	**Major enantiomer illustrated**	**Configur-ation assigned by rotn**	**HPLC conditions**	**Retention times**
This work	Low conv Not isolated. R in analogy with difluoro	n/a Not isolated.	OD-H Hex:IPA 80:20 1 mpm	20.6 (major) R 26.3 (minor) S
14. Wang 2017.		$[\alpha]_D^{20}$ = -15.0 (c=0.24, $CHCl_3$)	OD Hex:IPA 90:10 1 mpm	18.7 R minor 24.9 S major
17. Trost 2005		$[\alpha]_D$ = -13.5 (c=0.5, DCM)	OD Hept/IPA 90:10	11.5 15.0

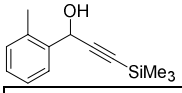


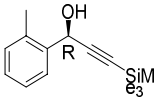
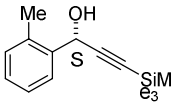
Reference	**Major enantiomer illustrated**	**Configuration assigned by rotn.**	**HPLC conditions**	**Retention times**

	(our configuration)			
This work.	 94% isolated	R $[\alpha]_D^{25}$ +17.8° (c 0.21 in $CHCl_3$)	OD Hex:IPA 90:10 1 mpm	15.3 (minor) S 16.9 (major) R
13. Guo 2011.		S $[\alpha]_D^{20}$ = -15.4 (c=1.1, $CHCl_3$)	AD Hex/IPA 95:5 1 mpm	8.85 (major) S 9.90 (minor) R



Reference	**Major enantiomer illustrated**	**Configur-ation assigned by rotn**	**HPLC conditions**	**Retention times**
This work.	 95% isolated	R $[\alpha]_D^{25}$ 14.8° (c 0.21 in $CHCl_3$)	GC used	96.2 (Minor) S 98.6 (Major) R
13. Guo 2011.		S $[\alpha]_D^{20}$ = -12.8 (c=1.17, $CHCl_3$)	AD Hex/IPA 98:2 1 mpm	10.48 (major) S 11.12 (minor) R



Reference	**Major enantiomer illustrated**	**Configur-ation assigned by rotn**	**HPLC conditions**	**Retention times**
This work.	 36% conv., not isolated.	Rotation not taken R by analogy.	OD-H, hexane/IPA 97:3 1.0 mpm	9.0 (minor) S 10.8 (major) R
13. Guo 2011.		S $[\alpha]_D^{20}$ = -14.8	AD Hex/IPA 98:2 1 mpm	8.77 (major) S 10.63 (minor) R

		(c=1.65, $CHCl_3$)		

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In addition, this paper was used to establish the absolute configuration of the S-MOM.tri(methoxy)aryl ortho-Br derivative **35** and hence reduction product **31**: Leblanc, M.; Fagnou, K. *Org. Lett.* **2005**, *7*, 2849-2852 (pinene and 9-BBN combination gives reduction of a derivative in 97% ee). Data for the *S*-derivative; HPLC was on AD-H column, 0.9 mpm, 90:10 hex:IPA 10.23 (minor), 11.03 (major), $[\alpha]_D^{22}$ = -22.5 (c=1, DCM). Our product had a (+) rotation which supports *R*, as predicted. We used an AD-H column as well 90:10, 1 mpm gives *R* at 10.6 (major) and S at 11.8 min (minor), so confirms the major configuration.