Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Dimethylzinc-mediated enantioselective addition of terminal alkynes to 1,2-diketones using perhydro-1,3-benzoxazines as ligands

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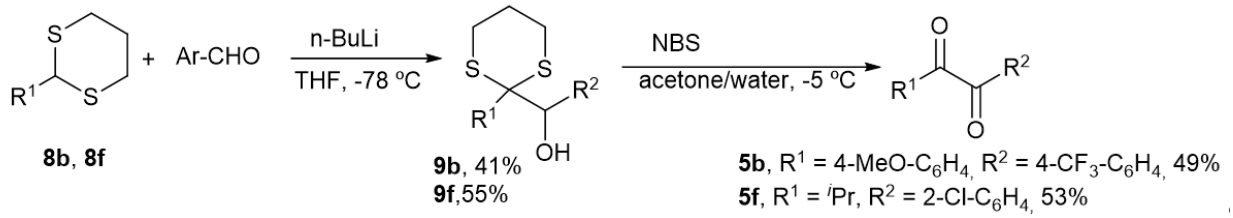
Synthesis of diketones 5b and 5f.

Diketones **5b** and **5f** were prepared in a two-step process involving (2-aryl-1,3-dithan-2-yl)lithium addition to arylaldehydes followed by treatment of the resulting alcohol with NBS in aqueous acetone.[1]



8b, **8f**

9b, 41%
9f,55%

5b, R^1 = 4-MeO-C_6H_4, R^2 = 4-CF_3-C_6H_4, 49%
5f, R^1 = ^{i}Pr, R^2 = 2-Cl-C_6H_4, 53%

Synthesis of 9b and 9f

To the solution of dithiane **8b** or **8f** (5 mmol), previously prepared according to the literature,[2] in dry THF (30 mL), *n*-BuLi (1.6 M) (5.5 mmol) was added at -78°C. After stirring at the same temperature for 2h, the corresponding aromatic aldehyde (5.5 mmol) was added slowly and the reaction was continued for 1h. After completion of the reaction, aqueous NH_4Cl was added to the reaction mixture. Solvent THF was evaporated and the residue was extracted with ethyl acetate. The organic layer was dried over anhydrous Mg_2SO_4, concentrated, and purified by column chromatography using mixtures of ethyl acetate and hexanes.

(2-(4-methoxyphenyl)-1,3-dithian-2-yl)(4-(trifluoromethyl)phenyl)methanol (9b). This compound was obtained from **8b** (1.13 g) and purified by flash chromatography (hexanes/ethyl acetate). Pale yellow oil; yield: 0.82 g, 41%; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.89-1.95 (m, 2H), 2.65-2.77 (m, 4H), 3.13 (d, J = 3.1 Hz, 1H), 3.82 (s, 3H), 5.00 (d, J = 3.1 Hz, 1H), 6.82 (d, J = 8.9 Hz, 2H), 7.00 (d, J = 8.3 Hz, 2 H), 7.38 (d, J = 8.3 Hz, 2H), 7.54 (d, J = 8.9 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 24.7, 26.8, 27.2, 55.3, 65.8, 80.4, 113.5 (2C), 124.1 (q, J = 272 Hz); 123.8 (q, J = 3.8 Hz, 2C), 128.6 (2C), 128.7, 130.0 (q, J = 32.3 Hz), 131.6 (2C), 141.3, 159.1; IR (neat) v: 3464, 1605, 1506, 1325, 1250, 1163, 1124, 840 cm^{-1}; HRMS (ESI-TOF) *m/z*: calcd. for $C_{19}H_{19}F_3NaO_2S_2^+$ $[M+Na]^+$ 423.0671, found 423.0666.

(2-chlorophenyl)(2-isopropyl-1,3-dithian-2-yl)methanol (9f). This compound was obtained from **9f** (0.85 g) and purified by flash chromatography (hexanes/ethyl acetate). Colorless oil; yield: 0.87 g, 55%; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.20 (d, J = 6.7 Hz, 3H) 1.28 (d, J = 6.8 Hz, 3H), 1.78 (m, 1H), 1.88 (m, 1H), 2.25 (hept, J = 6.7 Hz, 1H), 2.40 (ddd, J_1 = 14.1 Hz, J_2 = 9.7 Hz, J_3 = 4.2 Hz, 1H), 2.55 (m, 1H), 2.64 (dt, J_1 = 14.1 Hz, J_2 = 4.9 Hz, 1H), 2.97 (ddd, J_1 = 14.3 Hz, J_2 =10.2 Hz, J_3 = 4.2 Hz, 1H), 3.28 (d, J = 5.1 Hz, 1H), 5.60 (d, J = 51 Hz, 1H), 7.21-7.31 (2 H), 7.35 (dd, J_1 = 7.7 Hz, J_2 = 1.6 Hz, 1H), 7.90 (dd, J_1 = 7.7, J_2 = 1.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 19.0, 19.4, 23.9, 25.4, 27.5, 35.9, 63.9, 72.4, 126.2, 129.0, 129.5, 130.3, 135.0, 138.2; IR (neat) v: 3438, 2962, 2928, 2870, 1571, 1471, 1438, 1385, 1058, 1030, 756, 730, 703 cm^{-1}; HRMS (ESI-TOF) *m/z*: calcd. for $C_{14}H_{19}ClNaOS_2^+$ $[M+Na]^+$ 325.0458, found 325.0461.

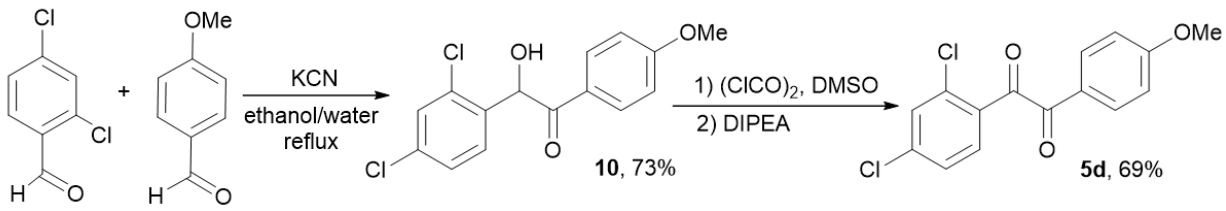
Synthesis of diketones 5b and 5f

A solution of dithiane **9b** or **9f** (2.0 mmol) in acetone (15 mL) was added dropwise over a period of 20 minutes to a solution of N-bromosuccinimide (5.3g 30 mmol) in 3% water/acetone (150 ml) at 5 ºC. The mixture was stirred and allowed to reach room temperature over 30 minutes, then poured onto a saturated aqueous sodium sulphite solution (120 mL) and dichloromethane (80 mL). After stirring for 10 minutes, the organic layer was separated, washed with water (3 x 50 mL) and dried ($MgSO_4$). The solvent was removed to yield the diketone which was purified by recrystallization or by column chromatography

1-(4-methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)ethane-1,2-dione (5b). This compound was obtained from **9b** (0.80 g) and purified by flash chromatography (hexanes/ethyl acetate). White solid; yield: 0.3 g, 49%; mp 97-99 ºC (from hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.90 (s, 3H), 6.99 (d, J = 8.9 Hz, 2H), 7.77 (d, J = 8.5 Hz, 2H), 7.96 (d, J = 8.9 Hz, 2H), 8.10 (d, J = 8.5 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 55.7, 114.5 (2C), 123.4 (q, J = 273 Hz); 125.7; 126.0 (q, J = 3.7 Hz, 2C), 130.2 (2C), 132.5 (2C), 135.7 (q, J = 33 Hz), 135.8, 165.2, 191.9, 193.3; IR (neat) v: 1680, 1657,1600,1575, 1510,1414, 1315, 1260, 1160,1123, 1066, 1016, 891, 854, 747, 642, 612 cm^{-1}; HRMS (ESI-TOF) *m/z*: calcd. for $C_{16}H_{11}F_3NaO_3^+$ $[M+Na]^+$ 331.0552, found 331.0556. NMR shift values are consistent with previously reported data.[3]

1-(2-chlorophenyl)-3-methylbutane-1,2-dione (5f). This compound was obtained from **9f** (0.85 g) and purified by flash chromatography (hexanes/ethyl acetate). Yellow oil; yield: 0.31 g, 53%. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.28 (d , J = 7.0 Hz, 6H), 3.39 (hept, J = 6.8 Hz, 1H), 7.37-7.42 (m, 2H), 7.49 (ddd, J_1 = 8.0 Hz, J_2 = 7.4 Hz, J_3 = 1.7 Hz 1H), 7.65 (dd, J_1 =7.7 Hz, J_2 = 1.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 17.7 (2C), 36.1, 127.2, 130.3, 131.5, 133.3, 133.8, 134.0, 193.4, 204.1; IR (neat) v: 2975, 2936, 2875, 1712, 1685, 1590, 1440, 1466, 1283, 1050, 908, 837, 744, 641 cm^{-1}; HRMS (ESI-TOF) *m/z*: calcd. for $C_{11}H_{11}ClNaO_2^+$ $[M+Na]^+$ 233.0340, found 233.0336.

Diketone **5d** was prepared in a two-step process involving a benzoin condensation between 2,4-dichlorobenzaldehyde and *p*-metoxibenzaldehyde to give the mixed benzoin[4] followed by a Swern oxidation.



2-(2,4-dichlorophenyl)-2-hydroxy-1-(4-methoxyphenyl)ethan-1-one (10)

A mixture of p-methoxybenzaldehyde (0.64 mL, 5.2 mmol).), 2,4-dichlorobenzaldehyde (0.92 g, 5 mL), potassium cyanide (0.22 g, 3.2 mmol), ethanol (6 mL) and water (3 mL) was charged in a microwave vial and heated at 80 ºC for 1 h. The mixture was and then quenched with water, extracted with dichloromethane, dried over anhydrous MgSO4 and concentrated in vacuo. The crude was purified by column chromatography using a mixture of hexanes and ethyl acetate as eluent to afford the pure hydroxyketone.as a pale yellow oil. Yield: 1.19 g, 73%. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.81 (s, 3H), 4.68 (s, 1H), 6.25 (s, 1H), 6.88 (d, J = 9.0 Hz, 2H), 7.04 (d, J = 8.4 Hz, 1H), 7.14 (dd, J_1 = 8.4 Hz, J_2 = 2.1 Hz, 1H), 7.42 (d, J = 2.1 Hz, 1H), 7.87 (d, J = 9.0 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 55.5, 71.6, 114.2 (2C), 125.7, 128.1, 129.9, 130.0, 131.3 (2C), 134.2, 135.1, 135.9, 164.4, 196.5; IR (neat) v: 3402, 2928, 1668, 1600, 1512, 1255, 1168, 1081, 978, 862, 795, 773, 624, 611 cm^{-1}; HRMS (ESI-TOF) m/z: calcd. for $C_{15}H_{12}Cl_2NaO_3^+$ $[M+Na]^+$ 333.0056, found 333.0061

1-(2,4-dichlorophenyl)-2-(4-methoxyphenyl)ethane-1,2-dione (5d).

To a solution of oxalyl chloride (0.4 mL, 4.75 mmol) in anhydrous dichloromethane (6 mL) cooled to -78 ºC was added dropwise, over a period of 10 min, a solution of anhydrous DMSO (0.62 mL, 8.36 mmol) in anhydrous dichloromethane (1.4 mL). After complete addition, the mixture was stirred at this temperature for further 10 min; then, the hydroxyketone **10** (1.18 g, 3.8 mmol) dissolved in anhydrous dichloromethane (1.5 mL) was added dropwise over a period of 15 min. The forming suspension was stirred at -78 ºC for 1 h and DIPEA (2.66 mL, 15.2 mmol) was added dropwise over a period of 5 min. The mixture was stirred at room temperature for 1 h. After full conversion, the reaction mixture was washed with a 5% aqueous solution of HCl (3 x 10 mL), water (20 mL), and brine, dried over anhydrous magnesium sulphate and concentrated in vacuo. The mixture was purified by column chromatography (hexanes/ethyl acetate). to afford the pure 1,2-diketone as a yellow solid. Yield 0.81 g, 69%; mp 121-122ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.91 (s, 3H), 7.01 (d, J = 9.0 Hz, 2H), 7.41 (dd, J_1 = 8.4 Hz, J_2 =1.9 Hz, 1H), 7.45 (d, J = 1.9 Hz, 1H), 7.84 (d, J = 8.4 Hz, 1H), 8.00 (d, J = 9.0 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 55.6, 114.4 (2C), 125.3, 127.8, 130.4, 132.5, 132.7 (2C), 133.0, 134.7, 140.3, 164.9, 190.4, 192.7; IR (neat) v: 1676, 1650, 1560, 1578, 1564, 1260, 1205, 1175, 1160, 878, 828, 744, 632, 613 cm^{-1}; HRMS (ESI-TOF) m/z: calcd. for $C_{15}H_{10}Cl_2NaO_3^+$ $[M+Na]^+$ 330.9899, found 330.9902.

[1] P. C. B. Page, A. E. Graham, B. K. Park, *Tetrahedron,* 1992*,* **48**, 7265.

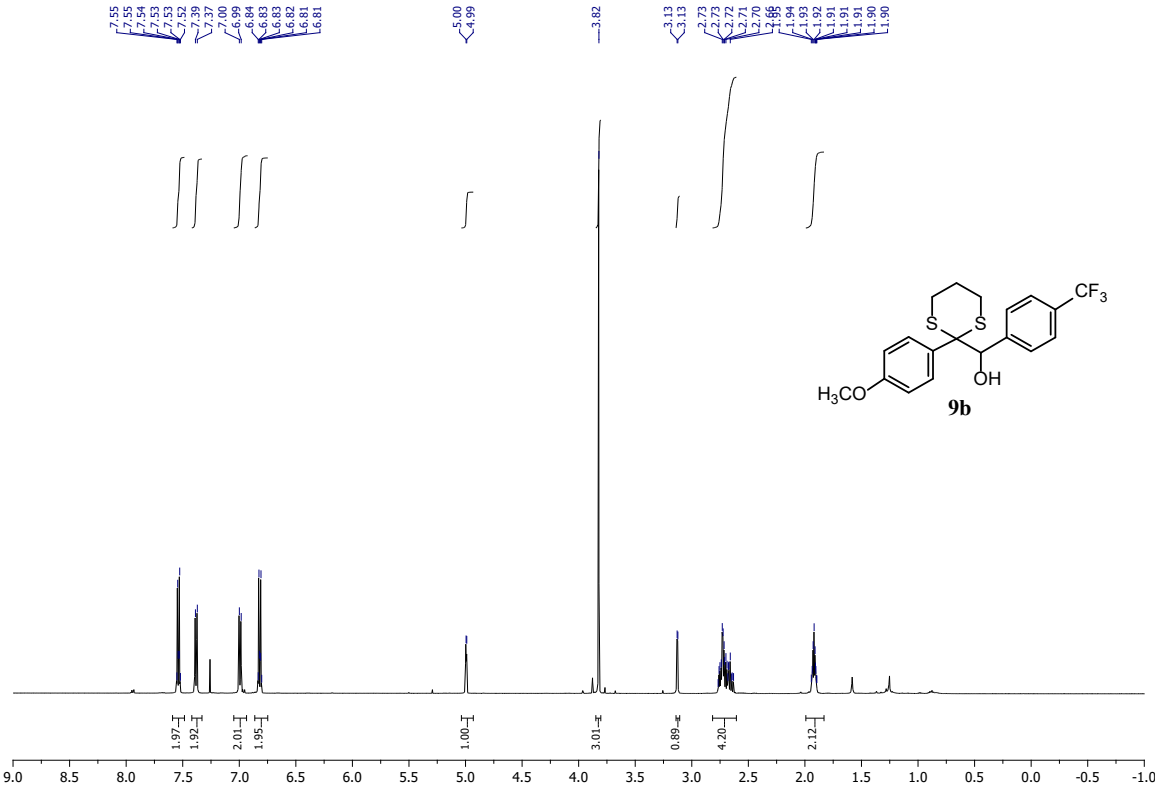
[2] R. B. Kothapalli, R. Niddana, R. Balamurugan, *Org. Lett.* 2014, **16**, 1278.

[3] Z. Wan, C. D. Jones, D. Mitchell, J. Y. Pu, T. Y. Zhang, *J. Org. Chem.* 2006, **71**, 826.

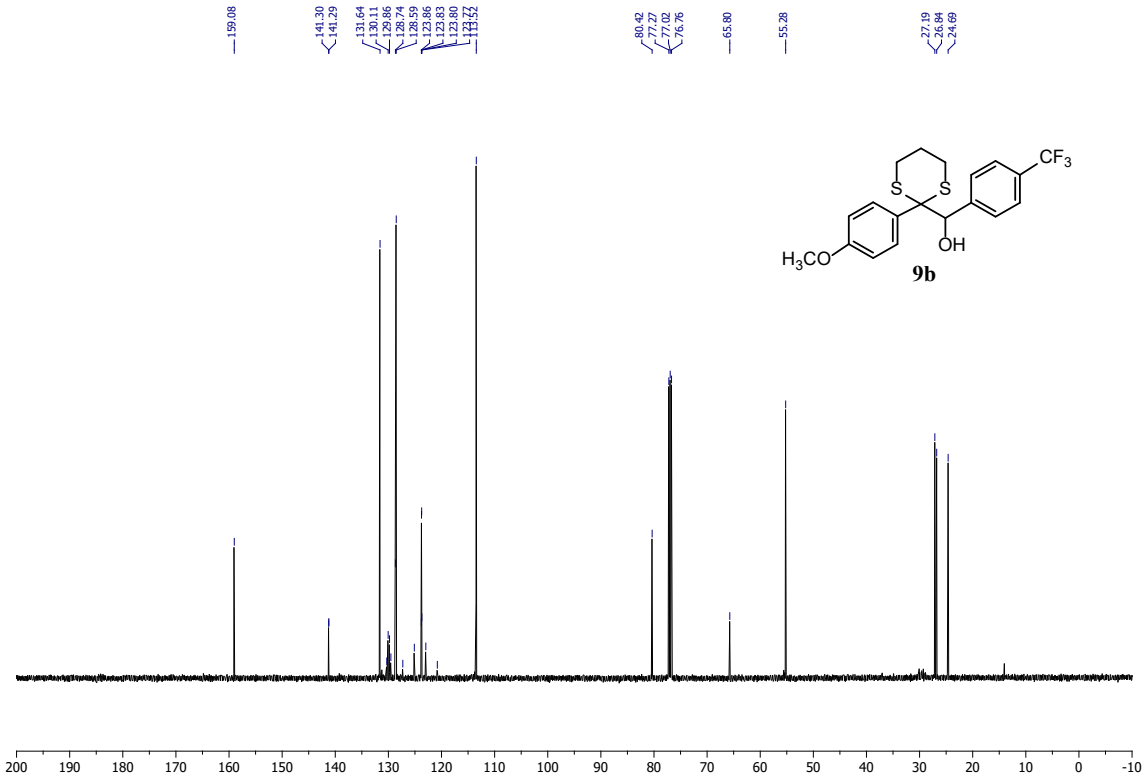
[4] J. S. Buck, W. S. Ide, *J. Am. Chem. Soc.*, 1930, **52**, 4107.

Copies of ^{1}H-NMR and ^{13}C-NMR Spectra

(2-(4-methoxyphenyl)-1,3-dithian-2-yl)(4-(trifluoromethyl)phenyl)methanol (9b) ^{1}H-NMR (500 MHz, $CDCl_3$)

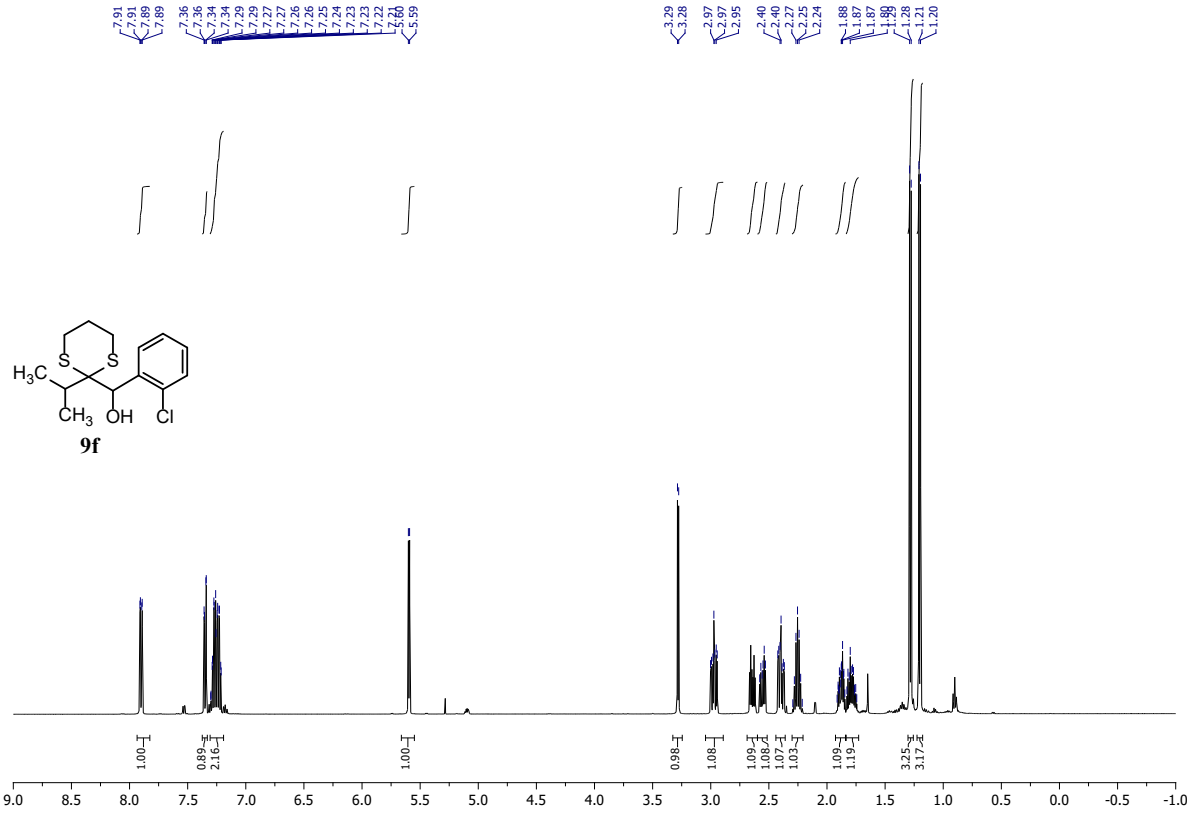


^{13}C-NMR (126 MHz, $CDCl_3$)



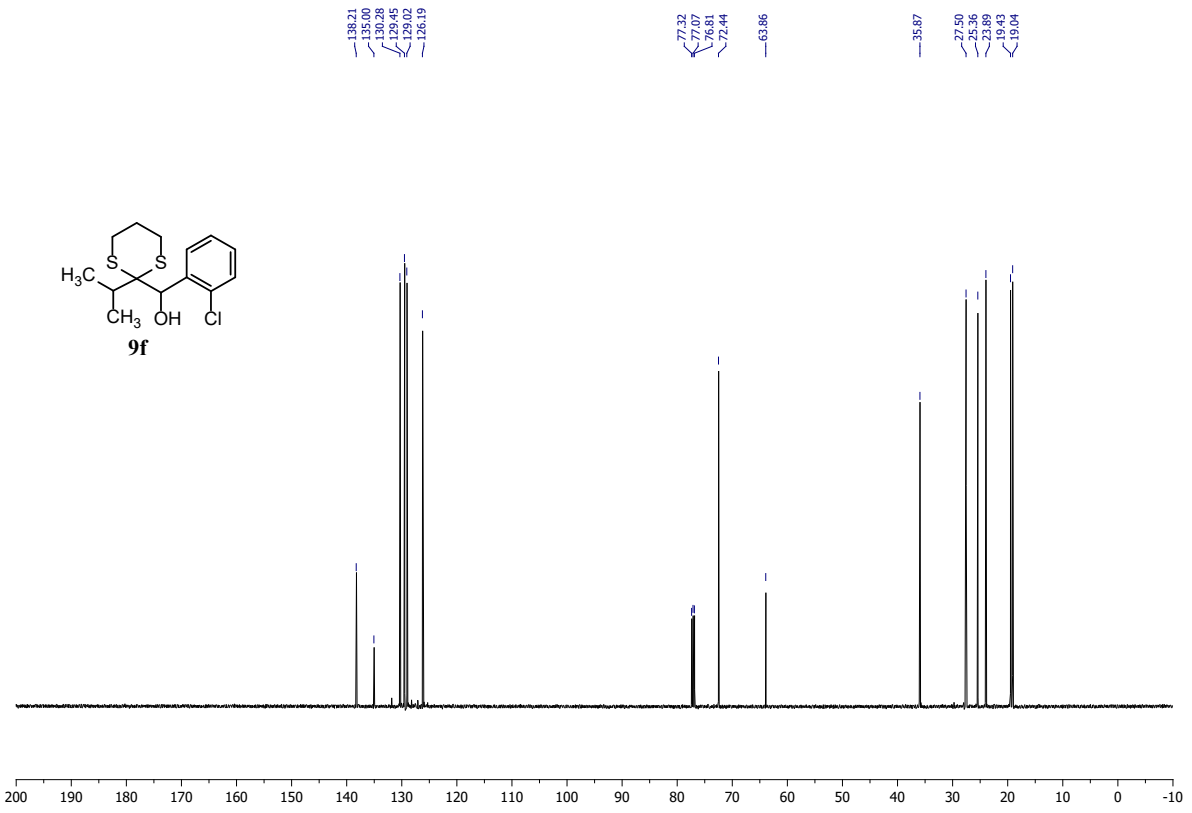
(2-chlorophenyl)(2-isopropyl-1,3-dithian-2-yl)methanol (9f).

^{1}H-NMR (500 MHz, $CDCl_3$)



9f

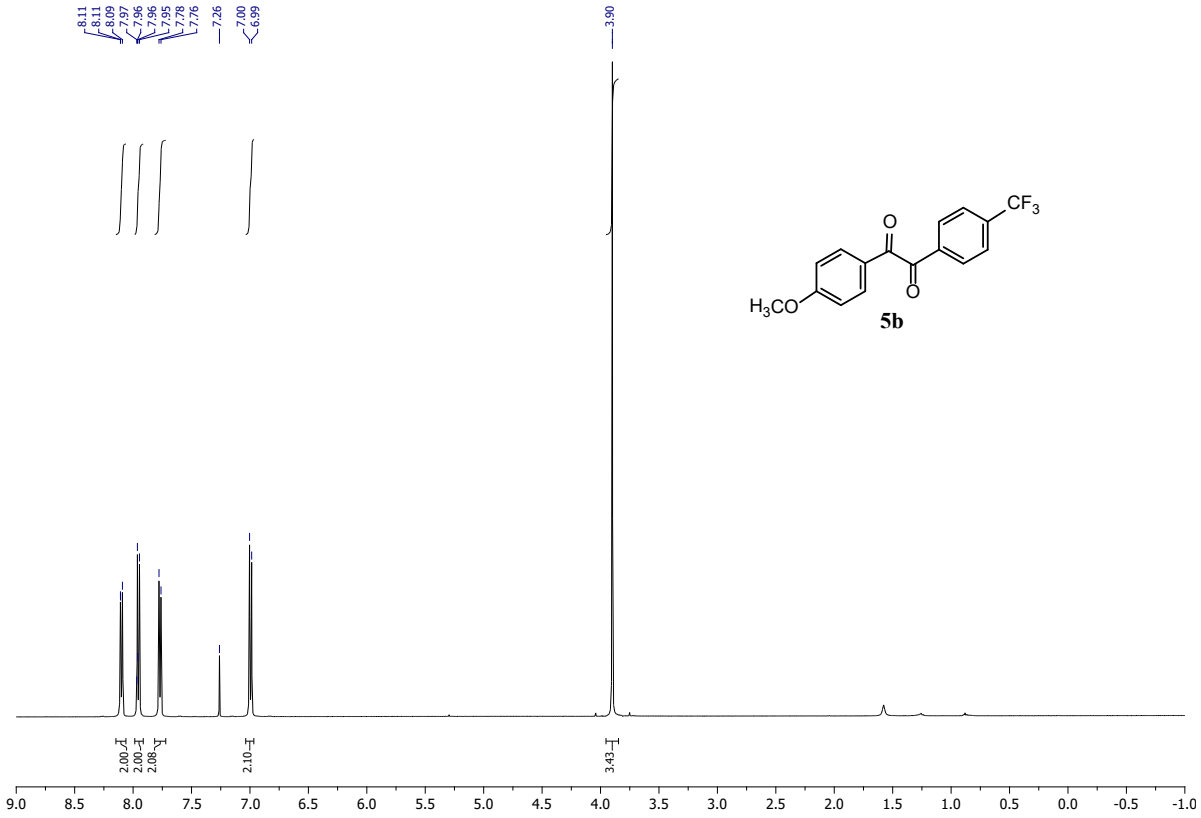
^{13}C-NMR (126 MHz, $CDCl_3$)



9f

1-(4-methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)ethane-1,2-dione (5b)

^{1}H-NMR (500 MHz, $CDCl_3$)



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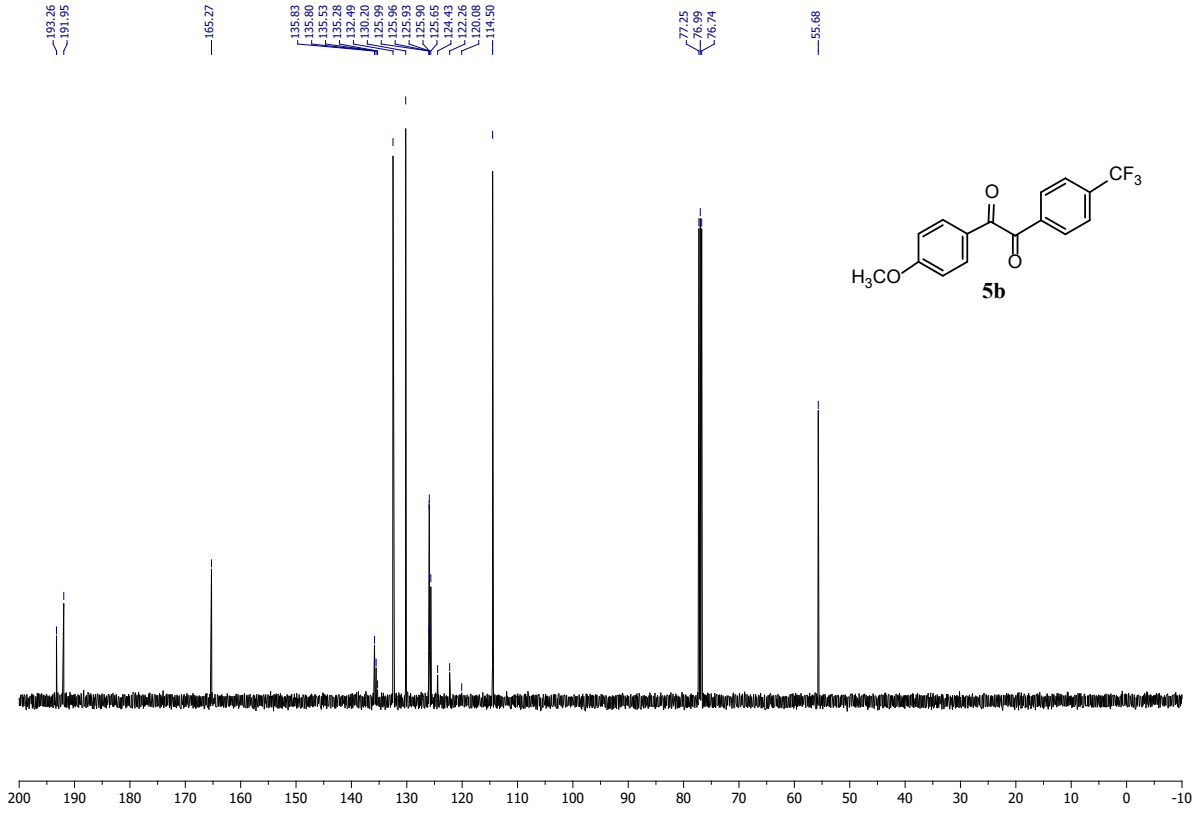
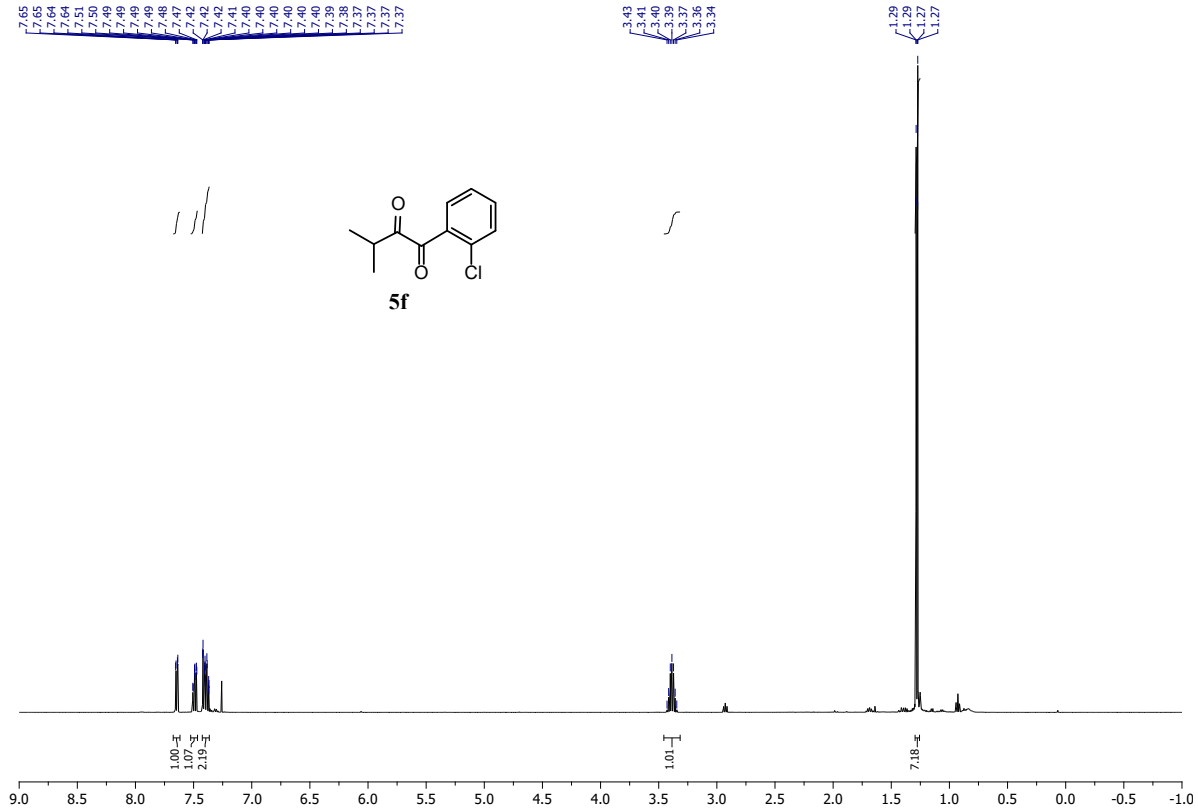


1-(2-chlorophenyl)-3-methylbutane-1,2-dione (5f)

^{1}H-NMR (500 MHz, $CDCl_3$)



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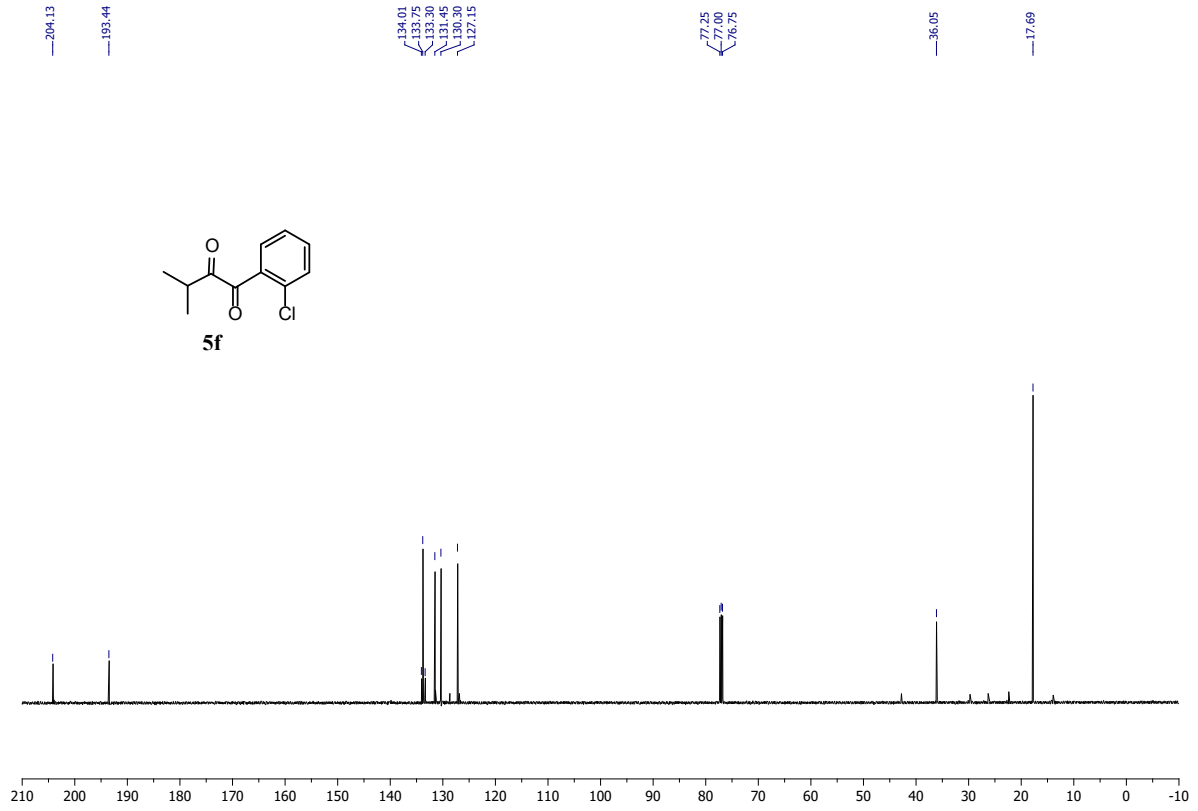
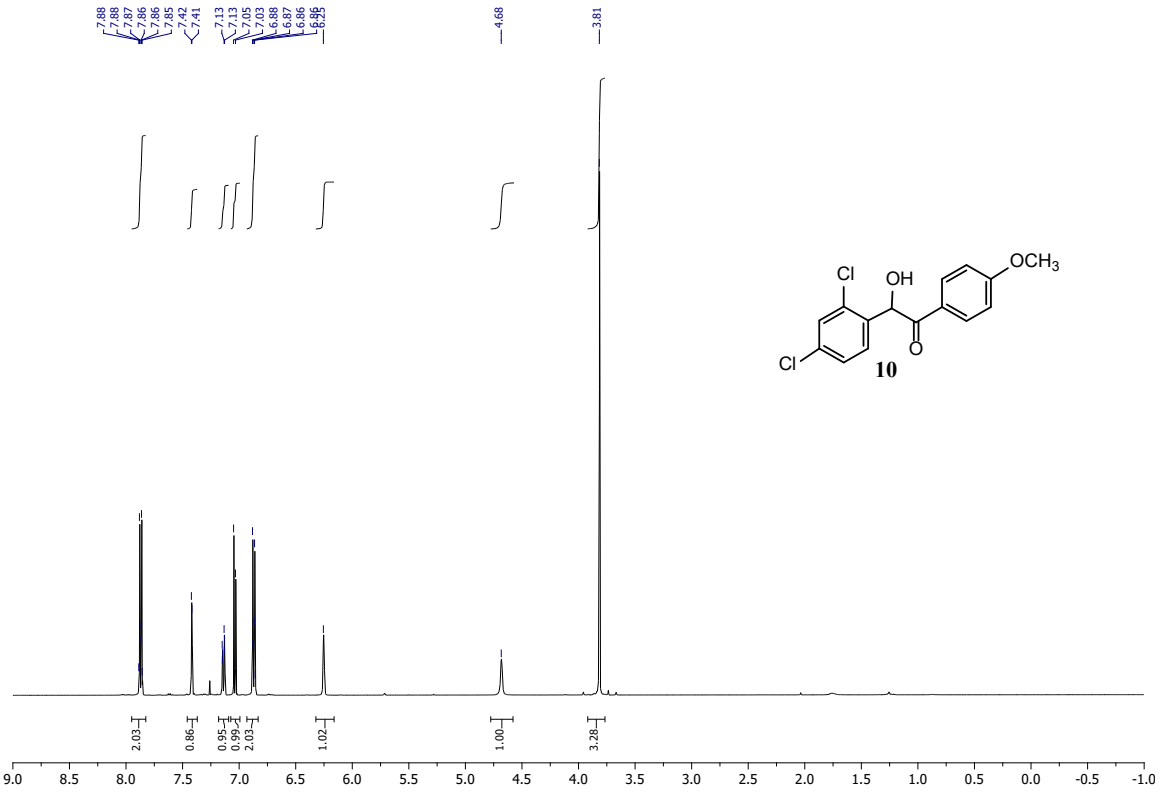
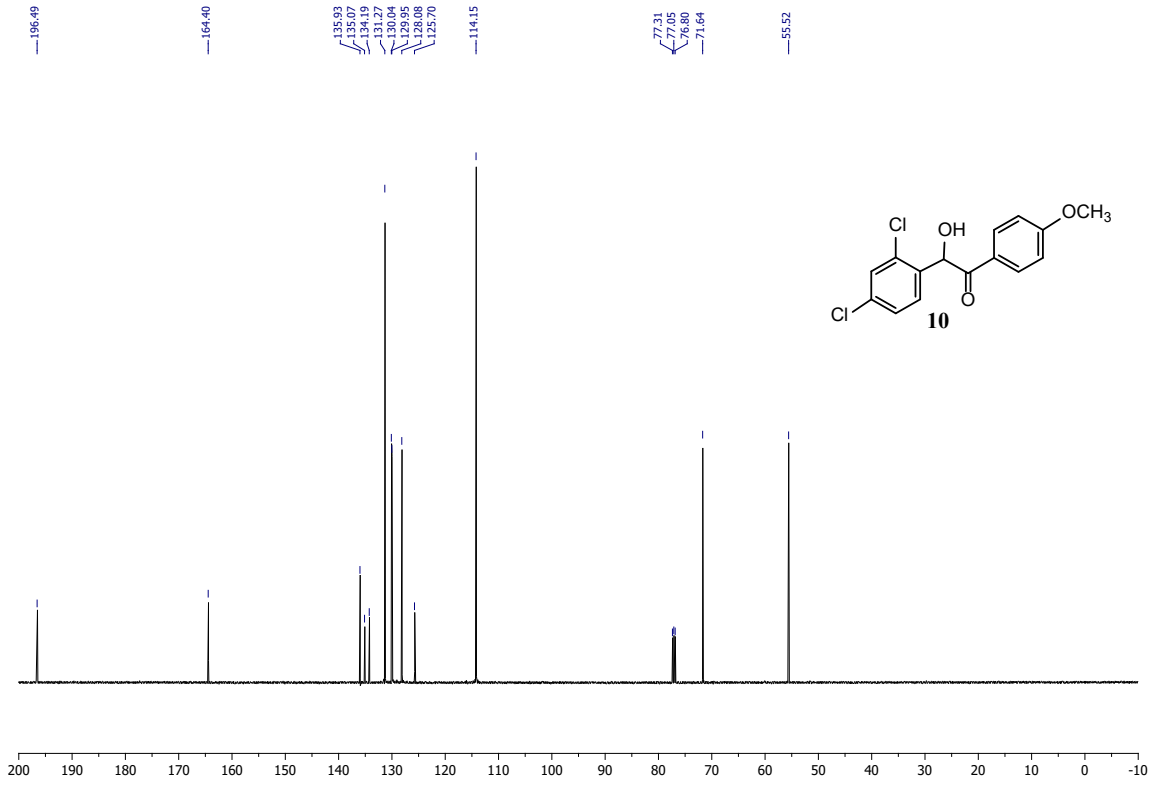


2-(2,4-dichlorophenyl)-2-hydroxy-1-(4-methoxyphenyl)ethan-1-one (10)

^{1}H-NMR (500 MHz, $CDCl_3$)

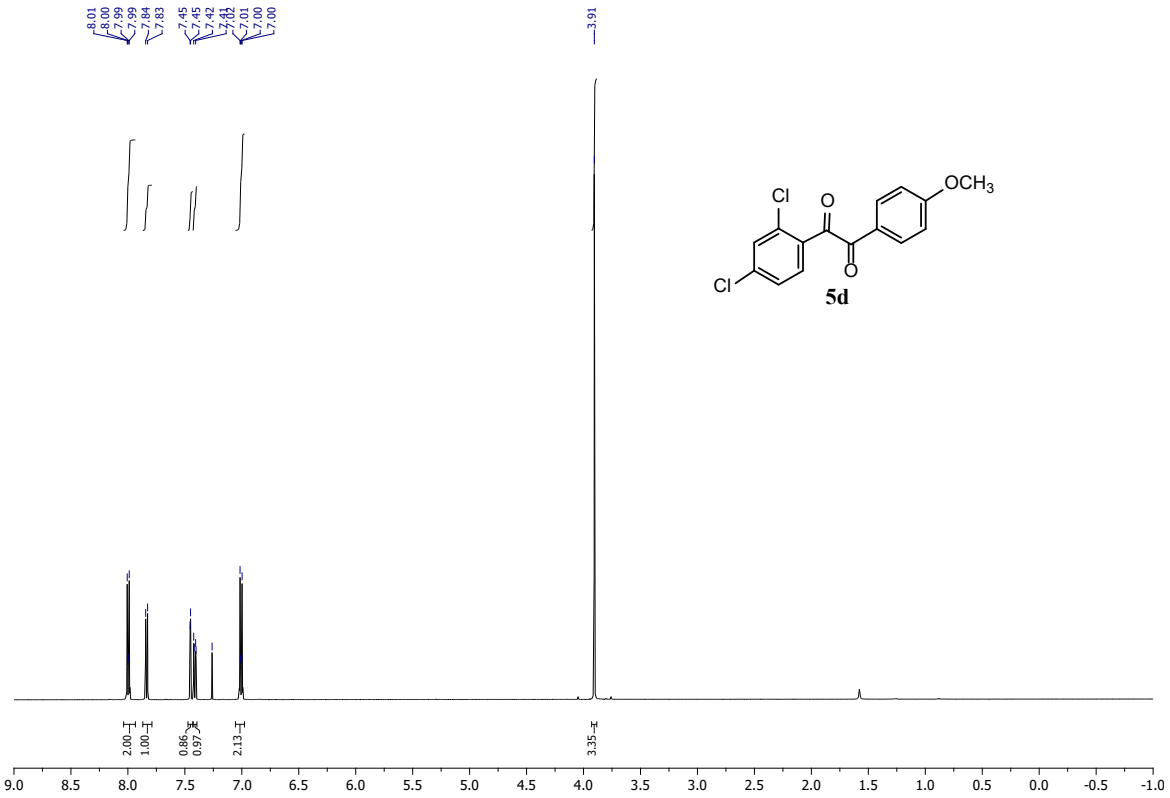


^{13}C-NMR (126 MHz, $CDCl_3$)

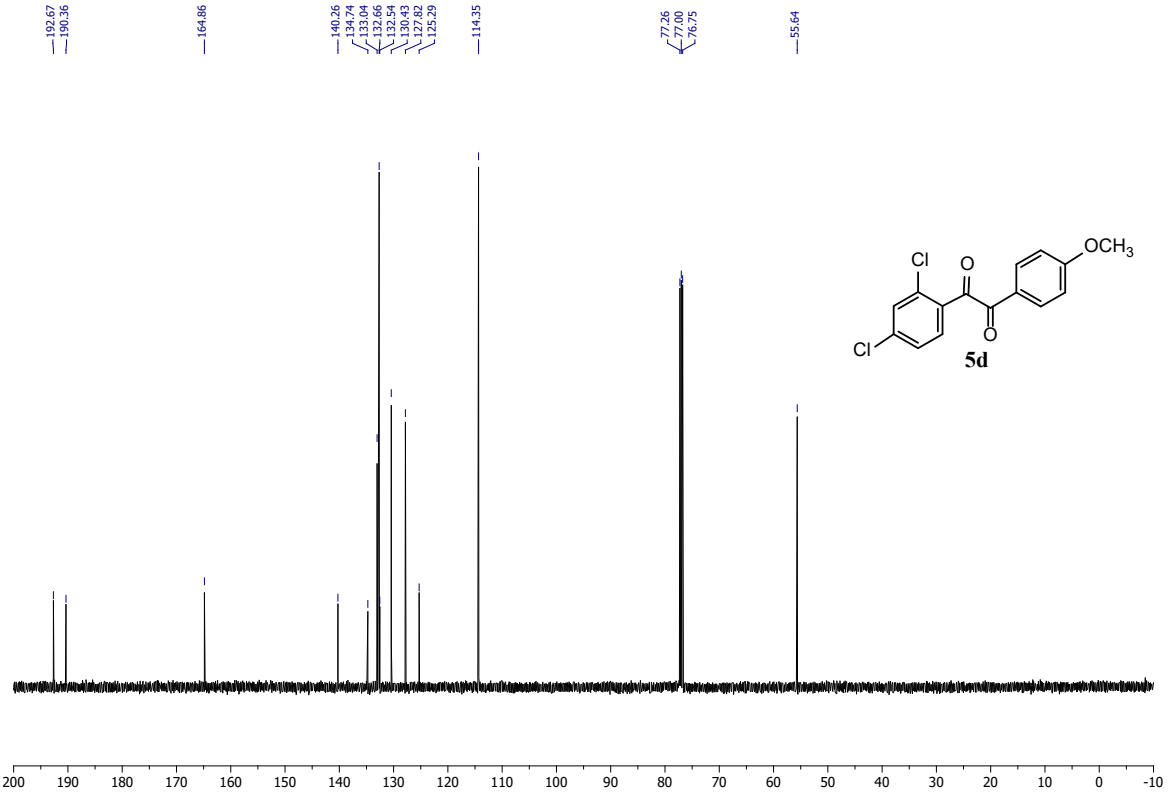


1-(2,4-dichlorophenyl)-2-(4-methoxyphenyl)ethane-1,2-dione (5d)

^{1}H-NMR (500 MHz, $CDCl_3$)

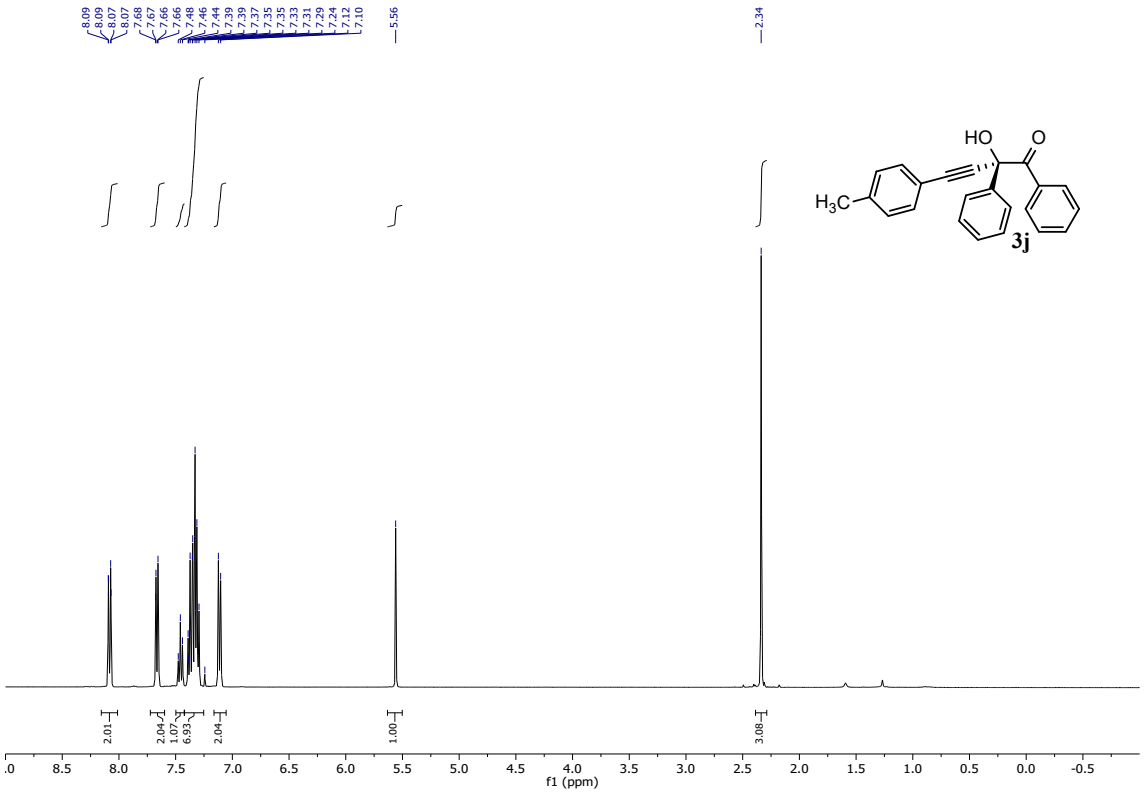


^{13}C-NMR (126 MHz, $CDCl_3$)

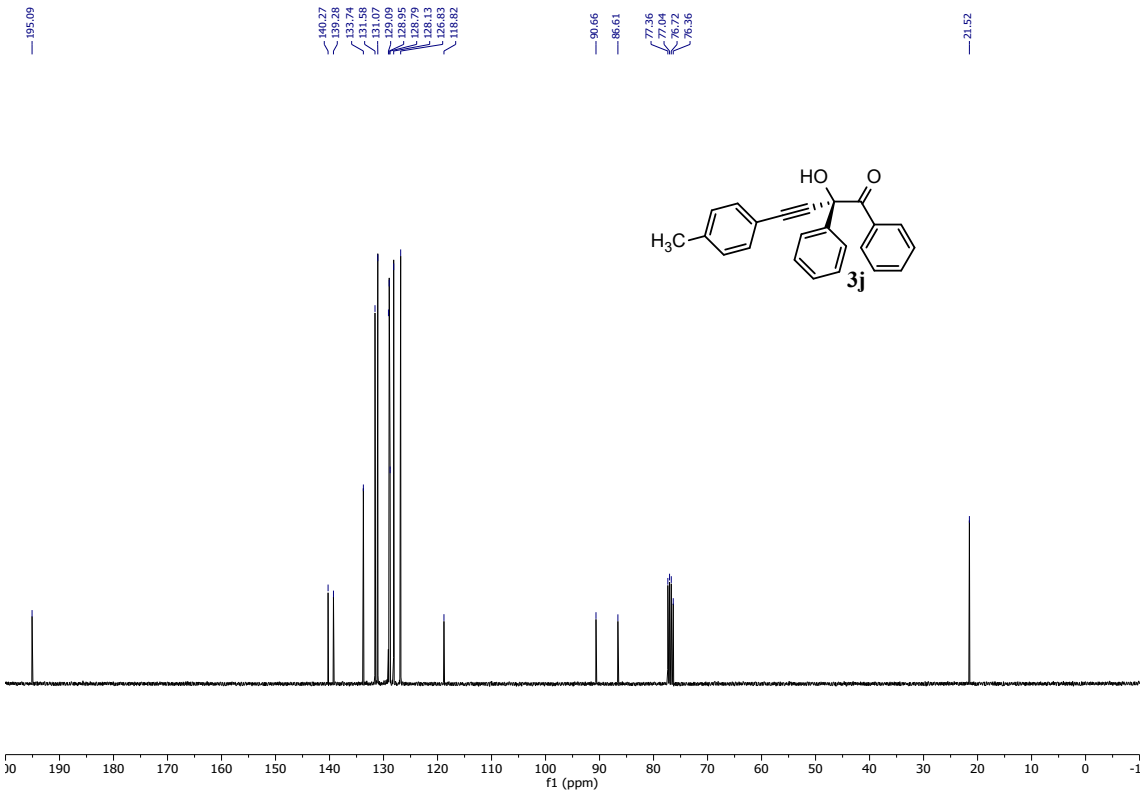


(*S*)-2-hydroxy-1,2-diphenyl-4-(p-tolyl)but-3-yn-1-one (3j)

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

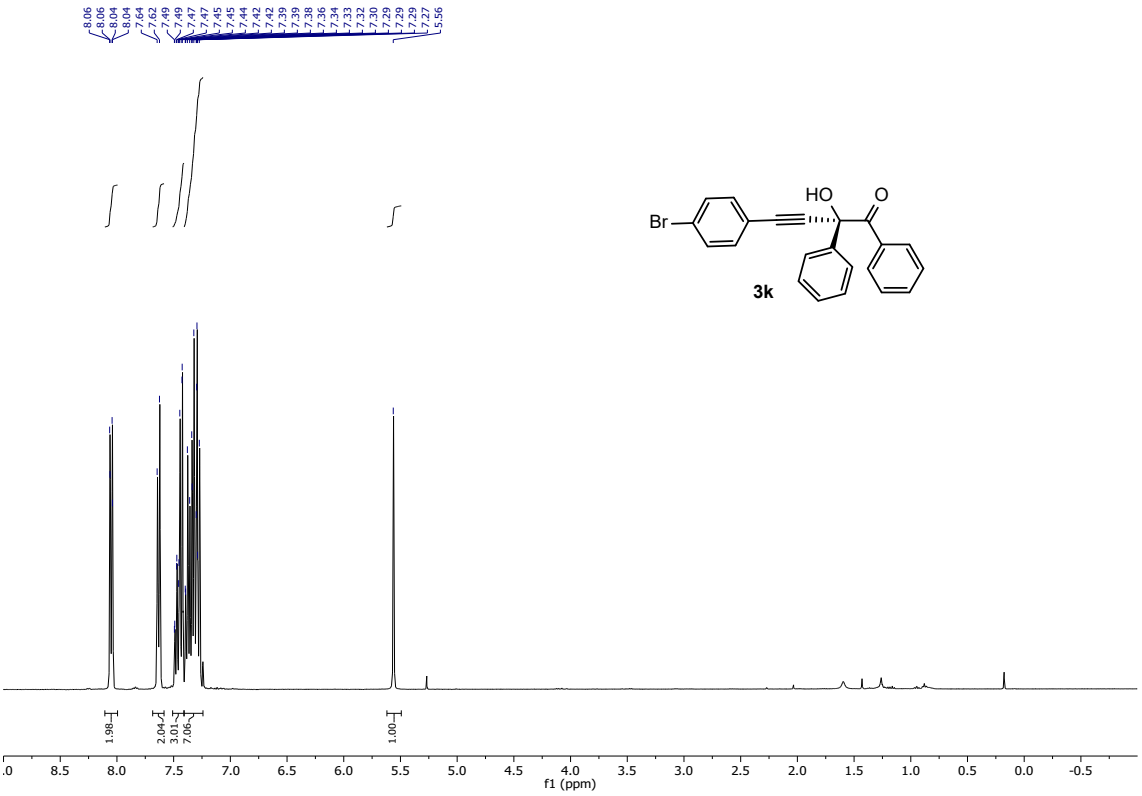


^{13}C-NMR (100 MHz, $CDCl_3$)



(*S*)-4-(4-bromophenyl)-2-hydroxy-1,2-diphenylbut-3-yn-1-one (3k)

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



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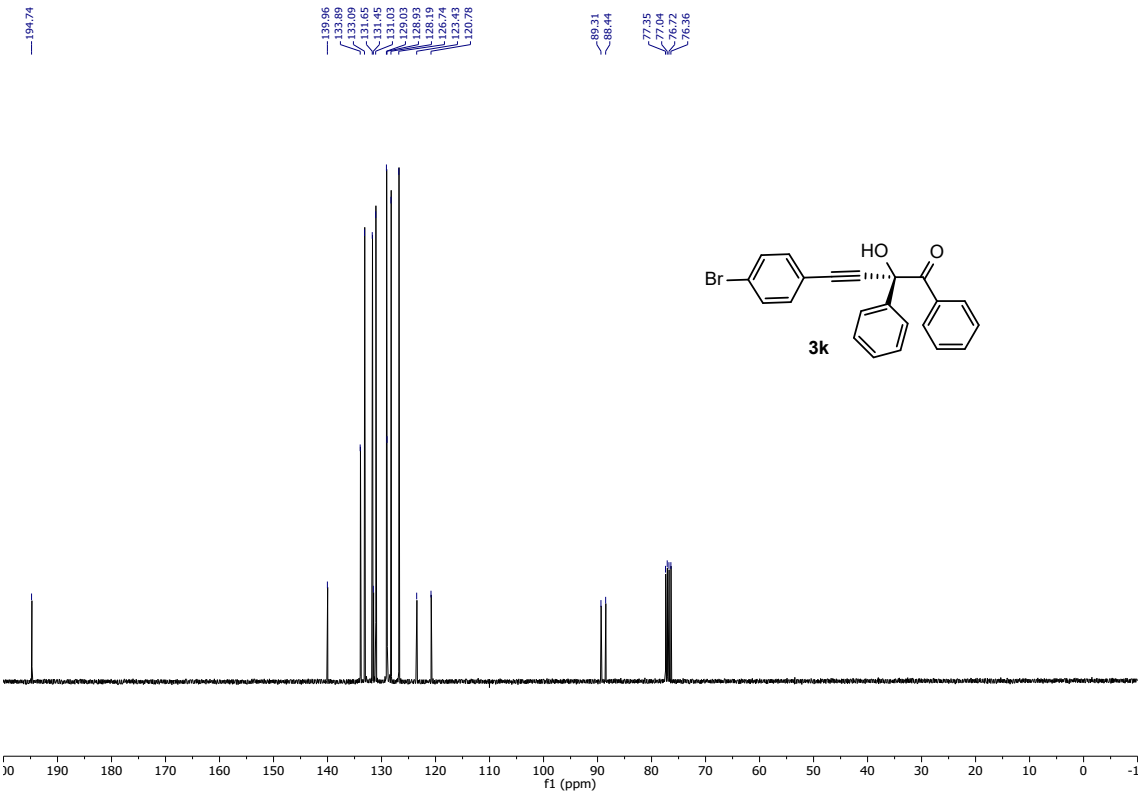

(*S*)-4-(2-fluorophenyl)-2-hydroxy-1,2-diphenylbut-3-yn-1-one (3l)

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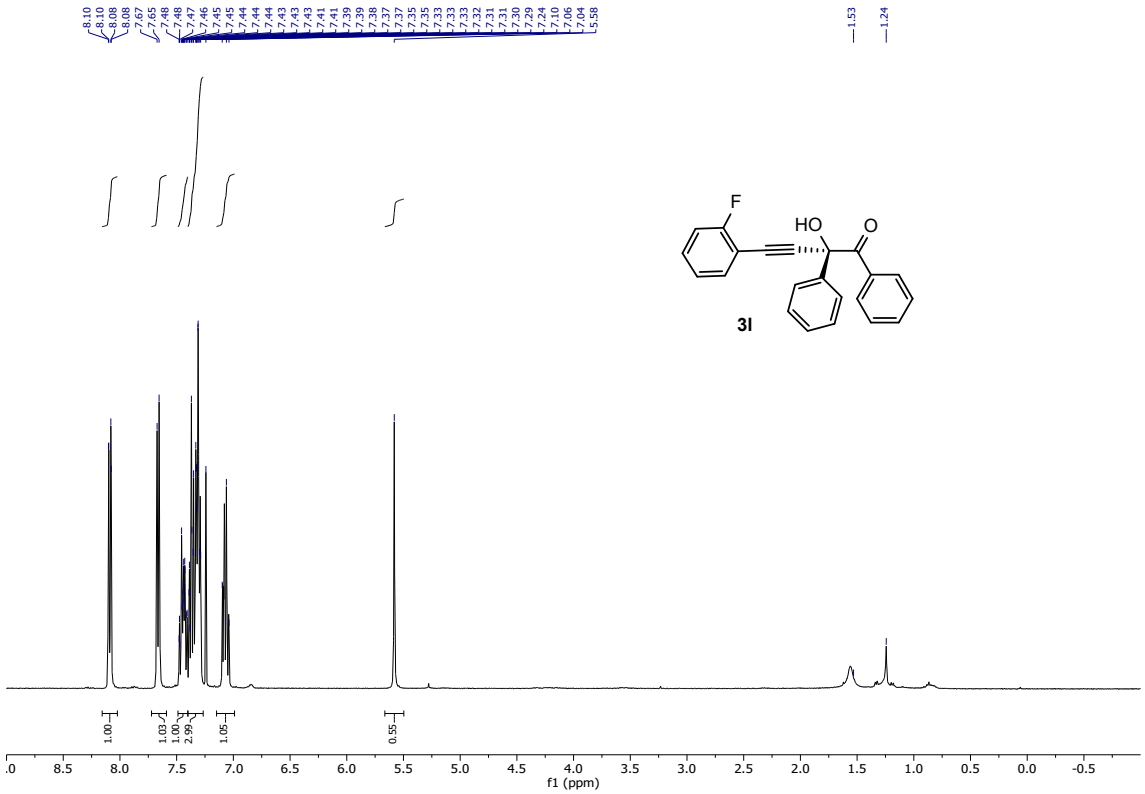

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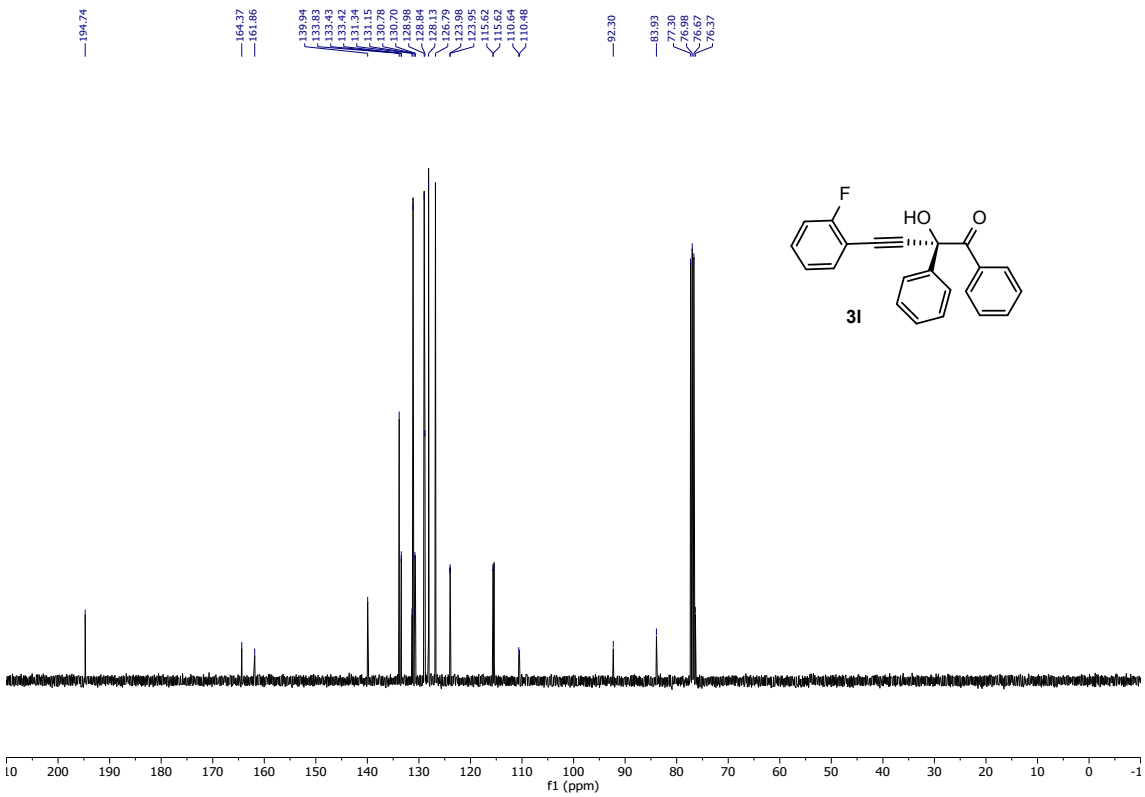

(*S*)-2-hydroxy-1,2-diphenyldec-3-yn-1-one (3n)

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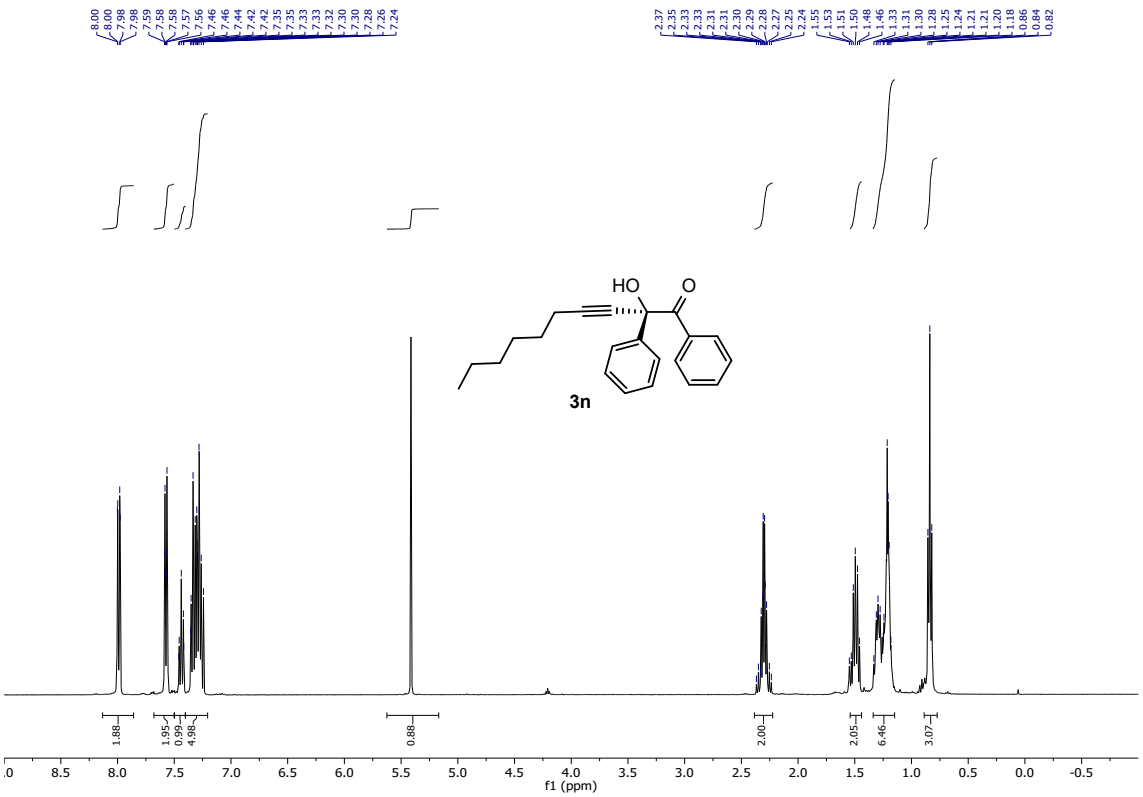

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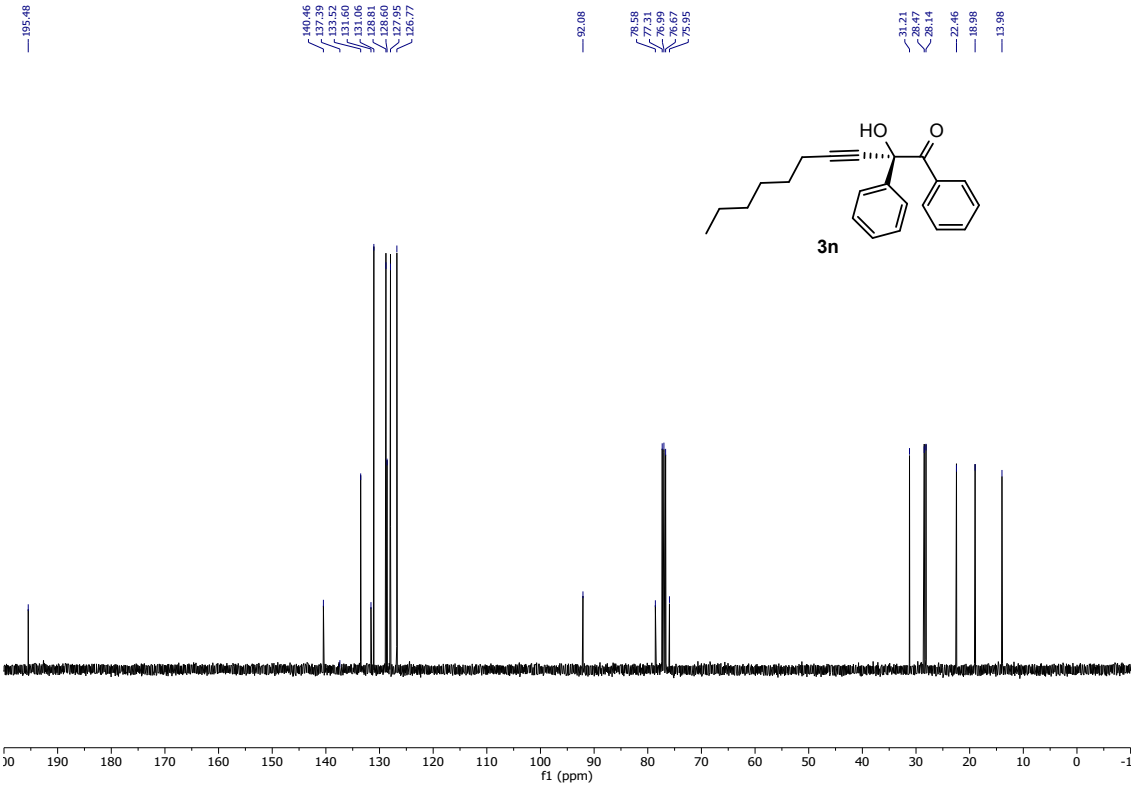

(*S*)-4-ethyl-4-hydroxy-6-(*p*-tolyl)hex-5-yn-3-one (4c)

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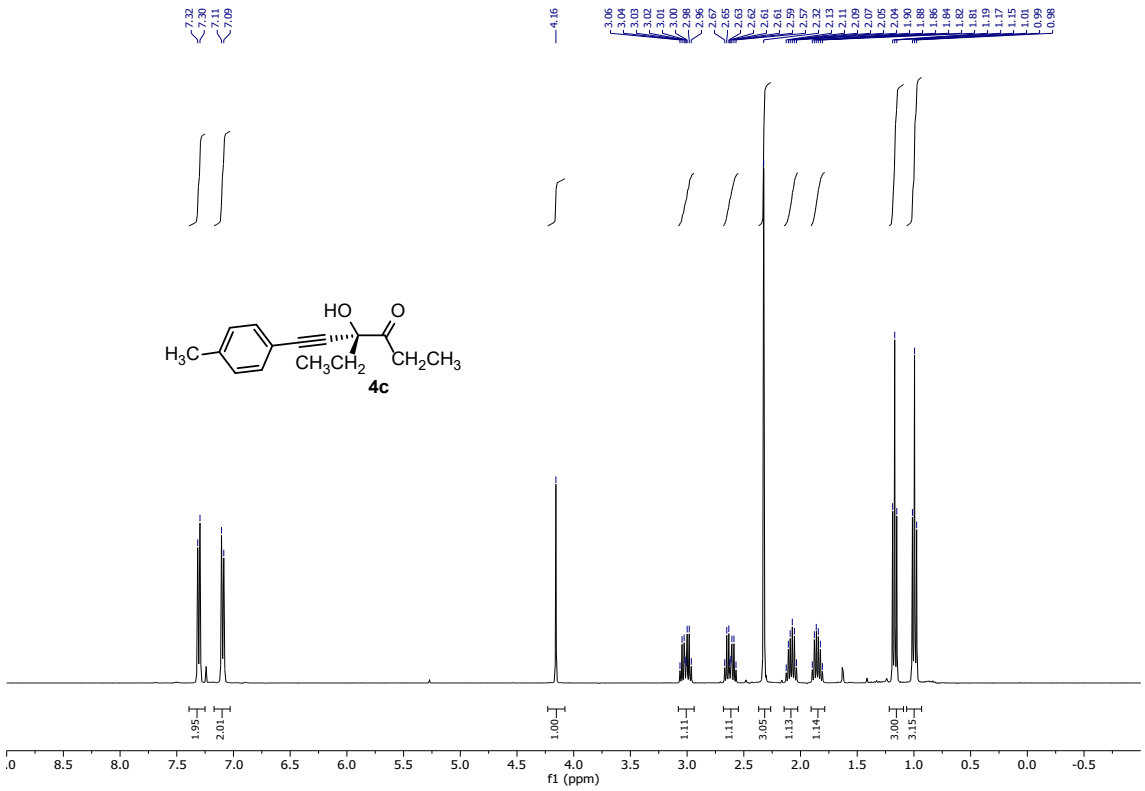
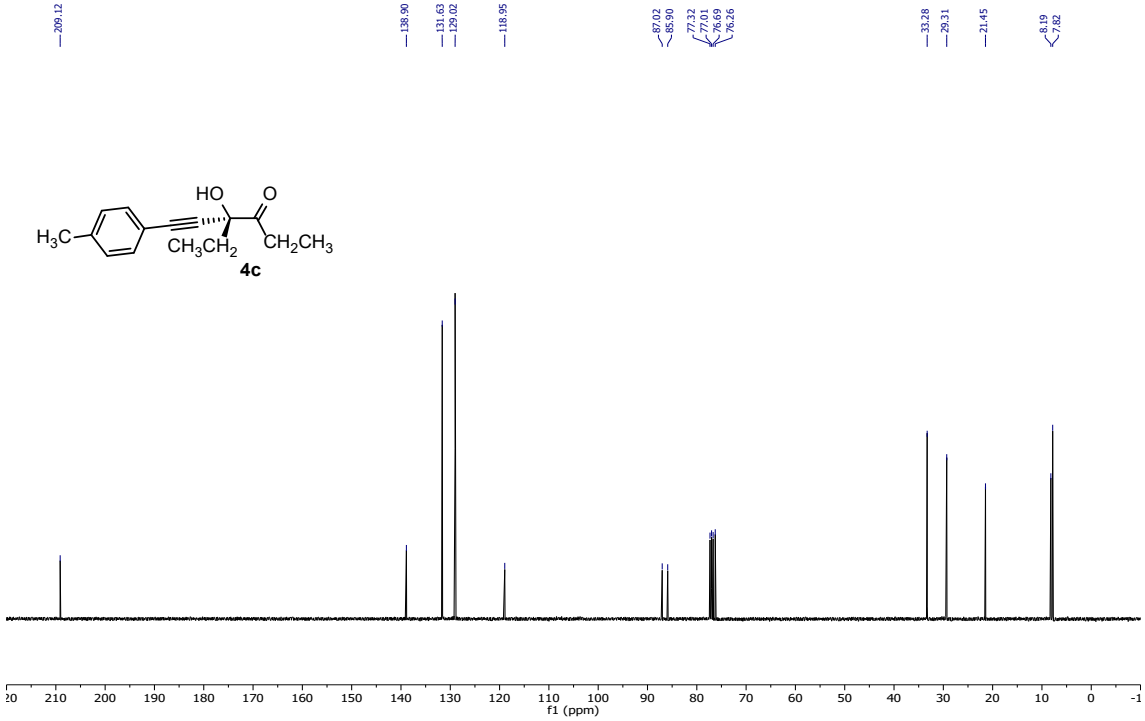
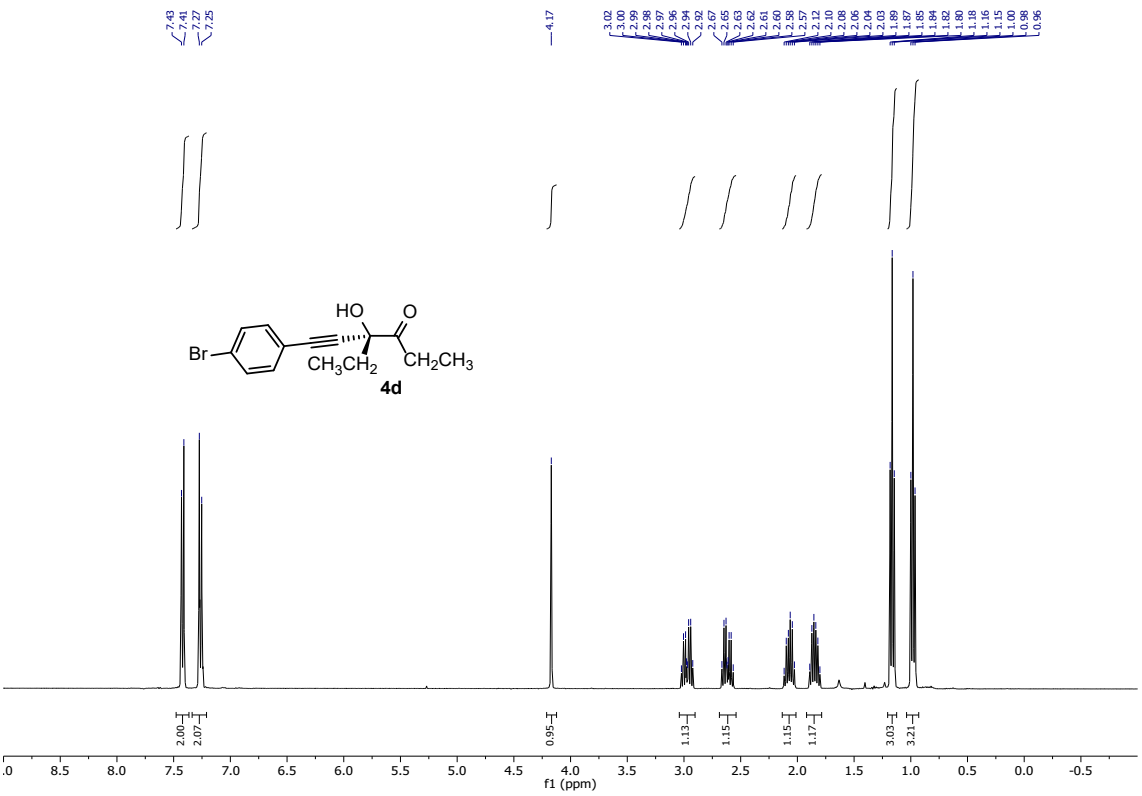


^{13}C-NMR (100 MHz, $CDCl_3$)

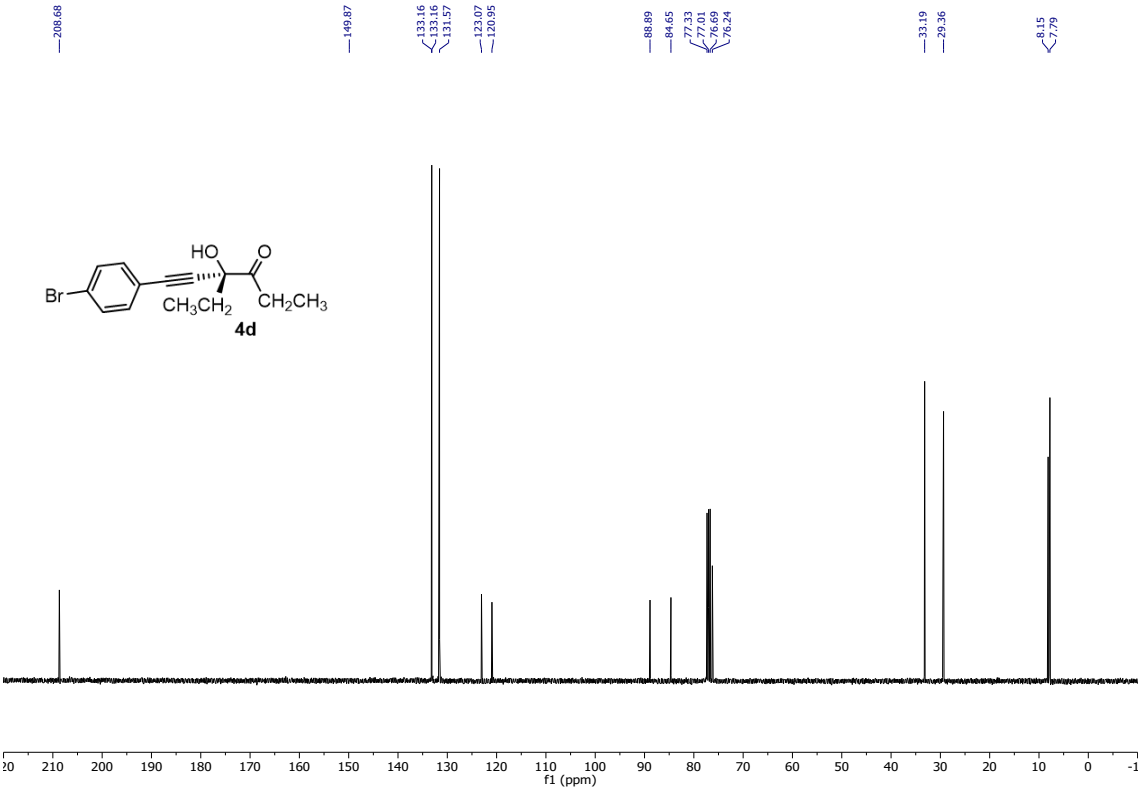


(*S*)-6-(4-bromophenyl)-4-ethyl-4-hydroxyhex-5-yn-3-one (4d)

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

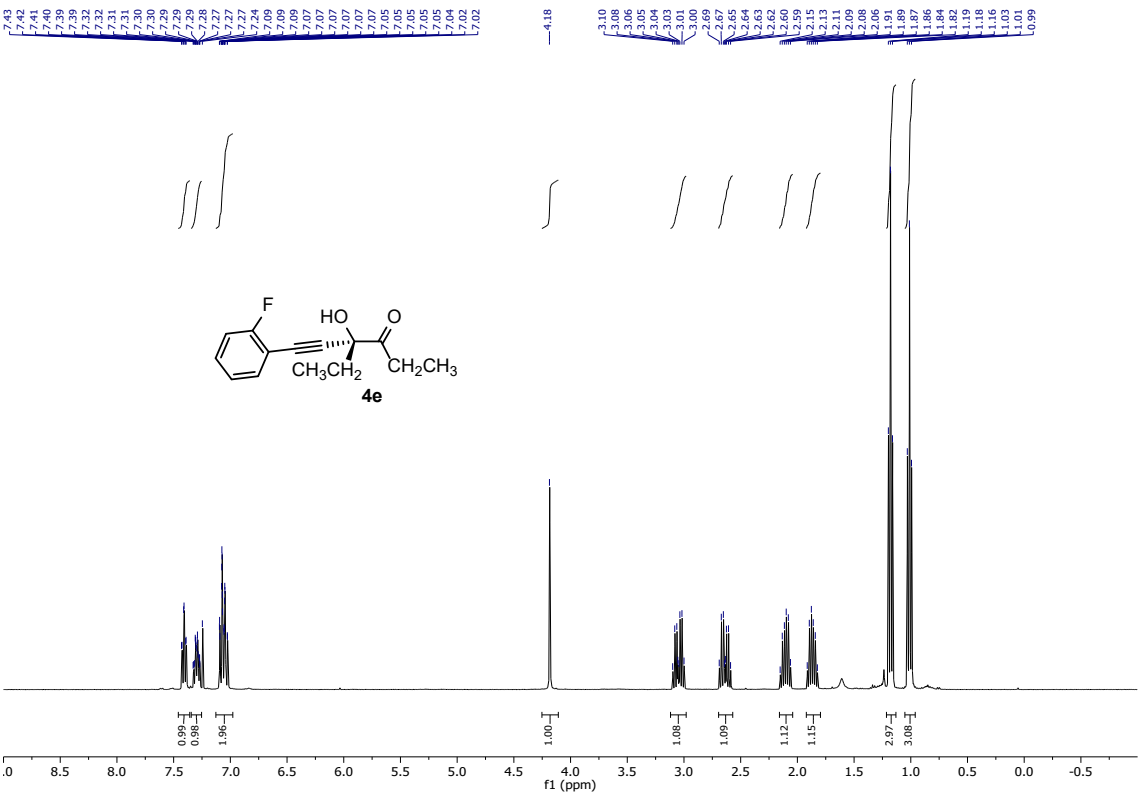


^{13}C-NMR (100 MHz, $CDCl_3$)

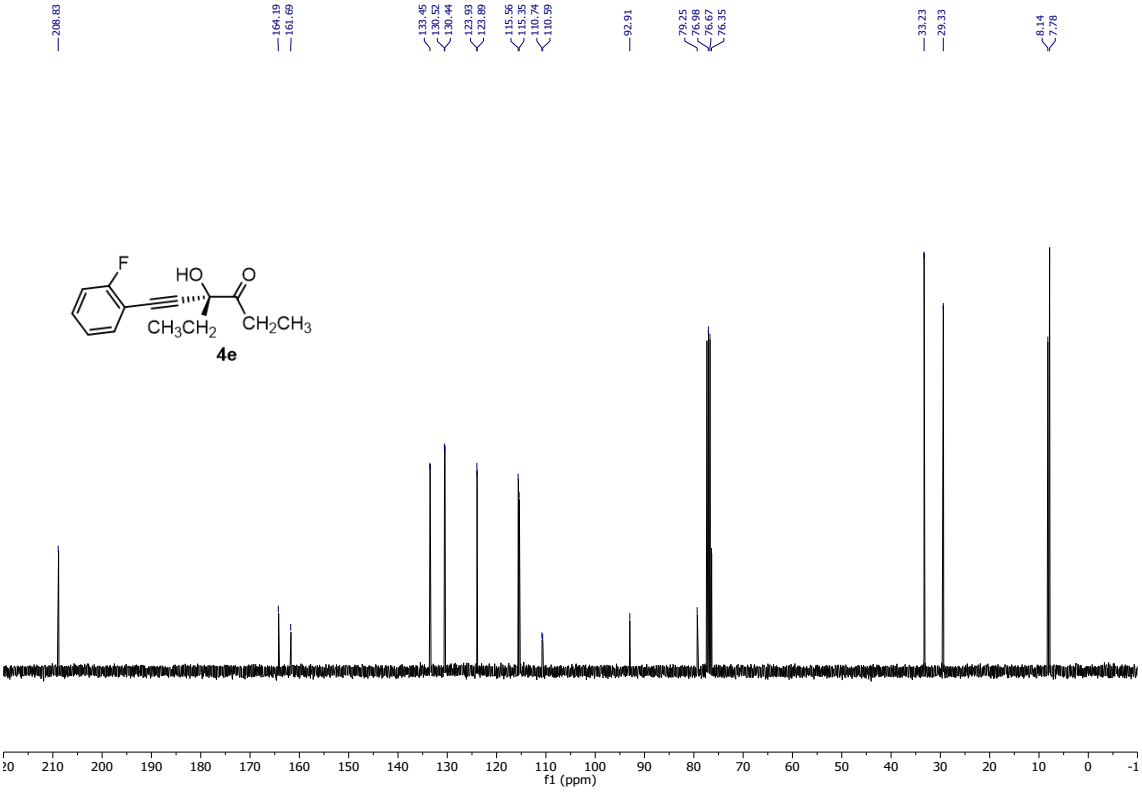


(*S*)-4-ethyl-6-(2-fluorophenyl)-4-hydroxyhex-5-yn-3-one (4e)

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

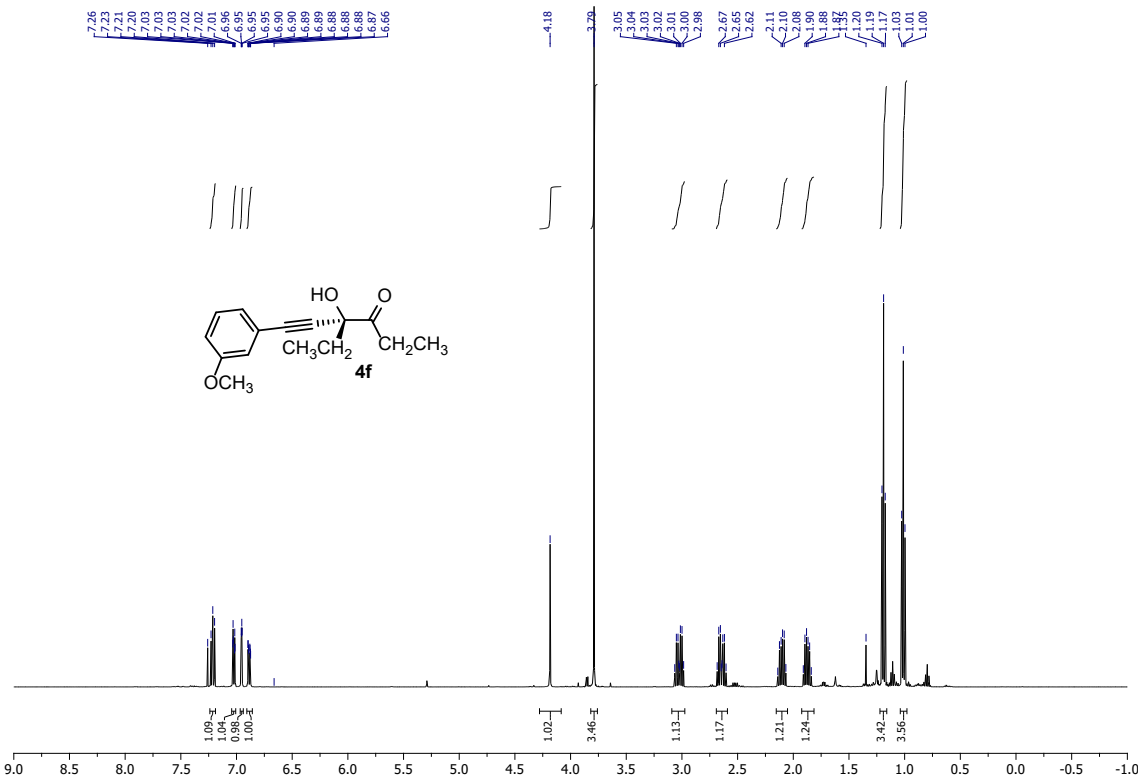


^{13}C-NMR (100 MHz, $CDCl_3$)

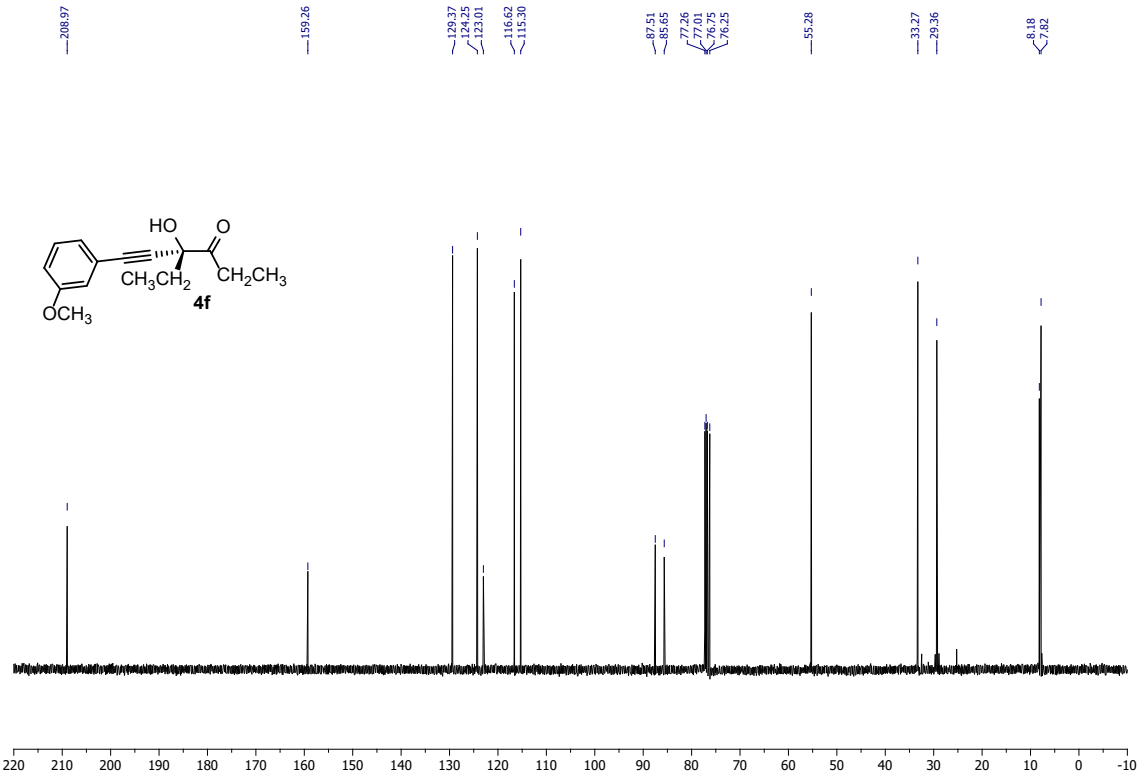


(*S*)-4-ethyl-4-hydroxy-6-(3-methoxyphenyl)hex-5-yn-3-one (4f)

^{1}H-NMR (500 MHz, $CDCl_3$)

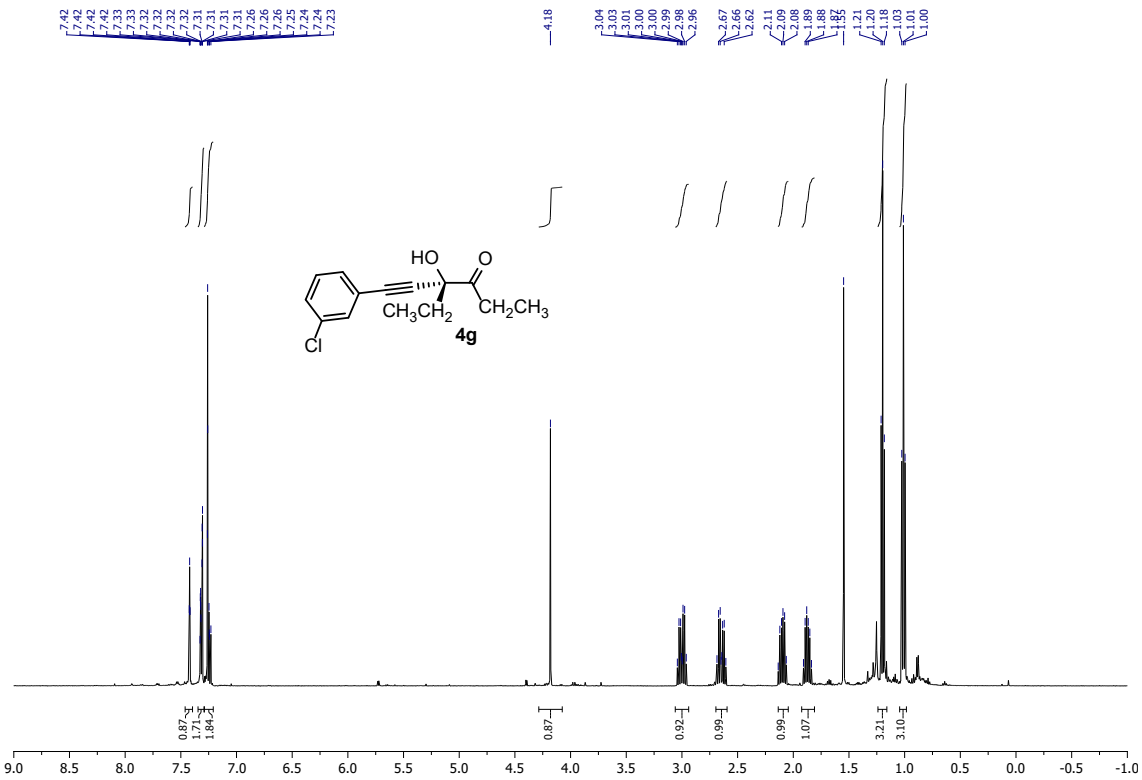


^{13}C-NMR (126 MHz, $CDCl_3$)

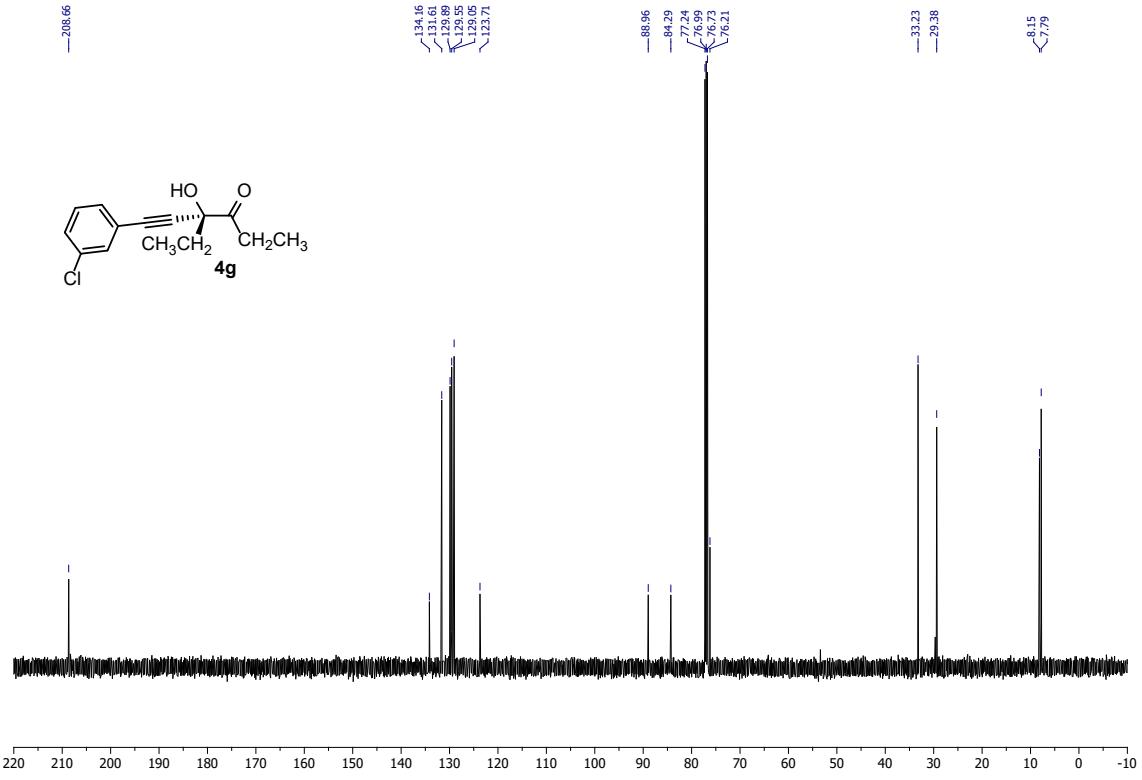


(*S*)-6-(3-chlorophenyl)-4-ethyl-4-hydroxyhex-5-yn-3-one (4g)

^{1}H-NMR (500 MHz, $CDCl_3$)

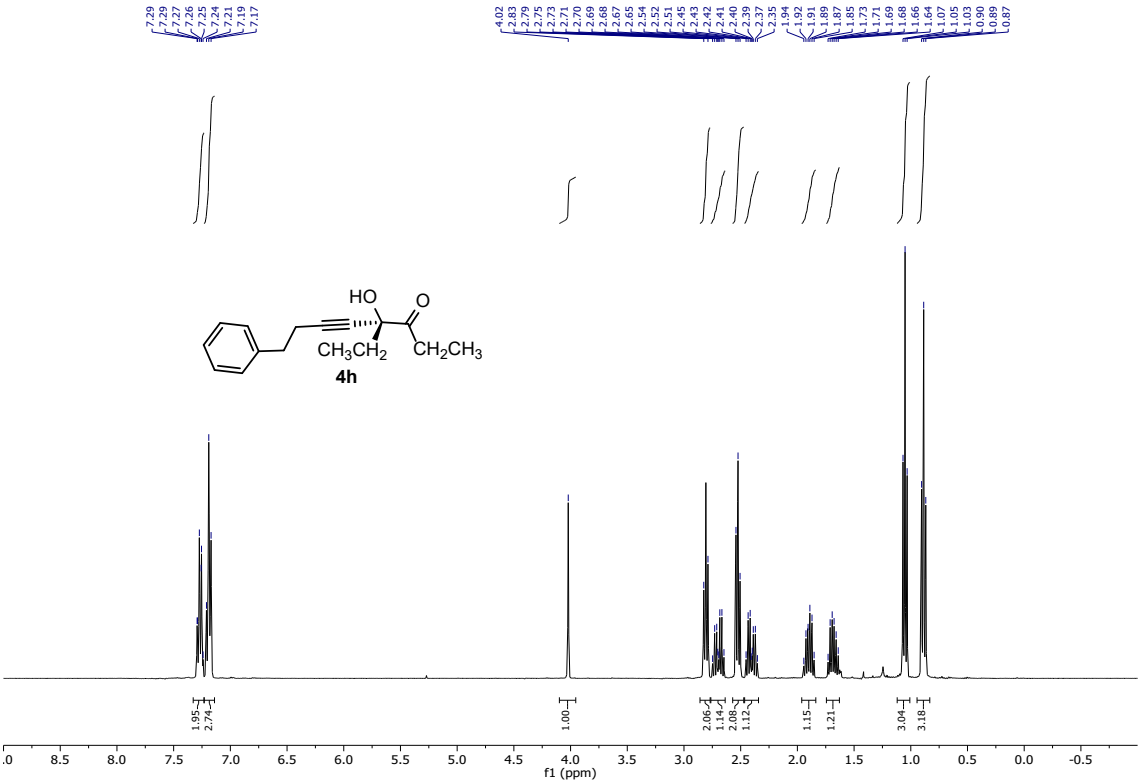


^{13}C-NMR (126 MHz, $CDCl_3$)

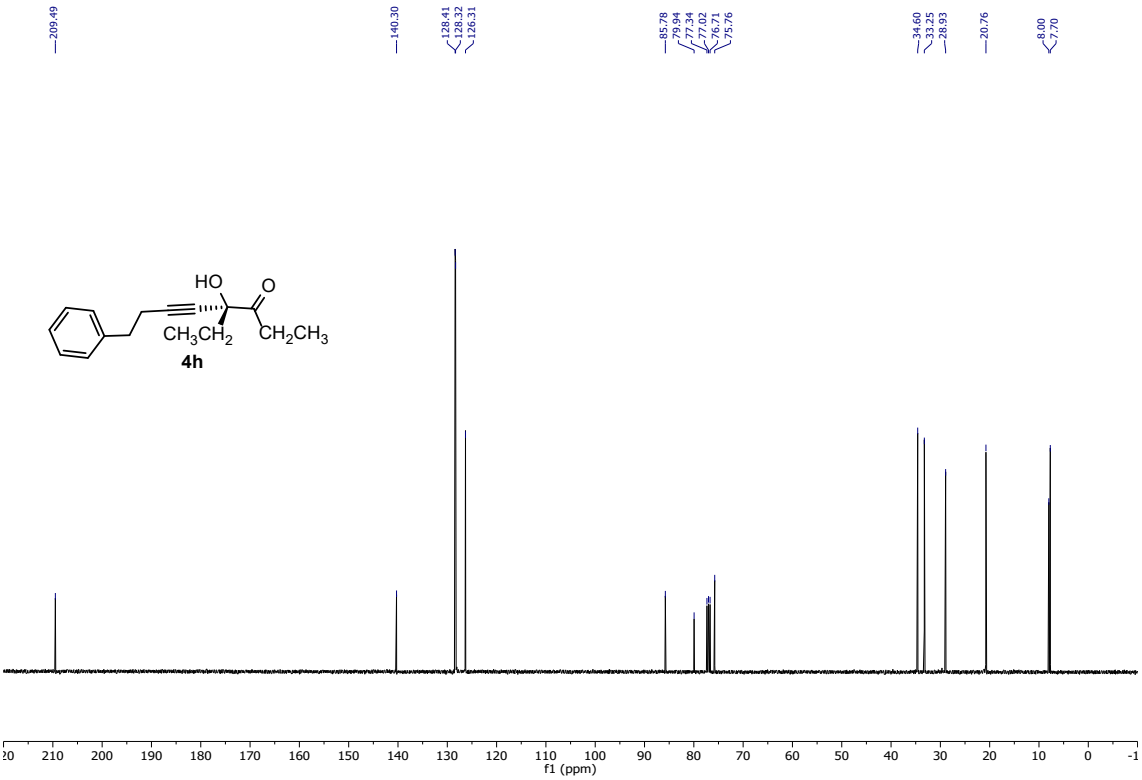


(*S*)-4-ethyl-4-hydroxy-8-phenyloct-5-yn-3-one (4h).

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

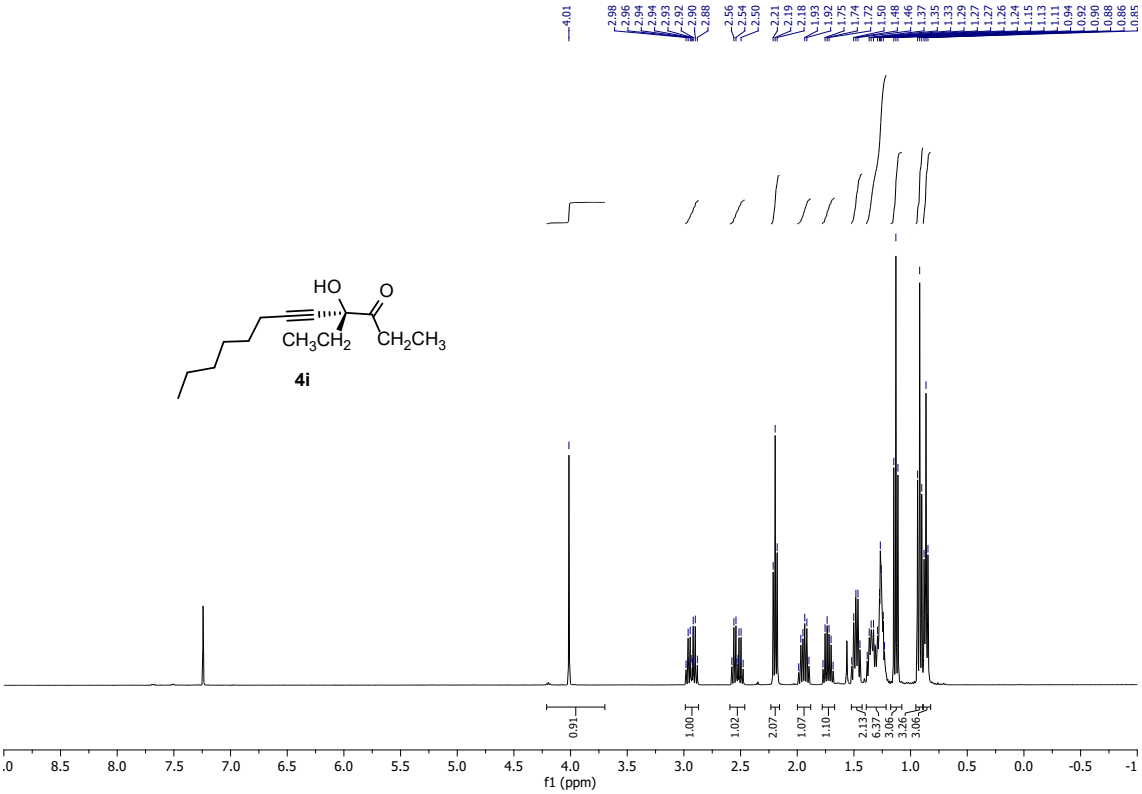


^{13}C-NMR (100 MHz, $CDCl_3$)

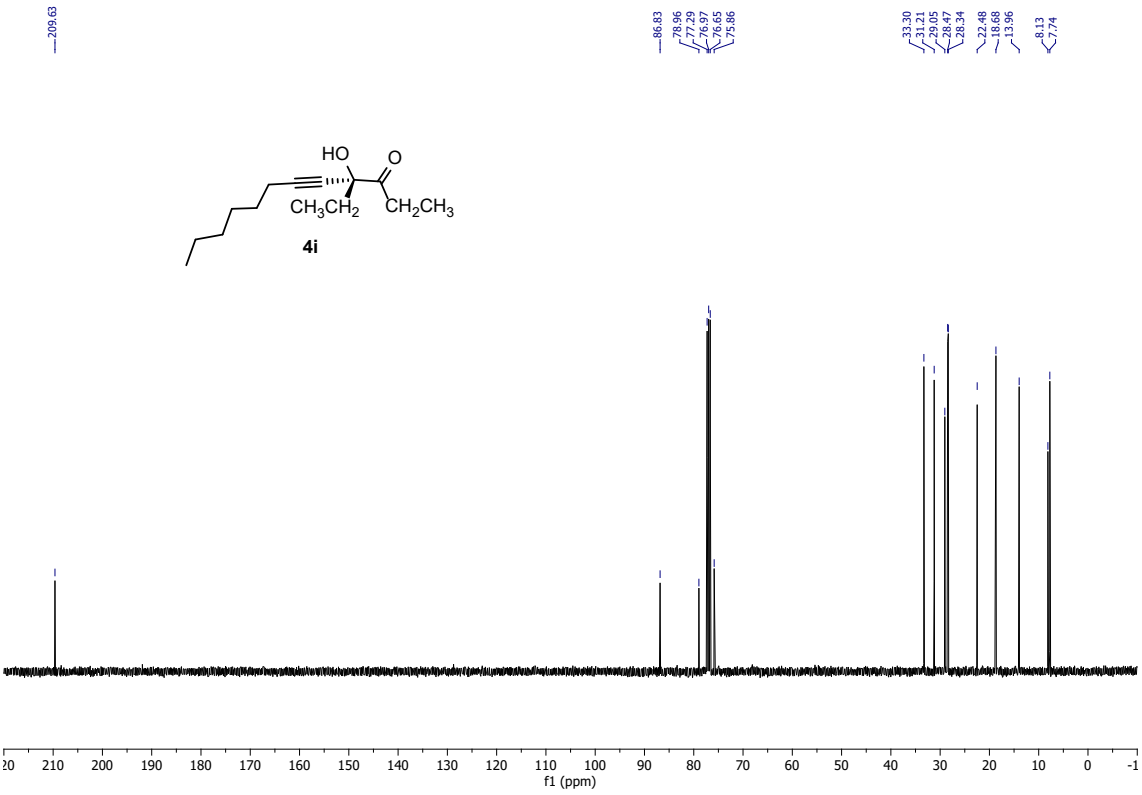


(*S*)-4-Ethyl-4-hydroxydodec-5-yn-3-one (4i)

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

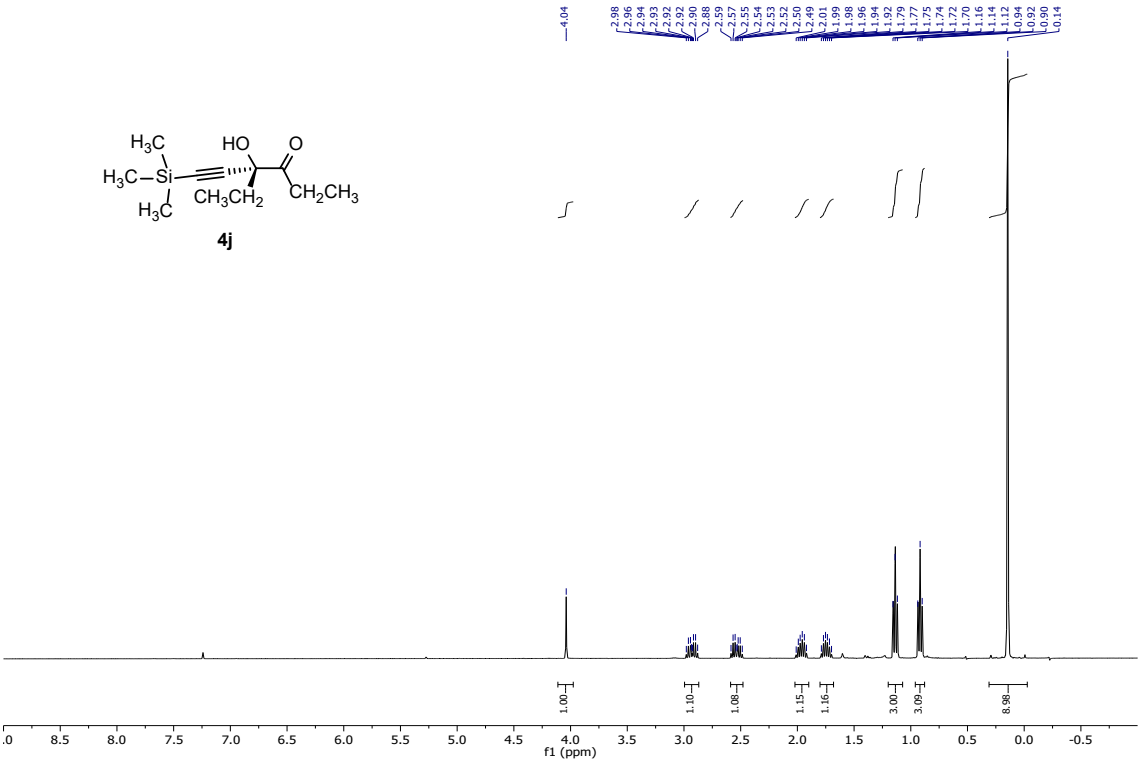


^{13}C-NMR (100 MHz, $CDCl_3$)

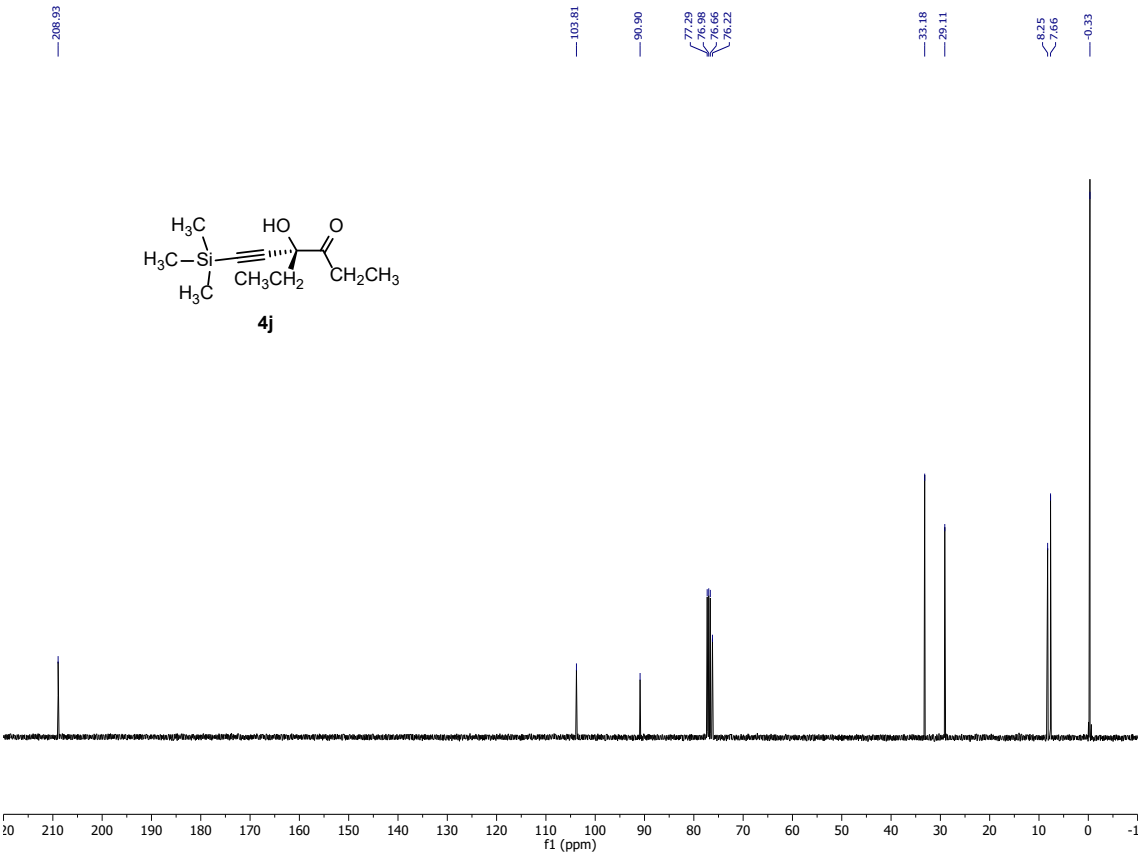


(*S*)-4-ethyl-4-hydroxy-6-(trimethylsilyl)hex-5-yn-3-one (4j)

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

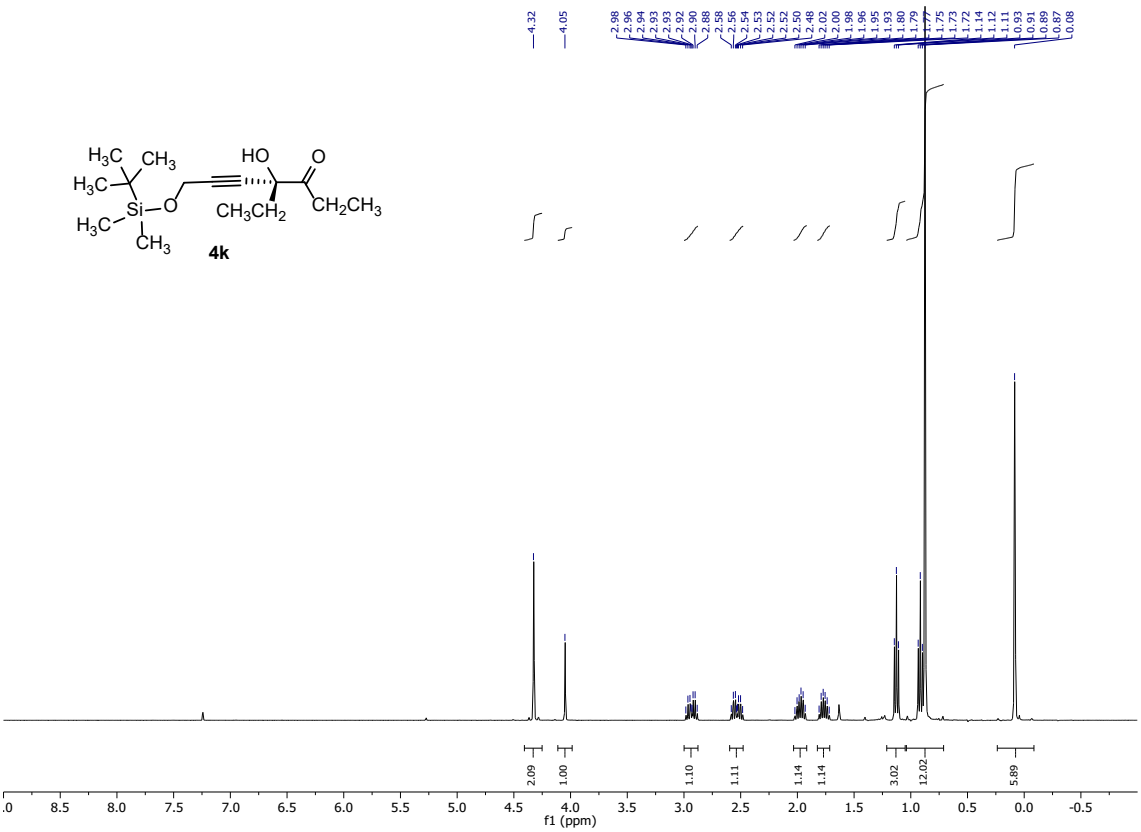


^{13}C-NMR (100 MHz, $CDCl_3$)



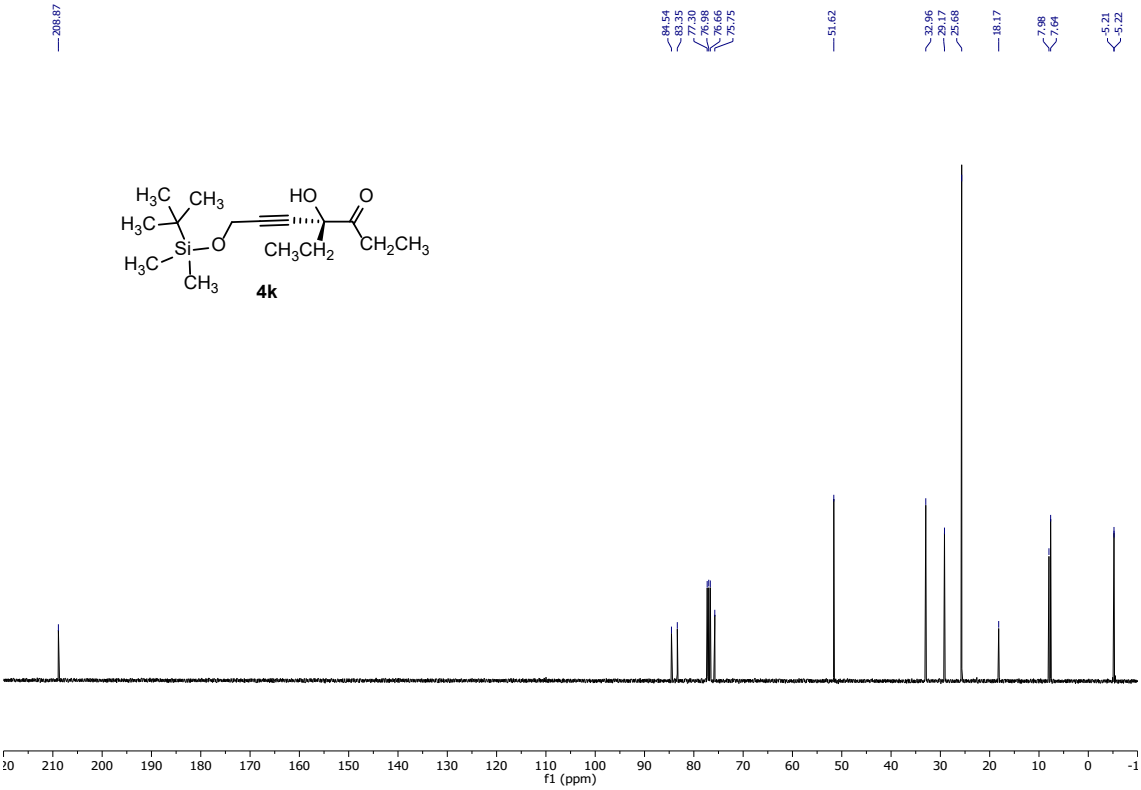
(*S*)-7-((tert-butyldimethylsilyl)oxy)-4-ethyl-4-hydroxyhept-5-yn-3-one (4k)

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



4k

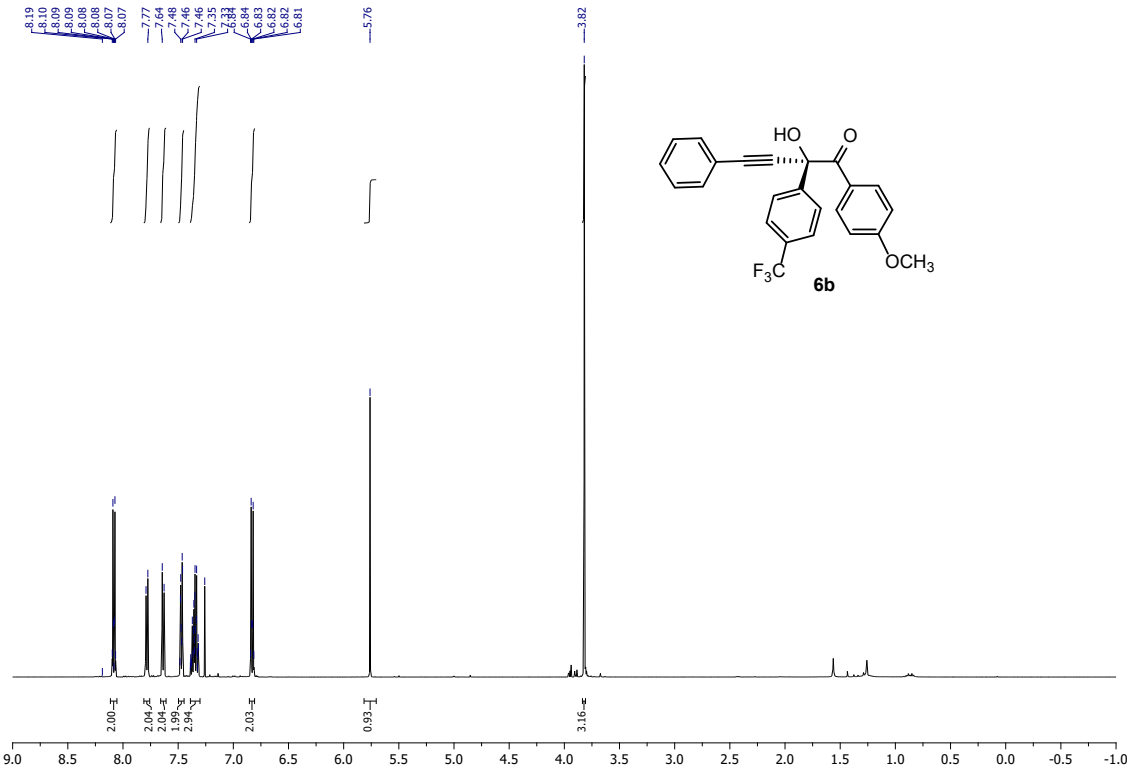
^{13}C-NMR (100 MHz, $CDCl_3$)



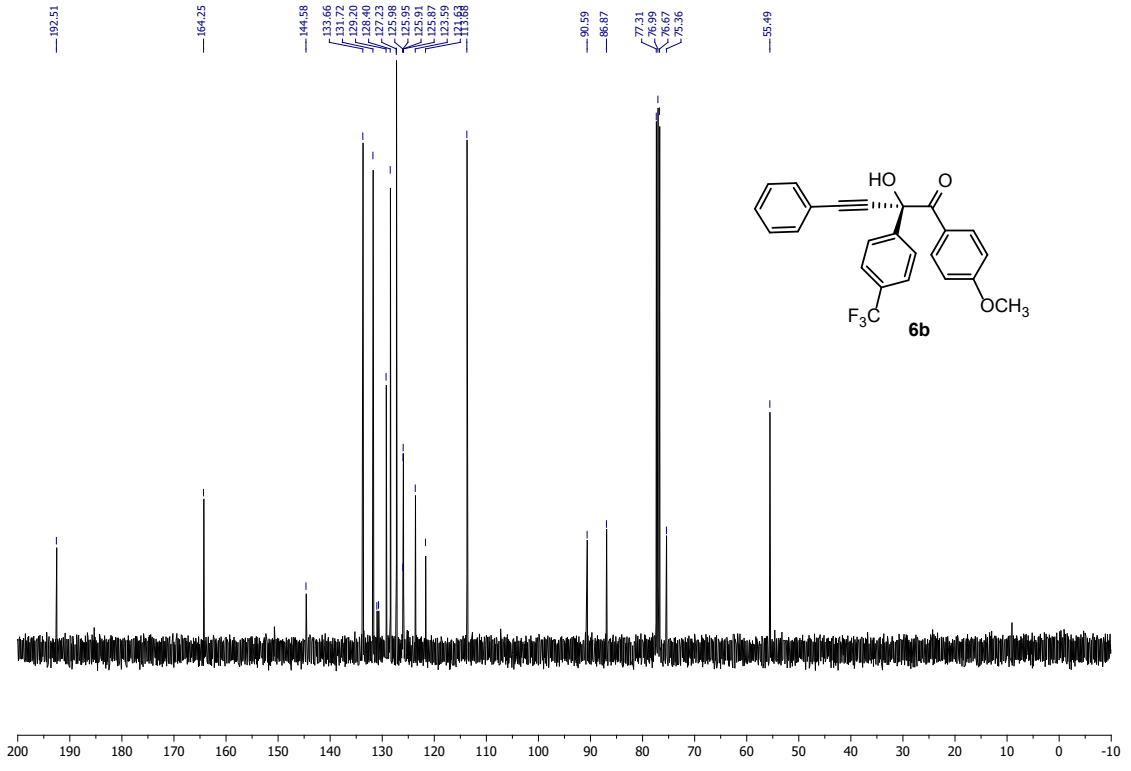
4k

(*S*)-2-hydroxy-1-(4-methoxyphenyl)-4-phenyl-2-(4-(trifluoromethyl)phenyl)but-3-yn-1-one (6b)

^{1}H-NMR (500 MHz, $CDCl_3$)

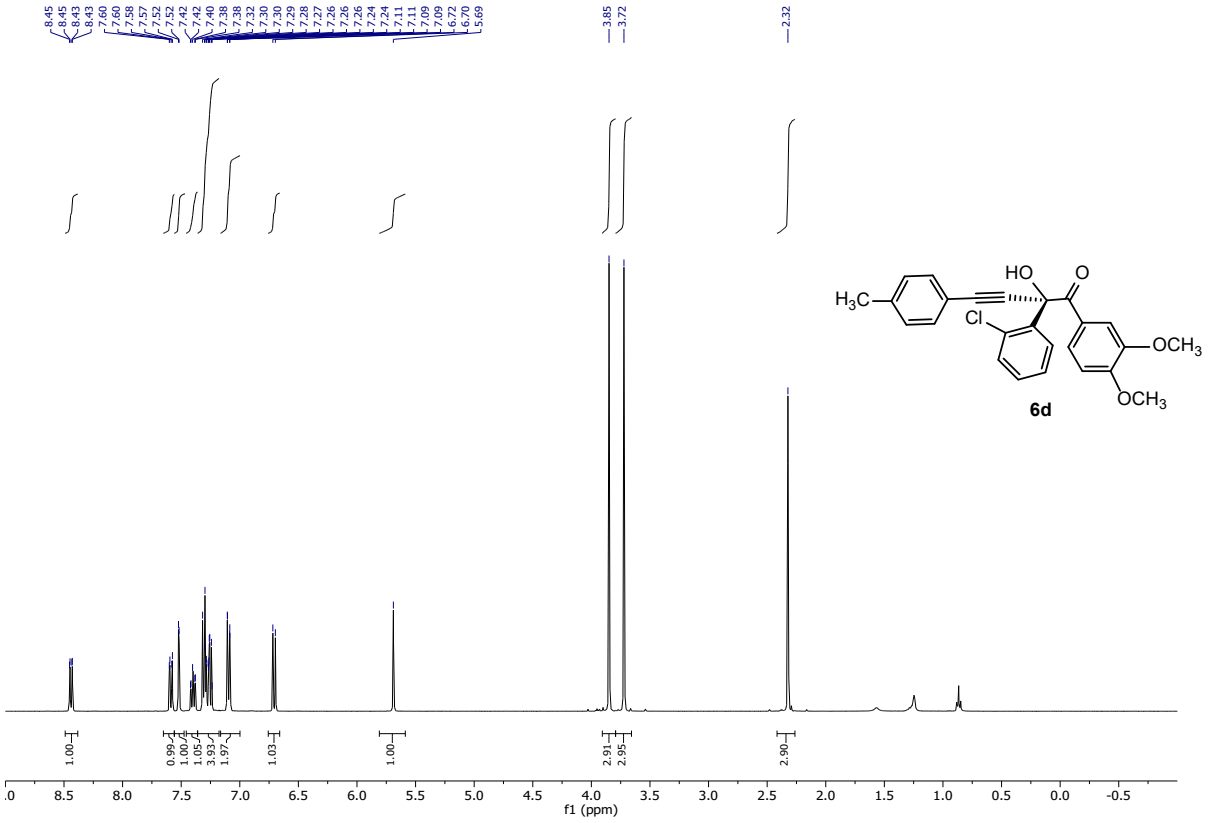


^{13}C-NMR (126 MHz, $CDCl_3$)

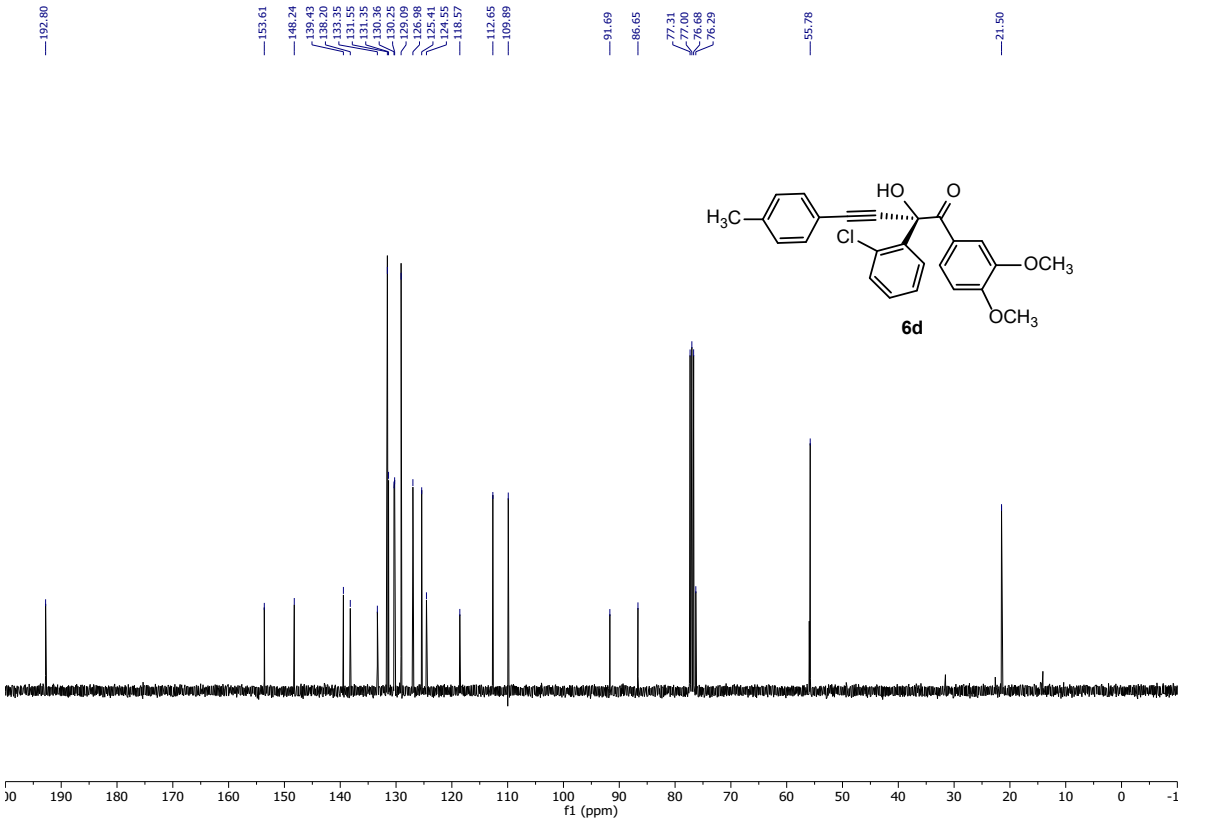


(*R*)-2-(2-chlorophenyl)-1-(3,4-dimethoxyphenyl)-2-hydroxy-4-(*p*-tolyl)but-3-yn-1-one (6d)

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

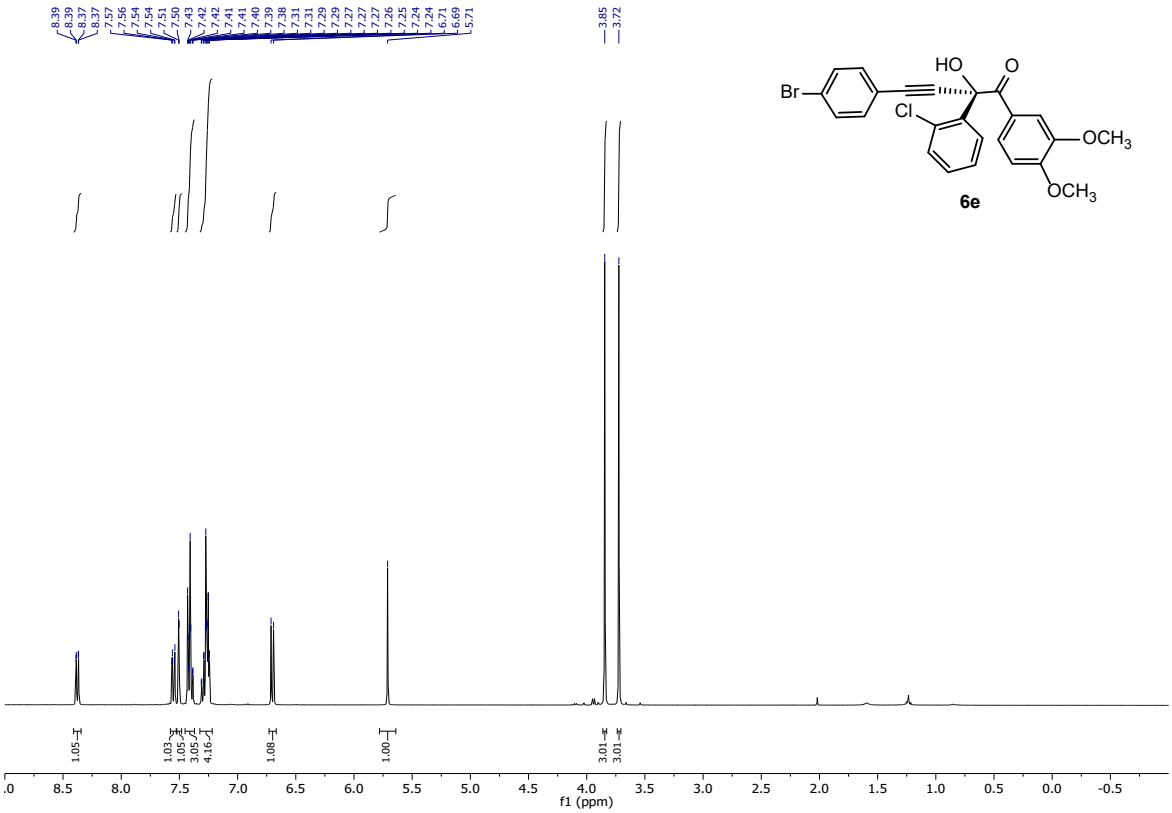


^{13}C-NMR (100 MHz, $CDCl_3$)

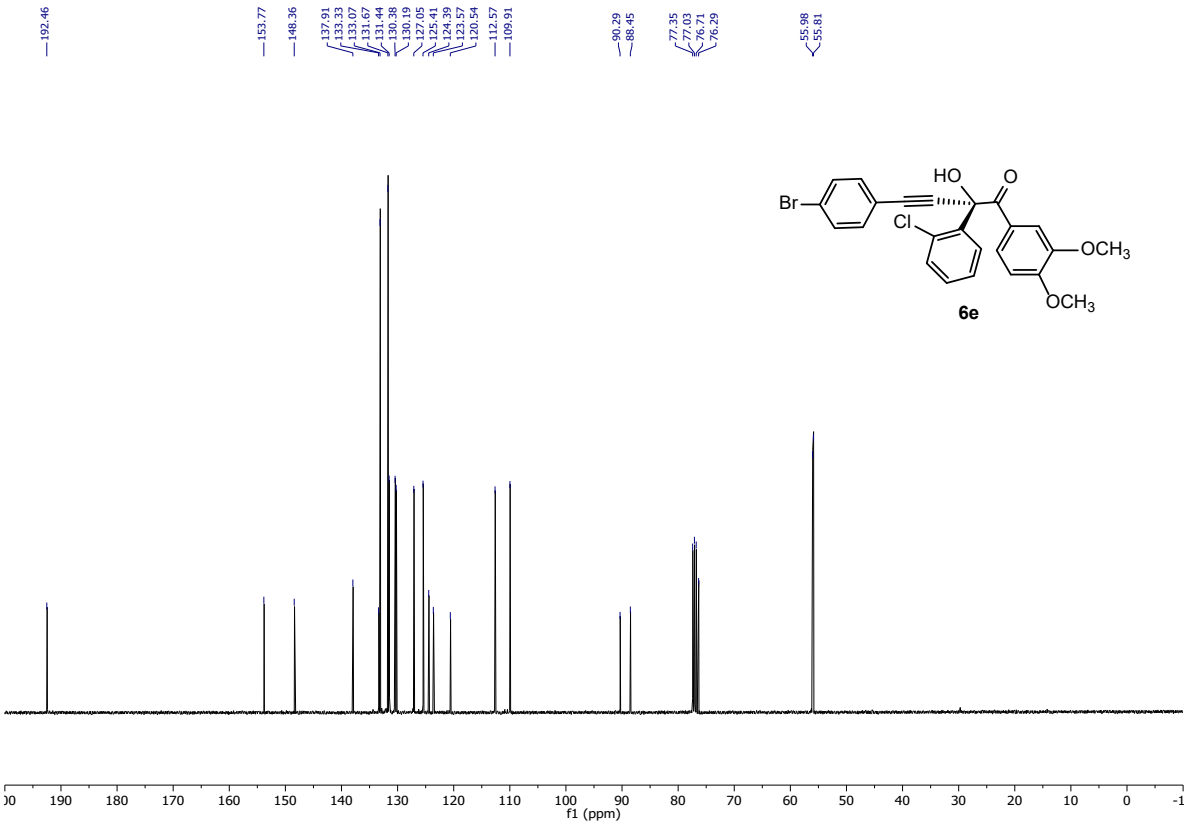


(*R*)-4-(4-bromophenyl)-2-(2-chlorophenyl)-1-(3,4-dimethoxyphenyl)-2-hydroxybut-3-yn-1-one (6e)

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

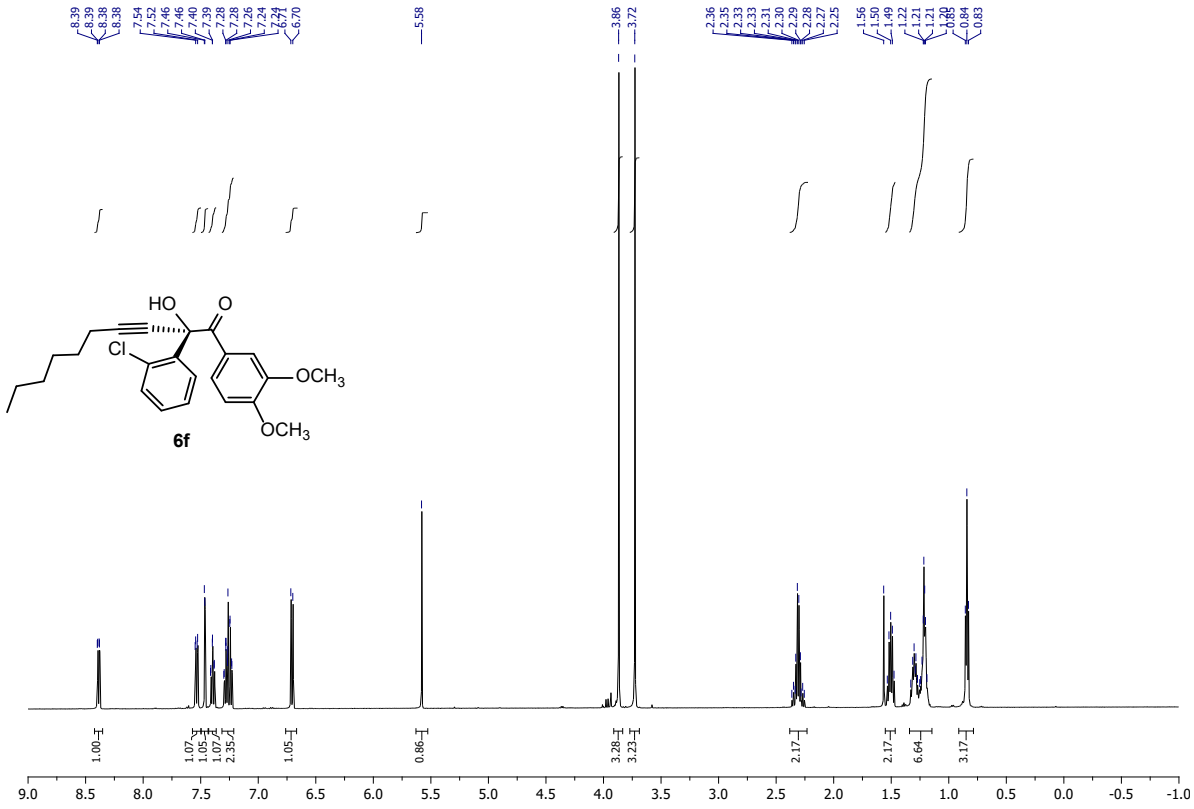


^{13}C-NMR (100 MHz, $CDCl_3$)

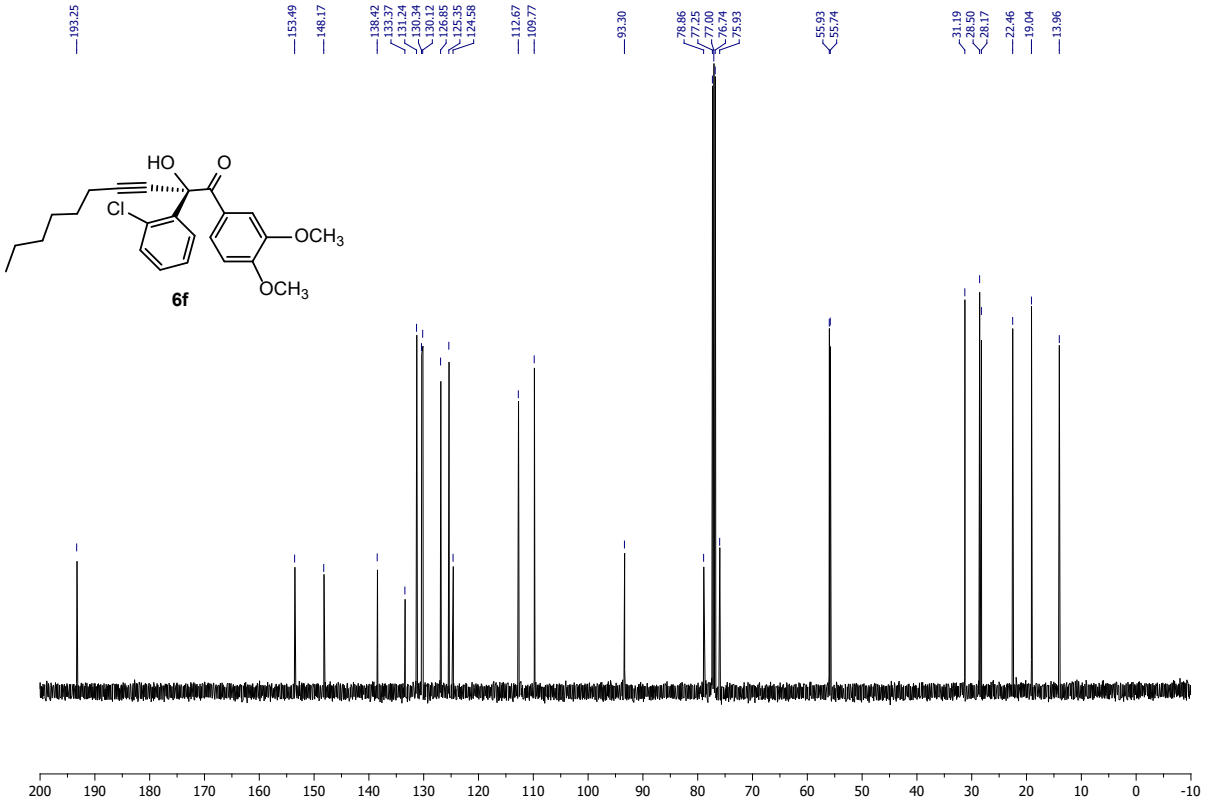


(*R*)-2-(2-chlorophenyl)-1-(3,4-dimethoxyphenyl)-2-hydroxydec-3-yn-1-one (6f)

^{1}H-NMR (500 MHz, $CDCl_3$)

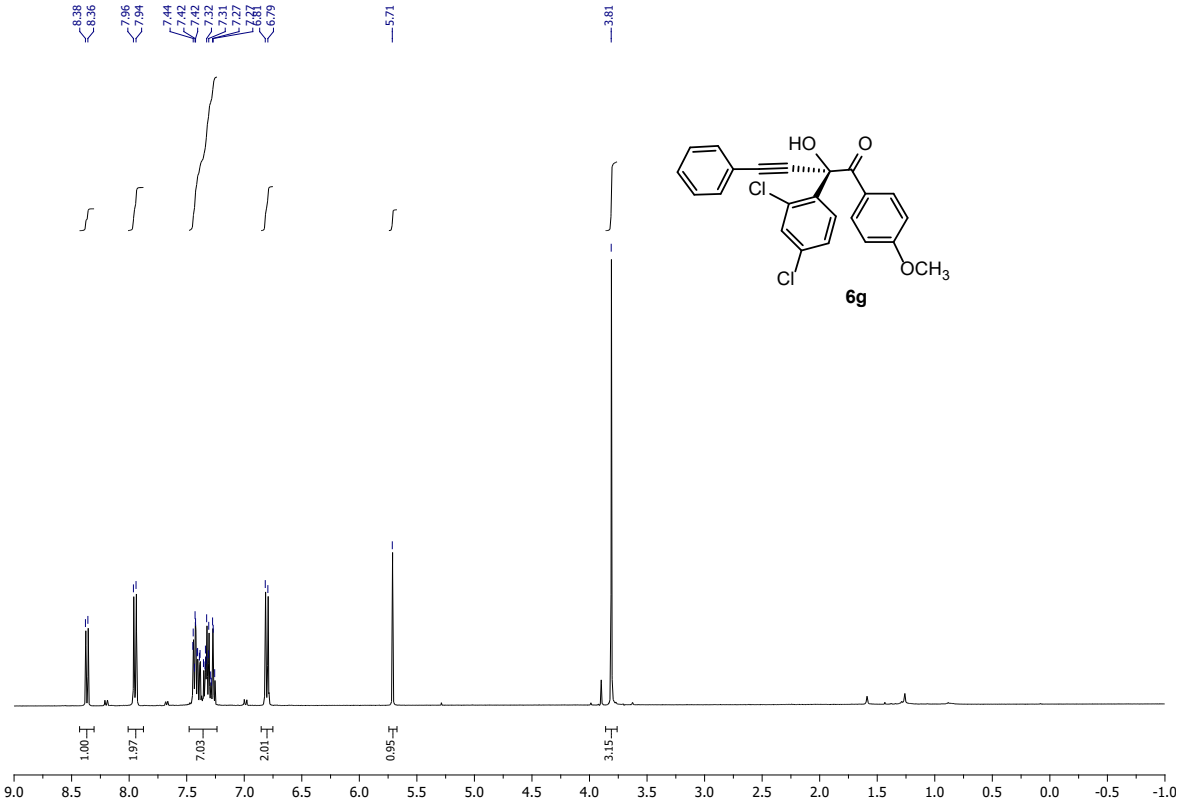


^{13}C-NMR (126 MHz, $CDCl_3$)

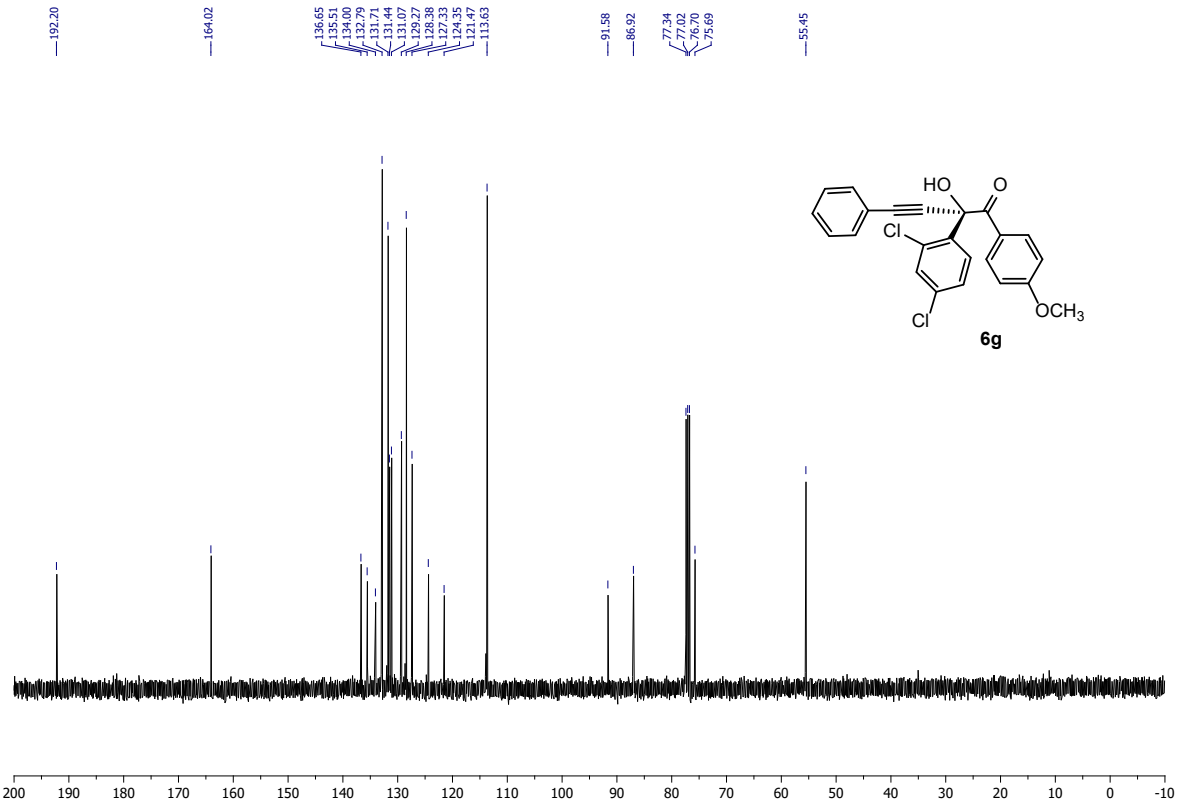


(R)-2-(2,4-dichlorophenyl)-2-hydroxy-1-(4-methoxyphenyl)-4-phenylbut-3-yn-1-one (6g)

^{1}H-NMR (500 MHz, $CDCl_3$)

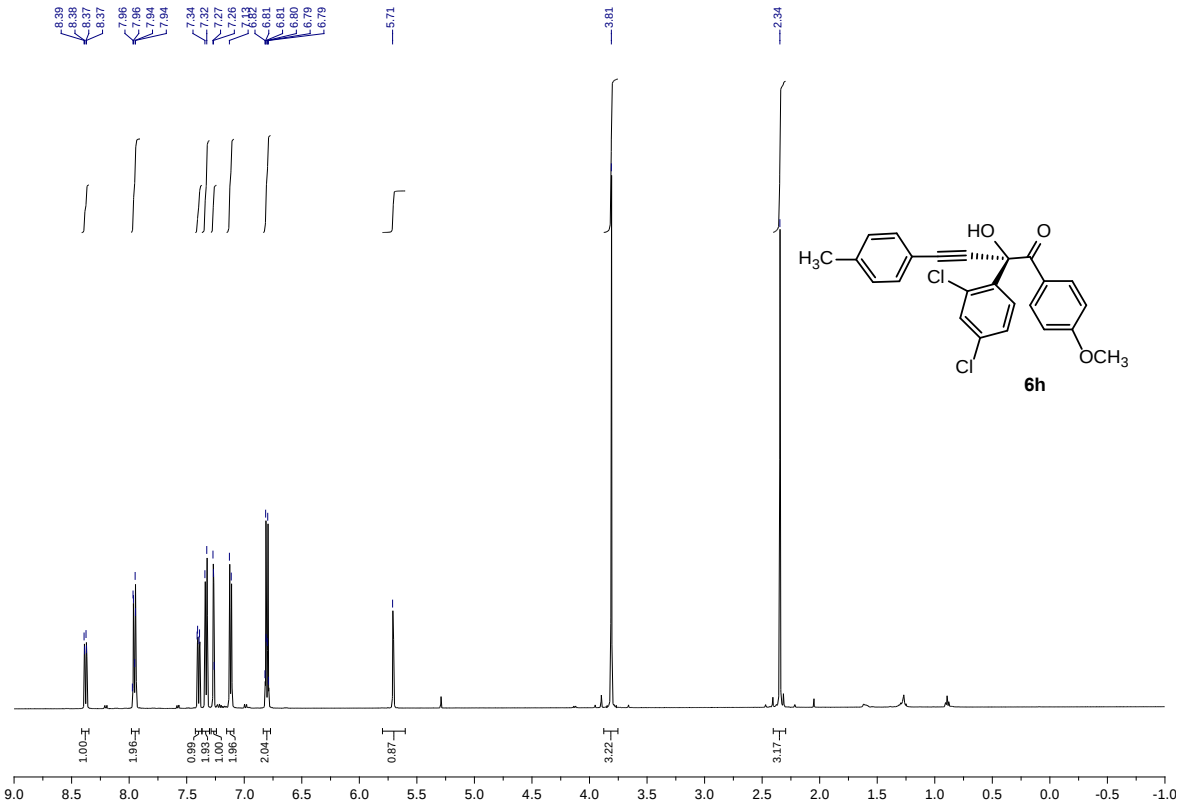


^{13}C-NMR (126 MHz, $CDCl_3$)

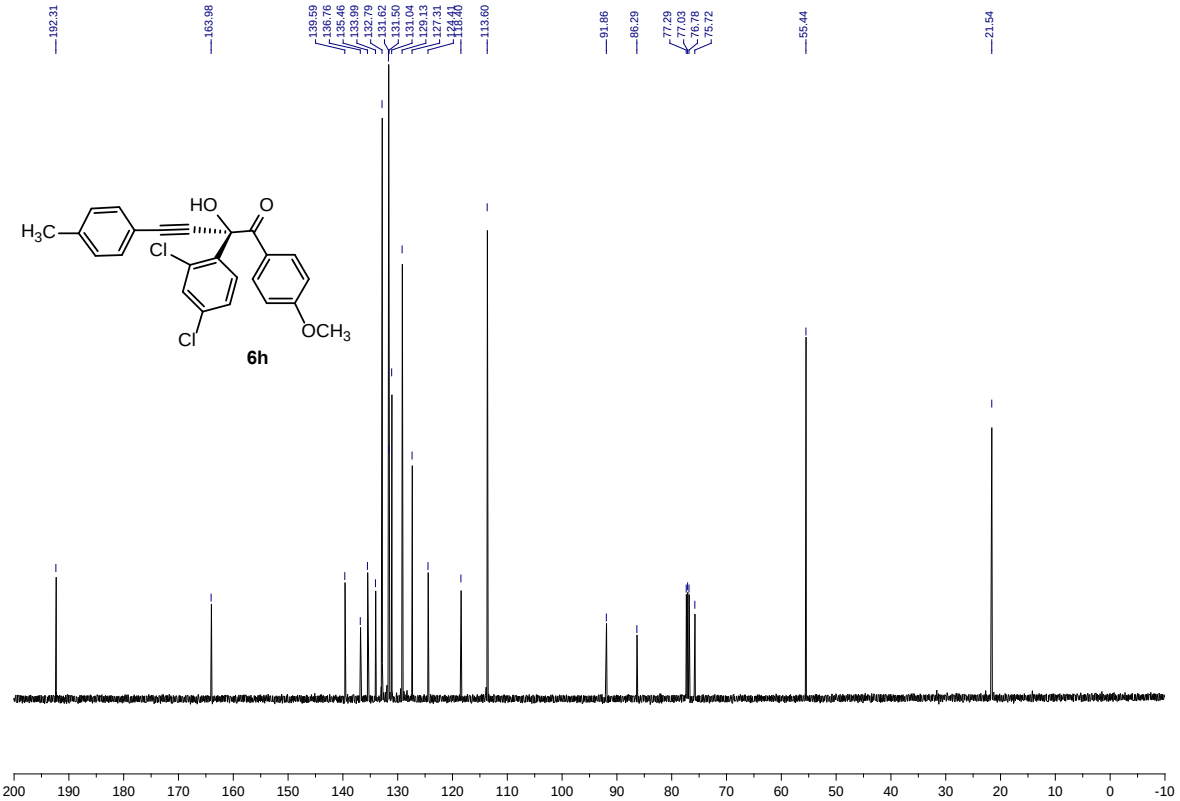


(*R*)-2-(2,4-dichlorophenyl)-2-hydroxy-1-(4-methoxyphenyl)-4-(*p*-tolyl)but-3-yn-1-one (6h)

^{1}H-NMR (500 MHz, $CDCl_3$)

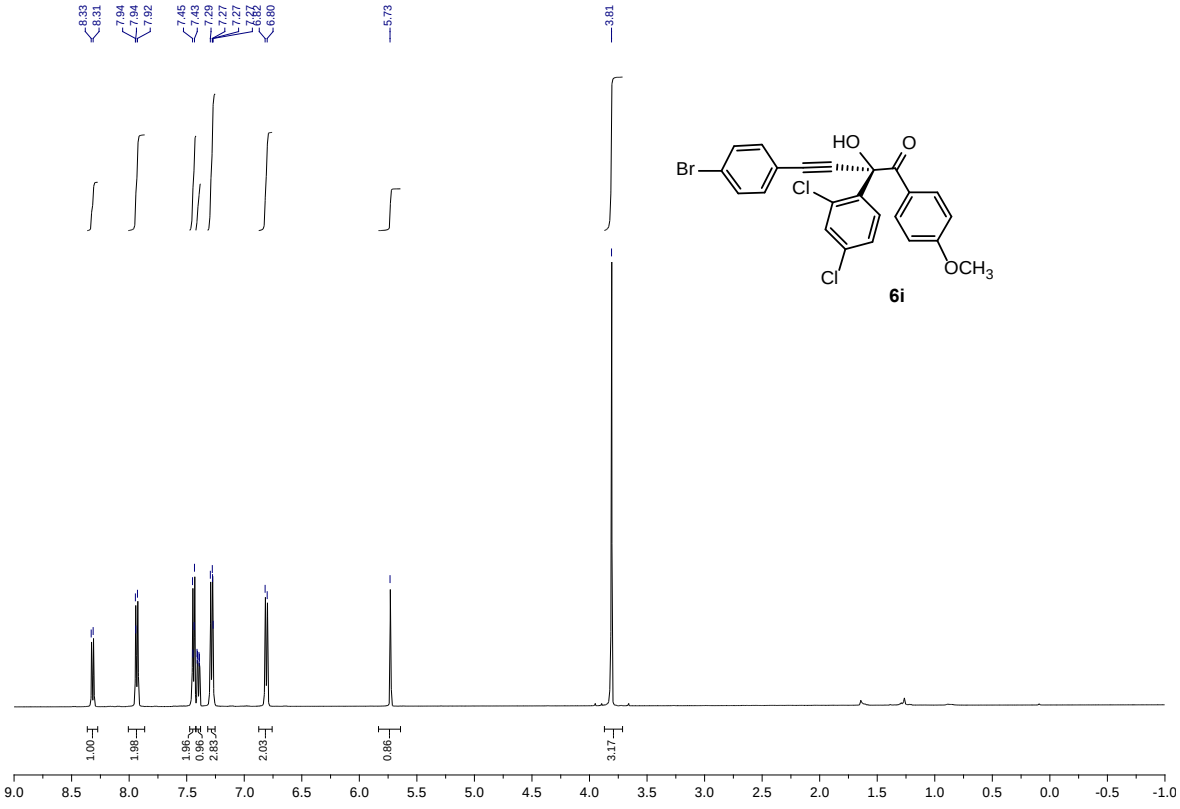


^{13}C-NMR (126 MHz, $CDCl_3$)

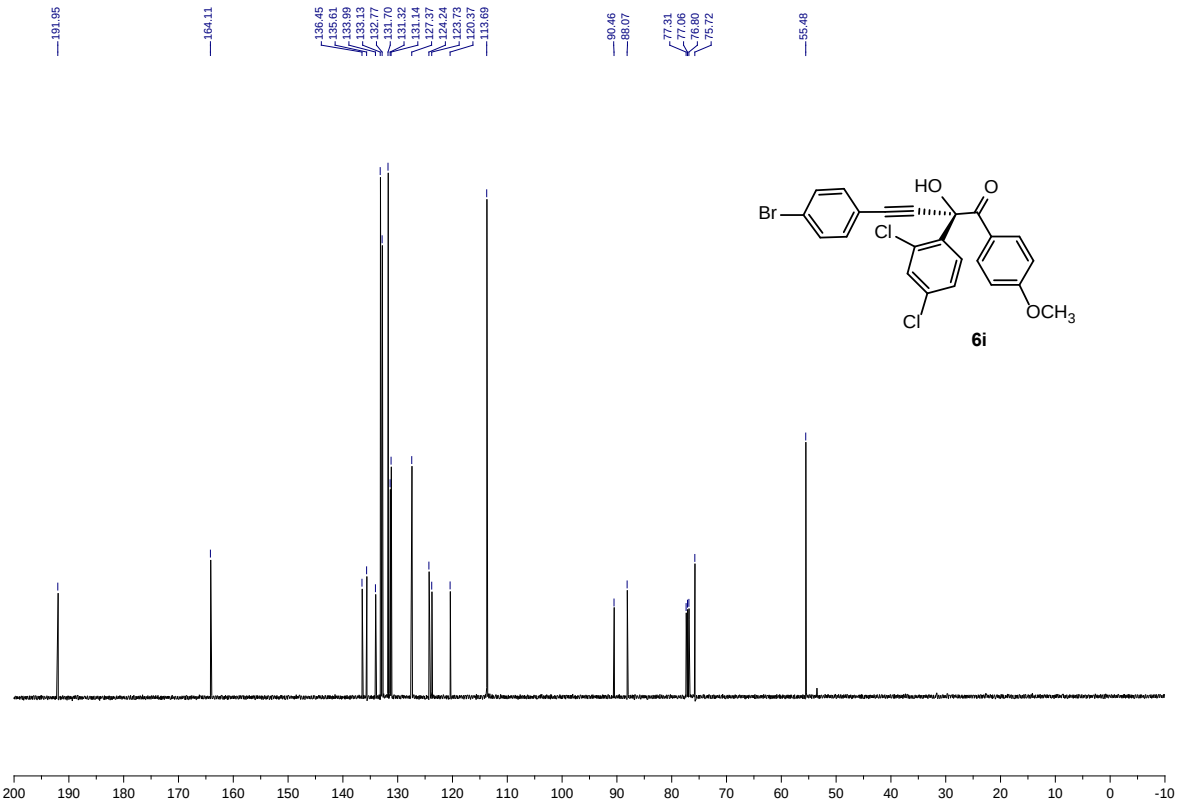


(*R*)-4-(4-bromophenyl)-2-(2,4-dichlorophenyl)-2-hydroxy-1-(4-methoxyphenyl)but-3-yn-1-one (6i)

^{1}H-NMR (500 MHz, $CDCl_3$)

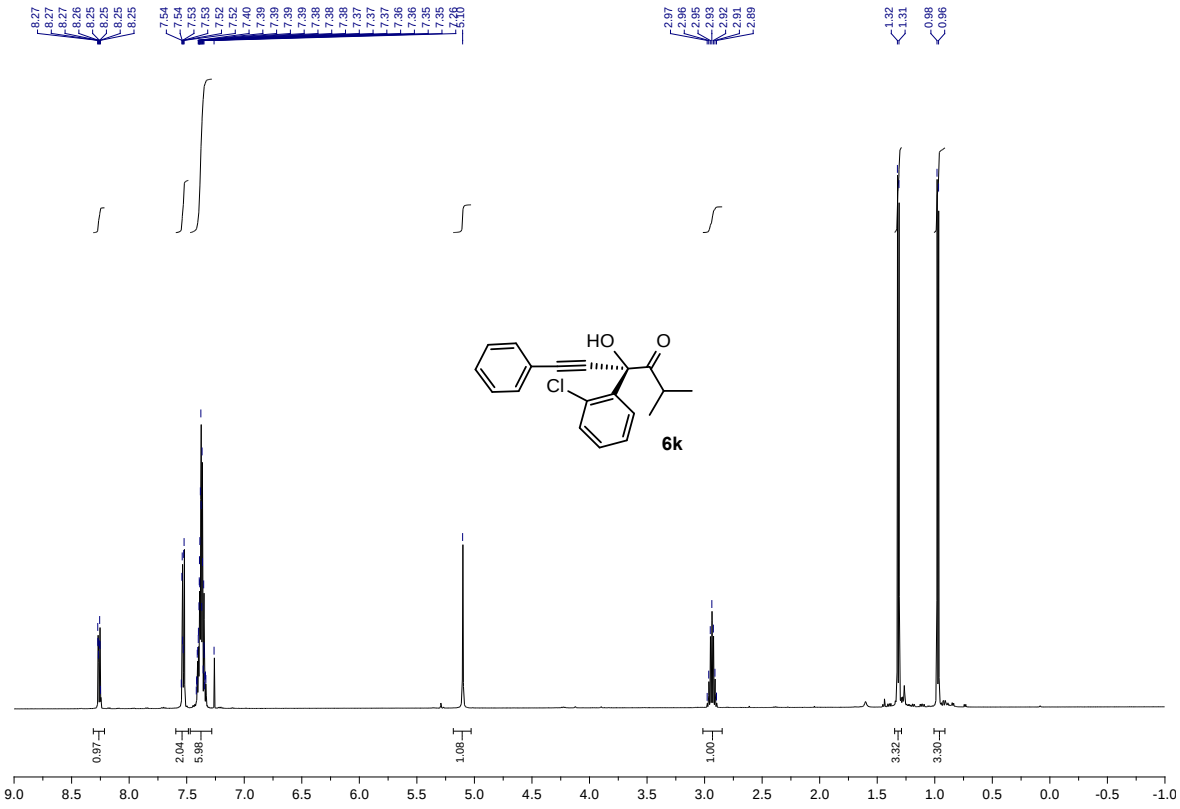


^{13}C-NMR (126 MHz, $CDCl_3$)

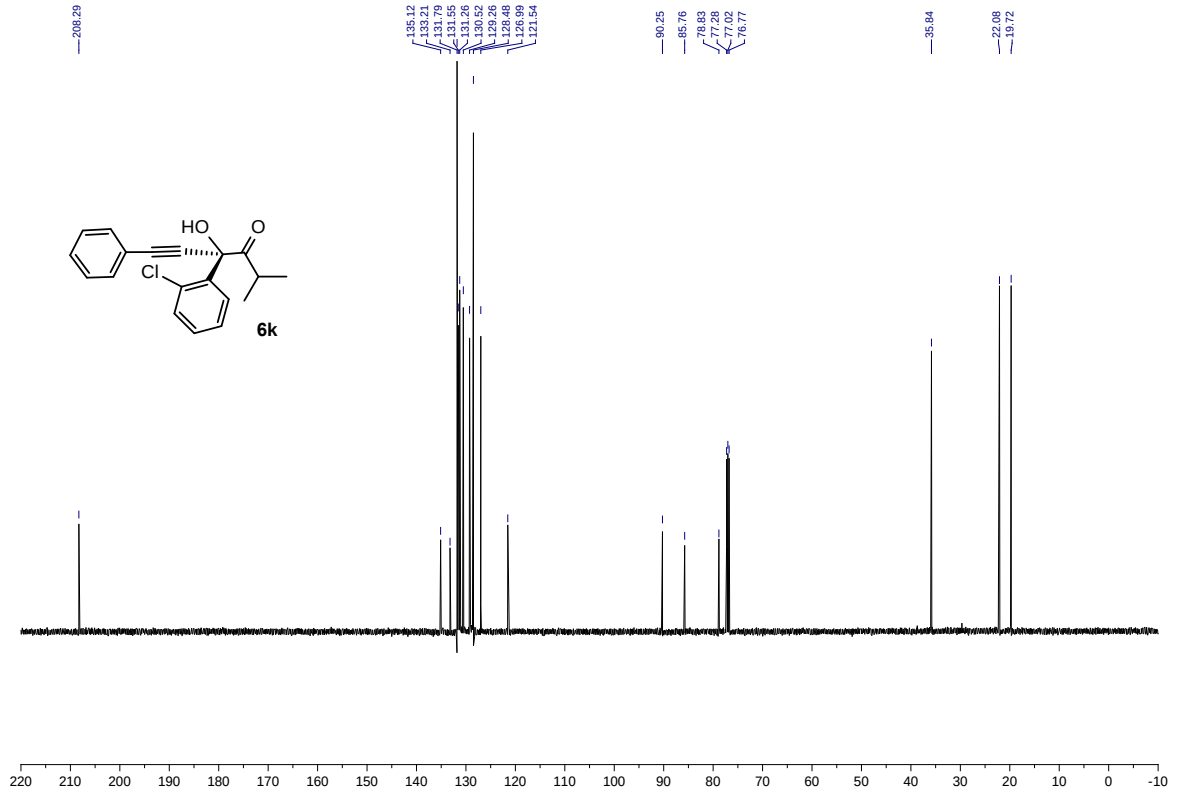


(*R*)-4-(2-chlorophenyl)-4-hydroxy-2-methyl-6-phenylhex-5-yn-3-one (6k)

^{1}H-NMR (500 MHz, $CDCl_3$)

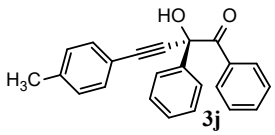


^{13}C-NMR (126 MHz, $CDCl_3$)



HPLC Data

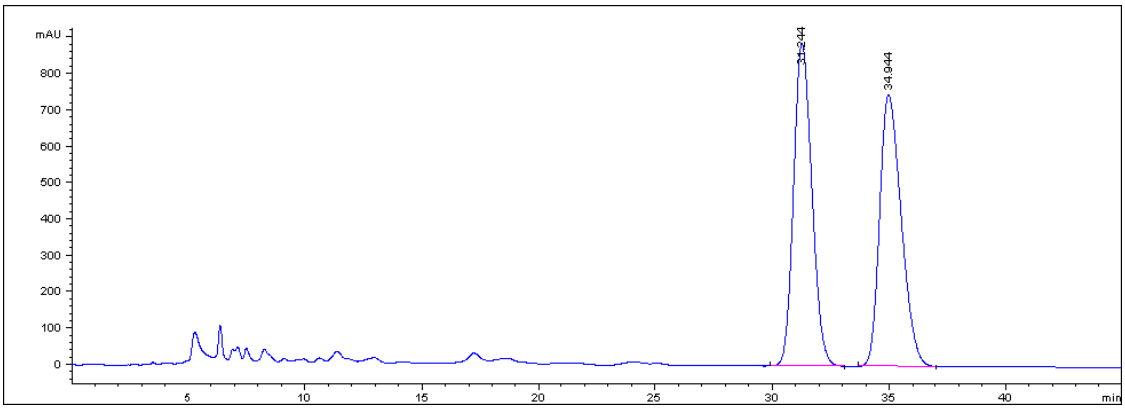
(*S*)-2-hydroxy-1,2-diphenyl-4-(p-tolyl)but-3-yn-1-one (3j)



3j

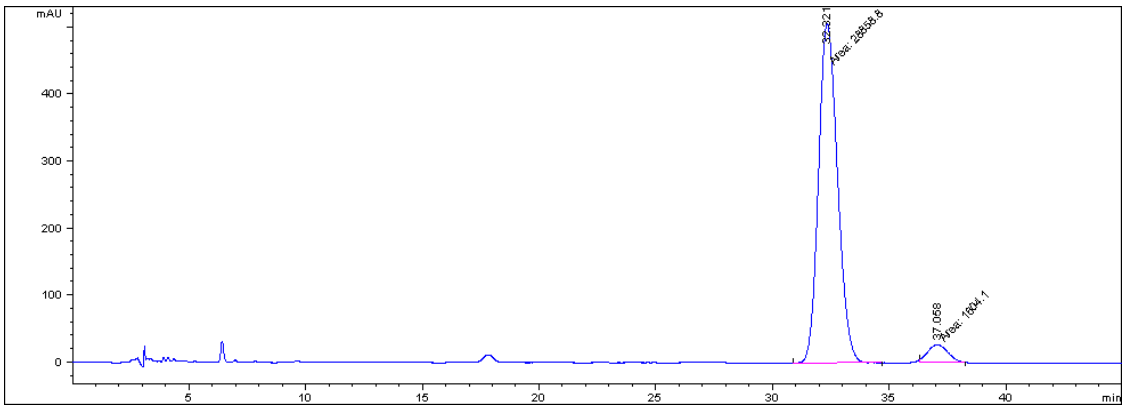
Lux-Amylose-1, hexane:isopropanol = 90:10, 1 mL min^{-1}, λ = 254 nm

Racemic Compound



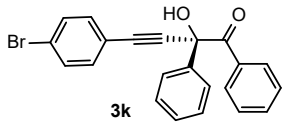
#	Time	Area	Height	Width	Area%	Symmetry
1	31.244	48180.4	887.4	0.8158	50.153	0.8
2	34.944	47887	747.5	0.9298	49.847	0.677

Asymmetric reaction: 95:5 er



#	Time	Area	Height	Width	Area%	Symmetry
1	32.321	28858.8	507.2	0.9484	94.734	0.809
2	37.058	1604.1	26.6	1.0053	5.266	0.969

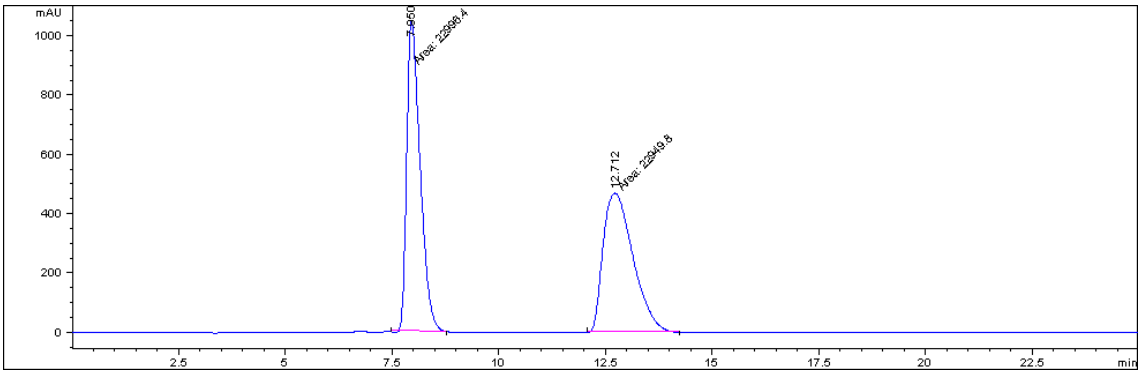
(*S*)-4-(4-bromophenyl)-2-hydroxy-1,2-diphenylbut-3-yn-1-one (3k)



3k

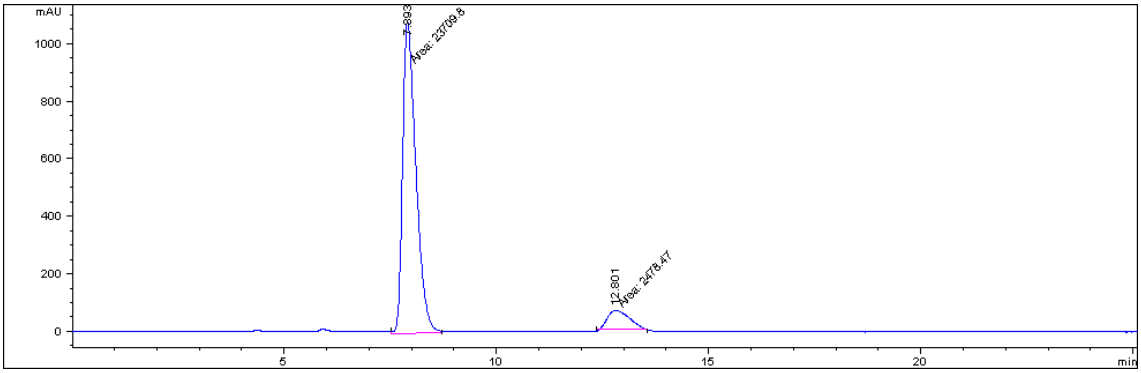
Chiralcel OD-H hexano:2-propanol = 90:10, 1.0 mL min^{-1}, λ = 254 nm

Racemic Compound



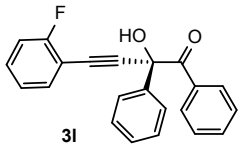
#	t_R	Area	Height	Width	Area%	Symmetry
1	7.95	22996.4	1046.9	0.3661	50.051	0.553
2	12.712	22949.8	469.3	0.8151	49.949	0.623

Asymmetric reaction: 91:9 er



#	t_R	Area	Height	Width	Area%	Symmetry
1	7.893	23709.8	1091.1	0.3622	90.536	0.555
2	12.801	2478.5	68	0.6076	9.464	0.586

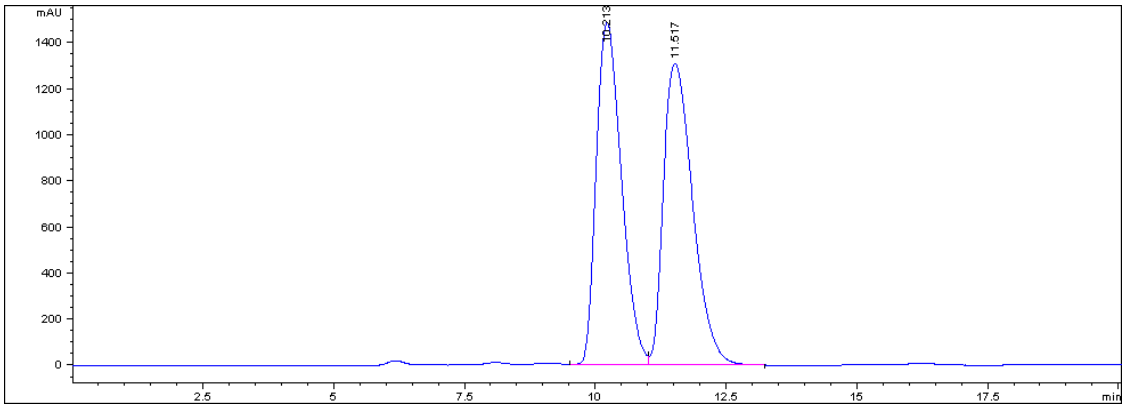
(*S*)-4-(2-fluorophenyl)-2-hydroxy-1,2-diphenylbut-3-yn-1-one (3l)



3l

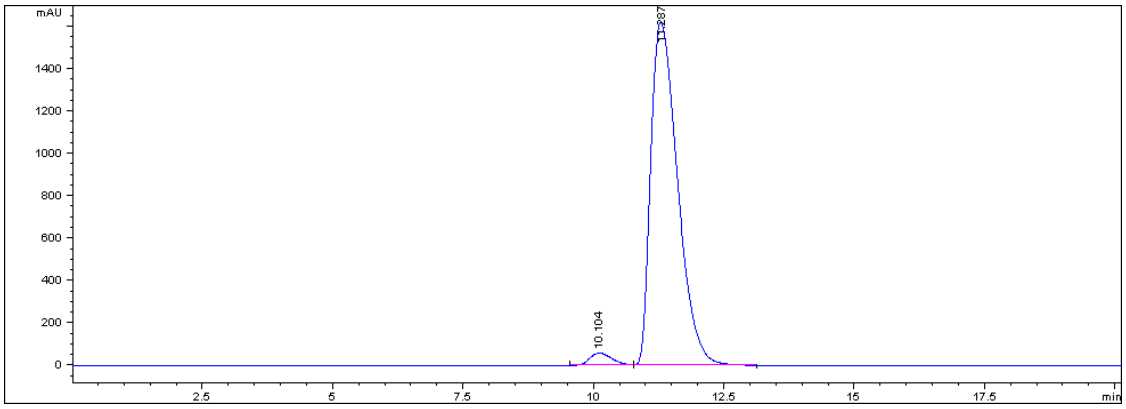
Chiralcel OD, hexane:isopropanol = 96:4, 1 mL min^{-1}, λ = 254 nm HPLC

Racemic Compound



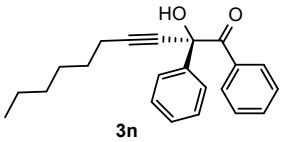
#	Time	Area	Height	Width	Area%	Symmetry
1	10.213	49899.9	1486.5	0.526	49.367	0.688
2	11.517	51179.5	1309.9	0.603	50.633	0.622

Asymmetric reaction: 97:3 er



#	Time	Area	Height	Width	Area%	Symmetry
1	10.104	1755.2	58	0.4522	2.929	0.72
2	11.287	58172.4	1617.4	0.5668	97.071	0.576

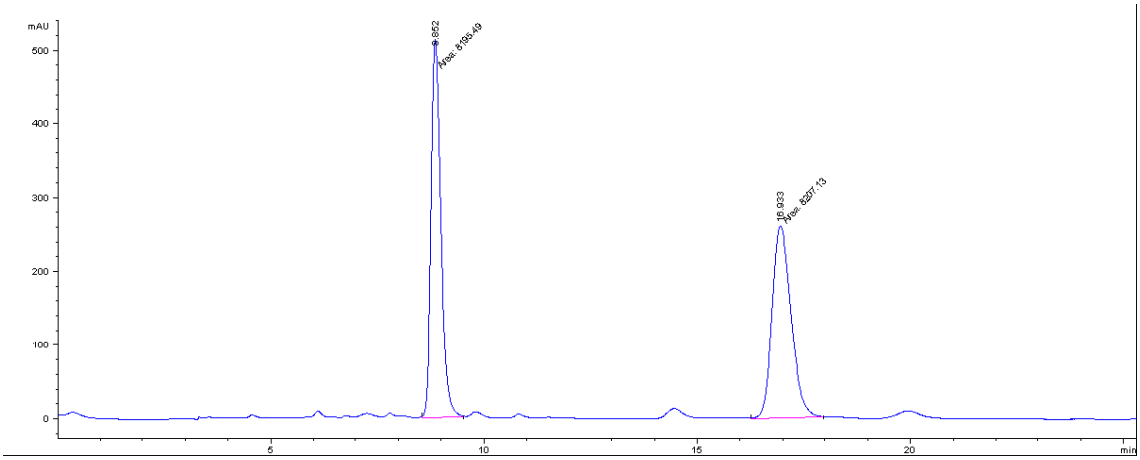
(*S*)-2-hydroxy-1,2-diphenyldec-3-yn-1-one (3n)



3n

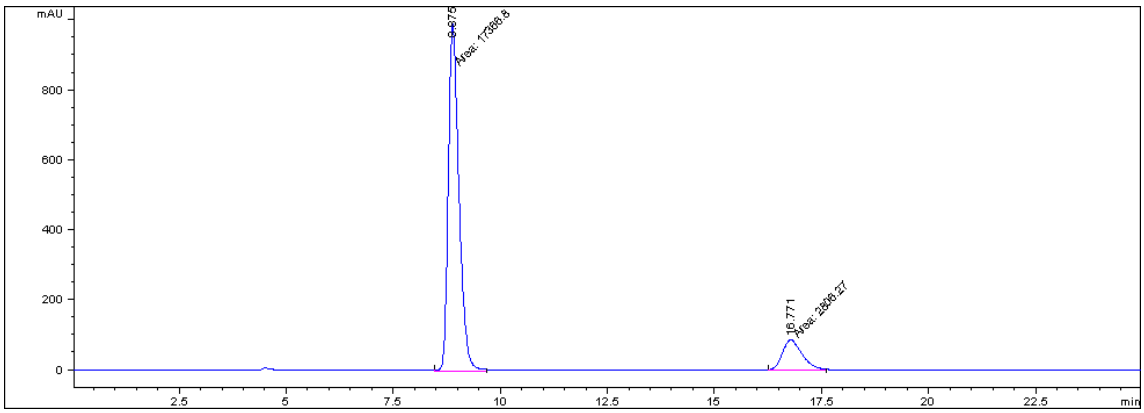
Chiralpak AD-H hexano: 2-propanol = 90 : 10, 1.0 mL min^{-1}, λ = 254 nm

Racemic compound



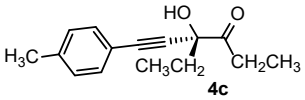
#	t_R	Area	Height	Width	Area%	Symmetry
1	8.852	8195.5	514.5	0.2655	49.965	0.722
2	116.933	8207.1	262.1	0.5219	50.035	0.748

Asymmetric reaction: 86:14 er



#	t_R	Area	Height	Width	Area%	Symmetry
1	8.875	17366.8	994.1	0.2912	86.089	0.663
2	16.771	2806.3	86.2	0.5424	13.911	0.707

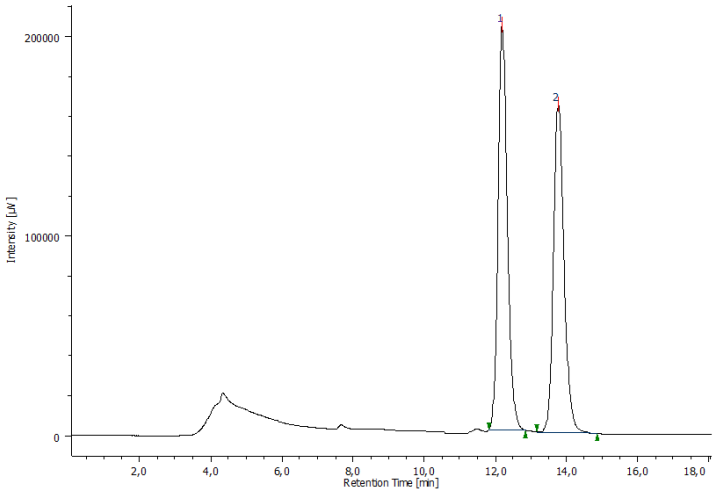
(*S*)-4-ethyl-4-hydroxy-6-(p-tolyl)hex-5-yn-3-one (4c)



4c

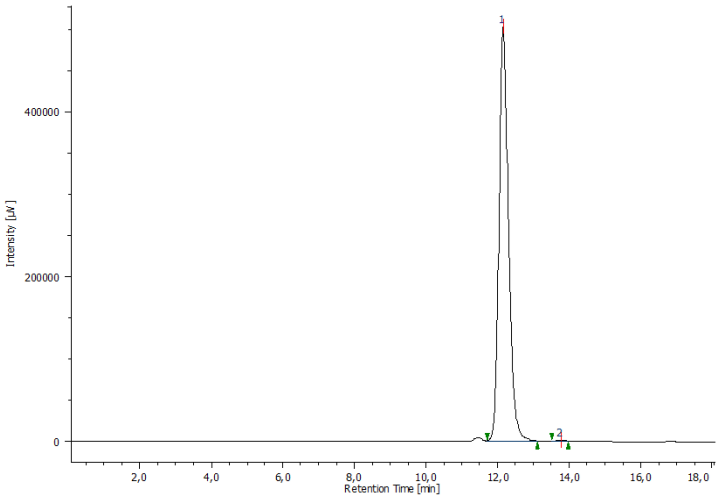
Chiralcel OJ, hexane:2-propanol = 96:4, 0.8 mL min^{-1}, λ = 254 nm

Racemic Compound



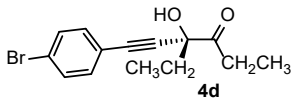
#	tR [min]	Area[µV.sec]	Height[µV]	Area %	Height %	Symmetry Factor
1	12.175	3682381	202687	52.117	55.281	1.212
2	13.750	3383252	163960	47.883	44.719	1.190

Asymmetric reaction: >99:1 er



#	tR [min]	Area[µV.sec]	Height[µV]	Area %	Height %	Symmetry Factor
1	12.142	9238289	502061	99.790	99.748	1.229
2	13.758	19416	1270	0.210	0.252	0.910

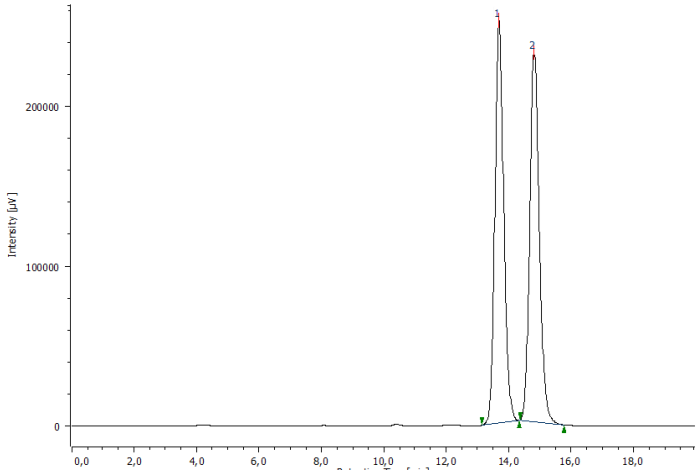
(*S*)-6-(4-bromophenyl)-4-ethyl-4-hydroxyhex-5-yn-3-one (4d)



4d

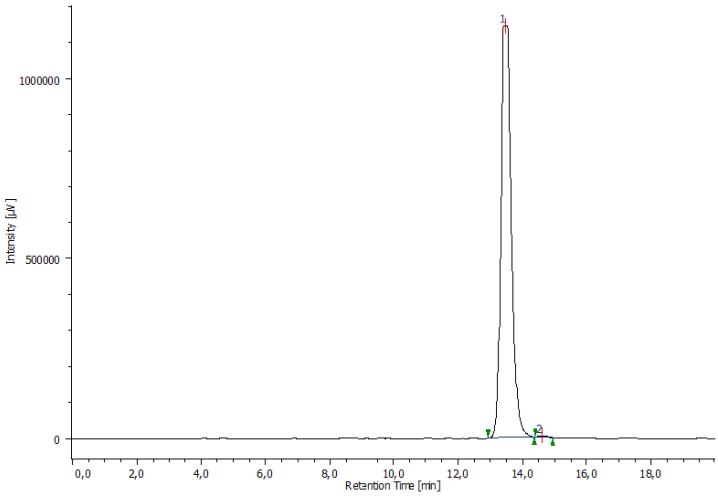
Chiralcel OJ, hexane : 2-propanol = 96 : 4, 0.8 mL min^{-1}, λ = 254 nm

Racemic Compound



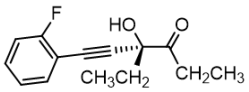
#	tR [min]	Area[µV.sec]	Height[µV]	Area %	Height %	Symmetry Factor
1	13.667	4936746	251123	50.081	52.156	1.150
2	14.792	4920805	230360	49.919	47.844	1.168

Asymmetric reaction: >99:1 er



#	tR [min]	Area[µV.sec]	Height[µV]	Area %	Height %	Symmetry Factor
1	13.458	26051820	1140634	99.751	99.678	1.223
2	14.600	65022	3683	0.249	0.322	1.273

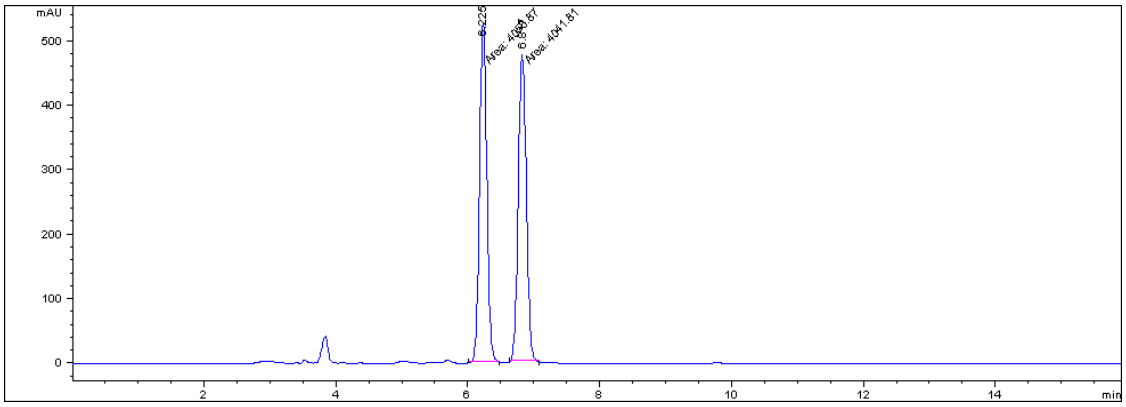
(*S*)-4-ethyl-6-(2-fluorophenyl)-4-hydroxyhex-5-yn-3-one (4e)



4e

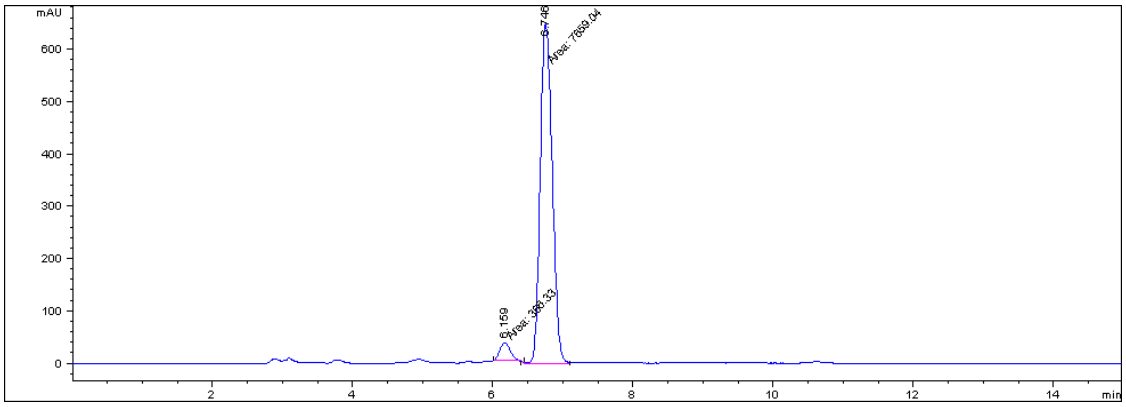
Lux-Amylose-1 hexane : 2-propanol = 96 : 4, 1.0 mL min^{-1}, λ = 254 nm

Racemic compound



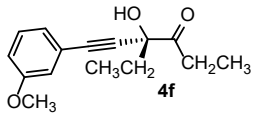
#	Time	Area	Height	Width	Area%	Symmetry
1	6.225	4056.9	527.8	0.1281	50.093	0.913
2	6.817	4041.8	476.7	0.1413	49.907	0.909

Asymmetric reaction: 95:5 er



#	Time	Area	Height	Width	Area%	Symmetry
1	6.159	366.3	34.4	0.1773	4.565	0.786
2	6.746	7659	652.6	0.1956	95.435	0.788

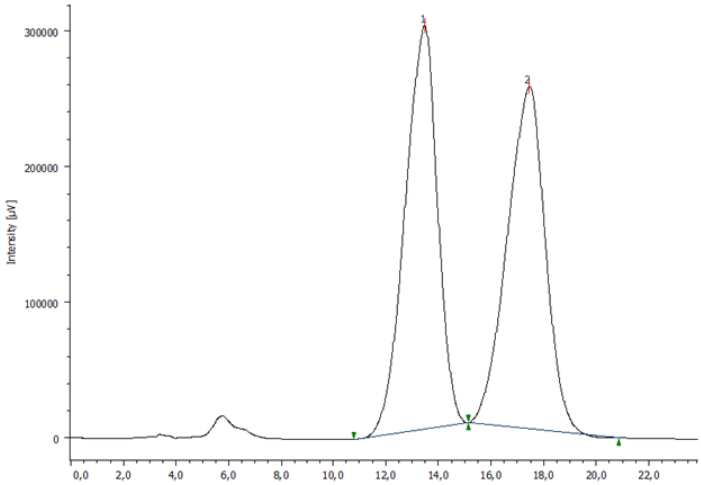
(*S*)-4-ethyl-4-hydroxy-6-(3-methoxyphenyl)hex-5-yn-3-one (4f)



4f

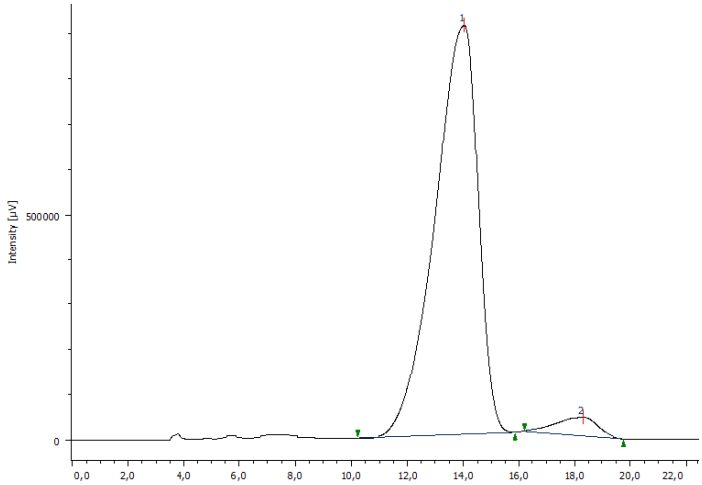
Chiralcel OD, hexane:isopropanol = 99:1, 1.0 mL min^{-1}, λ = 254 nm

Racemic compound



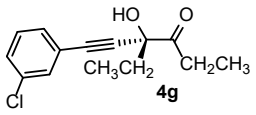
#	tR [min]	Area[µV.sec]	Height[µV]	Area %	Height %	Symmetry Factor
1	13.502	25491356	296704	50.143	54.109	0.856
2	17.862	25345674	251641	49.857	45.891	0.896

Asymmetric reaction: 96:4 er



#	tR [min]	Area[µV.sec]	Height[µV]	Area %	Height %	Symmetry Factor
1	14.608	97167786	905658	95.892	95.702	0.743
2	18.283	4163010	40669	4.108	4.298	0.790

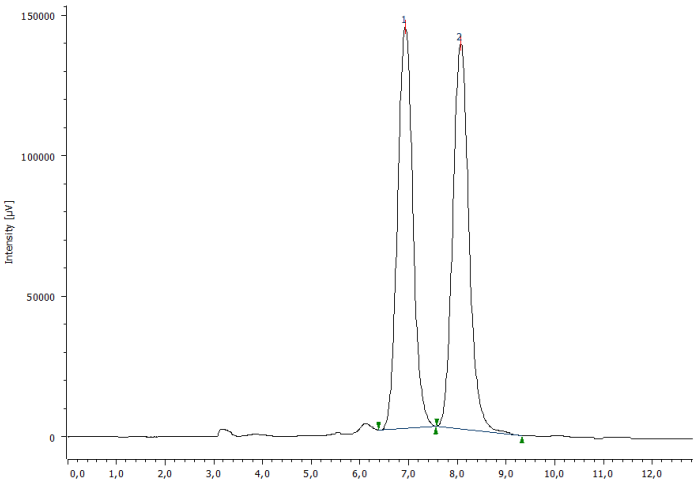
(*S*)-6-(3-chlorophenyl)-4-ethyl-4-hydroxyhex-5-yn-3-one (4g)



4g

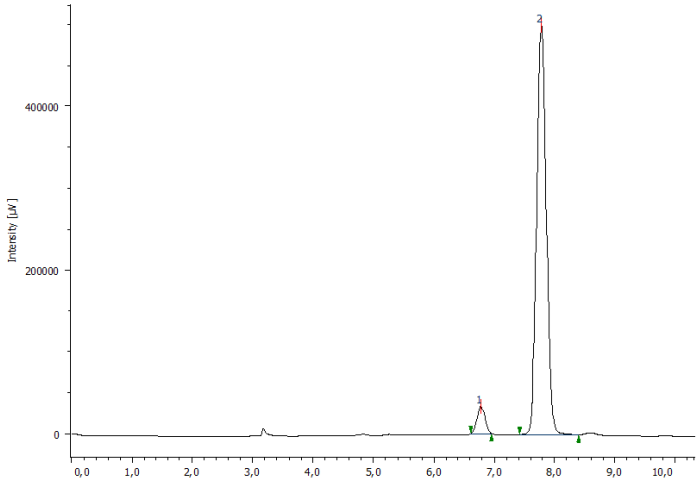
Lux-Cellulose-2, hexane:isopropanol = 98:2, 1.0 mL min-1, λ = 254 nm

Racemic compound



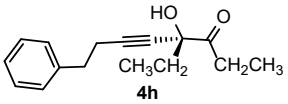
#	tR [min]	Area[µV.sec]	Height[µV]	Area %	Height %	Symmetry Factor
1	6.925	3122810	142683	49.779	51.048	1.056
2	8.058	3150592	136826	50.221	48.952	1.131

Asymmetric reaction: 95:5 er



#	tR [min]	Area[µV.sec]	Height[µV]	Area %	Height %	Symmetry Factor
1	6.767	305831	32603	5.177	6.142	1.010
2	7.775	5601551	498220	94.823	93.858	1.051

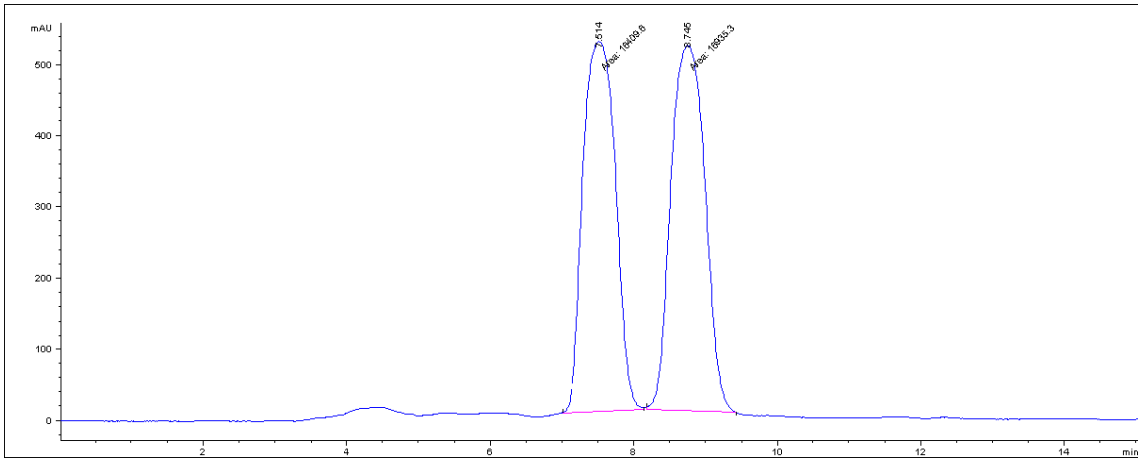
(*S*)-4-ethyl-4-hydroxy-8-phenyloct-5-yn-3-one (4h).



4h

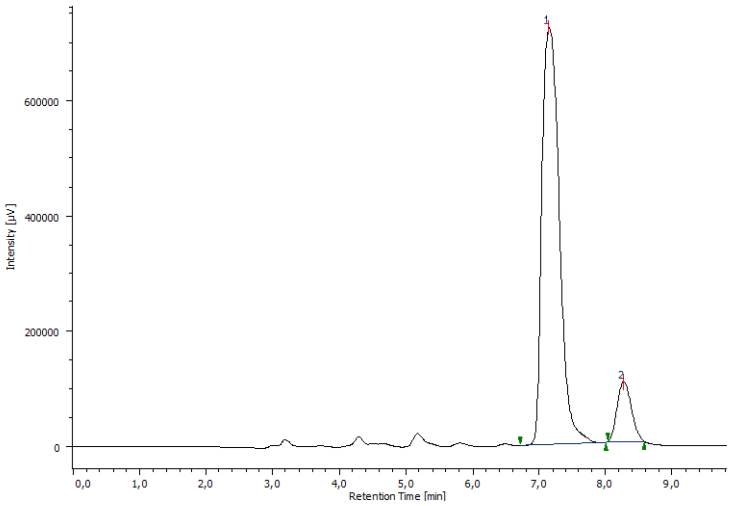
Chiralpak AD-H, hexane:isopropanol = 95:5, 1.0 mL min^{-1}, λ = 220 nm

Racemic Compound



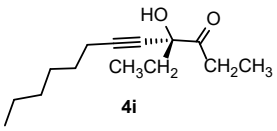
#	Time	Area	Height	Width	Area%	Symmetry
1	7.514	16409.6	520.9	0.5251	49.212	0.941
2	8.745	16935.3	513.8	0.5493	50.788	0.93

Asymmetric reaction: 90:10 er



#	tR [min]	Area[µV.sec]	Height[µV]	Area %	Height %	Symmetry Factor
1	7.133	13223206	720649	89.647	87.599	1.473
2	8.267	1527160	102017	10.353	12.401	1.136

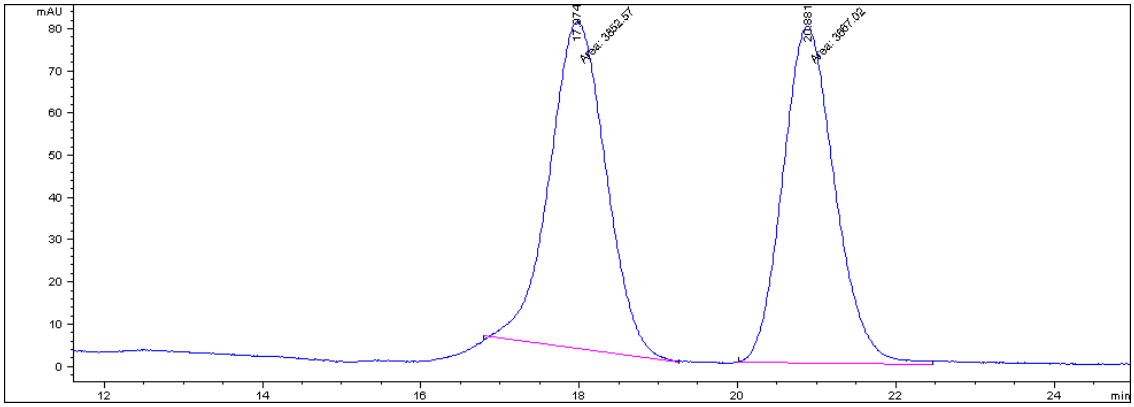
(*S*)-4-Ethyl-4-hydroxydodec-5-yn-3-one (4i)



4i

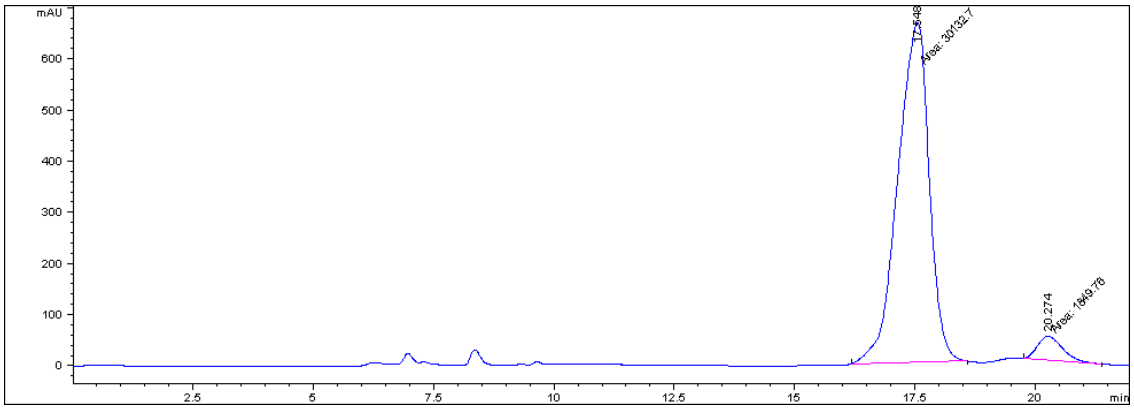
Chiralpak AD-H hexano:2-propanol = 99:1, 0.5 mL min^{-1}, λ = 210 nm

Racemic Compound



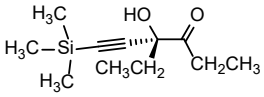
#	Time	Area	Height	Width	Area%	Symmetry
1	17.974	3852.6	77.6	0.8276	51.234	0.957
2	20.881	3667	80	0.7642	48.766	0.862

Asymmetric reaction: 94:6 er



#	Time	Area	Height	Width	Area%	Symmetry
1	17.548	30132.7	664.5	0.7557	94.216	1.644
2	20.274	1849.8	48.4	0.6369	5.784	0.628

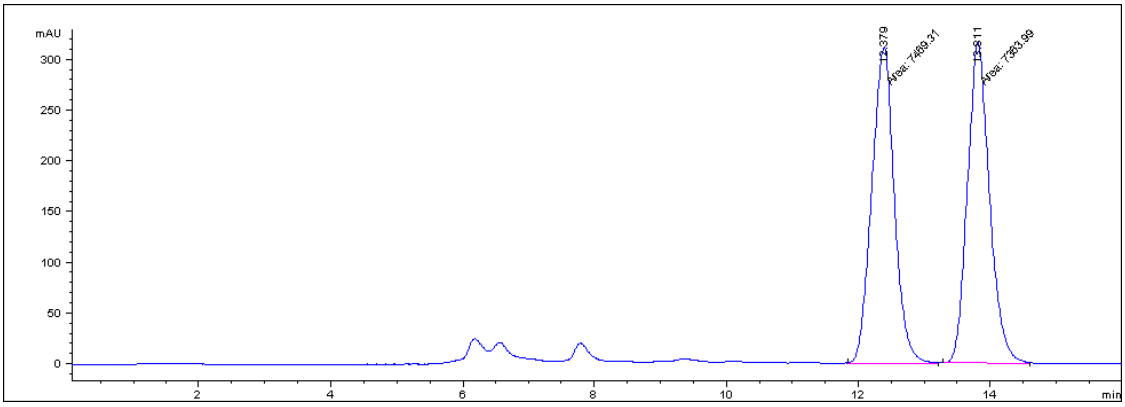
(*S*)-4-ethyl-4-hydroxy-6-(trimethylsilyl)hex-5-yn-3-one (4j)



4j

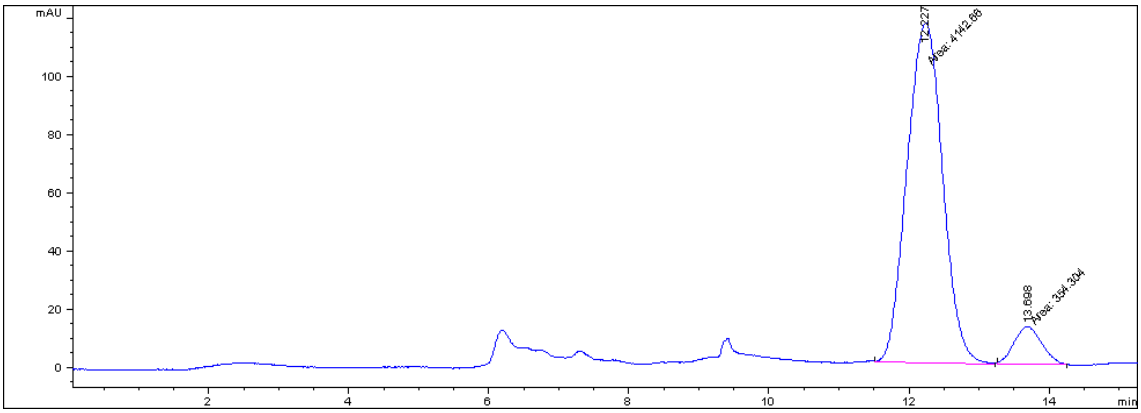
Chiralpak AD-H, hexane:isopropanol = 99:1, 0.5 mL min^{-1}, λ = 210 nm

Racemic Compound



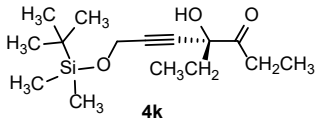
#	Time	Area	Height	Width	Area%	Symmetry
1	12.379	7469.3	312.6	0.3982	50.355	1.143
2	13.811	7364	316.4	0.3879	49.645	0.828

Asymmetric reaction: 92:8 er



#	Time	Area	Height	Width	Area%	Symmetry
1	12.227	4142.7	116.9	0.5905	92.121	1.027
2	13.698	354.3	12.8	0.4613	7.879	1.038

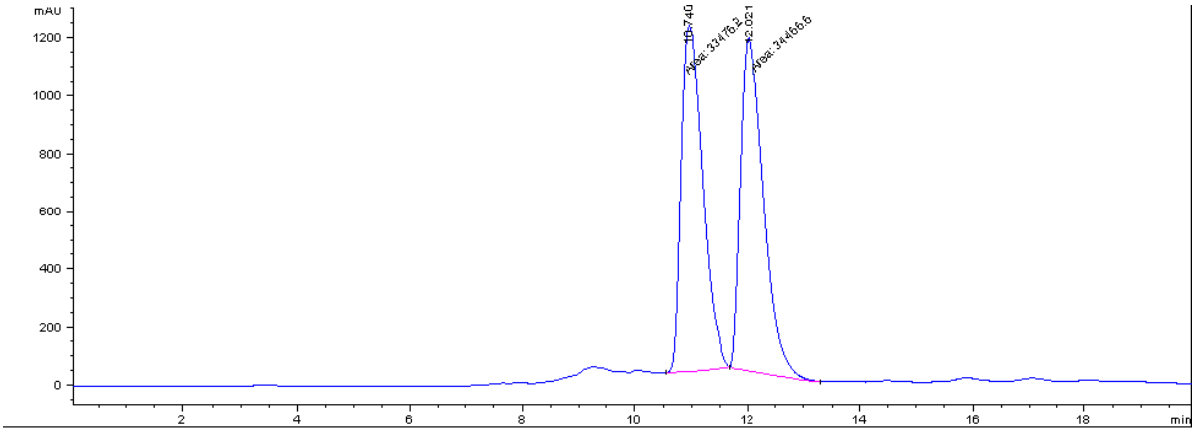
(*S*)-7-((tert-butyldimethylsilyl)oxy)-4-ethyl-4-hydroxyhept-5-yn-3-one (4k)



4k

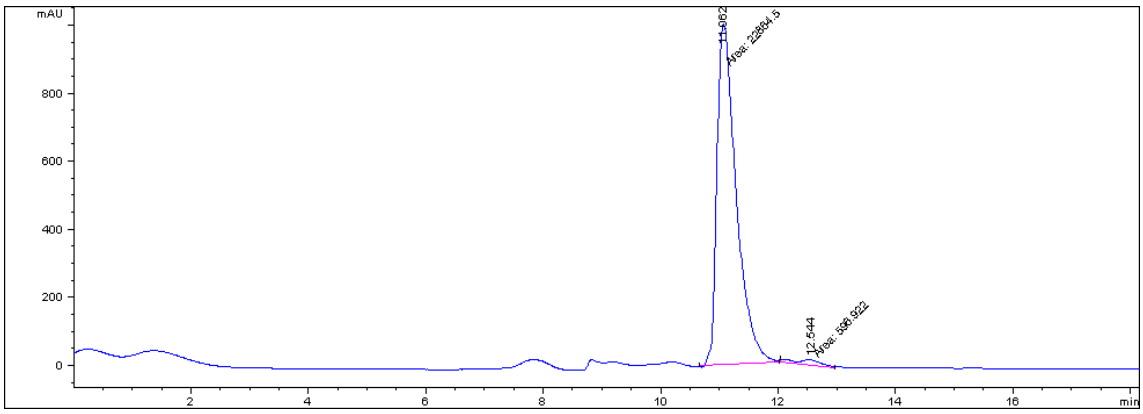
Chiralpak AD-H hexano:2-propanol = 95:5, 0.4 mL min^{-1}, λ = 210 nm

Racemic Compound



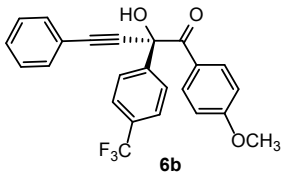
#	t_R	Area	Height	Width	Area%	Symmetry
1	10.740	33476.2	1208.2	0.4563	49.271	0.825
2	12.021	34466.6	1176.2	0.5006	50.729	0.683

Asymmetric reaction: 97:3 er



#	t_R	Area	Height	Width	Area%	Symmetry
1	11.062	22864.5	1001.4	0.3806	97.456	0.495
2	12.544	596.9	17.7	0.5622	2.544	1.003

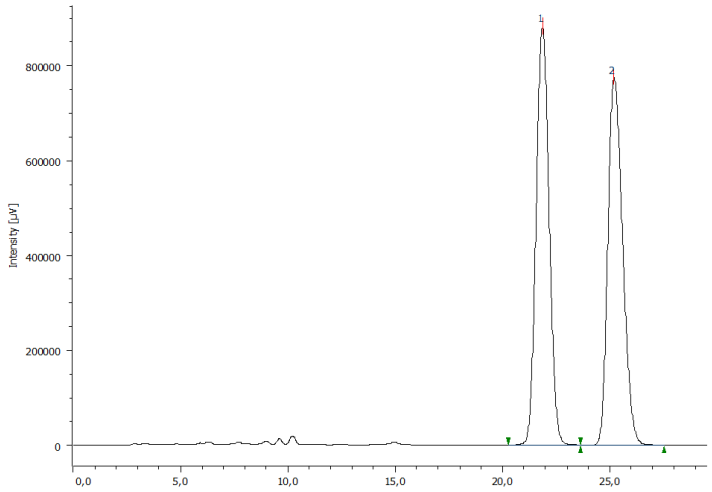
(*S*)-2-hydroxy-1-(4-methoxyphenyl)-4-phenyl-2-(4-(trifluoromethyl)phenyl)but-3-yn-1-one (6b).



6b

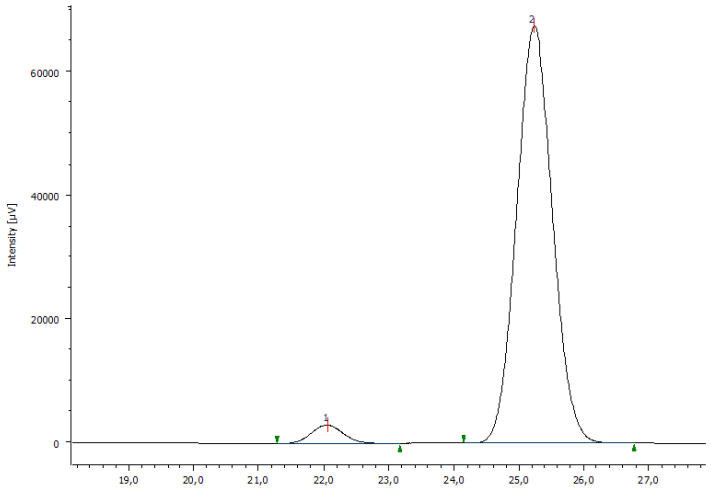
Lux-Amylose-1, hexane:isopropanol = 88:12, 1.0 mL min^{-1}, λ = 254 nm

Racemic compound



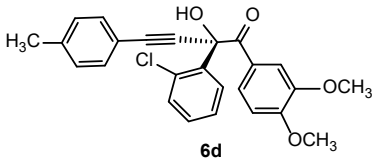
#	tR [min]	Area [µV.sec]	Height [µV]	Area %	Height %	Symmetry Factor
1	21.833	37183527	880517	50.042	53.210	1.073
2	25.167	37121562	774267	49.958	46.790	1.267

Asymmetric reaction: 96:4 er



#	tR [min]	Area [µV.sec]	Height [µV]	Area %	Height %	Symmetry Factor
1	22.050	103174	3024	3.776	4.294	1.044
2	25.225	2629514	67400	96.224	95.706	1.059

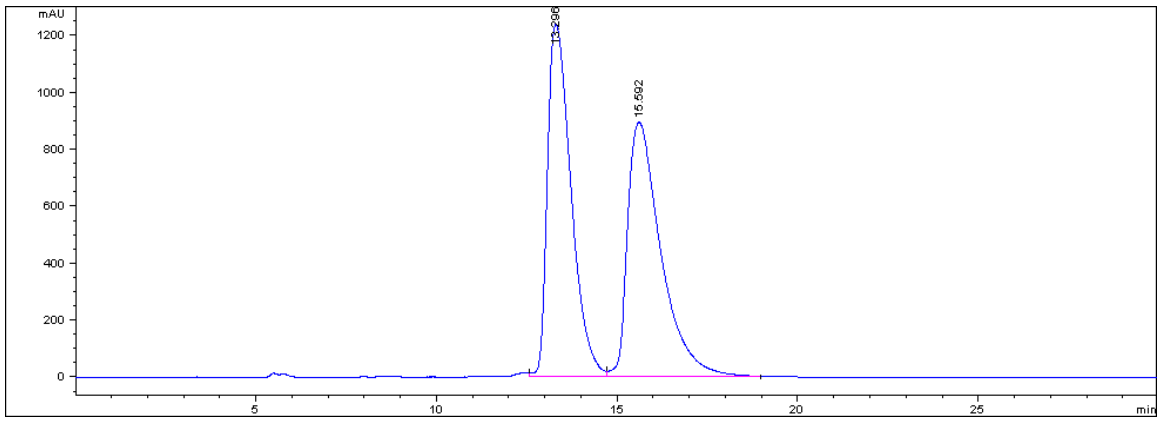
(*R*)-2-(2-chlorophenyl)-1-(3,4-dimethoxyphenyl)-2-hydroxy-4-(*p*-tolyl)but-3-yn-1-one (6d).



6d

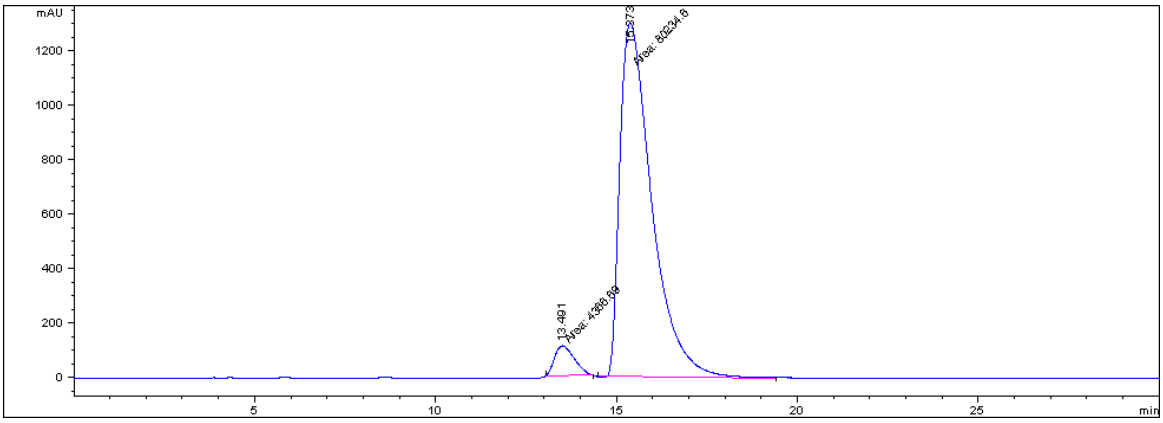
Chiralcel OD, hexane:isopropanol = 90:10, 1.0 mL min^{-1}, λ = 254 nm

Racemic Compound



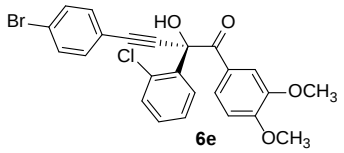
#	Time	Area	Height	Width	Area%	Symmetry
1	13.296	56507.1	1238.6	0.6474	49.631	0.545
2	15.592	57347.7	893.1	0.9475	50.369	0.482

Asymmetric reaction: 95:5 er



#	Time	Area	Height	Width	Area%	Symmetry
1	13.491	4366.7	113.1	0.6437	5.161	0.642
2	15.373	80234.6	1300.1	1.0285	94.839	0.467

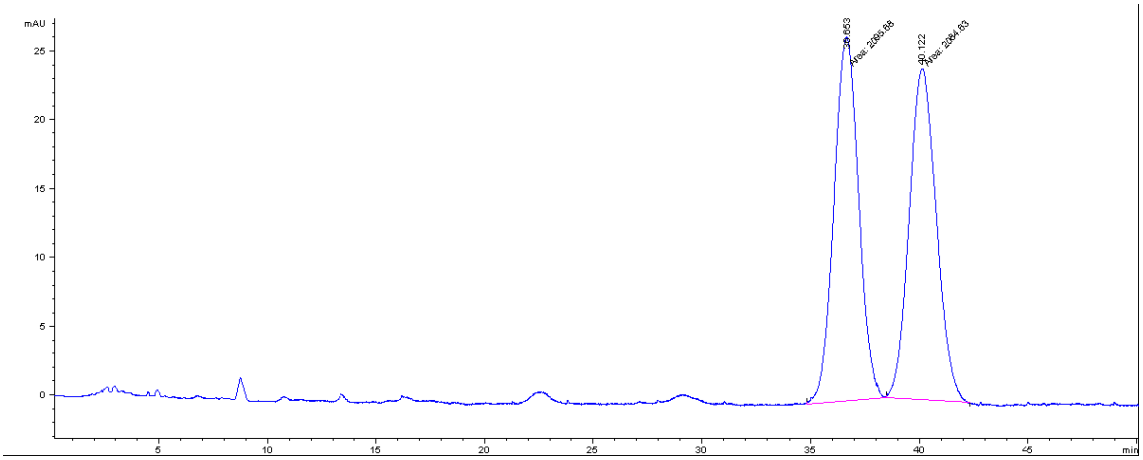
(*R*) -4-(4-bromophenyl)-2-(2-chlorophenyl)-1-(3,4-dimethoxyphenyl)-2-hydroxybut-3-yn-1-one (6e).



6e

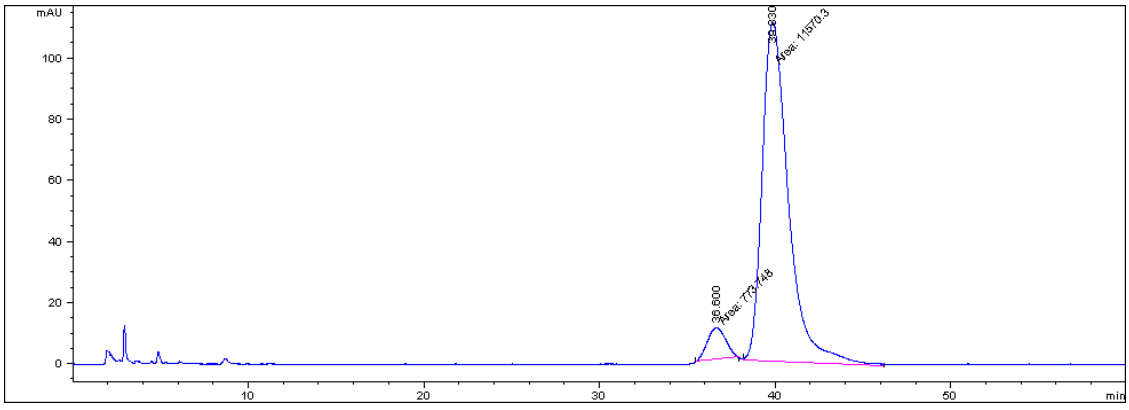
Chiralpak AD-H, hexane:isopropanol = 80:20, 1.5 mL min-1, λ = 254 nm

Racemic Compound



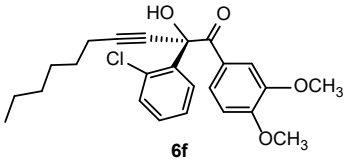
#	Time	Area	Height	Width	Area%	Symmetry
1	36.653	2095.7	26.5	1.3179	50.132	0.945
2	40.122	2084.6	24.1	1.4416	49.868	0.907

Asymmetric reaction: 94:6 er



#	Time	Area	Height	Width	Area%	Symmetry
1	36.6	773.7	10.6	1.2214	6.268	0.88
2	39.83	11570.3	110.9	1.7389	93.732	0.634

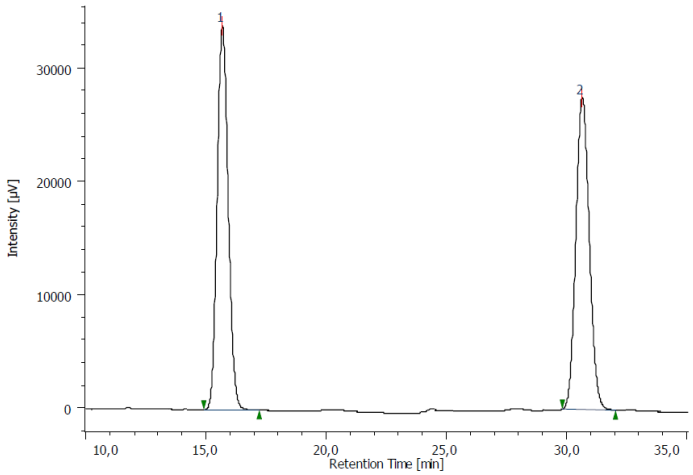
(*R*)-2-(2-chlorophenyl)-1-(3,4-dimethoxyphenyl)-2-hydroxydec-3-yn-1-one (6f)



6f

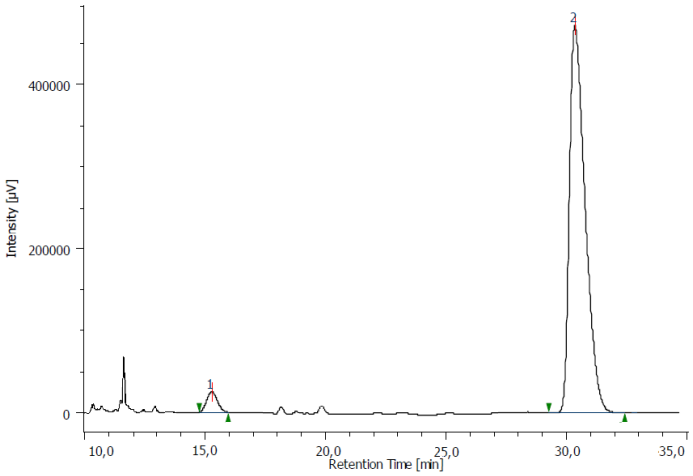
Lux-Cellulose-2, hexane:isopropanol = 90:10, 1.0 mL min^{-1}, λ = 254 nm

Racemic compound



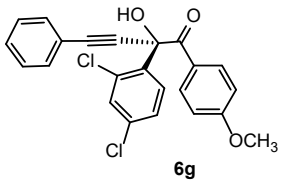
#	tR [min]	Area [µV.sec]	Height [µV]	Area %	Height %	Symmetry Factor
1	15.623	1075873	33834	50.134	55.153	1.102
2	30.613	1070101	27511	49.866	44.847	1.104

Asymmetric reaction: 97:3 er



#	tR [min]	Area [µV.sec]	Height [µV]	Area %	Height %	Symmetry Factor
1	15.304	740800	24868	3.336	5.125	1.116
2	30.336	21342378	471249	96.664	94.987	1.625

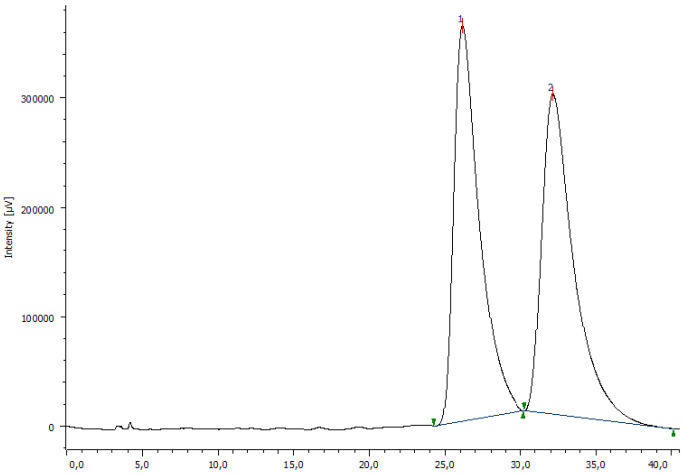
(*R*)-2-(2,4-dichlorophenyl)-2-hydroxy-1-(4-methoxyphenyl)-4-phenylbut-3-yn-1-one (6g)



6g

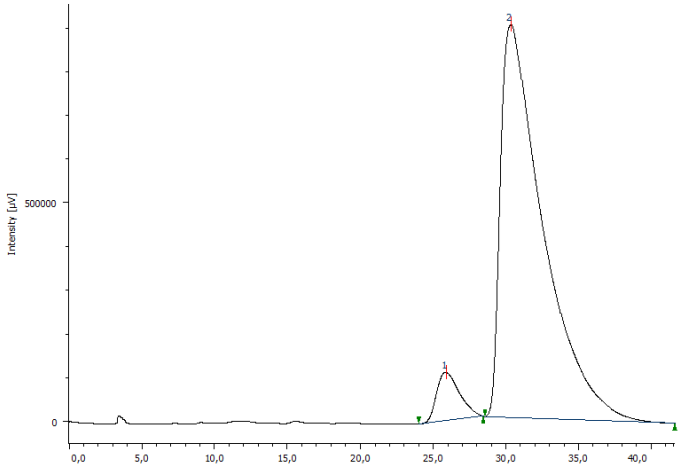
Chiralpak AS-H, hexane:isopropanol = 98:2, 1.0 mL min^{-1}, λ = 254 nm

Racemic compound



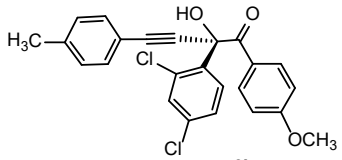
#	tR [min]	Area [µV.sec]	Height [µV]	Area %	Height %	Symmetry Factor
1	26.100	42872916	360589	50.021	55.214	1.867
2	32.108	42837095	292489	49.979	44.786	1.875

Asymmetric reaction: 94:6 er



#	tR [min]	Area [µV.sec]	Height [µV]	Area %	Height %	Symmetry Factor
1	25.833	11944713	110876	6.162	11.006	1.438
2	30.317	181899096	896541	93.838	88.994	2.870

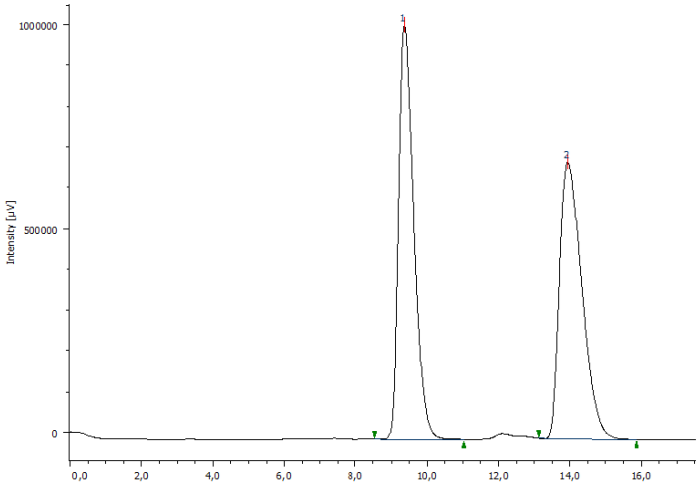
(*R*)-2-(2,4-dichlorophenyl)-2-hydroxy-1-(4-methoxyphenyl)-4-(p-tolyl)but-3-yn-1-one (6h)



6h

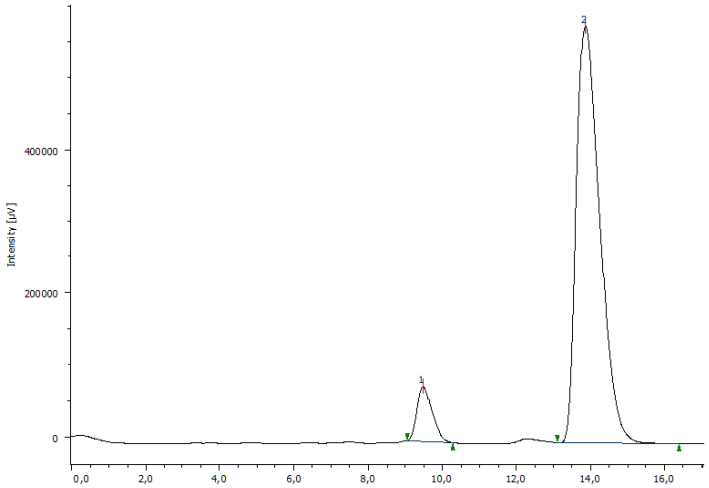
Chiralcel OD, hexane:isopropanol = 95:5, 1.0 mL min-1, λ = 254 nm

Racemic compound



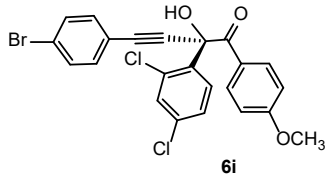
#	tR [min]	Area [µV.sec]	Height [µV]	Area %	Height %	Symmetry Factor
1	9.367	30322570	1013242	50.689	59.952	1.424
2	13.925	29498786	676834	49.311	40.048	1.548

Asymmetric reaction: 92:8 er



#	tR [min]	Area [µV.sec]	Height [µV]	Area %	Height %	Symmetry Factor
1	9.458	2143214	75316	7.798	11.532	1.386
2	13.842	25340977	577785	92.202	88.468	1.518

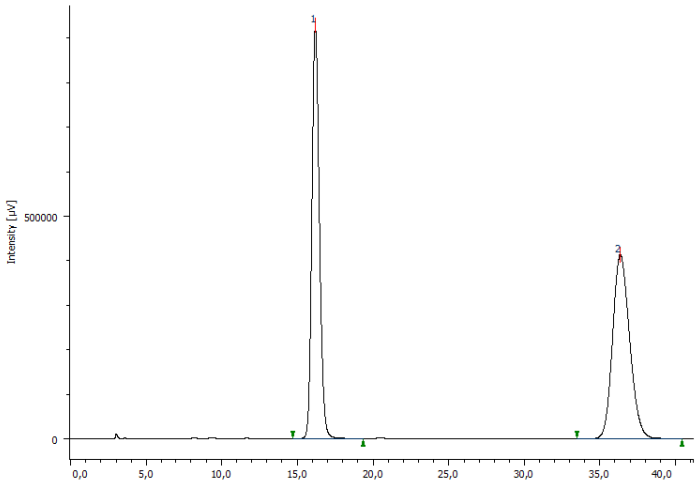
(*R*)-4-(4-bromophenyl)-2-(2,4-dichlorophenyl)-2-hydroxy-1-(4-methoxyphenyl)but-3-yn-1-one (6i)



6i

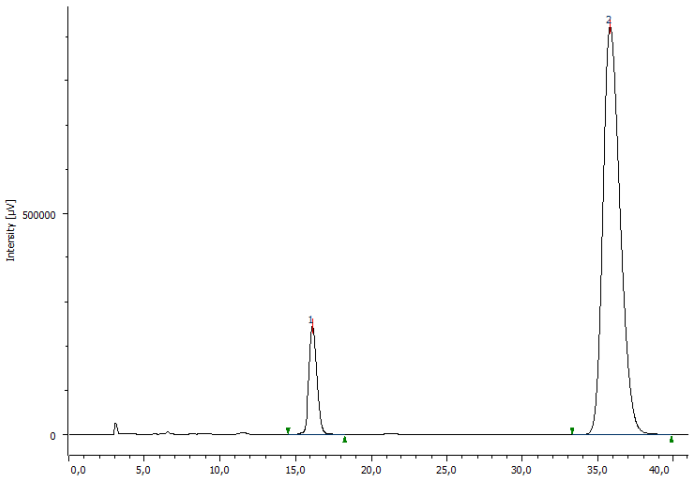
Lux-Cellulose-2, hexane:isopropanol = 95:5, 1.0 mL min-1, λ = 254 nm

Racemic compound



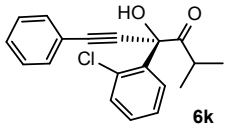
#	tR [min]	Area [µV.sec]	Height [µV]	Area %	Height %	Symmetry Factor
1	16.167	31837812	926004	49.836	69.246	1.175
2	36.308	32047438	411272	50.164	30.754	1.162

Asymmetric reaction: 98:11 er



#	tR [min]	Area [µV.sec]	Height [µV]	Area %	Height %	Symmetry Factor
1	16.108	9144864	244317	11.225	20.982	1.127
2	35.767	72326754	920079	88.775	79.018	1.265

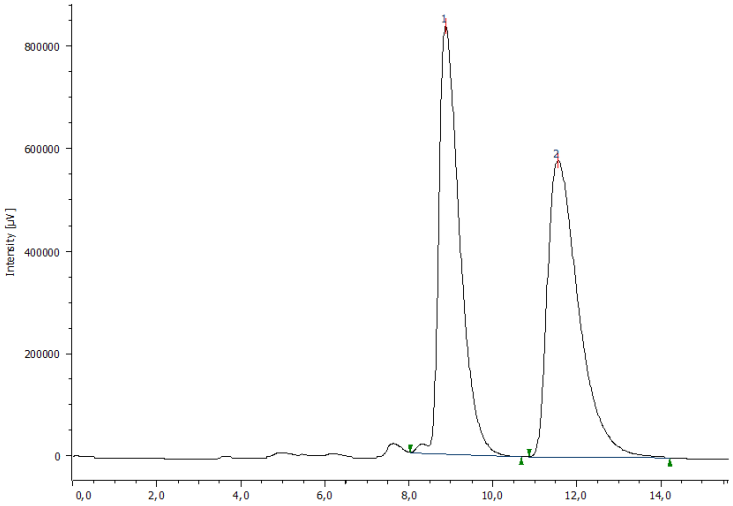
(R)-4-(2-chlorophenyl)-4-hydroxy-2-methyl-6-phenylhex-5-yn-3-one (6k)



6k

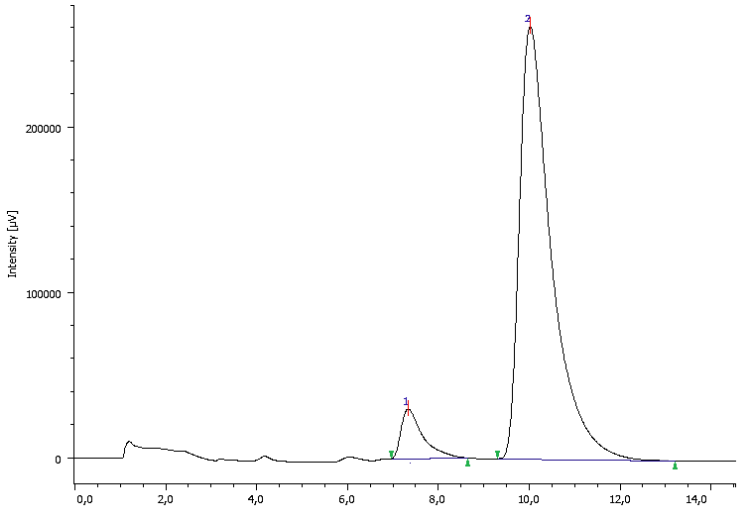
Chiralpak AS-H, hexane:isopropanol = 97:3, 1.0 mL min-1, λ = 254 nm

Racemic compound



#	tR [min]	Area [µV.sec]	Height [µV]	Area %	Height %	Symmetry Factor
1	8.867	28663811	832717	49.082	59.066	1.891
2	11.542	29735522	577098	50.918	40.934	1.862

Asymmetric reaction: 93:7 er



#	tR [min]	Area [µV.sec]	Height [µV]	Area %	Height %	Symmetry Factor
1	7.325	986741	29904	7.183	10.266	2.130
2	10.008	12750964	261398	92.817	89.734	1.967