Supplementary Information

Asymmetric Carbohydroxylation of Alkenes Using Photoenzymatic Catalysis

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Table of Contents

1. General information

General. Unless otherwise noted, all chemicals and reagents for chemical reactions were obtained from commercial suppliers and used as received (Sigma-Aldrich, Oakwood Chemical, Combi-Blocks, TCI, and VWR). GDH-105 was purchased as cell-free lysates from Codexis and were used as received. Silica gel chromatography purifications were carried out using AMD Silica Gel 60. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker UltraShield Plus (500 and 126 MHz, respectively) instrument, and are internally referenced to residual proton signals in $CDCl_3$ (7.26 ppm), CD_3CN (1.94 ppm) or CD_3OD (3.31 ppm). ^{19}F NMR spectra were recorded on a Bruker 282 MHz instrument. ^{1}H NMR data are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, dt = doublet of triplet, ddd = doublet of doublet of doublet), coupling constant (Hz), and integration. Data for ^{13}C NMR are reported in terms of chemical shift relative to $CDCl_3$ (77.16 ppm), CD_3CN (1.32 ppm and 118.26 ppm) or or CD_3OD (49.00 ppm). High resolution mass spectra (HRMS) were obtained on an Agilent 6220 LC/MS with an electrospray ionization time-of-flight (ESI-TOF) detector, or on an Agilent 7200 GC QTOF/MS with electron ionization mode, or on a Thermo Fisher Scientific Exactive series DART Mass Spectrometer.

Chromatography. Analytical high performance liquid chromatography (HPLC) and Electron Spray Ionization (ESI) mass spectrometry were carried out using an Agilent 1260 Infinity LCMS System. Yields and conversions were determined on a Poroshell C18 column (4.6 x 50 mm, 2.7 μm) against an internal standard 1,3,5-tribromobenzene (TBB) at 210 nm. Chiral HPLC was conducted using an Agilent 1260 Infinity Chiral HPLC system with isopropanol and hexanes as the mobile phases. Chiral OJ-H, OD-H, IA-H, IB-H, IC-H, and AS-H columns were used to separate enantiomers (4.6 x 250 mm, 5 μm).

Cloning. pET22b (+) was used as a cloning and expression vector for all enzymes described in this study. Genes for all 'ene'-reductases were purchased as gBlocks from IDT and cloned using the Gibson cloning method.[1] All C-terminal 6xHis tagged constructs were cloned directly between the NdeI and XhoI restriction sites. N-terminal 6xHis tagged constructs were created by the introduction of an N-terminal 6xHis sequence directly after the NdeI site and replacement of the C-terminal 6xHis tag with an XhoI cut site. Cloned plasmids were transformed into *E. coli.* DH5-α cells for storage, and *E. coli.* BL21 (DE3) electrocompetent cells for expression.

Protein and DNA Sequence.

Morphinone reductase (MorB). UniProtKB-Q51990 (Q51990_PSEPU)
Genebank accession number: AAC43569

Protein Sequence:

MPDTSFSNPGLFTPLQLGSLSLPNRVIMAPLTRSRTPDSVPGRLQQIYYGQRASAGLIISEATN
ISPTARGYVYTPGIWTDAQEAGWKGVVEAVHAKGGRIALQLWHVGRVSHELVQPDGQQP
VAPSALKAEGAECFVEFEDGTAGLHPTSTPRALETDEIPGIVEDYRQAAQRAKRAGFDMVE
VHAANACLPNQFLATGTNRRTDQYGGSIENRARFPLEVVDAVAEVFGPERVGIRLTPFLELF
GLTDDEPEAMAFYLAGELDRRGLAYLHFNEPDWIGGDITYPEGFREQMRQRFKGGLIYCG
NYDAGRAQARLDDNTADAVAFGRPFIANPDLPERFRLGAALNEPDPSTFYGGAEVGYTDY
PFLDNGHDRLGHHHHHH

DNA Sequence:

ATGCCCGACACTTCTTTTTCGAATCCAGGACTTTTTACTCCTCTTCAGTTGGGTAGTCTGTC
TCTTCCAAATCGTGTCATAATGGCACCTTTAACCCGCTCACGCACGCCAGATTCTGTACCT
GGACGCCTTCAACAGATATACTATGGTCAACGCGCCAGCGCCGGGTTAATCATCTCCGAA
GCGACAAATATCAGTCCCACCGCTCGGGGATACGTATACACGCCAGGCATTTGGACTGAC
GCTCAGGAGGCCGGTTGGAAAGGTGTGGTCGAAGCTGTCCATGCTAAAGGGGGTCGTATA
GCGTTGCAGTTATGGCATGTCGGCCGGGTCTCTCATGAGCTGGTGCAGCCAGACGGCCAA
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GATGGGACTGCTGGCCTGCACCCTACGTCAACTCCCAGAGCCCTGGAGACAGATGAGATA
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TTCCTGGAGTTATTTGGATTAACGGATGATGAACCCGAGGCAATGGCTTTTTACCTTGCGG
GAGAATTAGACCGGCGTGGTTTAGCGTATTTACACTTTAATGAACCCGATTGGATAGGTG
GGGACATCACGTACCCGGAAGGGTTTCGTGAGCAAATGCGTCAACGGTTCAAGGGGGGGC
TTATATATTGTGGAAACTACGACGCAGGTCGGGCCCAAGCCCGGCTTGACGACAATACAG
CAGATGCAGTGGCGTTTGGGCGTCCATTTATTGCCAACCCCGACTTGCCAGAACGTTTCCG
CTTAGGAGCAGCGCTGAACGAACCTGACCCCTCTACTTTTTACGGCGGGGCAGAGGTGGG
GTACACAGACTACCCGTTCCTGGACAACGGTCATGACCGCCTGGGACTCGAGCACCACCA
TCACCACCACTGA

Caulobacter segnis Alkene Reductase (CsER).

GenBank accession number: A0A2W5V2R8

CsER protein sequence:

MPNLFDPLRVGDLNLPNRVVMAPLTRLRAGPTHIPNALMAEYYGQRASAGLLITEGVPVAPQ
GVGYAGVPGIWSKEQTEGWKQVTKAVHDKGGRIFMQIWHVGRISDPELLNGELPIAPSAIAA
KGHVSLLRPQRDYPTPRALSTEEVAGVVEAFRQGAENAQAAGFDGVQLHGANGYLLDQFLQ

DGSNQRTDQYGGSIENRARLLLEAADAAISVWGADRVGVHLAPRADSHSMGDSNLAATFGH
VAKALGERKIGFVSAREYEAADSLGPDLKKAFGGVYIANEKFDLASANAAIEAGKADAIAFGK
AYIANPDLVERLKAGAALNTPDPATFYGFENGPRGYTDYPTLAQVREPALEHHHHHH.

CsER DNA sequence:

ATGCCGAATTTGTTTGATCCGCTTCGTGTGGGAGACCTTAATTTGCCTAATCGTGTCGTGA
TGGCACCCCTGACTCGCTTACGCGCTGGTCCTACACACATCCCGAACGCTCTGATGGCAGA
ATACTATGGGCAGCGTGCAAGTGCAGGCTTACTTATTACGGAGGGAGTTCCAGTGGCGCC
CCAAGGGGTTGGGTACGCTGGTGTTCCTGGAATTTGGTCCAAGGAACAGACCGAAGGCTG
GAAGCAAGTCACAAAAGCTGTCCACGACAAGGGCGGCCGCATCTTCATGCAAATCTGGCA
CGTTGGCCGCATCAGCGACCCGGAGTTGTTAAACGGAGAATTGCCGATTGCGCCAAGTGC
TATTGCCGCTAAAGGACATGTAAGCCTTTTACGCCCGCAACGCGATTACCCTACCCCCCGT
GCACTTTCAACCGAGGAGGTGGCAGGAGTAGTCGAAGCCTTCCGTCAGGGTGCTGAAAAT
GCTCAGGCAGCGGGCTTTGACGGGGTCCAGTTGCATGGAGCTAACGGCTACCTTTTGGAT
CAGTTTTTACAGGACGGGAGTAATCAACGCACGGATCAGTATGGGGGTTCGATTGAGAAC
CGTGCCCGCCTGCTGTTGGAGGCAGCCGATGCGGCAATTAGCGTCTGGGGAGCAGATCGC
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GCGACCTTTGGTCACGTAGCGAAGGCATTAGGGGAGCGCAAGATCGGTTTTGTCAGCGCA
CGCGAATATGAGGCCGCTGACTCTTTGGGACCGGATTTGAAGAAAGCATTCGGAGGAGTT
TATATTGCGAATGAGAAATTTGATCTTGCGTCTGCTAACGCCGCTATTGAGGCAGGCAAA
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AAGCCGGGGCAGCTTTAAACACCCCGGATCCGGCGACTTTCTATGGCTTCGAAAATGGTC
CTCGCGGGTATACGGATTACCCTACCTTGGCTCAGGTCCGCGAGCCCGCCCTCGAGCACCA
CCATCACCACCACTGA

Old yellow enzyme 2 (OYE2) from *Saccharomyces cerevisiae*.
Genbank accession number: AAA83386.1
OYE2 protein sequence:
MPFVKDFKPQALGDTNLFKPIKIGNNELLHRAVIPPLTRMRAQHPGNIPNRDWAVEYYAQRAQ
RPGTLIITEGTFPSPQSGGYDNAPGIWSEEQIKEWTKIFKAIHENKSFAWVQLWVLGWAAFPDT
LARDGLRYDSASDNVYMNAEQEEKAKKANNPQHSITKDEIKQYVKEYVQAAKNSIAAGADG
VEIHSANGYLLNQFLDPHSNNRTDEYGGSIENRARFTLEVVDAVVDAIGPEKVGLRLSPYGVF
NSMSGGAETGIVAQYAYVLGELERRAKAGKRLAFVHLVEPRVTNPFLTEGEGEYNGGSNKFAY
SIWKGPIIRAGNFALHPEVVREEVKDPRTLIGYGRFFISNPDLVDRLEKGLPLNKYDRDTFYKMS
AEGYIDYPTYEEALKLGWDKNHHHHHH.

OYE2 DNA sequence:
ATGCCCTTCGTGAAAGACTTCAAACCTCAAGCCCTGGGCGATACTAATTTATTTAAGCCAAT
TAAAATTGGAAACAATGAGTTGTTACACCGCGCTGTAATTCCACCCTTAACCCGCATGCGCG
CCCAACATCCAGGGAACATCCCTAATCGCGATTGGGCAGTCGAGTACTATGCTCAGCGTGCT
CAGCGTCCGGGTACCCTTATCATCACGGAAGGAACGTTTCCGTCGCCGCAATCGGGAGGGT
ATGACAACGCTCCCGGTATCTGGTCGGAAGAACAGATTAAAGAATGGACCAAAATCTTTAA
AGCAATTCATGAGAATAAATCTTTCGCCTGGGTCCAACTTTGGGTCCTGGGCTGGGCAGCC
TTCCCTGACACATTGGCGCGTGACGGGCTTCGTTATGATAGTGCTTCGGATAACGTGTATATG

AATGCTGAACAAGAAGAAAAGGCAAAAAAAGCAAACAATCCACAGCATTCGATTACTAAA
GACGAGATTAAGCAGTATGTTAAGGAATACGTACAAGCAGCAAAGAATTCTATTGCCGCAG
GGGCGGACGGGGTAGAAATCCACTCTGCTAATGGGTACTTGCTTAACCAGTTCCTGGACCC
GCATTCAAACAACCGCACTGATGAGTACGGAGGGTCCATCGAAAATCGTGCACGTTTTACT
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CGCATACGTCTTGGGAGAGCTGGAGCGTCGTGCTAAGGCTGGCAAGCGTTTAGCTTTTGTG
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GAGGATCGAATAAATTTGCGTATTCCATTGGAAGGGCCCGATCATTCGTGCCGGTAACTTTG
CCTTACATCCCGAAGTTGTTCGCGAGGAAGTAAAAGACCCACGTACCTTGATCGGGTATGG
CCGTTTCTTTATTTCAAACCCCGACTTGGTGGATCGCCTTGAAAAAGGTCTTCCCTTGAATA
AGTATGACCGTGATACGTTCTACAAAATGTCAGCCGAAGGTTACATCGACTACCCCACCTAC
GAAGAGGCTTTGAAACTTGGTTGGGACAAGAACCACCACCATCACCACCACTGA.

Gluconobacter oxydans enoate reductase (GluER) from *Gluconobacter oxydans 621H*.
Genbank accession number: AAW60280

GluER protein sequence:
MHHHHHHPTLFDPIDFGPIHAKNRIVMSPLTRGRADKEAVPTPIMAEYYAQRASAGLIITEATGI
SREGLGWPFAPGIWSDAQVEAWKPIVAGVHAKGGKIVCQLWHMGRMVHSSVTGTQPVSSSAT
TAPGEVHTYEGKKPFEQARAIDAADISRILNDYENAARNAIRAGFDGVQIHAANGYLIDEFLRN
GTNHRTDEYGGVPENRIRFLKEVTERVIAAIGADRTGVRLSPNGDTQGCIDSAPETVFVPAAKL
LQDLGVAWLELREPGPNGTFGKTDQPKLSPQIRKVFLRPLVLNQDYTFEAAQTALAEGKADAI
AFGRKFISNPDLPERFARGIALQPDDMKTWYSQGPEGYTDYPSATSGPN.

GluER DNA sequence:
ATGCACCACCATCACCACCACCCGACCCTTTTCGACCCCATCGATTTCGGACCTATCCACGC
CAAGAATCGTATCGTCATGTCCCCCCTGACTCGCGGTCGCGCTGACAAAGAGGCGGTTCCA
ACCCCCATTATGGCTGAATACTACGCCCAACGCGCTTCGGCGGGTTTAATTATCACTGAAGC
GACGGGGATTTCACGCGAAGGCTTAGGTTGGCCGTTTGCGCCGGGAATTTGGTCCGATGCA
CAGGTTGAGGCGTGGAAACCTATCGTCGCGGGTGTCCATGCAAAGGGCGGCAAGATCGTAT
GTCAGCTTTGGCATATGGGCCGTATGGTACATTCTTCAGTTACAGGGACGCAGCCCGTAAGC
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AAGCGCGTGCAATCGATGCTGCAGACATCTCCCGCATCCTTAACGATTACGAAAATGCAGC
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TCCAGACTTGCCTGAGCGCTTTGCCCGTGGCATCGCACTGCAACCAGACGATATGAAAACA
TGGTACTCCCAAGGCCCAGAGGGTTACACAGACTATCCATCCGCAACTTCTGGGCCGAACT

GA.

Geobacillus kaustophilus old yellow enzyme (GkOYE).
UniProtKB accession number: Q5KXG9.

GkOYE protein sequence
MNTMLFSPYTIRGLTLKNRIVMSPMCMYSCDTKDGAVRTWHKIHYPARAVGQVGLIIVEATGV
TPQGRISERDLGIWSDDHIAGLRELVGLVKEHGAAIGIQLAHAGRKSQVPGEIIAPSAVPFDDSSP
TPKEMTKADIEETVQAFQNGARRAKEAGFDVIEIHAAHGYLINEFLSPLSNRRQDEYGGSPENR
YRFLGEVIDAVREVWDGPLFVRISASDYHPDGLTAKDYVPYAKRMKEQGVDLVDVSSGAIVPA
RMNVYPGYQVPFAELIRREADIPTGAVGLITSGWQAEEILQNGRADLVFLGRELLRNPYWPYA
AARELGAKISAPVQYERGWRFLEHHHHH.

GkOYE DNA sequence
ATGAATACAATGTTGTTCAGTCCTTATACAATCCGTGGTCTGACACTGAAAAACAGAATTGT
GATGTCTCCCATGTGCATGTATTCCTGCGACACCAAAGATGGCGCAGTCCGTACATGGCACA
AAATTCATTATCCGGCGCGTGCAGTGGGCCAGGTAGGCCTGATTATTGTGGAAGCAACAGG
TGTGACTCCGCAGGGCCGTATCTCCGAACGCGATTTGGGAATCTGGTCAGACGACCATATTG
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GTTCGCTGAACTTATTAGAAGAGAAGCGGACATTCCTACAGGAGCGGTTGGTCTGATTACG
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GCGAACTGCTGCGGAATCCCTATTGGCCCTACGCGGCTGCCAGAGAACTGGGAGCCAAGAT
TTCCGCGCCAGTTCAATACGAGCGCGGGTGGAGATTTCTCGAGCACCACCACCACCACCAC
TGA.

Nicotinamide-dependent cyclohexanone reductase (NCR) from *Zymomonas mobiles*.
GenBank accession number: AAV90509.

NCR protein sequence:
MPSLFDPIRFGAFTAKNRIWMAPLTRGRATRDHVPTEIMAEYYAQRASAGLIISEATGISQEGLG
WPYAPGIWSDAQVEAWLPITQAVHDAGGLIFAQLWHMGRMVPSNVSGMQPVAPSASQAPGLG
HTYDGKKPYDVARALRLDEIPRLLDDYEKAARHALKAGFDGVQIHAANGYLIDEFIRDSTNHR
HDEYGGAVENRIRLLKDVTERVIATIGKERTAVRLSPNGEIQGTVDSHPEQVFIPAAKMLSDLDI
AFLGMREGAVDGTFGKTDQPKLSPEIRKVFKPPLVLNQDYTFETAQAALDSGVADAISFGRPFI
GNPDLPRRFFEKAPLTKDVIETWYTQTPKGYTDYPLLGDHHHHHH.

NCR DNA sequence:
ATGCCGTCACTGTTCGATCCAATCCGCTTTGGGGCTTTCACTGCAAAAAATCGTATCTGGAT
GGCGCCGTTAACACGGGGTCGGGCAACCCGTGACCATGTCCCAACAGAGATAATGGCTGA
ATACTATGCCCAACGCGCATCCGCGGGCTTGATCATCAGCGAGGCGACCGGGATCAGCCAA
GAGGGCCTGGGCTGGCCCTATGCACCAGGAATCTGGAGTGATGCGCAGGTCGAGGCATGG
TTACCCATAACCCAAGCGGTACACGATGCCGGAGGTTTGATATTTGCACAACTGTGGCACAT
GGGGCGTATGGTGCCTTCCAACGTTTCTGGAATGCAACCTGTCGCACCTAGCGCTTCACAA
GCGCCCGGCTTGGGCCATACTTATGATGGCAAAAAGCCATACGATGTAGCCAGAGCATTGA
GACTTGACGAGATCCCACGGCTGCTGGACGACTATGAAAAGGCAGCTCGGCACGCACTGA
AAGCTGGGTTCGATGGAGTTCAGATTCATGCTGCCAACGGATACCTGATTGACGAGTTCATC
CGGGATTCAACAAATCATAGACACGACGAATACGGGGGGGCGGTTGAGAACAGAATACGG
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GTTTAAGTCCGAATGGAGAGATACAAGGCACAGTAGACTCGCATCCAGAACAGGTATTTAT
CCCGGCTGCAAAGATGTTATCTGATTTAGATATCGCGTTCCTTGGGATGCGCGAGGGTGCTG
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CAAGCCACCCCTTGTTCTGAATCAAGATTACACTTTCGAGACTGCCCAGGCTGCGTTAGATT
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AGATTCTTTGAAAAGGCACCGTTAACTAAGGACGTAATTGAGACTTGGTACACTCAGACTC
CCAAAGGTTACACCGACTATCCACTGTTAGGTGATCTCGAGCACCACCATCACCACCACTG
A

The detailed expression and purification information of other tested ‘ene’-reductases in this study, namely old yellow enzyme 2 (OYE2), gluconobacter oxydans enoate reductase (GluER), Geobacillus kaustophilus old yellow enzyme (GKOYE), Caulobacter segnis Alkene Reductase (CSER) and Nicotinamide-dependent cyclohexanone reductase (NCR), were described elsewhere[2-5].

MorB Protein Expression and Purification.

Morphinone reductase (MorB) was produced in *E. coli* BL21 transformed with plasmid encoding MorB. Transformed glycerol stocks were used to initiate a 5 mL overnight culture in Luria-Bertani (LB) media with ampicillin (100 µg/mL at 37 °C and 250 rpm. Expression culture (500 mL in a 2 L baffled shake flask) containing ampicillin (100 µg/mL) and autoinducing mixtures (sterile filtered mixture of 1% glucose, 4% lactose and 15% glycerol, 40 mL/L media) was inoculated with 5 mL of the overnight culture, then grown at 30 ºC and 250 rpm for 24 h. The cells were harvested by centrifugation (4000 x g, 20 min, 4 °C) and frozen at -80 °C for further purification.

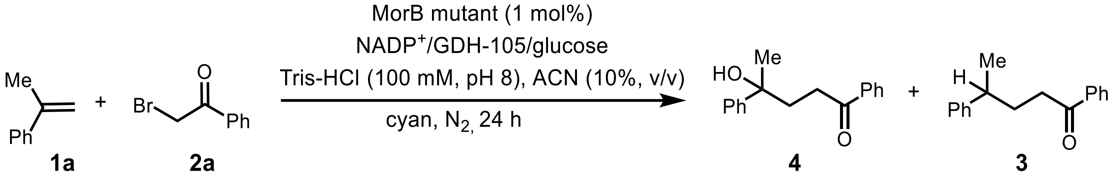
Frozen cells were thawed and resuspended in buffer A (20 mM KPi pH 7, 300 mM NaCl, 25 mM imidazole) to a final concentration of 2 mL/g of wet cells. The resuspended cells were supplemented with lysozyme (1 mg/mL), FMN (1 mg/mL), DNase I (0.1 mg/mL), phenylmethylsulfonyl fluoride (PMSF, 1 mM) and allowed to shake for 30 min at 37 ºC. The cells were further disrupted by sonication (2 x 4 min, output control 5, 35% duty cycle, Sonicator QSonica Q500 Ultra Sonicator). Lysates were centrifuged (20,000 x g, 1 h, 4 °C) to pellet insoluble materials. Proteins were purified using a nickel-NTA column (5 mL HisTrap HP, GE Healthcare, Piscataway, NJ) *via* an AKTAStart purifier FPLC system (GE

Healthcare). Enzymes were eluted with buffer B (20 mM KPi pH 7, 300 mM NaCl, 250 mM imidazole) over five column volumes. Yellow fractions containing MorB enzymes were pooled, concentrated through buffer exchange into an imidazole free storage buffer (20 mM KPi, pH 7, 300 mM NaCl). Concentrated enzymes were aliquoted, flash-frozen in liquid N_2, and then stored at -80 °C until later use. Protein purity was assessed with SDS-PAGE.

Protein concentrations were determined using the extinction coefficient (12.2 x mM^{-1} cm^{-1} at 446 nm) for free FMN released after protein denaturation. Extinction coefficient for MorB: $\varepsilon = 10.7$ x mM^{-1} cm^{-1} at 463 nm. Both the WT and the final mutant MorB-B3 expressed pretty well, with approximate yield of 150 mg protein/L culture.

2. Detailed experimental procedures

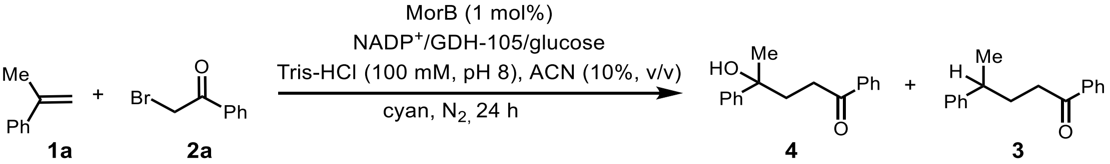
Supplementary Table 1. Initial panel of 'ene'-reductases screened for carbohydroxylation.



entry	'ene'-reductases	yield[a] of **4**	er[b]	yield[a] of **3**
1	GluERT36A	26%	62:38	29%
2	NCR	10%	59:41	18%
3	MorB	45%	75:25	10%
4	CSAR	7%	58:42	29%
5	GKOYE	4%	n.d.[c]	2%
6	OYE2	10%	66:34	26%
7	No enzyme	0%	n.d.[c]	0

Reaction conditions: α-methylstyrene (1.3 uL, 0.01 mmol, 1.0 eq, 16.6 mM), α-bromoketone (5.94 mg, 0.03 mmol, 3 eq), GDH-105 (0.12 mg), NADP$^+$ (0.4 mg), glucose (1.8 mg) and purified 'ene'-reductases (1 mol% based on α-methylstyrene) in 100 mM Tris-HCl buffer pH 8.0, with 10% CH_3CN (*v/v*) as cosolvent, final total volume is 660 µL. Reaction mixtures were stirred under anaerobic conditions and irradiated with cyan LED at room temperature for 24 h. [a] Yield determined via LCMS relative to an internal standard (TBB). [b]Enantiomeric ratio (er) determined by HPLC on a chiral stationary phase. [c]n.d., not determined.

Supplementary Table 2. Control experiments.



entry	variation	yield[a] of **4**	er[b]	yield[a] of **3**
1	-	45%	75:25	10%
2	w/o cofactor regeneration	28%	75:25	3%
3	50% glucose	26%	75:25	2%
4	w/o MorB, 1% FMN	2%	50:50	0
5	blue Kessil	32%	75:25	8%
6	dark	14%	75:25	trace
7	w/o cofactor regeneration, dark	0	n.d.[c]	0

Reaction conditions: α-methylstyrene (1.3 uL, 0.01 mmol, 1.0 eq, 16.6 mM), α-bromoketone (5.94 mg, 0.03 mmol, 3 eq), GDH-105 (0.12 mg), NADP$^+$ (0.4 mg), glucose (1.8 mg) and purified ‘ene’-reductases (1 mol% based on α-methylstyrene) in 100 mM Tris-HCl buffer pH 8.0, with 10% CH_3CN (*v*/*v*) as cosolvent, final total volume is 660 µL. Reaction mixtures were stirred under anaerobic conditions and irradiated with cyan LED at room temperature for 24 h. [a] Yield determined via LCMS relative to an internal standard (TBB). [b]Enantiomeric ratio (er) determined by HPLC on a chiral stationary phase. [c]n.d., not determined.

Site Saturation Mutagenesis of MorB catalysts for carbohydroxylation

Site saturation mutagenesis primers were designed using the PCR protocol from Kille *et al*[6]. The PCR products were digested with DpnI, repaired using Gibson Mix™, and used to directly transform *E. coli.* BL21 electrocompetent cells and plated on LB agar plates containing ampicillin (100 µg/mL).

Screening procedure for carbohydroxylation with MorB mutants in 96-well plates

Single colonies were picked with sterile toothpicks and used to inoculate 500 µL of LB media containing ampicillin (100 µg/mL) in deep-well 96-well plates, and cultured overnight (30 °C, 250 rpm). Wells A2, B4, C6, D8, E10, F12, and G2 were embedded controls of the parent protein for that round of engineering. Well H12 was used as blank control. A glycerol stock plate of the library was prepared by mixing sterilized glycerol solution (50% *v*/*v*, 50 µL/well) with the overnight cell cultures (50 µL/well). The library was sealed and stored at -80 °C. The expression cultures (950 µL of autoinducing Turbo Broth™ media containing 100 µg/mL of ampicillin) in 96-well plates were inoculated by adding 50 µL of the overnight cultures, and grown for 24 h (30 ºC, 250 rpm). After growth and expression, cells were harvested by centrifugation (4000 x g, 20 min, 4 °C) and frozen at -80 ºC for later screening.

The cell libraries were thawed and resuspended with lysis buffer (100 µL/well) and allowed to shake for 1 h at 30 ºC. The crude cell lysates were centrifuged (4000 x g, 20 min, 4 °C) and the supernatants (90 µL/well) were transferred into a new white plastic 96-well plate for screening assay immediately.

In the Coy$^{@}$ chamber, the freshly prepared cofactor regeneration mix (38 µL/well) and substrates (alkene: 0.4 mg/well, bromoacetophenone: 2 mg/well in 10 µL CH_3CN) were added to the supernatants (90 µL/well), and the 96-well plate was sealed with adhesive plate-sealing film and shaken under anaerobic conditions with a fan cooling and irradiated using a Lumidox 96-well Cyan LED array at room temperature for 20 h. Upon completion, the reaction was quenched with acetonitrile (700 µL/well), and the plate was sealed with a reusable silicone mat, shaken for 60 min, and centrifuged (4500 × g, 20 min). The supernatant (200 µL/well) was filtered through a Millipore 96-well filter plate into a shallow-well plate (1000 x g, 1 min), and the filtrate was retained for LCMS analysis. Promising hits were chosen and subjected to cultivation in shaking flasks for further confirmation. The DNA plasmids of hits were extracted and submitted for sequencing to identify their mutations.

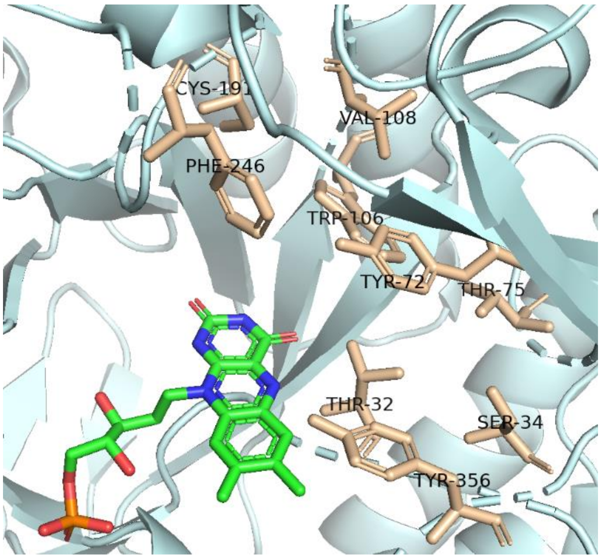
Recipe for Auto Inducing TB Media. For autoinducing cultures, Turbo Broth^{TM} media was supplemented with a sterile-filtered solution of 1.25% glucose, 5% lactose, and 15% glycerol (40 mL/L media).

Lysis buffer. 100 mM Tris-HCl (pH 8.0) buffer containing lysozyme (1 mg/mL), DNase I (0.1 mg/mL), FMN (1 mg/mL), and PMSF (1 mM).

cofactor regeneration. 100 mM Tris-HCl (pH 8.0) buffer containing GDH-105 (1.25 mg/mL), FMN (0.5 mg/mL), $NADP^+$ (8.5 mg/mL), and glucose (108 mg/mL).

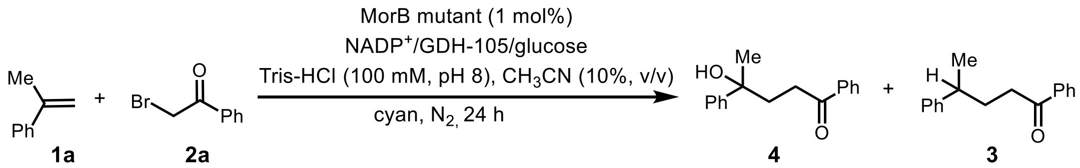
Site saturation mutagenesis **Round 1**

Supplementary Table 3. Template and target sites of the 1st round of SSM on MorB



Template	Target sites	Beneficial mutations
MorB-WT	Y72, C191, F246, S34, T32, T75,	Y72C
	V108, W106, N189, F246, Y356	F246T
		F246P
		N189S

Supplementary Table 4. Summary of the 1st round of SSM on MorB for carbohydroxylation.



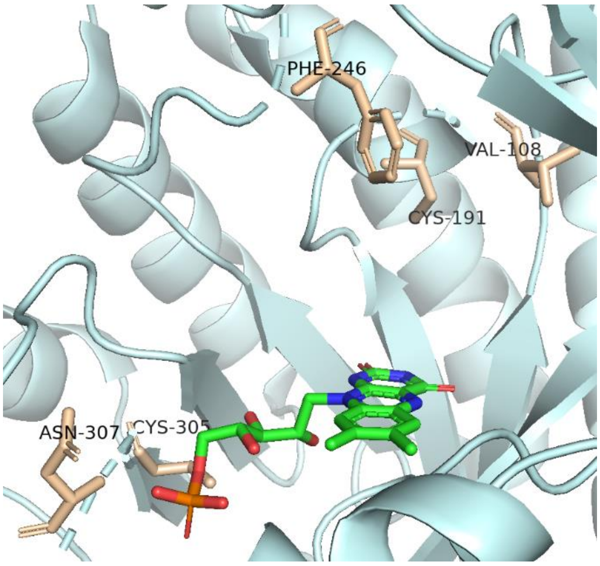
Entry	MorB mutants	Yield of **4** (%)^a	er^b	Yield of **3** (%)^a
1	WT	45	75:25	10
2	Y72C	66	79:21	9
3	F246T	44	77:23	6
4	F246P	53	76:24	8
5	N189S	56	77:23	8

Reaction conditions: α-methylstyrene (0.65 uL, 0.005 mmol, 1.0 eq, 8.3 mM), α-bromoketone (2.98 mg, 0.015 mmol, 3.0 eq), GDH-105 (0.06 mg, 10 wt%), NADP$^+$ (0.2 mg, 5 mol%), glucose (0.9 mg, 1.0 eq) and purified ‘ene’-reductases (1 mol% based on α-methylstyrene) in 100 mM Tris-HCl buffer pH 8.0, with 10% CH_3CN (*v*/*v*) as cosolvent, final total volume is 600 μL. Reaction mixtures were stirred under anaerobic conditions and irradiated with cyan LED at room temperature for 24 h. ^{a} Yield determined via LCMS relative to an internal standard (TBB). ^{b} Enantiomeric ratio (er) determined by

HPLC on a chiral stationary phase.

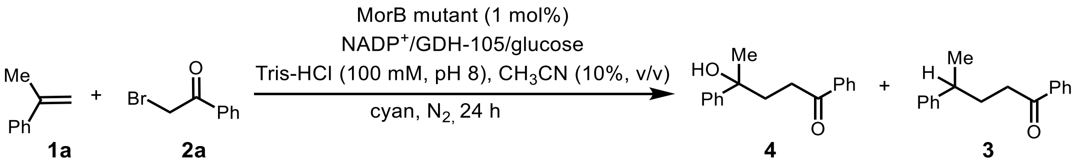
Site saturation mutagenesis **Round 2**

Supplementary Table 5. Templates and target sites of the 2nd round of SSM on MorB for carbohydroxylation.



Template	Target sites	Beneficial mutations
Y72C	C191, F246, V108, C305, N307	Y72C/C191G
		Y72C/C191D
		Y72C/F246L
		Y72C/N307D

Supplementary Table 6. Summary of the 2nd round of SSM on MorB for carbohydroxylation.

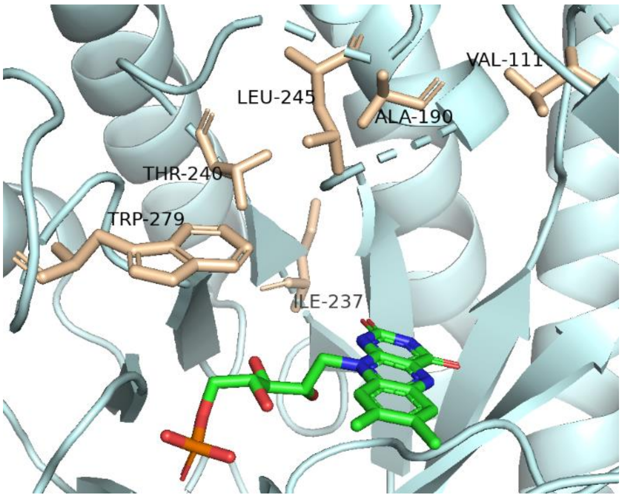


Entry	MorB mutants	Yield of **4** (%)[a]	er[b]	Yield of **3** (%)[a]
1	Y72C	66	79:21	9
2	Y72C/C191G	74	80:20	6
3	Y72C/C191D	70	80:20	6
4	Y72C/F246L	66	78:22	7
5	Y72C/N307D	70	80:20	14

Reaction condition is described in Supplementary Table 4.

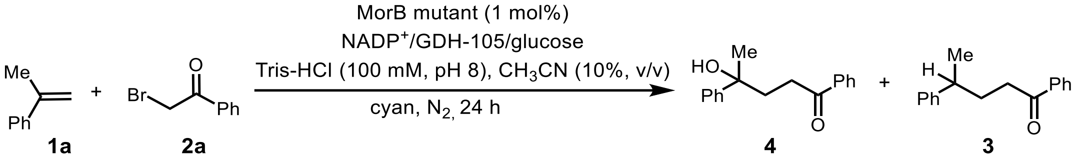
Site saturation mutagenesis **Round 3**

Supplementary Table 7. Templates and target sites of the 3rd round of SSM on MorB for carbohydroxylation.



Template	Target sites	Beneficial mutations
Y72C/C191G	A190, V111, T240, W279, L245, I237	Y72C/C191G/T240E Y72C/C191G/T240Q Y72C/C191G/V111T Y72C/C191G/V111G

Supplementary Table 8. Summary of the 3rd round of SSM on MorB for carbohydroxylation.

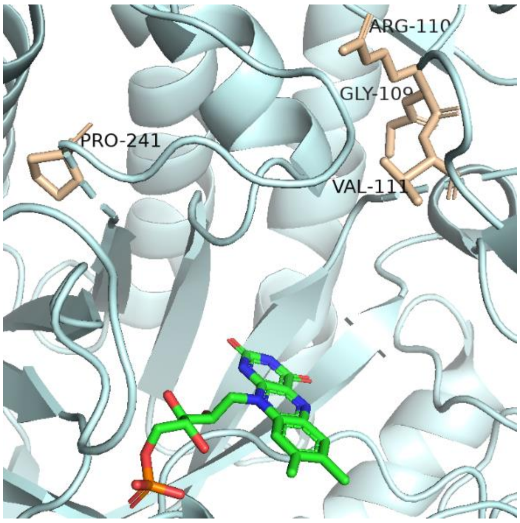


Entry	MorB mutants	Yield of **4** (%)^a	er^b	Yield of **3** (%)^a
1	Y72C/C191G	74	80:20	6
2	Y72C/C191G/T240E	86	86:14	4
3	Y72C/C191G/T240Q	81	80:20	5
4	Y72C/C191G/V111T	86	83:17	6
5	Y72C/C191G/V111G	90	79:21	8

Reaction condition is described in Supplementary Table 4.

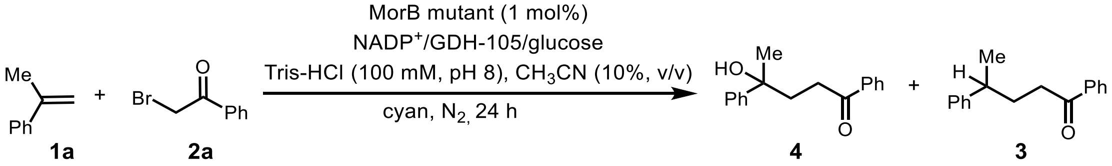
Site saturation mutagenesis **Round 4**

Supplementary Table 9. Templates and target sites of the 4th round of SSM on MorB for hydroxylation.



Template	Target sites	Beneficial mutations
Y72C/C191G/T240E	G109, R110, R111, P241	Y72C/C191G/T240E/R110L 72C/C191G/T240E/R110Q Y72C/C191G/T240E/P241M

Supplementary Table 10. Summary of the 4th round of SSM on MorB for carbohydroxylation.

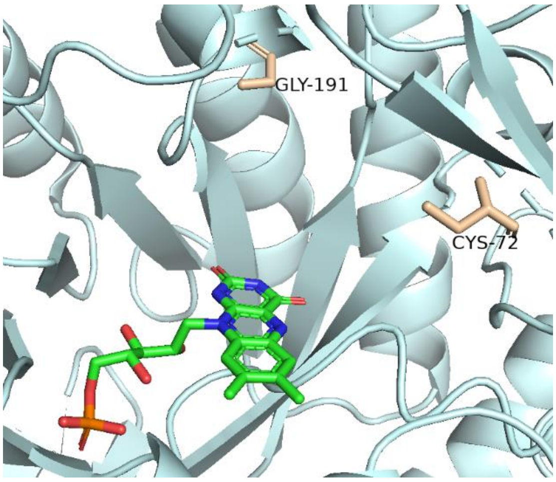


Entry	MorB mutants	Yield of **4** (%)[a]	er[b]	Yield of **3** (%)[a]
1	Y72C/C191G/T240E	80	85:15	4
2	Y72C/C191G/T240E/R110C	81	87:13	3
3	Y72C/C191G/T240E/R110L	83	87:13	3
4	Y72C/C191G/T240E/R110Q	79	87:13	3
5	Y72C/C191G/T240E/P241M	72	87:13	3

Reaction condition is the same as described in Supplementary Table 4.

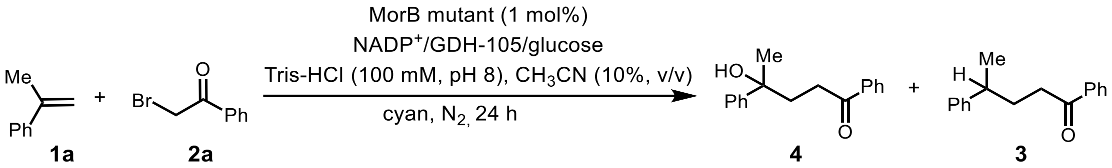
Site saturation mutagenesis **Round 5**

Supplementary Table 11. Templates and target sites of the 5th round of SSM on MorB for carbohydroxylation.



Template	Target sites	Beneficial mutations
Y72C/C191G/T240E/R110L	C72	Y72C/C191G/T240E/R110L/C72T Y72C/C191G/T240E/R110L/C72Q Y72C/C191G/T240E/R110L/C72E

Supplementary Table 12. Summary of the 5th round of SSM on MorB for carbohydroxylation.

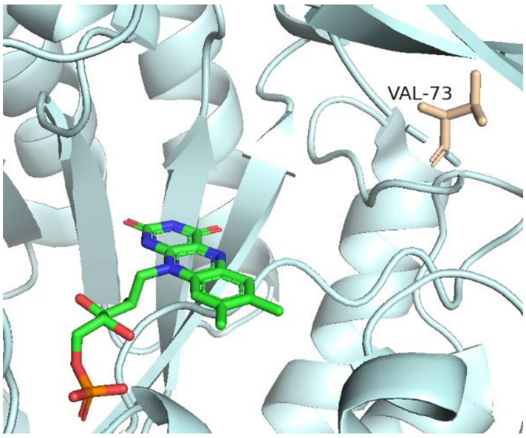


Entry	MorB mutants	Yield of **4** (%)^a	er^b	Yield of **3** (%)^a
1	Y72C/C191G/T240E/R110L	83	87:13	3
2	Y72C/C191G/T240E/R110L/C72Q	92	92:8	3
3	Y72C/C191G/T240E/R110L/C72T	94	92:8	3
4	Y72C/C191G/T240E/R110L/C72E	86	91:9	3

Reaction condition is the same as described in Supplementary Table 4.

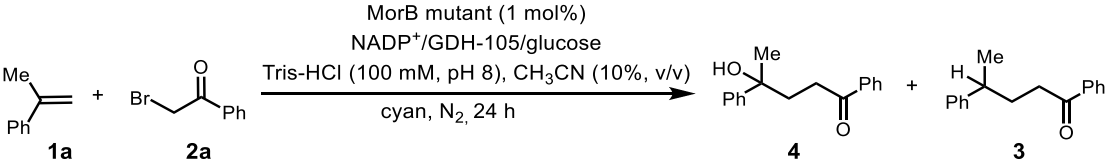
Site saturation mutagenesis **Round 6**

Supplementary Table 13. Templates and target sites of the 6th round of SSM on MorB for carbohydroxylation.



Template	Target sites	Beneficial mutations
Y72C/C191G/T240E/R110L/C72T	V73	Y72C/C191G/T240E/R110L/C72T/V73D Y72C/C191G/T240E/R110L/C72T/V73S

Supplementary Table 14. Summary of the 6th round of SSM on MorB for carbohydroxylation.

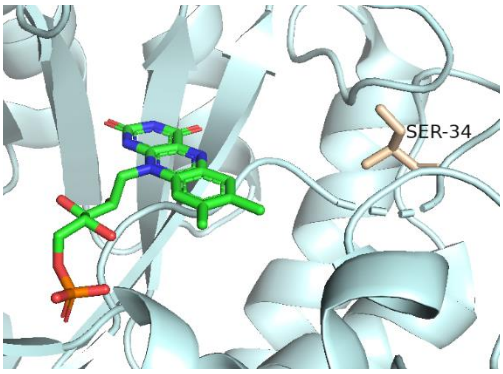


Entry	MorB mutants	Yield of **4** (%)[a]	er[b]	Yield of **3** (%)[a]
1	Y72C/C191G/T240E/R110L/C72T	94	92:8	3
2	Y72C/C191G/T240E/R110L/C72T/V73D	96	93:7	2
3	Y72C/C191G/T240E/R110L/C72T/V73S	92	92:8	3

Reaction condition is the same as described in Supplementary Table 4.

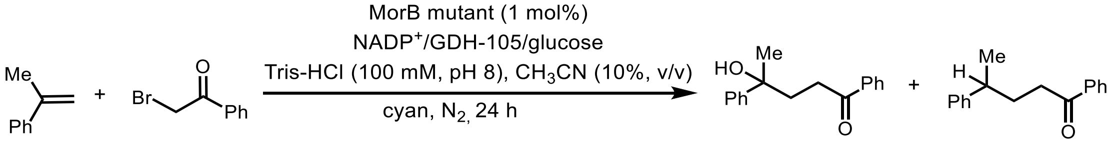
Site saturation mutagenesis **Round 7**

Supplementary Table 15. Templates and target sites of the 7th round of SSM on MorB for carbohydroxylation.



Template	Target sites	Beneficial mutations
Y72C/C191G/T240E/R110L/C72T/V73D	S34	Y72C/C191G/T240E/R110L/C72T/V73D/S34Q Y72C/C191G/T240E/R110L/C72T/V73D/S34T

Supplementary Table 16. Summary of the 7th round of SSM on MorB for carbohydroxylation.

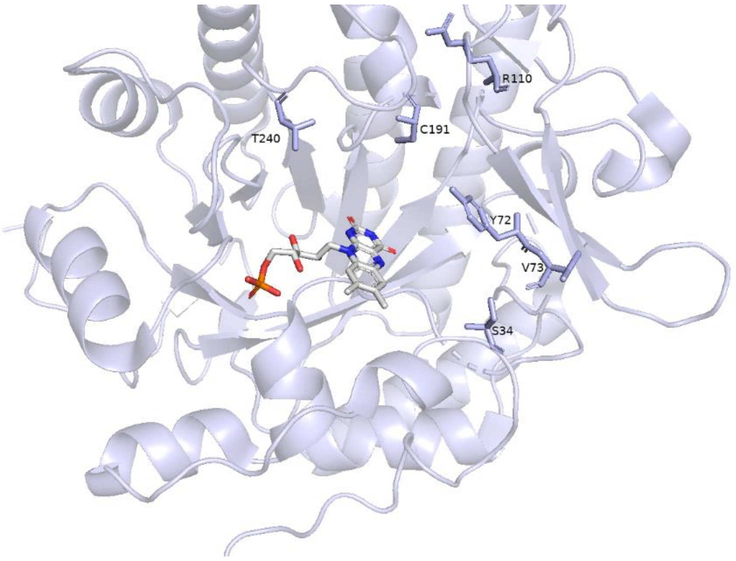


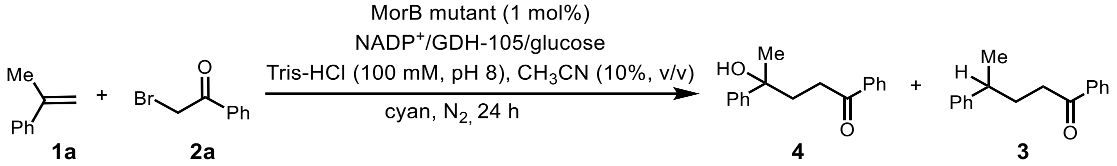
1a **2a** **4** **3**

Entry	MorB mutants	Yield of **4** (%)[a]	er[b]	Yield of **3** (%)[a]
1	Y72C/C191G/T240E/R110L/C72T/V73D/	96	93:7	2
2	Y72C/C191G/T240E/R110L/C72T/V73D/S34Q	96	95:5	trace
3	Y72C/C191G/T240E/R110L/C72T/V73D/S34T	94	95:5	trace

Reaction condition is the same as described in Supplementary Table 4.

Supplementary Table 17. Summary of the site saturation mutagenesis results.





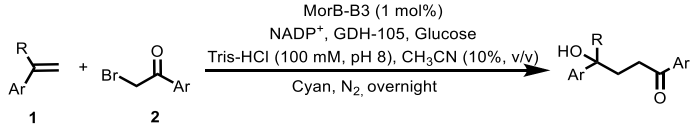
Entry	MorB mutants	Yield[a] of **4**	er[b]	Yield[a] of **3**
1	WT	45%	75:25	10%
2	Y72C	66%	79:21	9%
3	Y72C/C191G	74%	80:20	6%
4	Y72C/C191G/T240E	80%	85:15	4%
5	Y72C/C191G/T240E/R110L	83%	87:13	3%
6	Y72C/C191G/T240E/R110L/C72T	94%	92:8	3%
7	Y72C/C191G/T240E/R110L/C72T/V73D	96%	93:7	2%
8	Y72C/C191G/T240E/R110L/C72T/V73D/S34Q (MorB-B3)	96%	95:5	trace

Reaction conditions: α-methylstyrene (0.65 uL, 0.005 mmol, 1.0 eq), α-bromoketone (2.98 mg, 0.015 mmol, 3.0 eq), GDH-105 (0.06 mg), NADP$^+$ (0.2 mg), glucose (0.9 mg) and purified ‘ene’-reductases (1 mol% based on α-methylstyrene) in 100 mM Tris-HCl buffer pH 8.0, with 10% CH_3CN (*v*/*v*) as cosolvent, final total volume is 600 μL. Reaction mixtures were stirred under anaerobic conditions and irradiated with cyan LED at room temperature for 24 h. [a] Yield determined via LCMS relative to an internal standard (TBB). [b] Enantiomeric ratio (er) determined by HPLC on a chiral stationary phase.

MorB-B3 catalyzed asymmetric carbohydroxylation reaction

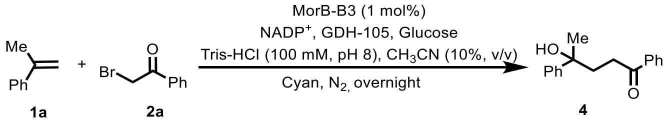
General procedure for enzymatic reaction

General procedure I for enzymatic reaction

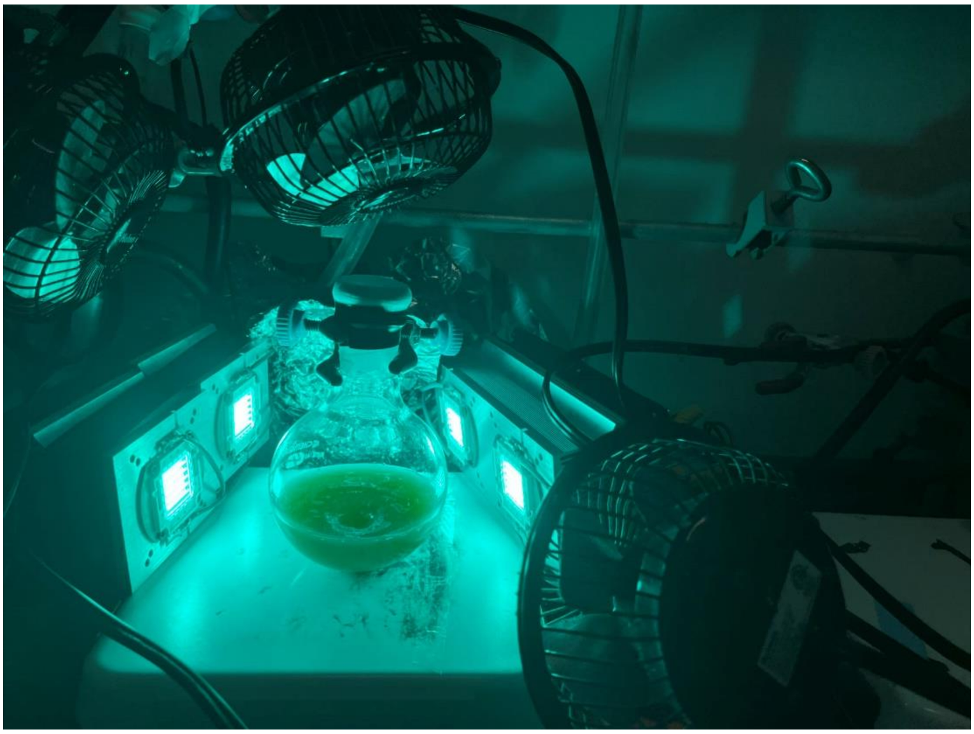


In the Coy® chamber (Vinyl Anaerobic Chamber, Type A), to a 1.5 mL GC vial was charged with GDH-105 (24 µL, 5 mg/mL stock solution in 100 mM Tris-HCl buffer pH 8.0, 10 wt%), glucose (18 µL, 100 mg/mL stock solution, 1 eq), NADP$^+$ (26.7 µL, 15 mg/mL stock solution, 10 mol%), MorB-B3 (1.0 mol%) and substrates (**1**, 0.01 mmol; **2**, 0.03 mmol). Buffer (100 mM Tris-HCl buffer pH 8.0) was added to bring the total volume to 660 µL with 10% CH_3CN (*v*/*v*) as cosolvent. The vial was sealed with a screw cap and shaken under cyan light irradiation and anaerobic conditions at room temperature for 24 h. Upon completion, the reaction was quenched with 1.5 mL of acetonitrile and 100 µL of 2 mg/mL 1,3,5-tribromobenzene (TBB) in acetonitrile as the internal standard. The mixture was shaken for 30 min, centrifuged (12000 x g, 5 mins), and the supernatant was filtered and retained for LCMS analysis for yield calculation. After LCMS analysis, the supernatant was concentrated under reduced pressure, extracted with EtOAc, the combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting crude residue was dissolved in 20% isopropanol/hexanes (*v*/*v*) for chiral HPLC analysis.

General Procedure II for 1 mmol preparative scale reaction

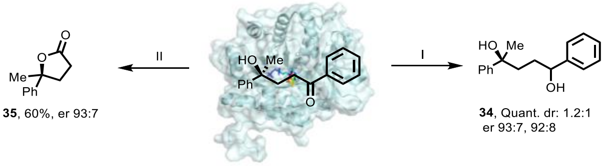


In the Coy® chamber (Vinyl Anaerobic Chamber, Type A), a 200 mL vial was charged with GDH-105 (12 mg), glucose (180 mg), NADP$^+$ (40 mg), Buffer (60 mL, 100 mM tris buffer pH 8.0) was added. MorB-B3 (1.0 mol%) was resuspended in the buffer. Substrates (**1a**, 130 µL, 1.0 mmol, and **2a**, 594 mg in 6 mL CH_3CN) were added to bring the total volume to 66 mL. The vial was sealed with a screw cap and stirred under anaerobic conditions with cyan light irradiation at room temperature for 48 h. Upon completion, the reaction was centrifuged at 4000 g, 15 min. The supernatant was combined and the cell pellet was washed with CH_3CN. The combined solution was further quenched with 30 mL of acetonitrile. The mixture was stirred for 30 min, centrifuged (4000 g, 10 min), and the supernatant was concentrated, and extracted with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to provide the crude product, which was purified by flash chromatography (EtOAc/Hexanes, 10%, *v*/*v*) to give the pure product as a yellow oil (139.7 mg, 55% yield).



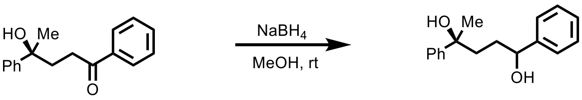
Supplementary Figure 1. Scale-up reaction set-up.

Product derivatization



Supplementary Figure 2. Product derivatization.

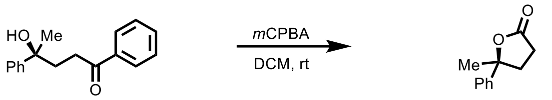
General procedure I for product derivatization



34, Quant. dr 1.2:1
er 93:7, 92:8

To a 1.5 mL GC vial equipped with a magnetic stir bar was charged with (*S*)-4-hydroxy-1,4-diphenylpentan-1-one (**4,** 17.0 mg, 0.067 mmol). MeOH (600 uL) was added, followed by the addition of $NaBH_4$ (3 eq, 7.6 mg, 0.2 mmol). The reaction mixture was allowed to stir at room temperature overnight. Upon completion, water was added and extracted with DCM. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford the target product **34** (colorless oil, quant.).

General procedure II for product derivatization

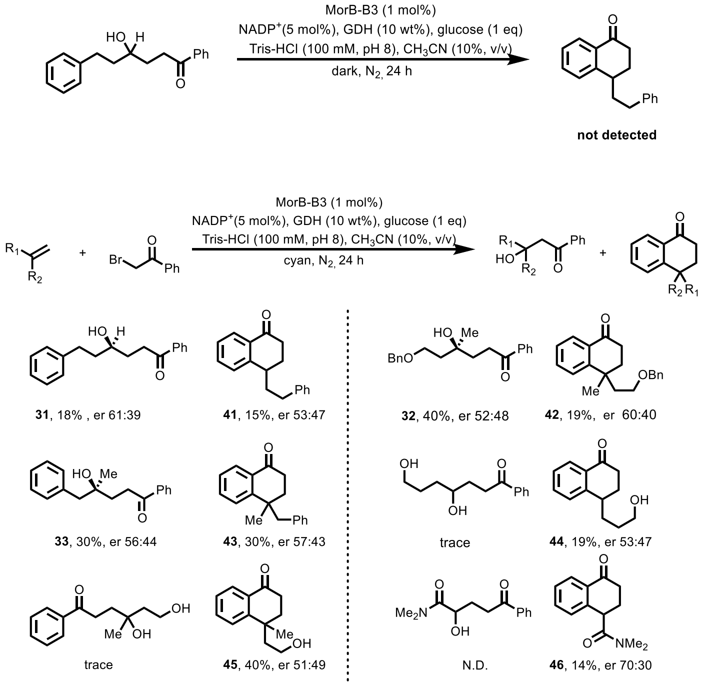


35, 60%, er 93:7

To a 1.5 mL GC vial equipped with a magnetic stir bar was charged with (*S*)-4-hydroxy-1,4-diphenylpentan-1-one (**4,** 25.4 mg, 0.1 mmol). CH_2Cl_2 (500 uL) was added, followed by the addition of *m*CPBA (3 eq, 51.6mg, 0.3 mmol). The reaction mixture was allowed to stir at room temperature for 24 h. Upon completion, water was added and extracted with DCM. The combined organic layers were washed with sat. Na_2SO_3 and brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Further purified with preparative TLC afford the target product **35** (colorless oil, 60%).

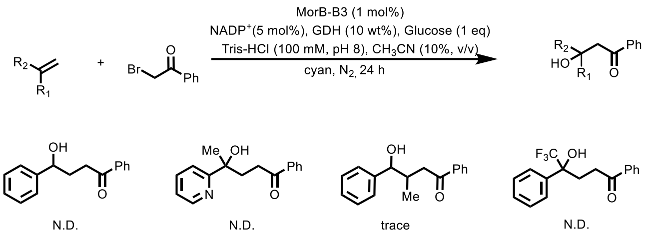
Substrates with cyclization coproducts.

For those unactivated alkenes, the cyclohexanone coproduct was observed as shown below. Control experiment showed that the cyclohexanone coproduct couldn’t be formed through hydroxylation product. We reasoned the radical intermediate underwent the radical addition to the arene, after aromatization to give the product.



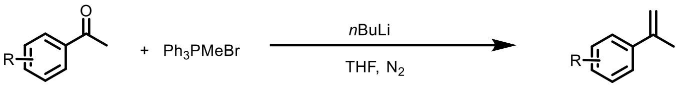
Supplementary Figure 3. Substrates with cyclization coproducts.

Substrates limitations



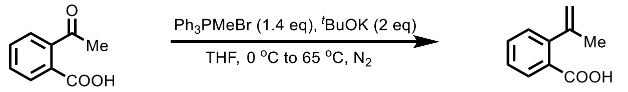
Supplementary Figure 4. Substrates limitations.

General procedures for the preparation of alkenes

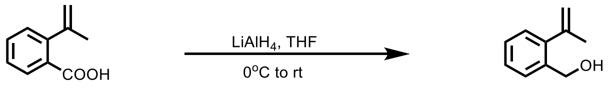


Substrates **1b-1k**, **36,** and **38** were prepared according to literatures[8-16]. Other substrates were commercially available and used without any purification.

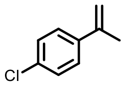
Methyltriphenylphosphonium bromide (1.5 mmol) in dry THF (10 mL) under N_2 atmosphere was cooled to 0 °C. Then, *n*-BuLi (2.5 M solution in hexane, 1.5 mmol) was added slowly to the solution. After, the resulting orange mixture was maintained at 0 °C for 0.5-1 h, a solution of the corresponding ketone (1.0 mmol) in dry THF was added dropwise at 0 °C. The reaction was allowed to warm up to rt, stirred overnight (monitored by TLC), and finally quenched sat. NH_4Cl. The resulting mixture was extracted with DCM. The combined organic phase was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The resulting crude product was purified by flash column chromatography to give the corresponding alkenes.



Methyltriphenylphosphonium bromide (1.4 mmol) in dry THF (10 mL) under N_2 atmosphere was cooled to 0 °C. Then, *t*BuOK (2 mmol) was added slowly to the solution. After, the resulting orange mixture was maintained at 0 °C for 0.5-1 h, a solution of the corresponding ketone (1.0 mmol) in dry THF was added dropwise at 0 °C. The reaction was stirred overnight at 65 ºC, and finally quenched with sat. NH_4Cl. The resulting mixture was extracted with DCM. The combined organic phase was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The resulting crude product was purified by flash column chromatography to give the corresponding alkene.



2-(Prop-1-en-2-yl)benzoic acid (0.5 mmol) dissolved in dry THF was cooled to 0 °C. Then, $LiAlH_4$ (1 mmol) was added slowly to the solution. The solution was allowed to stir at rt for 2 h. The reaction was quenched by 10% NaOH solution and extracted with DCM. The combined organic phase was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The resulting crude product was purified by flash column chromatography to give the corresponding alcohol.

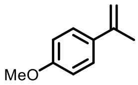


1-chloro-4-(prop-1-en-2-yl)benzene (1b)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.40 (m, 2H), 7.34 – 7.30 (m, 2H), 5.38 (t, *J* = 1.1 Hz, 1H), 5.12 (p, *J* = 1.5 Hz, 1H), 2.17 – 2.14 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.2, 139.7, 133.2, 128.3, 126.8, 113.0, 21.8.

The NMR spectra is in agreement with published data[8].

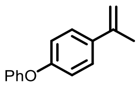


1-methoxy-4-(prop-1-en-2-yl)benzene (1c)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 5.29 (s, 1H), 4.99 (s, 1H), 3.82 (s, 3H), 2.13 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.1, 142.6, 133.7, 126.6, 113.5, 110.7, 55.3, 21.9.

The NMR spectra is in agreement with published data[8].

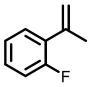


1-phenoxy-4-(prop-1-en-2-yl)benzene (1d)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 2H), 7.31 – 7.23 (m, 2H), 7.07 – 7.00 (m, 1H), 6.96 – 6.92 (m, 2H), 6.92 – 6.86 (m, 2H), 5.25 (dd, *J* = 1.5, 0.8 Hz, 1H), 4.97 (p, *J* = 1.5 Hz, 1H), 2.07 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.2, 156.7, 142.5, 136.3, 129.8, 126.9, 123.3, 118.9, 118.5, 111.7, 21.9.

The NMR spectra is in agreement with published data[9].



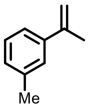
1-fluoro-2-(prop-1-en-2-yl)benzene (1e)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.7 Hz, 1H), 7.28 – 7.19 (m, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.04 (dd, *J* = 11.1, 8.3 Hz, 1H), 5.24 (s, 2H), 2.15 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 160.0 (d, *J* = 248.2 Hz), 140.2, 130.3 (d, *J* = 13.5 Hz), 129.4 (d, *J* = 4.4 Hz), 128.7 (d, *J* = 8.4 Hz), 123.9, 116.6 (d, *J* = 4.0 Hz), 115.8 (d, *J* = 23.0 Hz), 23.1 (d, *J* = 3.5 Hz).

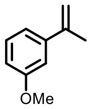
^{19}F NMR (470 MHz, $CDCl_3$) δ -114.54 (s).

The NMR spectra is in agreement with published data[10].

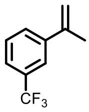


1-methyl-3-(prop-1-en-2-yl)benzene (1f)

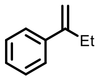
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.20 (m, 3H), 7.12 (d, *J* = 7.4 Hz, 1H), 5.38 (d, *J* = 1.9 Hz, 1H), 5.10 (p, *J* = 1.5 Hz, 1H), 2.40 (s, 3H), 2.18 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 143.4, 141.3, 137.7, 128.2, 128.1, 126.3, 122.6, 112.3, 21.9, 21.5.
The NMR spectra is in agreement with published data[10].



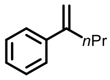
1-methoxy-3-(prop-1-en-2-yl)benzene (1g)
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 9.7, 6.2 Hz, 1H), 7.09 (d, *J* = 7.7 Hz, 1H), 7.05 – 6.96 (m, 1H), 6.85 (dd, *J* = 8.2, 2.0 Hz, 1H), 5.39 (s, 1H), 5.11 (s, 1H), 3.85 (s, 3H), 2.17 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 159.5, 143.2, 142.8, 129.2, 118.1, 112.7, 112.6, 111.5, 55.2, 21.9.
The NMR spectra is in agreement with published data[10].



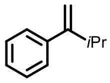
1-(prop-1-en-2-yl)-3-(trifluoromethyl)benzene (1h)
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 1H), 5.43 (s, 1H), 5.18 (s, 1H), 2.18 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 142.1, 142.0, 130.6 (q, *J* = 32.0 Hz), 128.7 (q, *J* = 1.1 Hz), 128.7, 124.2 (q, *J* = 272.3 Hz), 124.0 (q, *J* = 3.8 Hz), 122.3 (q, *J* = 3.8 Hz), 114.0, 21.7.
^{19}F NMR (470 MHz, $CDCl_3$) δ -62.65 (s, 3F)
The NMR spectra is in agreement with published data[11].



but-1-en-2-ylbenzene (1i)
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.30 – 7.22 (m, 1H), 5.28 (s, 1H), 5.06 (d, *J* = 1.2 Hz, 1H), 2.52 (q, *J* = 7.4 Hz, 2H), 1.11 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 150.1, 141.5, 128.2, 127.3, 126.0, 110.9, 28.1, 13.0.
The NMR spectra is in agreement with published data[12].



pent-1-en-2-ylbenzene (1j)
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 2H), 7.38 – 7.32 (m, 2H), 7.32 – 7.27 (m, 1H), 5.30 (d, *J* = 1.7 Hz, 1H), 5.08 (q, *J* = 1.5 Hz, 1H), 2.54 – 2.48 (m, 2H), 1.51 (h, *J* = 7.4 Hz, 2H), 0.95 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 148.5, 141.5, 128.2, 127.2, 126.2, 112.2, 37.5, 21.4, 13.8.
The NMR spectra is in agreement with published data[12].

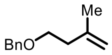


(3-methylbut-1-en-2-yl)benzene (1k)

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.40 – 7.32 (m, 4H), 7.31 – 7.26 (m, 1H), 5.23 – 5.15 (m, 1H), 5.07 (t, *J* = 1.4 Hz, 1H), 2.87 (pd, *J* = 6.8, 1.4 Hz, 1H), 1.13 (s, 3H), 1.12 (s, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 155.8, 142.9, 128.1, 127.0, 126.6, 110.0, 32.3, 22.1.

The NMR spectra is in agreement with published data[13].

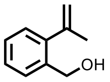


(((3-methylbut-3-en-1-yl)oxy)methyl)benzene (1o)

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.34 (d, *J* = 4.4 Hz, 4H), 7.31 – 7.27 (m, 1H), 4.94 – 4.61 (m, 2H), 4.53 (s, 2H), 3.59 (t, *J* = 6.9 Hz, 2H), 2.68 – 2.06 (m, 2H), 1.92 – 1.61 (m, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 142.9, 138.5, 128.4, 127.7, 127.6, 111.5, 72.9, 68.7, 37.8, 22.7.

The NMR spectra is in agreement with published data[14].

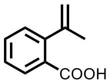


(2-(prop-1-en-2-yl)phenyl)methanol (36)

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.51 – 7.45 (m, 1H), 7.30 (ddt, *J* = 9.5, 5.5, 2.4 Hz, 2H), 7.23 – 7.17 (m, 1H), 5.28 – 5.24 (m, 1H), 4.93 (dd, *J* = 2.1, 1.1 Hz, 1H), 4.73 (s, 2H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 144.8, 143.0, 137.3, 128.2, 128.1, 127.5, 127.3, 115.5, 63.3, 25.1.

The NMR spectra is in agreement with published data[15].



2-(prop-1-en-2-yl)benzoic acid (38)

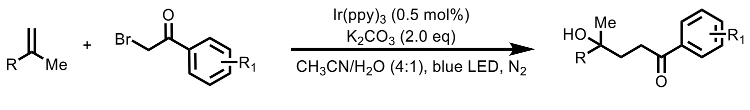
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.98 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.53 (td, *J* = 7.5, 1.4 Hz, 1H), 7.38 (td, *J* = 7.6, 1.3 Hz, 1H), 7.29 (d, *J* = 6.8 Hz, 1H), 5.16 (t, *J* = 1.7 Hz, 1H), 4.97 – 4.89 (m, 1H), 2.15 (s, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 171.9, 146.6, 146.2, 132.6, 130.7, 129.7, 127.9, 127.1, 114.0, 24.3.

The NMR spectra is in agreement with published data[16].

General procedure for the preparation of racemic compounds

General procedure I for the preparation of racemic compounds[6]

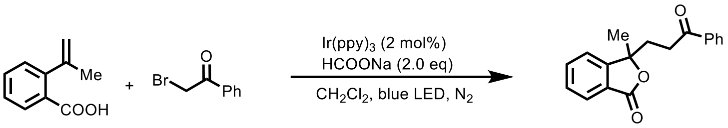


In the glovebox, to a 20 mL vial equipped with a magnetic stir bar was charged with Ir(ppy)$_3$ (0.5 mol%), K$_2$CO$_3$ (2.0 eq), alkene (1.0 mmol, 1.0 eq.) and bromoacetophenone (1.0 eq.). Degassed CH$_3$CN (3.2 mL) and water (0.8 mL) were added. The vial was placed under Kessil Blue LED (465 nm) overnight. Upon completion (monitored by LCMS), the mixtures were extracted with EtOAc and washed with brine. The combined organic layers were dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure to provide the crude product, which was purified by flash chromatography.

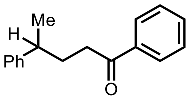
The cyclization coproducts **41-46** were isolated as minor products under the same reaction conditions.

Note: Some of the hydroxylation products were unstable in the silicon column. If necessary, purification with reverse phase C18 column was applied.

General procedure II for the preparation of racemic compounds[7]



In a glovebox, to a 20 mL vial equipped with a magnetic stir bar was charged with Ir(ppy)$_3$ (2 mol%), HCOONa (2.0 eq), alkene (1.0 mmol, 1.0 eq.) and bromoacetophenone (1.0 eq.). Degassed DCM (2 mL) was added. The vial was placed under Kessil Blue LED (465 nm) overnight. Upon completion (monitored by LCMS), water was added and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure to provide the crude product, which was purified by flash chromatography.

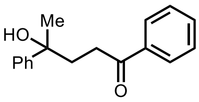


1,4-diphenylpentan-1-one (3)

Product standard was prepared according to the reported method[5]. Overall yield: 35%.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.87 (d, *J* = 7.0 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.18 (m, 3H), 3.03 – 2.74 (m, 3H), 2.10 (ddt, *J* = 15.0, 9.2, 6.0 Hz, 1H), 2.06 – 1.95 (m, 1H), 1.34 (d, *J* = 7.0 Hz, 3H).

The NMR spectra is in agreement with published data[5].



4-hydroxy-1,4-diphenylpentan-1-one (4)

Product standard was prepared according to the General procedure I for the preparation of racemic compounds. Overall yield: 55%.

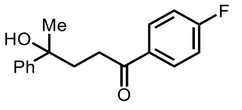
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.87 (d, *J* = 7.4 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.47 (d, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.24 (d, *J* = 7.3 Hz, 1H), 3.01 (dt, *J* = 17.7, 7.4 Hz, 1H), 2.88 (ddd, *J* = 17.7, 7.5, 6.3 Hz, 1H), 2.57 (s, 1H), 2.40 – 2.22 (m, 2H), 1.63 (s, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 201.2, 147.2, 136.8, 133.1, 128.5, 128.3, 128.1, 126.7, 124.8, 74.2, 37.7, 33.8, 31.4.

HRMS (DART-MS): m/z calcd for $C_{17}H_{17}O$ [M-OH]$^+$: 237.12739, found: 237.12624.

IR (neat, cm^{-1}): 3492, 3059, 2971, 1716, 1598, 1447, 1273, 1068, 1025, 697.

The NMR spectra is in agreement with published data[6].



1-(4-fluorophenyl)-4-hydroxy-4-phenylpentan-1-one (5)

Product standard was prepared according to the General procedure I for the preparation of racemic compounds. Overall yield: 25%.

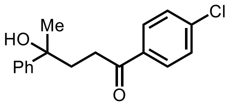
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 8.6, 5.5 Hz, 2H), 7.46 (d, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.25 (d, *J* = 6.3 Hz, 1H), 7.08 (t, *J* = 8.6 Hz, 2H), 3.01 – 2.95 (m, 1H), 2.85 – 2.79 (m, 1H), 2.43 (s, 1H), 2.36 – 2.19 (m, 2H), 1.63 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 199.4, 165.73 (d, *J* = 254.7 Hz), 147.1, 133.2 (d, *J* = 3.0 Hz), 130.7 (d, *J* = 9.3 Hz), 128.3, 126.7, 124.8, 115.6 (d, *J* = 21.8 Hz), 74.1, 37.7, 33.6, 31.4.

^{19}F NMR (470 MHz, $CDCl_3$) δ -105.31 – -105.26 (m, 1F).

HRMS (DART-MS): m/z calcd for $C_{17}H_{16}OF$ [M-OH]$^+$: 255.11797, found: 255.11679.

IR (neat, cm^{-1}): 3492, 2970, 1738, 1598, 1365, 1216, 1070, 1009, 699.



1-(4-chlorophenyl)-4-hydroxy-4-phenylpentan-1-one (6)

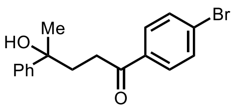
Product standard was prepared according to the General procedure I for the preparation of racemic compounds. Overall yield: 17%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 7.3 Hz, 2H), 7.36 (dd, *J* = 17.1, 8.3 Hz, 4H), 7.25 (d, *J* = 7.3 Hz, 1H), 3.01 – 2.95 (m, 1H), 2.84 – 2.78 (m, 1H), 2.38 (s, 1H), 2.30 – 2.26 (m, 2H), 1.63 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 199.8, 147.0, 139.5, 135.1, 129.5, 128.8, 128.3, 126.7, 124.8, 74.1, 37.7, 33.7, 31.4.

HRMS (DART-MS): m/z calcd for $C_{17}H_{16}OCl$ [M-OH]$^+$: 271.08842, found: 271.08708.

IR (neat, cm^{-1}): 3444, 2970, 1723, 1676, 1588, 1399, 1090, 830, 696.



1-(4-bromophenyl)-4-hydroxy-4-phenylpentan-1-one (7)

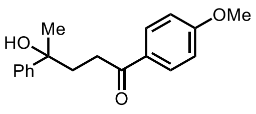
Product standard was prepared according to the General procedure I for the preparation of racemic compounds. Overall yield: 15%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 8.6 Hz, 2H), 7.45 (d, *J* = 7.3 Hz, 2H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.24 (d, *J* = 7.3 Hz, 1H), 2.97 (ddd, *J* = 17.6, 7.9, 6.9 Hz, 1H), 2.80 (ddd, *J* = 17.7, 7.6, 6.4 Hz, 1H), 2.34 (s, 1H), 2.31 – 2.23 (m, 2H), 1.63 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 200, 147.0, 135.5, 131.8, 129.6, 128.3, 128.2, 126.7, 124.8, 74.2, 37.7, 33.7, 31.4.

HRMS (DART-MS): m/z calcd for $C_{17}H_{16}OBr$ [M-OH]$^+$: 315.03790, found: 315.03638.

IR (neat, cm^{-1}): 3498, 3057, 2968, 1720, 1673, 1585, 1396, 1069, 1009, 696.



4-hydroxy-1-(4-methoxyphenyl)-4-phenylpentan-1-one (8)

Product standard was prepared according to the General procedure I for the preparation of racemic compounds. Overall yield: 30%.

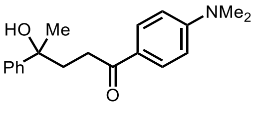
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.9 Hz, 2H), 7.47 (d, *J* = 7.3 Hz, 2H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.24 (t, *J* = 7.3 Hz, 1H), 6.88 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 2.96 – 2.82 (m, 2H), 2.76 (s, 1H), 2.33 – 2.23 (m, 2H), 1.62 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 199.8, 163.5, 147.3, 130.4, 129.8, 128.3, 126.6, 124.9, 113.6, 74.1, 55.5, 37.8, 33.4, 31.4.

HRMS (DART-MS): m/z calcd for $C_{18}H_{19}O_2$ $[M\text{-}OH]^+$: 267.13796, found: 267.13662.

IR (neat, cm^{-1}): 3443, 2969, 2932, 1715, 1666, 1597, 1445, 1254, 1167, 699.

The NMR spectra is in agreement with published data[17].



1-(4-(dimethylamino)phenyl)-4-hydroxy-4-phenylpentan-1-one (9)

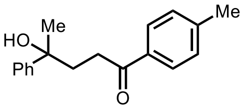
Product standard was prepared according to the General procedure I for the preparation of racemic compounds. Overall yield: 17%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.9 Hz, 2H), 7.47 (d, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 6.60 (d, *J* = 9.0 Hz, 2H), 3.40 (s, 1H), 3.04 (s, 6H), 2.95 – 2.73 (m, 2H), 2.27 (dtd, *J* = 21.2, 14.4, 6.8 Hz, 2H), 1.61 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 199.6, 153.5, 147.7, 130.4, 128.2, 126.4, 125.0, 124.6, 110.6, 74.1, 40.0, 38.1, 33.0, 31.4.

HRMS (DART-MS): m/z calcd for $C_{19}H_{22}NO$ $[M\text{-}OH]^+$: 280.16959, found: 280.16835.

IR (neat, cm^{-1}): 3456, 2922, 1711, 1590, 1365, 1167, 1065, 818, 700.



4-hydroxy-4-phenyl-1-(p-tolyl)pentan-1-one (10)

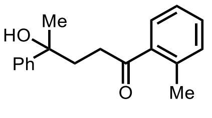
Product standard was prepared according to the General procedure I for the preparation of racemic compounds. Overall yield: 45%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.1 Hz, 2H), 7.46 (d, *J* = 7.4 Hz, 2H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.25 – 7.16 (m, 3H), 2.96 (dt, *J* = 17.6, 7.4 Hz, 1H), 2.94 – 2.79 (m, 1H), 2.67 (s, 1H), 2.38 (s, 3H), 2.35 – 2.20 (m, 2H), 1.62 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 200.9, 147.3, 143.9, 134.3, 129.2, 128.3, 128.2, 126.6, 124.9, 74.2, 37.8, 33.7, 31.4, 21.6.

HRMS (DART-MS): m/z calcd for $C_{18}H_{19}O$ $[M\text{-}OH]^+$: 251.14304, found: 251.14190.

IR (neat, cm^{-1}): 3456, 2970, 1737, 1675, 1606, 1365, 1104, 754, 698.



4-hydroxy-4-phenyl-1-(o-tolyl)pentan-1-one (11)

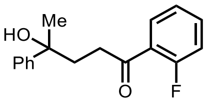
Product standard was prepared according to the General procedure I for the preparation of racemic compounds. Overall yield: 33%.

^{1}H NMR (500 MHz, CD_3CN) δ 7.52 (d, *J* = 7.9 Hz, 1H), 7.48 (d, *J* = 7.0 Hz, 2H), 7.40 – 7.34 (m, 3H), 7.25 (td, *J* = 7.7, 2.5 Hz, 3H), 2.92 (ddd, *J* = 17.1, 8.9, 6.6 Hz, 1H), 2.66 (ddd, *J* = 17.2, 8.9, 6.1 Hz, 1H), 2.38 (s, 3H), 2.17 – 2.10 (m, 2H), 1.54 (s, 3H).

^{13}C NMR (126 MHz, CD_3CN) δ 204.9, 148.2, 138.7, 137.1, 131.5, 130.9, 128.1, 128.0, 126.3, 125.7, 124.9, 73.3, 38.1, 36.8, 30.1, 20.0.

HRMS (DART-MS): m/z calcd for $C_{18}H_{19}O$ $[M-OH]^+$: 251.14304, found: 251.14179.

IR (neat, cm^{-1}): 3454, 2970, 1738, 1675, 1445, 1370, 1216, 1068, 749.



1-(2-fluorophenyl)-4-hydroxy-4-phenylpentan-1-one (12)

Product standard was prepared according to the General procedure I for the preparation of racemic compounds. Overall yield: 20%.

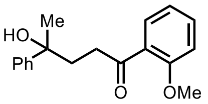
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (td, *J* = 7.7, 1.5 Hz, 1H), 7.46 (d, *J* = 7.3 Hz, 3H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.26 – 7.15 (m, 2H), 7.08 (dd, *J* = 10.7, 8.8 Hz, 1H), 3.08 – 2.97 (m, 1H), 2.96 – 2.84 (m, 1H), 2.40 (s, 1H), 2.28 (dd, *J* = 13.6, 6.3 Hz, 2H), 1.62 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 199.5 (d, *J* = 4.2 Hz), 161.8 (d, *J* = 254.9 Hz), 147.3, 134.5 (d, *J* = 9.0 Hz), 130.6 (d, *J* = 2.6 Hz), 128.3, 126.7, 124.8, 124.4, 124.3, 116.7 (d, *J* = 23.8 Hz), 74.1, 38.7 (d, *J* = 7.5 Hz), 37.6 (d, *J* = 1.6 Hz), 31.0.

^{19}F NMR (470 MHz, CD_3CN) δ -112.02 – -112.97 (m, 1F).

HRMS (DART-MS): m/z calcd for $C_{17}H_{16}OF$ $[M-OH]^+$: 255.11797, found: 255.11673.

IR (neat, cm^{-1}): 3456, 2970, 1737, 1680, 1608, 1450, 1212, 1026, 756.



4-hydroxy-1-(2-methoxyphenyl)-4-phenylpentan-1-one (13)

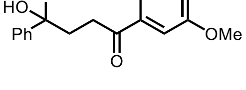
Product standard was prepared according to the General procedure I for the preparation of racemic compounds. Overall yield: 32%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.49 – 7.45 (m, 2H), 7.45 – 7.39 (m, 1H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.23 (t, *J* = 7.3 Hz, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 3.79 (s, 3H), 2.95 (td, *J* = 7.2, 4.5 Hz, 2H), 2.76 (s, 1H), 2.25 (qd, *J* = 14.4, 7.1 Hz, 2H), 1.60 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 203.8, 158.4, 147.7, 133.4, 130.2, 128.3, 128.1, 126.5, 124.9, 120.6, 111.5, 74.2, 55.4, 39.0, 38.1, 31.0.

HRMS (DART-MS): m/z calcd for $C_{18}H_{19}O_2$ $[M-OH]^+$: 267.13796, found: 267.13678.

IR (neat, cm^{-1}): 3443, 2970, 1737, 1667, 1597, 1370, 1241, 1021, 753.



4-hydroxy-1-(3-methoxyphenyl)-4-phenylpentan-1-one (14)

Product standard was prepared according to the General procedure I for the preparation of racemic compounds. Overall yield: 15%.

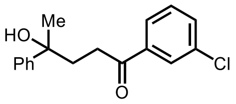
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.4 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 2H), 7.35 (dd, *J* = 13.1, 5.2

Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.24 (t, *J* = 7.3 Hz, 1H), 7.08 (dd, *J* = 8.2, 1.9 Hz, 1H), 3.83 (s, 3H), 2.99 (ddd, *J* = 17.6, 7.8, 7.0 Hz, 1H), 2.86 (ddd, *J* = 17.7, 7.5, 6.3 Hz, 1H), 2.51 (s, 1H), 2.35 – 2.20 (m, 2H), 1.63 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 201.0, 159.8, 147.2, 138.1, 129.5, 128.3, 126.7, 124.8, 120.8, 119.6, 112.4, 74.2, 55.4, 37.8, 33.9, 31.3.

HRMS (DART-MS): m/z calcd for $C_{18}H_{19}O_2$ $[M-OH]^+$: 267.13796, found: 267.13670.

IR (neat, cm^{-1}): 3464, 2969, 1722, 1676, 1582, 1252, 1028, 867, 762.



1-(3-chlorophenyl)-4-hydroxy-4-phenylpentan-1-one (15)

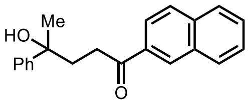
Product standard was prepared according to the General procedure for the preparation of racemic compounds. Overall yield: 17%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.50 (dd, *J* = 8.0, 0.9 Hz, 1H), 7.46 (d, *J* = 7.3 Hz, 2H), 7.36 (td, *J* = 7.7, 2.6 Hz, 3H), 7.28 – 7.24 (m, 1H), 3.02 – 2.96 (m, 1H), 2.81 (dt, *J* = 17.8, 6.9 Hz, 1H), 2.30 – 2.27 (m, 3H), 1.63 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 199.7, 147.0, 138.3, 134.9, 133.0, 129.9, 128.4, 128.2, 126.8, 126.2, 124.8, 74.1, 37.6, 33.8, 31.4.

HRMS (DART-MS): m/z calcd for $C_{17}H_{16}OCl$ $[M-OH]^+$: 271.08842, found: 271.08712.

IR (neat, cm^{-1}): 3455, 2970, 1736, 1682, 1570, 1370, 1201, 1068, 697.



4-hydroxy-1-(naphthalen-2-yl)-4-phenylpentan-1-one (16)

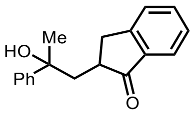
Product standard was prepared according to the General procedure I for the preparation of racemic compounds. Overall yield: 33%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.96 (dd, *J* = 8.7, 1.5 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 8.5 Hz, 2H), 7.58 (t, *J* = 7.0 Hz, 1H), 7.56 – 7.47 (m, 3H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.31 – 7.23 (m, 1H), 3.14 (dt, *J* = 17.5, 7.4 Hz, 1H), 3.02 (ddd, *J* = 17.5, 7.3, 6.4 Hz, 1H), 2.60 (s, 1H), 2.42 – 2.30 (m, 2H), 1.66 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 201.1 147.2, 135.6, 134.1, 132.5, 129.8, 129.6, 128.5, 128.4, 128.3, 127.7, 126.7, 126.7, 124.9, 123.9, 74.2, 37.9, 33.8, 31.5.

HRMS (DART-MS): m/z calcd for $C_{21}H_{19}O$ $[M-OH]^+$: 287.14304, found: 287.14176.

IR (neat, cm^{-1}): 3456, 2970, 1738, 1672, 1365, 1217, 1027, 762, 699.



2-(2-hydroxy-2-phenylpropyl)-2,3-dihydro-1H-inden-1-one (17)

Product standard was prepared according to the General procedure I for the preparation of racemic compounds. Overall yield: 38%.

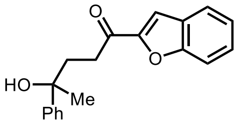
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.7 Hz, 1H), 7.62 – 7.47 (m, 3H), 7.42 (d, *J* = 7.7 Hz, 1H), 7.39 – 7.31 (m, 3H), 7.24 (t, *J* = 7.4 Hz,1H), 3.38 (dd, *J* = 17.3, 8.1 Hz, 1H), 3.14 (s, 1H), 2.92 (dd, *J* =

17.3, 4.7 Hz, 1H), 2.71 (tt, *J* = 8.0, 5.0 Hz, 1H), 2.50 (dd, *J* = 14.5, 5.2 Hz, 1H), 1.96 (dd, *J* = 14.5, 7.9 Hz, 1H), 1.67 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 209.7, 154.0, 148.0, 136.2, 134.9, 128.3, 127.4, 126.7, 126.3, 124.8, 124.0, 74.4, 45.2, 44.9, 34.9, 30.7.

HRMS (DART-MS): m/z calcd for $C_{18}H_{17}O$ $[M-OH]^+$: 249.12739, found: 249.12617.

IR (neat, cm^{-1}): 3456, 2970, 1738, 1365, 1216, 911, 756, 701.



1-(benzofuran-2-yl)-4-hydroxy-4-phenylpentan-1-one (18)

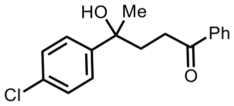
Product standard was prepared according to the General procedure I for the preparation of racemic compounds. Overall yield: 12%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.9 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.46 (td, *J* = 8.2, 4.2 Hz, 3H), 7.41 (s, 1H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.32 – 7.28 (m, 1H), 7.28 – 7.22 (m, 1H), 3.01 (dt, *J* = 17.3, 7.4 Hz, 1H), 2.87 (dt, *J* = 17.4, 7.0 Hz, 1H), 2.44 (s, 1H), 2.32 (t, *J* = 7.3 Hz, 2H), 1.64 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 191.9, 155.6, 152.3, 147.0, 128.3, 128.2, 127.0, 126.8 124.9, 123.9, 123.3, 113.0, 112.5, 74.1, 37.6, 34.0, 31.3.

HRMS (DART-MS): m/z calcd for $C_{19}H_{17}O_2$ $[M-OH]^+$: 277.12231, found: 277.12106.

IR (neat, cm^{-1}): 3483, 2970, 1738, 1670, 1560, 1365, 1216, 1011, 745.



4-(4-chlorophenyl)-4-hydroxy-1-phenylpentan-1-one (19)

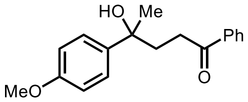
Product standard was prepared according to the General procedure I for the preparation of racemic compounds. Overall yield: 26%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.3 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.48 – 7.39 (m, 4H), 7.33 (dd, *J* = 12.0, 5.0 Hz, 2H), 3.09 – 2.96 (m, 2H), 2.90 (ddd, *J* = 17.8, 7.5, 6.2 Hz, 1H), 2.38 – 2.21 (m, 2H), 1.62 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 201.2, 145.9, 136.6, 133.3, 132.4, 128.6, 128.4, 128.1, 126.5, 73.9, 37.6, 33.7, 31.3.

HRMS (DART-MS): m/z calcd for $C_{17}H_{16}OCl$ $[M-OH]^+$: 271.08842, found: 271.08738.

IR (neat, cm^{-1}): 3480, 2961, 1673, 1487, 1206, 1088, 736, 686.



4-hydroxy-4-(4-methoxyphenyl)-1-phenylpentan-1-one (20)

Product standard was prepared according to the General procedure I for the preparation of racemic compounds. Overall yield: 37%.

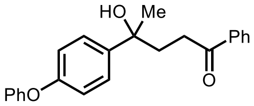
^{1}H NMR (500 MHz, CD_3CN) δ 7.88 (d, *J* = 7.5 Hz, 2H), 7.63 – 7.56 (m, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 6.91 (d, *J* = 8.1 Hz, 2H), 3.79 (s, 3H), 3.08 – 2.98 (m, 1H), 2.79 (ddd, *J* = 17.2, 9.1, 6.0 Hz, 1H), 2.21 (s, 1H), 2.18 – 2.12 (m, 2H), 1.54 (s, 3H).

^{13}C NMR (126 MHz, CD_3CN) δ 200.6, 158.2, 140.2, 137.1, 132.9, 128.6, 127.9, 126.2, 113.2, 73.1, 54.8, 38.2, 33.6, 30.1.

HRMS (DART-MS): m/z calcd for $C_{18}H_{19}O_2$ $[M-OH]^+$: 267.13796, found: 267.13683.

IR (neat, cm^{-1}): 3471, 2968, 1676, 1610, 1509, 1244, 1176, 1030, 831, 743.

The NMR spectra is in agreement with published data[18].



4-hydroxy-4-(4-phenoxyphenyl)-1-phenylpentan-1-one (21)

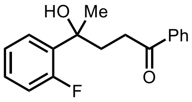
Product standard was prepared according to the General procedure I for the preparation of racemic compounds. Overall yield: 15%.

^{1}H NMR (500 MHz, CD_3CN) δ 7.89 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.63 – 7.57 (m, 1H), 7.48 (dt, *J* = 7.4, 3.4 Hz, 4H), 7.42 – 7.34 (m, 2H), 7.14 (t, *J* = 7.4 Hz, 1H), 7.04 – 6.94 (m, 4H), 3.31 (s, 1H), 3.04 (ddd, *J* = 17.1, 9.4, 6.1 Hz, 1H), 2.83 (ddd, *J* = 17.1, 9.4, 5.6 Hz, 1H), 2.29 – 2.09 (m, 2H), 1.57 (s, 3H).

^{13}C NMR (126 MHz, CD_3CN) δ 200.5, 157.5, 155.6, 143.3, 137.1, 132.9, 129.9, 128.6, 127.9, 126.7, 123.3, 118.6, 118.3, 73.2, 38.2, 33.5, 30.1.

HRMS (DART-MS): m/z calcd for $C_{23}H_{21}O_2$ [M-OH]$^+$: 329.15361**,** found: 329.15211.

IR (neat, cm^{-1}): 3490, 2969, 1738, 1667, 1365, 1231, 1078, 825, 761.



4-(2-fluorophenyl)-4-hydroxy-1-phenylpentan-1-one (22)

Product standard was prepared according to the General procedure I for the preparation of racemic compounds. Overall yield: 8%.

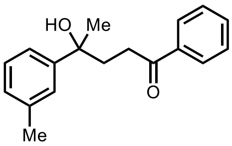
^{1}H NMR (500 MHz, CD_3CN) δ 7.87 (d, *J* = 8.5 Hz, 2H), 7.68 (td, *J* = 8.2, 1.6 Hz, 1H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.30 (tdd, *J* = 7.1, 5.0, 1.8 Hz, 1H), 7.20 (td, *J* = 7.6, 1.2 Hz, 1H), 7.08 (ddd, *J* = 12.4, 8.1, 1.1 Hz, 1H), 3.05 (ddd, *J* = 17.0, 9.6, 5.8 Hz, 1H), 2.79 (ddd, *J* = 17.2, 9.6, 5.3 Hz, 1H), 2.44 – 2.33 (m, 1H), 2.26 – 2.15 (m, 2H), 1.63 (d, *J* = 0.8 Hz, 3H).

^{13}C NMR (126 MHz, CD_3CN) δ 200.5, 159.4 (d, *J* = 243.8 Hz), 137.0, 134.3 (d, *J* = 12.8 Hz), 132.9, 128.78 (d, *J* = 8.6 Hz), 128.6, 127.9, 127.8, 124.1 (d, *J* = 3.3 Hz), 115.7 (d, *J* = 24.0 Hz), 72.4 (d, *J* = 4.1 Hz), 36.0 (d, *J* = 4.0 Hz), 33.7 (s), 28.6 (d, *J* = 4.1 Hz).

^{19}F NMR (470 MHz, CD_3CN) δ -114.06 (s).

HRMS (DART-MS): m/z calcd for $C_{17}H_{16}OF$ [M-OH]$^+$: 255.11797, found: 255.11675.

IR (neat, cm^{-1}): 3442, 2970, 1673, 1579, 1483, 1446, 1207, 1068, 757.



4-hydroxy-1-phenyl-4-(m-tolyl)pentan-1-one (23)

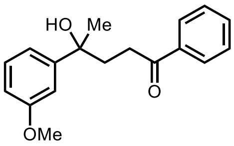
Product standard was prepared according to the General procedure I for the preparation of racemic compounds. Overall yield: 20%.

^{1}H NMR (500 MHz, CD_3CN) δ 7.87 (d, *J* = 7.2 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.34 (s, 1H), 7.29 (d, *J* = 7.9 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 7.3 Hz, 1H), 3.04 (ddd, *J* = 16.8, 9.4, 6.3 Hz, 1H), 2.78 (ddd, *J* = 17.0, 9.3, 5.8 Hz, 1H), 2.36 (s, 3H), 2.17 (dt, *J* = 9.2, 5.5 Hz, 2H), 1.55 (s, 3H).

^{13}C NMR (126 MHz, CD_3CN) δ 200.5, 148.2, 137.6, 137.0, 132.9, 128.6, 128.0, 127.9, 127.0, 125.7, 122.0, 73.3, 38.1, 33.6, 30.1, 20.7.

HRMS (DART-MS): m/z calcd for $C_{18}H_{19}O$ $[M\text{-}OH]^+$: 251.14304, found: 251.14183.

IR (neat, cm^{-1}): 3475, 2970, 1674, 1597, 1447, 1007, 742, 688.



4-hydroxy-4-(3-methoxyphenyl)-1-phenylpentan-1-one (24)

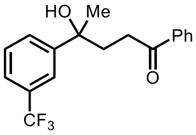
Product standard was prepared according to the General procedure for the preparation of racemic compounds. Overall yield: 11%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, J = 7.4 Hz, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.41 (t, J = 7.7 Hz, 2H), 7.27 – 7.24 (m, 1H), 7.06 (s, 1H), 7.01 (d, J = 7.7 Hz, 1H), 6.78 (dd, J = 8.1, 1.8 Hz, 1H), 3.81 (s, 3H), 3.01 (dt, J = 17.6, 7.4 Hz, 1H), 2.89 (dt, J = 17.8, 6.9 Hz, 1H), 2.65 (s, 1H), 2.39 – 2.18 (m, 2H), 1.61 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 201.2, 159.6, 149.1, 136.8, 133.1, 129.3, 128.5, 128.1, 117.3, 111.8, 111.0, 74.1, 55.2, 37.7, 33.8, 31.4.

HRMS (DART-MS): m/z calcd for $C_{18}H_{19}O_2$ $[M\text{-}OH]^+$: 267.13796, found: 267.13678.

IR (neat, cm^{-1}): 3473, 2953, 1674, 1558, 1134, 1030, 766, 689.



4-hydroxy-1-phenyl-4-(3-(trifluoromethyl)phenyl)pentan-1-one (25)

Product standard was prepared according to the General procedure I for the preparation of racemic compounds. Overall yield: 15%.

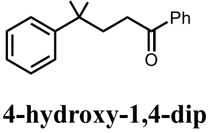
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, J = 7.4 Hz, 2H), 7.77 (s, 1H), 7.64 (d, J = 7.7 Hz, 1H), 7.59 – 7.48 (m, 2H), 7.44 (dt, J = 19.7, 7.7 Hz, 3H), 3.06 – 2.83 (m, 3H), 2.32 (ddq, J = 28.4, 14.5, 7.1 Hz, 2H), 1.64 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 201.1, 148.5, 136.6, 133.3, 130.6 (q, J = 32.0 Hz), 128.7, 128.6, 128.4, 128.1, 124.3 (q, J = 272.3 Hz), 123.6 (q, J = 3.8 Hz), 121.8 (q, J = 3.8 Hz), 74.0, 37.6, 33.6, 31.3.

^{19}F NMR (470 MHz, $CDCl_3$) δ -62.43 (s).

HRMS (DART-MS): m/z calcd for $C_{18}H_{16}OF_3$ $[M\text{-}OH]^+$: 305.11478, found: 305.11332.

IR (neat, cm^{-1}): 3494, 2969, 1666, 1597, 1320, 1131, 1068, 809, 744.



4-hydroxy-1,4-diphenylhexan-1-one (26)

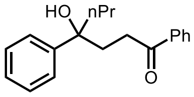
Product standard was prepared according to the General procedure I for the preparation of racemic compounds. Overall yield: 58%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 – 7.81 (m, 2H), 7.52 (t, J = 7.4 Hz, 1H), 7.40 (dd, J = 11.9, 5.3 Hz, 4H), 7.35 (t, J = 7.7 Hz, 2H), 7.23 (t, J = 7.3 Hz, 1H), 3.00 (ddd, J = 17.8, 8.0, 6.8 Hz, 1H), 2.81 (ddd, J = 17.8, 7.9, 5.8 Hz, 1H), 2.52 (s, 1H), 2.38 – 2.20 (m, 2H), 2.01 – 1.81 (m, 2H), 0.80 (t, J = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 201.4, 145.2, 136.9, 133.1, 128.5, 128.2, 128.1, 126.5, 125.5, 76.7, 36.5, 36.3, 33.5, 7.8.

HRMS (DART-MS): m/z calcd for $C_{18}H_{19}O$ $[M-OH]^+$: 251.14304, found: 251.14186.

IR (neat, cm^{-1}): 3420, 2968, 1717, 1665, 1446, 1273, 978, 686.



4-hydroxy-1,4-diphenylheptan-1-one (27)

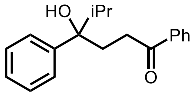
Product standard was prepared according to the General procedure I for the preparation of racemic compounds. Overall yield: 21%.

^{1}H NMR (500 MHz, CD_3CN) δ 7.85 (d, *J* = 7.4 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.9 Hz, 4H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.24 (t, *J* = 7.3 Hz, 1H), 3.08 – 2.98 (m, 1H), 2.68 (ddd, *J* = 17.1, 9.2, 5.8 Hz, 1H), 2.25 – 2.14 (m, 3H), 1.92 – 1.75 (m, 2H), 1.43 – 1.29 (m, 1H), 1.09 – 0.93 (m, 1H), 0.85 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD_3CN) δ 200.7, 146.3, 137.0, 132.9, 128.6, 127.9, 127.8, 126.1, 125.5, 75.9, 45.6, 37.1, 33.2, 16.6, 13.7.

HRMS (DART-MS): m/z calcd for $C_{19}H_{21}O$ $[M-OH]^+$: 265.15869, found: 265.15744.

IR (neat, cm^{-1}): 3502, 2955, 1711, 1660, 1595, 1577, 1468, 1174, 922, 701.



4-hydroxy-5-methyl-1,4-diphenylhexan-1-one (28)

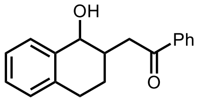
Product standard was prepared according to the General procedure I for the preparation of racemic compounds. Overall yield: 15%.

^{1}H NMR (500 MHz, CD_3CN) δ 7.84 – 7.80 (m, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.47 – 7.42 (m, 4H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.25 (t, *J* = 7.3 Hz, 1H), 2.94 (ddd, *J* = 17.2, 9.7, 5.8 Hz, 1H), 2.61 (ddd, *J* = 17.3, 9.4, 5.4 Hz, 1H), 2.28 (dddd, *J* = 18.7, 14.3, 9.2, 5.1 Hz, 2H), 2.08 (dt, *J* = 13.6, 6.8 Hz, 1H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.70 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, CD_3CN) δ 200.9, 145.5, 137.0, 132.9, 128.6, 127.8, 127.7, 126.1, 126.0, 78.1, 38.3, 33.8, 33.7, 17.0, 16.1.

HRMS (DART-MS): m/z calcd for $C_{19}H_{21}O$ $[M-OH]^+$: 265.15869, found: 265.15748.

IR (neat, cm^{-1}): 3464, 2962, 1665, 1593, 1359, 1219, 1016, 951, 764.



2-(1-hydroxy-1,2,3,4-tetrahydronaphthalen-2-yl)-1-phenylethan-1-one (29)

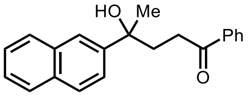
Product standard was prepared according to the General procedure I for the preparation of racemic compounds. Overall yield: 50%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.0 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.35 (d, *J* = 5.2 Hz, 1H), 7.22 (td, *J* = 7.2, 1.8 Hz, 2H), 7.14 (d, *J* = 6.6 Hz, 1H), 4.73 (t, *J* = 4.3 Hz, 1H), 3.34 (dd, *J* = 16.8, 7.2 Hz, 1H), 3.17 – 3.05 (m, 1H), 2.96 – 2.81 (m, 2H), 2.56 (ddq, *J* = 10.6, 6.9, 3.3 Hz, 1H), 1.99 – 1.71 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 200.3, 138.1, 137.2, 136.6, 133.2, 129.9, 129.1, 128.6, 128.3, 128.0, 126.3, 69.7, 40.5, 35.9, 28.8, 23.5.

HRMS (DART-MS): m/z calcd for $C_{18}H_{17}O$ $[M-OH]^+$: 249.12739, found: 249.12632.

IR (neat, cm^{-1}): 3510, 3453, 2929, 1738, 1676, 1578, 1447, 1365, 1205, 1102, 738.



4-hydroxy-4-(naphthalen-2-yl)-1-phenylpentan-1-one (30)

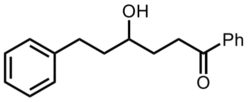
Product standard was prepared according to the General procedure I for the preparation of racemic compounds. Overall yield: 26%.

^{1}H NMR (500 MHz, CD_3CN) δ 8.02 (s, 1H), 7.94 – 7.82 (m, 5H), 7.63 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.51 (tt, *J* = 6.8, 5.1 Hz, 2H), 7.44 (t, *J* = 7.8 Hz, 2H), 3.07 (ddd, *J* = 17.1, 9.8, 5.7 Hz, 1H), 2.80 (ddd, *J* = 17.2, 9.7, 5.4 Hz, 1H), 2.39 – 2.21 (m, 2H), 1.66 (s, 3H).

^{13}C NMR (126 MHz, CD_3CN) δ 200.5, 145.7, 137.0, 133.2, 132.9, 132.2, 128.5, 128.0, 127.8, 127.6, 127.4, 126.0, 125.6, 124.0, 123.3, 73.6, 37.9, 33.6, 30.1.

HRMS (DART-MS): m/z calcd for $C_{21}H_{19}O$ $[M-OH]^+$: 287.14304, found: 287.14175.

IR (neat, cm^{-1}): 3455, 2970, 1673, 1597, 1447, 1370, 1121, 819, 742.



4-hydroxy-1,6-diphenylhexan-1-one (31)

Product standard was prepared according to the General procedure I for the preparation of racemic compounds. Overall yield: 23%.

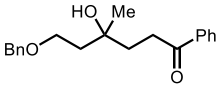
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.3 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.20 (dd, *J* = 15.0, 7.4 Hz, 3H), 3.72 (s, 1H), 3.22 – 3.07 (m, 2H), 2.87 – 2.78 (m, 1H), 2.76 – 2.65 (m, 1H), 2.06 – 1.97 (m, 1H), 1.93 (d, *J* = 5.2 Hz, 1H), 1.92 – 1.85 (m, 1H), 1.86 – 1.79 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 200.8, 142.0, 136.9, 133.2, 128.6, 128.5, 128.4, 128.1, 125.9, 70.9, 39.5, 35.0, 32.1, 31.4.

HRMS (DART-MS): m/z calcd for $C_{18}H_{19}O$ $[M-OH]^+$: 251.14304, found: 251.14228.

IR (neat, cm^{-1}): 3455, 3024, 2970, 1738, 1447, 1365, 1216, 1068, 902, 685.

The NMR spectra is in agreement with published data[19].



6-(benzyloxy)-4-hydroxy-4-methyl-1-phenylhexan-1-one (32)

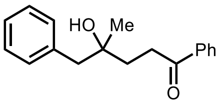
Product standard was prepared according to the General procedure I for the preparation of racemic compounds. Overall yield: 8%.

^{1}H NMR (500 MHz, CD_3CN) δ 8.01 (d, *J* = 7.2 Hz, 2H), 7.61-7.64 (m, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.32 - 7.36 (m, 4H), 7.30-7.32 (m, 1H), 4.51 (s, 2H), 3.69 (td, *J* = 6.5, 1.8 Hz, 2H), 3.11 (ddd, *J* = 8.6, 6.6, 1.8 Hz, 2H), 3.00 (s, 1H),1.77-1.91 (m, 4H), 1.20 (s, 3H).

^{13}C NMR (126 MHz, CD_3CN) δ 200.6, 138.7, 137.2, 132.9, 128.6, 128.3, 127.9, 127.7, 127.5, 72.6, 70.9, 66.9, 40.5, 36.0, 33.3, 26.3.

HRMS (DART-MS): m/z calcd for $C_{20}H_{23}O_2$ $[M-OH]^+$: 295.16926, found: 295.16823.

IR (neat, cm^{-1}): 3463, 2928, 1679, 1597, 1449, 1284, 1097, 697.



4-hydroxy-4-methyl-1,5-diphenylpentan-1-one (33)

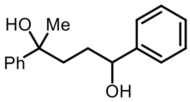
Product standard was prepared according to the General procedure I for the preparation of racemic compounds. Overall yield: 20%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.3 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 3H), 7.28 – 7.21 (m, 2H), 3.26 – 3.09 (m, 2H), 2.83 (dd, *J* = 30.5, 13.2 Hz, 2H), 2.09 – 1.89 (m, 2H), 1.20 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 200.7, 137.2 136.9, 133.1, 130.6, 128.6, 128.3, 128.1, 126.6, 72.0, 48.8, 35.3, 33.2, 26.5.

HRMS (DART-MS): m/z calcd for $C_{18}H_{19}O$ $[M-OH]^+$: 251.14304, found: 251.14190.

IR (neat, cm^{-1}): 3464, 2970, 1738, 1365, 1228, 1216, 1034, 809, 698.



1,4-diphenylpentane-1,4-diol (34)

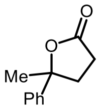
Product standard was prepared according to the General procedure I for the product derivatization. Yield: Quant.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (ddd, *J* = 8.1, 6.9, 1.5 Hz, 2H), 7.36 – 7.27 (m, 3H), 7.28 – 7.19 (m, 5H), 4.64 (ddd, *J* = 16.6, 7.9, 4.9 Hz, 1H), 2.72 (br, 1H), 2.51 (br, 1H), 2.12 – 1.90 (m, 1H), 1.86-1.60 (m, 3H), 1.55 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 147.8, 147.7, 144.6, 144.5, 128.4, 128.2, 128.2, 127.5, 127.5, 126.6, 126.5, 125.8, 124.9, 124.8, 74.9, 74.4, 74.4, 74.4, 40.5, 39.9, 33.7, 33.5, 31.0, 30.5.

HRMS (DART-MS): m/z calcd for $C_{17}H_{17}$ $[M-H_2O-OH]^+$: 221.13248, found: 221.13182.

The NMR spectra is in agreement with published data[19].



5-methyl-5-phenyldihydrofuran-2(3H)-one (35)

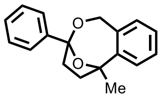
Product standard was prepared according to the General procedure II for the product derivatization. Yield: 62%.

^{1}H NMR (500 MHz, CD_3CN) δ 7.46 – 7.40 (m, 4H), 7.34 (ddt, *J* = 8.5, 5.0, 3.0 Hz, 1H), 2.75 – 2.58 (m, 1H), 2.56 – 2.41 (m, 3H), 1.70 (s, 3H).

^{13}C NMR (126 MHz, CD_3CN) δ 176.4, 145.1, 128.5, 127.5, 124.2, 86.6, 35.5, 28.6, 28.3.

HRMS (DART-MS): m/z calcd for $C_{11}H_{13}O_2$ $[M+H]^+$: 177.09101, found: 177.09027.

The NMR spectra is in agreement with published data[20].



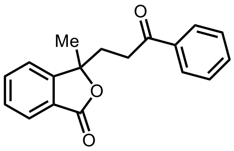
6-methyl-3-phenyl-3,4,5,6-tetrahydro-1H-3,6-epoxybenzo[c]oxocine (37)

Product standard was prepared according to the General procedure I for the preparation of racemic compounds. Overall yield: 33%.

^{1}H NMR (500 MHz, CD_3CN) δ 7.67 (dt, *J* = 6.5, 1.4 Hz, 2H), 7.49 – 7.41 (m, 2H), 7.42 – 7.34 (m, 2H), 7.34 – 7.26 (m, 1H), 7.21 (td, *J* = 7.4, 1.4 Hz, 1H), 7.12 (d, *J* = 7.4 Hz, 1H), 4.96 (d, *J* = 14.1 Hz, 1H), 4.45 (d, *J* = 14.2 Hz, 1H), 2.37 (ddd, *J* = 11.6, 5.7, 3.9 Hz, 1H), 2.27 – 2.21 (m, 2H), 2.14 (dd, *J* = 12.1, 9.4 Hz, 1H), 1.85 (s, 3H).

^{13}C NMR (126 MHz, CD_3CN) δ 148.01, 140.5, 138.1, 128.2, 128.2, 127.7, 127.4, 126.3, 126.1, 124.8, 109.30, 86.7, 65.3, 40.9, 39.9, 26.7.

HRMS (DART-MS): m/z calcd for $C_{18}H_{19}O_2$ $[M+H]^+$: 267.13796, found: 267.13697.



3-methyl-3-(3-oxo-3-phenylpropyl)isobenzofuran-1(3H)-one (40)

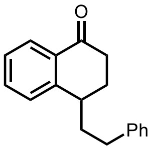
Product standard was prepared according to the General procedure II for the preparation of racemic compounds. Overall yield: 15%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.6 Hz, 1H), 7.82 (d, *J* = 7.4 Hz, 2H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.52 (q, *J* = 7.0 Hz, 2H), 7.41 (t, *J* = 7.9 Hz, 3H), 3.12 – 3.01 (m, 1H), 2.66 – 2.50 (m, 2H), 2.42 – 2.33 (m, 1H), 1.71 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 198.7, 169.8, 153.2, 136.4, 134.4, 133.3, 129.3, 128.6, 128.0, 125.9, 121.1, 87.0, 33.7, 32.6, 26.3.

HRMS (ESI): m/z calcd for $C_{18}H_{17}O_3$ $[M+H]^+$: 2881.11932, found: 281.11722.

IR (neat, cm^{-1}): 2982, 1748, 1708, 1680, 1465, 1220, 1031, 718, 608.



4-phenethyl-3,4-dihydronaphthalen-1(2H)-one (41)

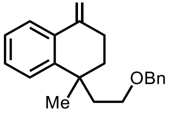
Product standard was prepared according to the General procedure I for the preparation of racemic compounds. Overall yield: 6%.

^{1}H NMR (500 MHz, CD_3CN) δ 7.96 (d, *J* = 7.7 Hz, 1H), 7.56 (td, *J* = 7.7, 1.3 Hz, 1H), 7.42 – 7.26 (m, 6H), 7.21 (t, *J* = 7.1 Hz, 1H), 3.02 (m, 1H), 2.88 – 2.78 (m, 2H), 2.75 – 2.65 (m, 1H), 2.55 (dt, *J* = 17.7, 4.9 Hz, 1H), 2.35 – 2.22 (m, 1H), 2.18 (m, 1H), 2.09 – 2.00 (m, 2H).

^{13}C NMR (126 MHz, CD_3CN) δ 197.7, 148.5, 142.3, 133.4, 131.9, 128.6, 128.4, 128.4, 126.6, 126.6, 125.8, 37.4, 36.1, 34.5, 33.4, 26.2.

HRMS (DART-MS): m/z calcd for $C_{18}H_{19}O$ $[M+H]^+$: 251.14304, found: 251.14183.

IR (neat, cm^{-1}): 3024, 2925, 1738, 1680, 1599, 1477, 1282, 763, 697.



6-(benzyloxy)-4-hydroxy-4-methyl-1-phenylhexan-1-one (42)

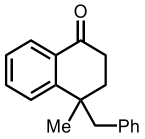
Product standard was prepared according to the General procedure I for the preparation of racemic compounds. Overall yield: 3%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.54 – 7.48 (m, 1H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.32 (dd, *J* = 13.1, 6.7 Hz, 3H), 7.28 (d, *J* = 7.0 Hz, 3H), 4.44 (s, 2H), 3.56 – 3.44 (m, 2H), 2.82 – 2.64 (m, 2H), 2.24 – 2.10 (m, 2H), 1.97 (dq, *J* = 9.3, 6.2 Hz, 2H), 1.42 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 198.3, 151.0, 138.2, 133.7, 131.6, 128.4, 127.6, 127.5, 126.5, 126.1, 73.1, 67.1, 40.6, 36.2, 34.8, 34.3, 28.0.

HRMS (DART-MS): m/z calcd for $C_{20}H_{23}O_2$ $[M+H]^+$: 295.16926, found: 295.16786.

IR (neat, cm^{-1}): 2929, 2861, 1738, 1680, 1597, 1452, 1284, 1095, 734, 696.



4-benzyl-4-methyl-3,4-dihydronaphthalen-1(2H)-one (43)

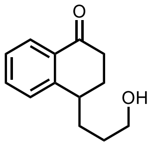
Product standard was prepared according to the General procedure I for the preparation of racemic compounds. Overall yield: 9%.

^{1}H NMR (500 MHz, MeOD) δ 7.99 (d, *J* = 7.8 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.42 – 7.31 (m, 2H), 7.26 – 7.17 (m, 3H), 7.05 – 6.97 (m, 2H), 3.01 (dd, *J* = 31.0, 13.4 Hz, 2H), 2.91 – 2.77 (m, 1H), 2.62 (dt, *J* = 17.7, 5.1 Hz, 1H), 2.08 (dt, *J* = 13.6, 5.3 Hz, 1H), 1.99 – 1.91 (m, 1H), 1.38 (s, 3H).

^{13}C NMR (126 MHz, MeOD) δ 199.1, 151.2, 137.7, 133.5, 131.4, 130.2, 127.5, 127.0, 126.7, 126.2, 126.1, 46.7, 37.6, 34.3, 33.7, 26.6.

HRMS (DART-MS): m/z calcd for $C_{18}H_{19}O$ $[M+H]^+$: 251.14304, found: 251.14201.

IR (neat, cm^{-1}): 3026, 2921, 1738, 1679, 1451, 1284, 910, 770, 604.



4-(3-hydroxypropyl)-3,4-dihydronaphthalen-1(2H)-one (44)

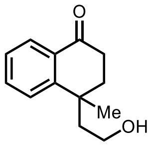
Product standard was prepared according to the General procedure I for the preparation of racemic compounds. Overall yield: 3%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.7 Hz, 1H), 7.48 (td, *J* = 7.6, 1.2 Hz, 1H), 7.41 – 7.22 (m, 2H), 3.69 (t, *J* = 6.2 Hz, 2H), 3.01 – 2.90 (m, 1H), 2.82 – 2.73 (m, 1H), 2.59 (dt, *J* = 17.8, 5.0 Hz, 1H), 2.27 (ddd, *J* = 11.8, 9.0, 7.2 Hz, 1H), 2.15 – 2.00 (m, 1H), 1.77 (tdd, *J* = 16.9, 10.7, 5.9 Hz, 3H), 1.69 – 1.61 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 198.3, 148.0, 133.5, 131.9, 128.3, 127.4, 126.7, 62.8, 37.9, 34.9, 30.8, 30.7, 26.9.

HRMS (DART-MS): m/z calcd for $C_{13}H_{17}O_2$ $[M+H]^+$: 205.12231, found: 205.12231.

IR (neat, cm^{-1}): 3398, 2933, 1678, 1597, 1283, 1053, 765, 550.



4-(2-hydroxyethyl)-4-methyl-3,4-dihydronaphthalen-1(2H)-one (45)

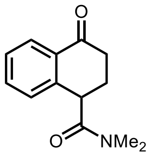
Product standard was prepared according to the General procedure I for the preparation of racemic compounds. Overall yield: 5%.

^{1}H NMR (500 MHz, CD_3CN) δ 7.96 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.60 (td, *J* = 7.6, 1.5 Hz, 1H), 7.51 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.38 – 7.32 (m, 1H), 3.55 (td, *J* = 7.3, 5.1 Hz, 2H), 2.84 – 2.61 (m, 2H), 2.57 (p, *J* = 5.3 Hz, 1H), 2.30 – 2.11 (m, 2H), 2.07 – 2.00 (m, 1H), 1.91 – 1.80 (m, 1H), 1.42 (s, 3H).

^{13}C NMR (126 MHz, CD_3CN) δ 197.8, 151.7, 133.6, 131.5, 126.8, 126.5, 126.3, 58.3, 43.4, 35.9, 34.5, 33.8, 27.1.

HRMS (DART-MS): m/z calcd for $C_{13}H_{17}O_2$ $[M+H]^+$: 205.12231, found: 205.12135.

IR (neat, cm^{-1}): 3396, 2931, 1737, 1674, 1597, 1478, 1285, 1047, 1015, 756.



***N, N*-dimethyl-4-oxo-1,2,3,4-tetrahydronaphthalene-1-carboxamide (46)**

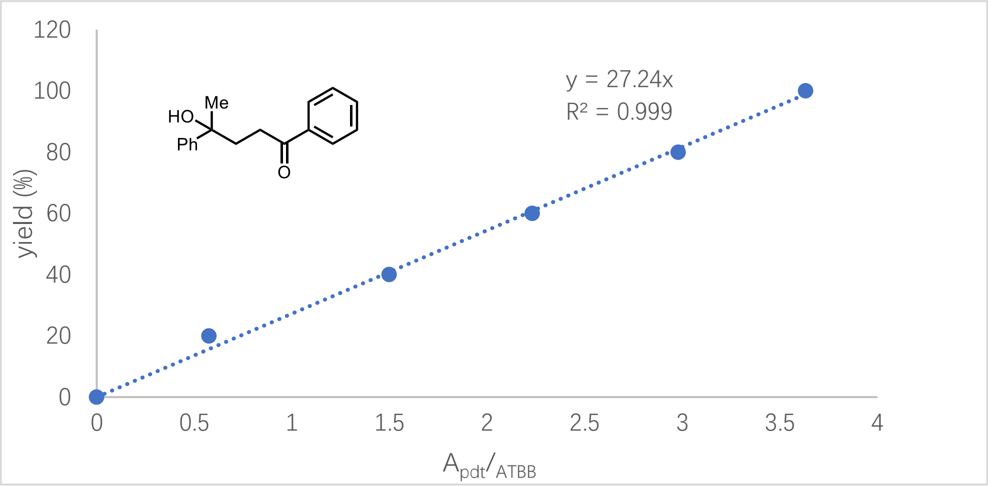
Product standard was prepared according to the General procedure I for the preparation of racemic compounds. Overall yield: 3%.

^{1}H NMR (500 MHz, CD_3CN) δ 7.98 (d, *J* = 7.8 Hz, 1H), 7.55 (tt, *J* = 7.5, 1.4 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 7.7 Hz, 1H), 4.44 (t, *J* = 5.6 Hz, 1H), 3.23 (d, *J* = 1.3 Hz, 3H), 2.97 (d, *J* = 1.2 Hz, 3H), 2.81 – 2.68 (m, 1H), 2.58 (dtd, *J* = 17.4, 6.4, 1.2 Hz, 1H), 2.41 – 2.24 (m, 2H).

^{13}C NMR (126 MHz, CD_3CN) δ 197.3, 172.3, 143.5, 133.3, 133.2, 128.3, 127.2, 126.5, 41.1, 37.1, 35.4, 34.9, 25.9.

HRMS (DART-MS): m/z calcd for $C_{13}H_{16}NO_2$ $[M+H]^+$: 218.11756, found: 218.11648.

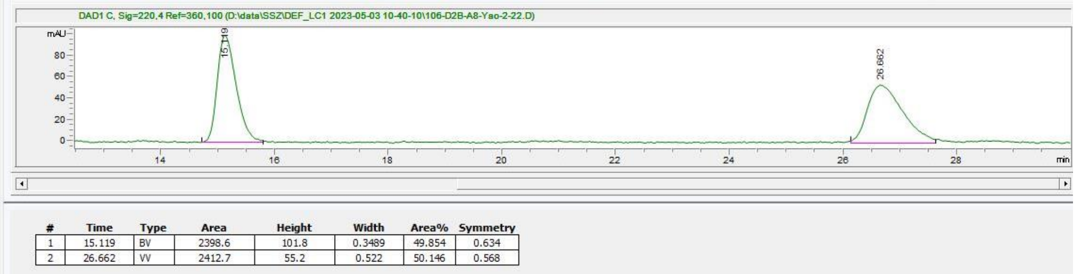
IR (neat, cm^{-1}): 2970, 1738, 1680, 1365, 1216, 1010, 827, 769.



Enzymatic reaction was conducted according to the general procedure for hydroxylation reaction in vials using prop-1-en-2-ylbenzene (**1a**) and 2-bromo-1-phenylethan-1-one (**2a**) as the starting materials.

Yield: 96%. 1 mmol scale: 55% isolated yield.

Enantioselectivity: 95:5 er. Chiral HPLC method: OJ-H column, 220 nm, 10% isopropanol/hexanes, flow rate 1.0 mL/min, room temperature, t_R (major) = 25.00 min, t_R (minor) = 15.11 min.



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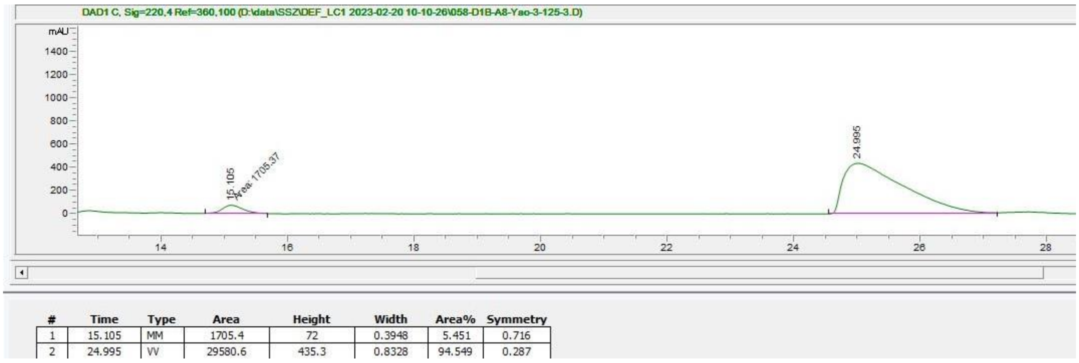
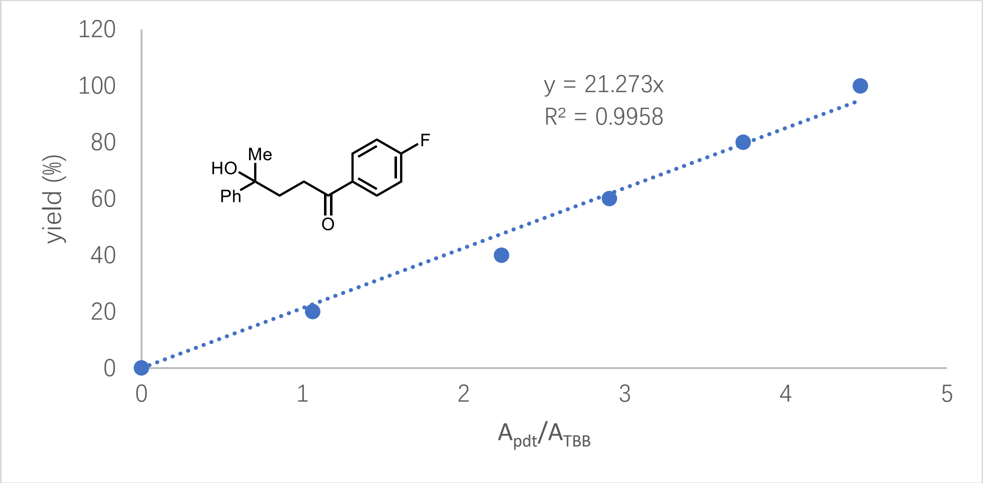
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	15.119	BV	2398.6	101.8	0.3489	49.854	0.634
2	26.662	VV	2412.7	55.2	0.522	50.146	0.568



DAD1 C, Sig=220,4 Ref=360,100 (D:\data\SSZ\DEF_LC1 2023-02-20 10-10-26\058-D1B-A8-Yao-3-125-3.D)

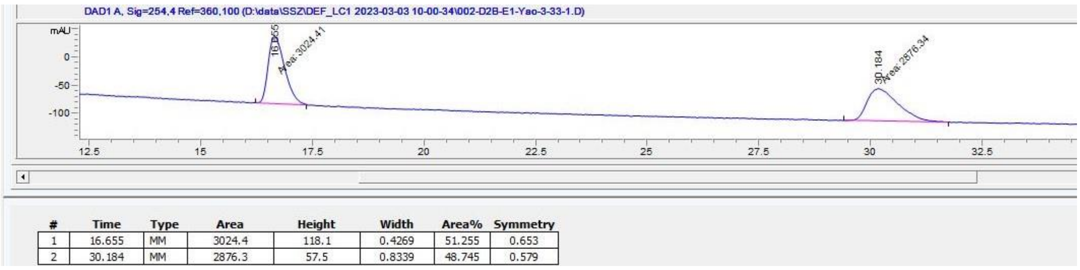
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	15.105	MM	1705.4	72	0.3948	5.451	0.716
2	24.995	VV	29580.6	435.3	0.8328	94.549	0.287



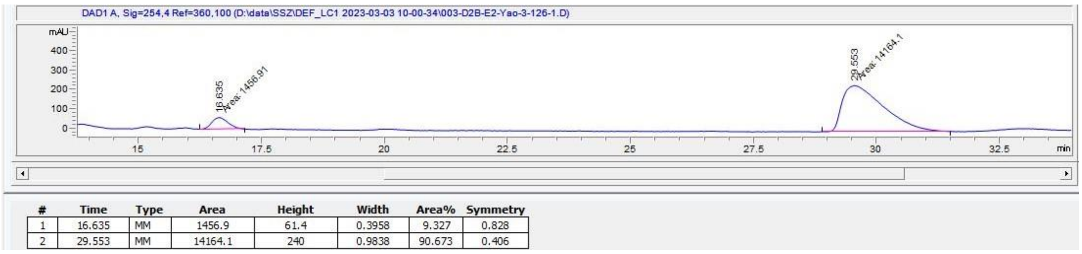
Enzymatic reaction was conducted according to the general procedure for hydroxylation reaction in vials using prop-1-en-2-ylbenzene (**1a)** and 2-bromo-1-(4-fluorophenyl)ethan-1-one (**2b)** as the starting materials.

Yield: 50% (1.5 mol% S34Q).

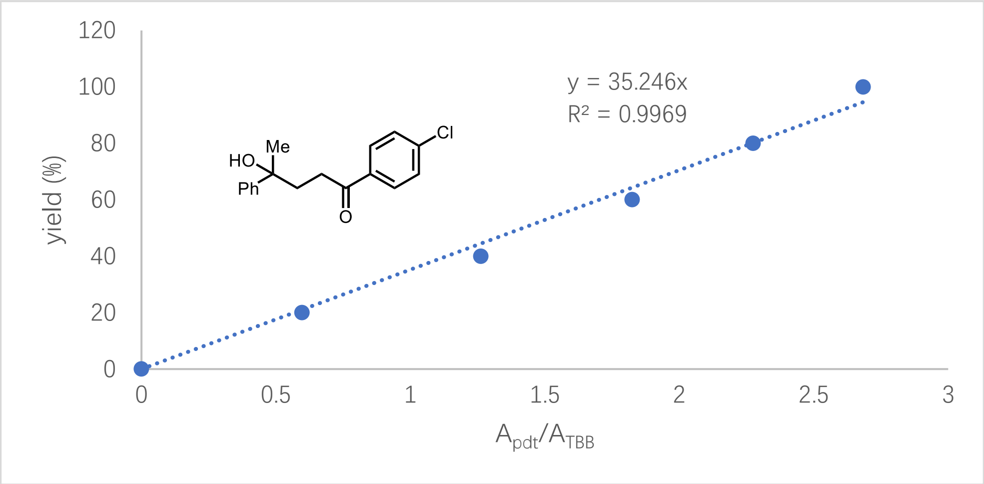
Enantioselectivity: 91:9 er. Chiral HPLC method: OJ-H column, 254 nm, 7% isopropanol/hexanes, flow rate 1.0 mL/min, room temperature, t_R (major) = 29.55 min, t_R (minor) = 16.64 min.


DAD1 A, Sig=254,4 Ref=360,100 (D:\data\SSZ\DEF_LC1 2023-03-03 10-00-34\002-D2B-E1-Yao-3-33-1.D)

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	16.655	MM	3024.4	118.1	0.4269	51.255	0.653
2	30.184	MM	2876.3	57.5	0.8339	48.745	0.579


DAD1 A, Sig=254,4 Ref=360,100 (D:\data\SSZ\DEF_LC1 2023-03-03 10-00-34\003-D2B-E2-Yao-3-126-1.D)

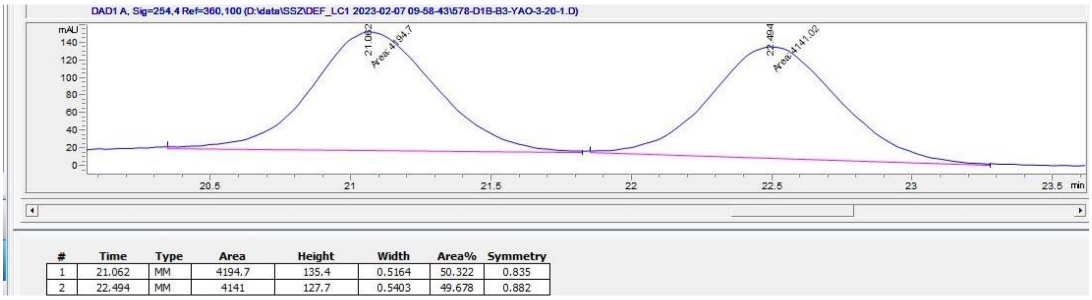
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	16.635	MM	1456.9	61.4	0.3958	9.327	0.828
2	29.553	MM	14164.1	240	0.9838	90.673	0.406



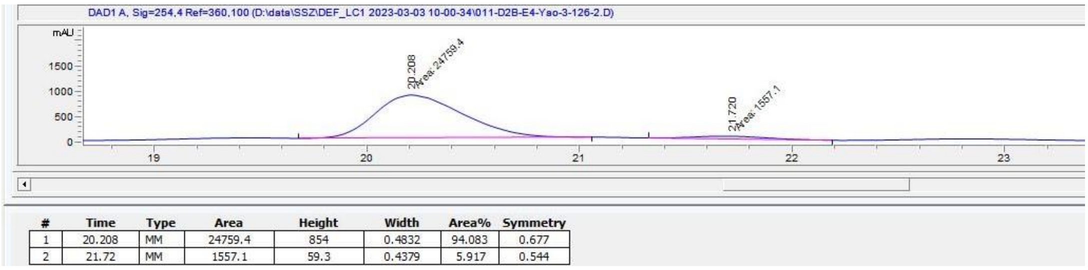
Enzymatic reaction was conducted according to the general procedure for hydroxylation reaction in vials using prop-1-en-2-ylbenzene (**1a)** and 2-bromo-1-(4-chlorophenyl)ethan-1-one (**2c)** as the starting materials.

Yield: 47%.

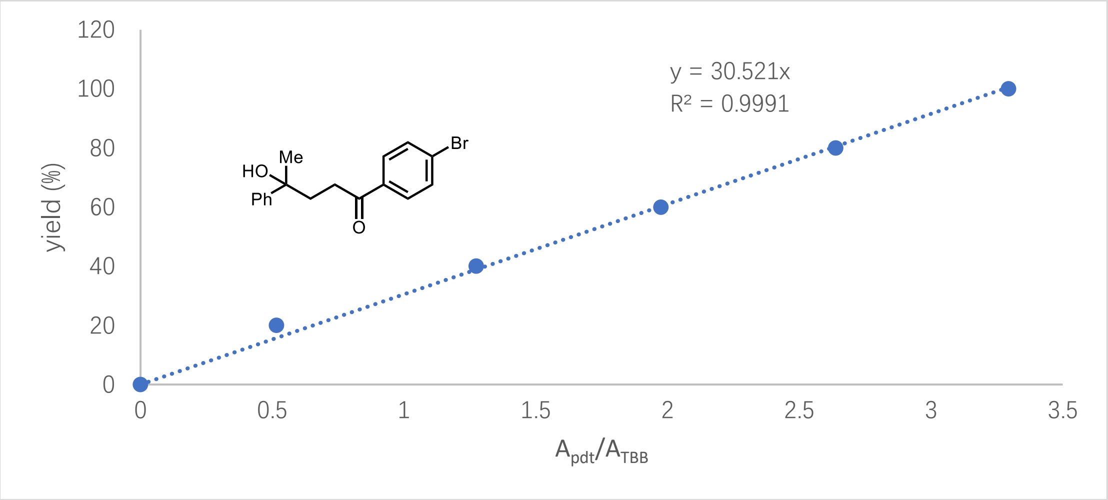
Enantioselectivity: 94:6 er. Chiral HPLC method: IA-H column, 254 nm, 5% isopropanol/hexanes, flow rate 1.0 mL/min, room temperature, t_R (major) = 20.21 min, t_R (minor) = 21.72 min.


DAD1 A, Sig=254,4 Ref=360,100 (D:\data\SSZ\DEF_LC1 2023-02-07 09-58-43\578-D1B-B3-YAO-3-20-1.D)

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	21.062	MM	4194.7	135.4	0.5164	50.322	0.835
2	22.494	MM	4141	127.7	0.5403	49.678	0.882


DAD1 A, Sig=254,4 Ref=360,100 (D:\data\SSZ\DEF_LC1 2023-03-03 10-00-34\011-D2B-E4-Yao-3-126-2.D)

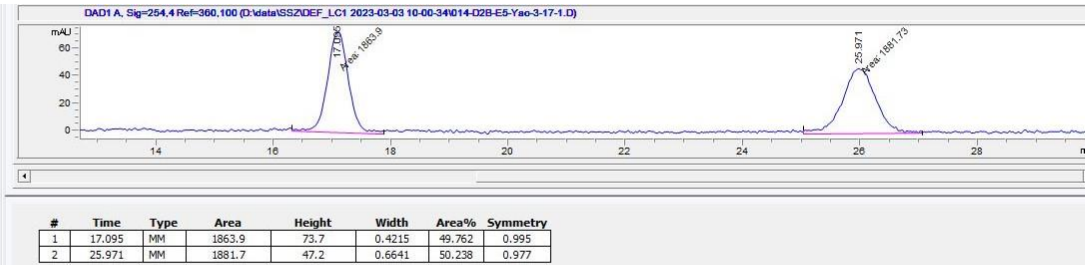
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	20.208	MM	24759.4	854	0.4832	94.083	0.677
2	21.72	MM	1557.1	59.3	0.4379	5.917	0.544



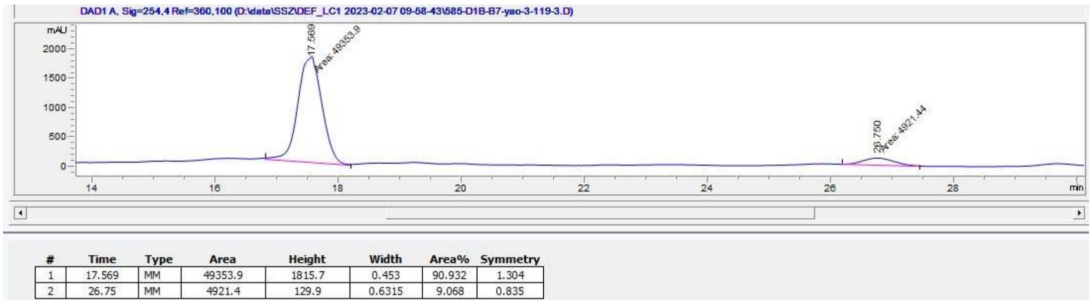
Enzymatic reaction was conducted according to the general procedure for hydroxylation reaction in vials using prop-1-en-2-ylbenzene (**1a**) and 2-bromo-1-(4-bromophenyl)ethan-1-one (**2d**) as the starting materials.

Yield: 46% (1.5 mol% S34Q)

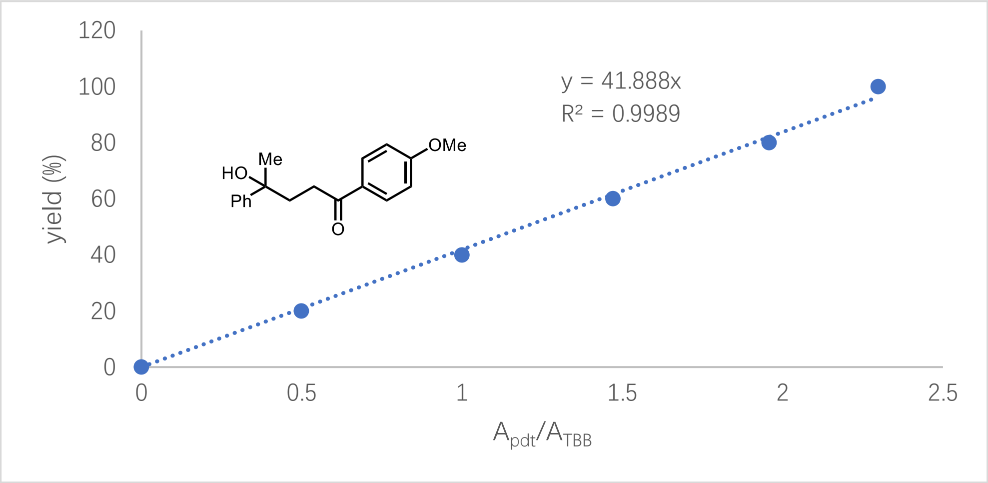
Enantioselectivity: 91:9 er. Chiral HPLC method: IC-H column, 254 nm, 4% isopropanol/hexanes, flow rate 1.0 mL/min, room temperature, t_R (major) = 17.57 min, t_R (minor) = 26.75 min.


DAD1 A, Sig=254,4 Ref=360,100 (D:\data\SSZ\DEF_LC1 2023-03-03 10-00-34\014-D2B-E5-Yao-3-17-1.D)

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	17.095	MM	1863.9	73.7	0.4215	49.762	0.995
2	25.971	MM	1881.7	47.2	0.6641	50.238	0.977


DAD1 A, Sig=254,4 Ref=360,100 (D:\data\SSZ\DEF_LC1 2023-02-07 09-58-43\585-D1B-B7-yao-3-119-3.D)

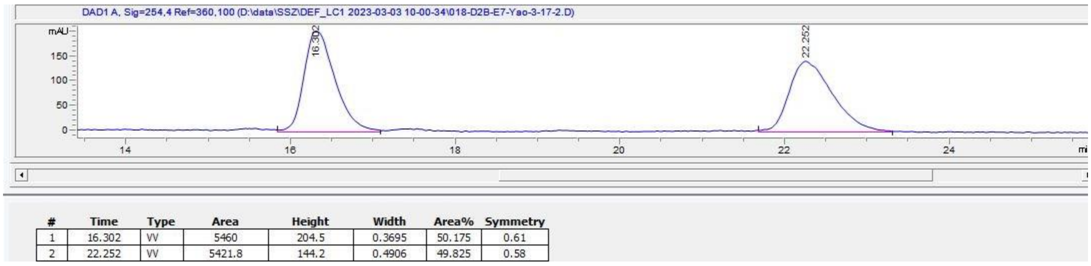
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	17.569	MM	49353.9	1815.7	0.453	90.932	1.304
2	26.75	MM	4921.4	129.9	0.6315	9.068	0.835



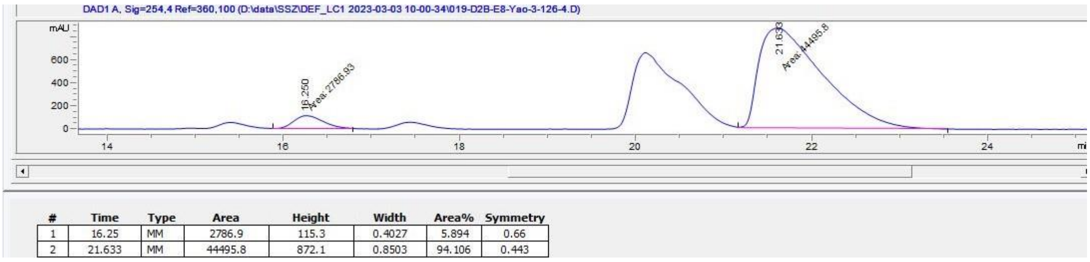
Enzymatic reaction was conducted according to the general procedure for hydroxylation reaction in vials using prop-1-en-2-ylbenzene (**1a)** and 2-bromo-1-(4-methoxyphenyl)ethan-1-one (**2e)** as the starting materials.

Yield: 73%.

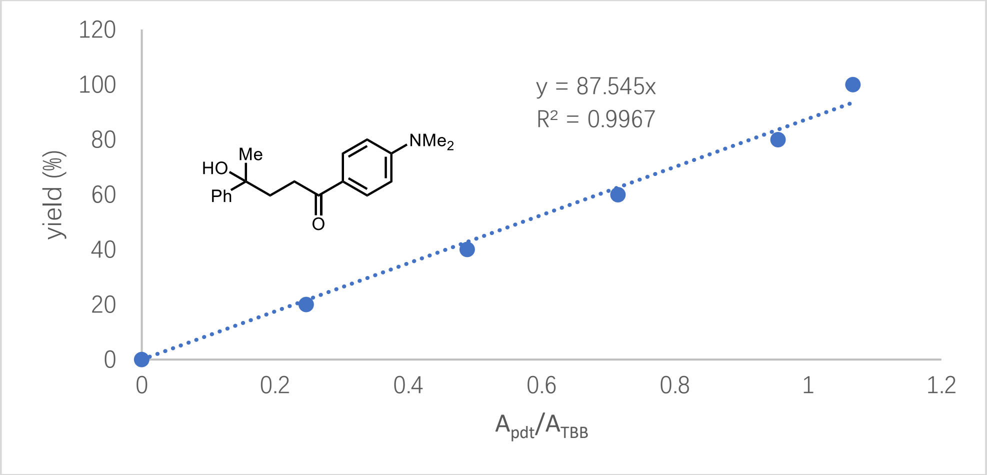
Enantioselectivity: 94:6 er. Chiral HPLC method: OJ-H column, 254 nm, 15% isopropanol/hexanes, flow rate 1.0 mL/min, room temperature, t_R (major) = 21.63 min, t_R (minor) = 16.25 min.



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	16.302	VV	5460	204.5	0.3695	50.175	0.61
2	22.252	VV	5421.8	144.2	0.4906	49.825	0.58



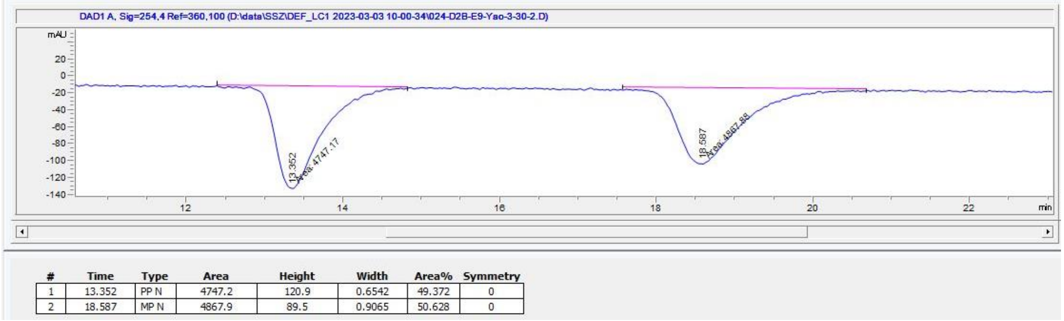
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	16.25	MM	2786.9	115.3	0.4027	5.894	0.66
2	21.633	MM	44495.8	872.1	0.8503	94.106	0.443



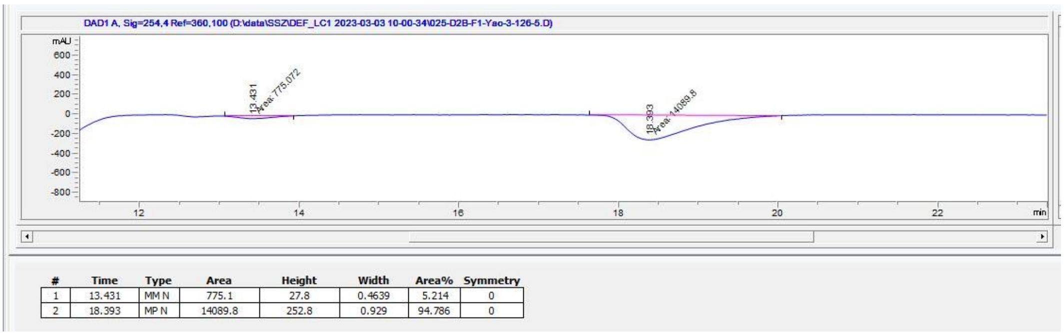
Enzymatic reaction was conducted according to the general procedure for hydroxylation reaction in vials using prop-1-en-2-ylbenzene (**1a)** and 2-bromo-1-(4-(dimethylamino)phenyl)ethan-1-one (**2f)** as the starting materials.

Yield: 79%.

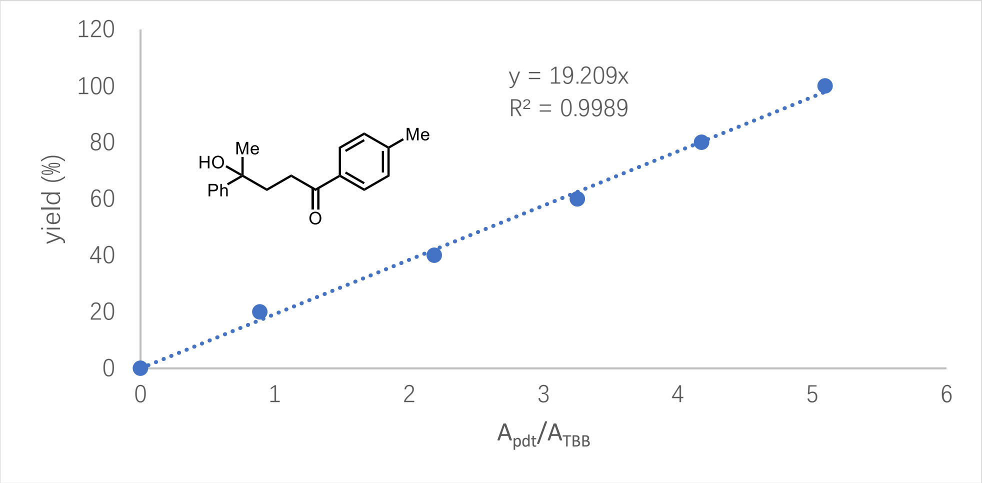
Enantioselectivity: 95:5 er. Chiral HPLC method: OD-H column, 254 nm, 15% isopropanol/hexanes, flow rate 1.0 mL/min, room temperature, t_R (major) = 18.39 min, t_R (minor) = 13.40 min.


DAD1 A, Sig=254,4 Ref=360,100 (D:\data\SSZ\DEF_LC1 2023-03-03 10-00-34\024-D2B-E9-Yao-3-30-2.D)

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	13.352	PP N	4747.2	120.9	0.6542	49.372	0
2	18.587	MP N	4867.9	89.5	0.9065	50.628	0


DAD1 A, Sig=254,4 Ref=360,100 (D:\data\SSZ\DEF_LC1 2023-03-03 10-00-34\025-D2B-F1-Yao-3-126-5.D)

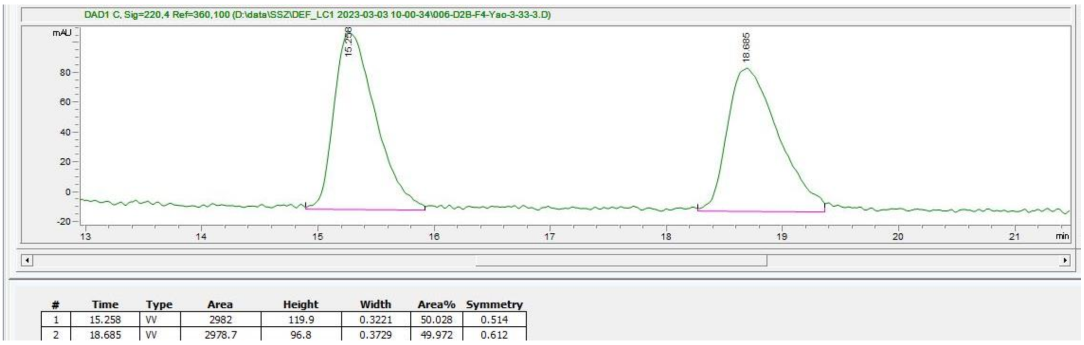
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	13.431	MM N	775.1	27.8	0.4639	5.214	0
2	18.393	MP N	14089.8	252.8	0.929	94.786	0



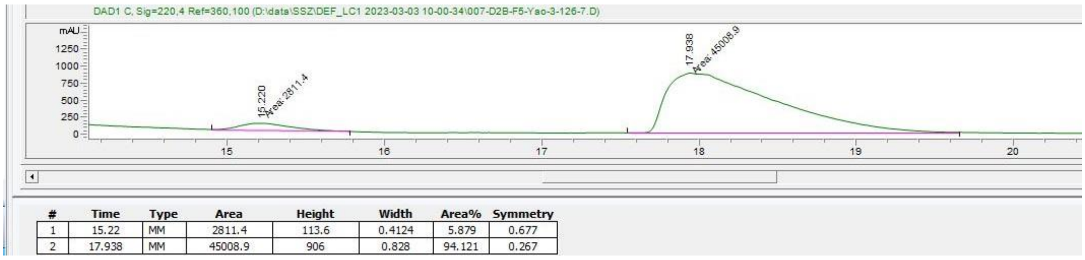
Enzymatic reaction was conducted according to the general procedure for hydroxylation reaction in vials using prop-1-en-2-ylbenzene (**1a**) and 2-bromo-1-(p-tolyl)ethan-1-one (**2g**) as the starting materials.

Yield: 76%.

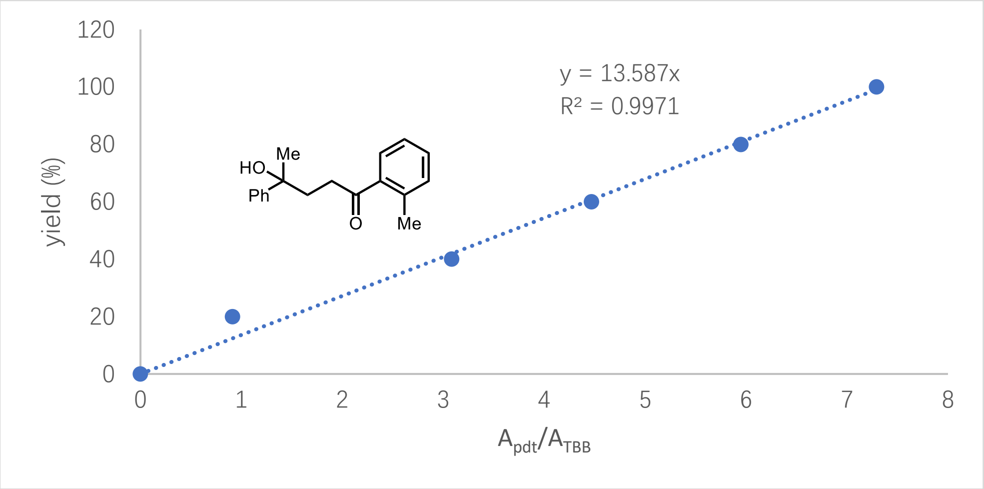
Enantioselectivity: 94:6 er. Chiral HPLC method: OJ-H column, 220 nm, 7% isopropanol/hexanes, flow rate 1.0 mL/min, room temperature, t_R (major) = 17.94 min, t_R (minor) = 15.22 min.


DAD1 C, Sig=220,4 Ref=360,100 (D:\data\SSZ\DEF_LC1 2023-03-03 10-00-34\006-D2B-F4-Yao-3-33-3.D)

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	15.258	VV	2982	119.9	0.3221	50.028	0.514
2	18.685	VV	2978.7	96.8	0.3729	49.972	0.612


DAD1 C, Sig=220,4 Ref=360,100 (D:\data\SSZ\DEF_LC1 2023-03-03 10-00-34\007-D2B-F5-Yao-3-126-7.D)

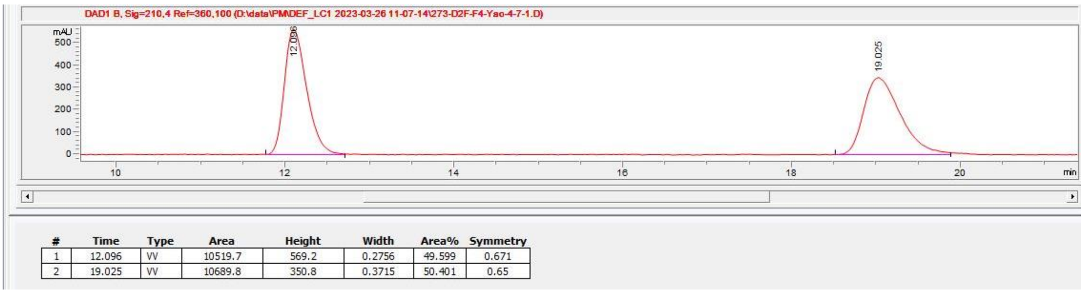
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	15.22	MM	2811.4	113.6	0.4124	5.879	0.677
2	17.938	MM	45008.9	906	0.828	94.121	0.267



Enzymatic reaction was conducted according to the general procedure for hydroxylation reaction in vials using prop-1-en-2-ylbenzene (**1a)** and 2-bromo-1-(o-tolyl)ethan-1-one (**2h)** as the starting materials.

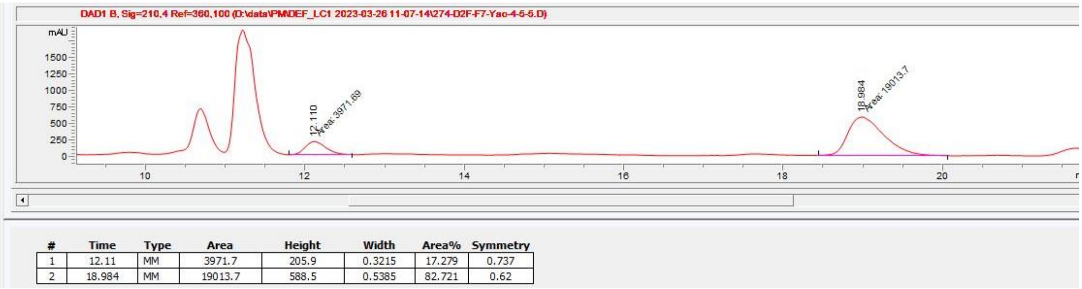
Yield: 14%.

Enantioselectivity: 83:17 er. Chiral HPLC method: IC-H column, 210 nm, 4% isopropanol/hexanes, flow rate 1.0 mL/min, room temperature, t_R (major) =18.98 min, t_R (minor) = 12.11 min.



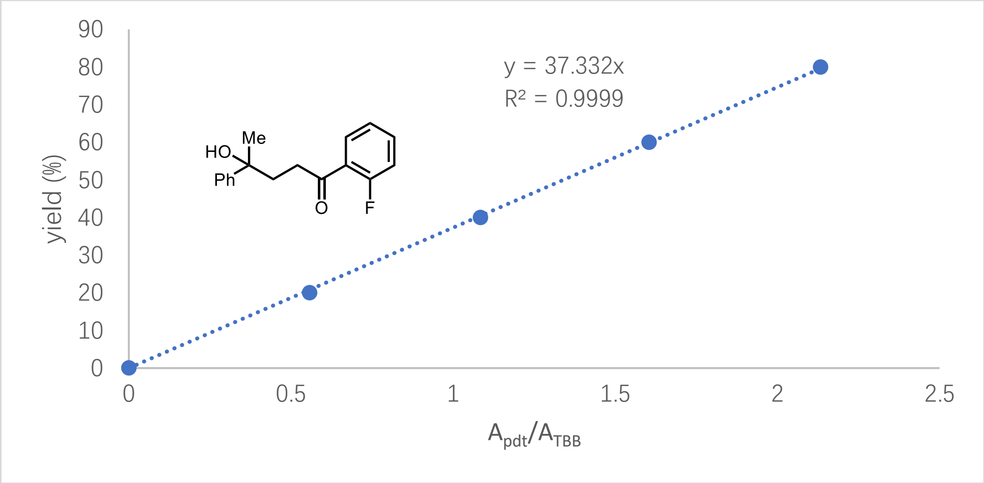
DAD1 B, Sig=210,4 Ref=360,100 (D:\data\PMDEF_LC1 2023-03-26 11-07-14\273-D2F-F4-Yao-4-7-1.D)

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	12.096	VV	10519.7	569.2	0.2756	49.599	0.671
2	19.025	VV	10689.8	350.8	0.3715	50.401	0.65



DAD1 B, Sig=210,4 Ref=360,100 (D:\data\PMDEF_LC1 2023-03-26 11-07-14\274-D2F-F7-Yao-4-5-5.D)

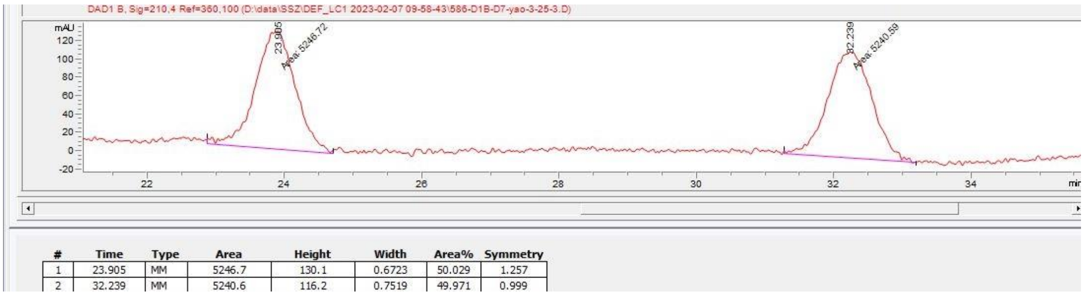
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	12.11	MM	3971.7	205.9	0.3215	17.279	0.737
2	18.984	MM	19013.7	588.5	0.5385	82.721	0.62



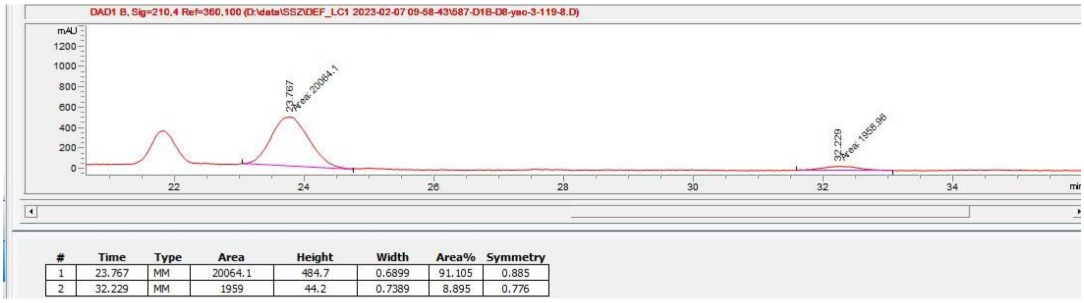
Enzymatic reaction was conducted according to the general procedure for hydroxylation reaction in vials using prop-1-en-2-ylbenzene (**1a**) and 2-bromo-1-(2-fluorophenyl)ethan-1-one (**2i)** as the starting materials.

Yield: 56%.

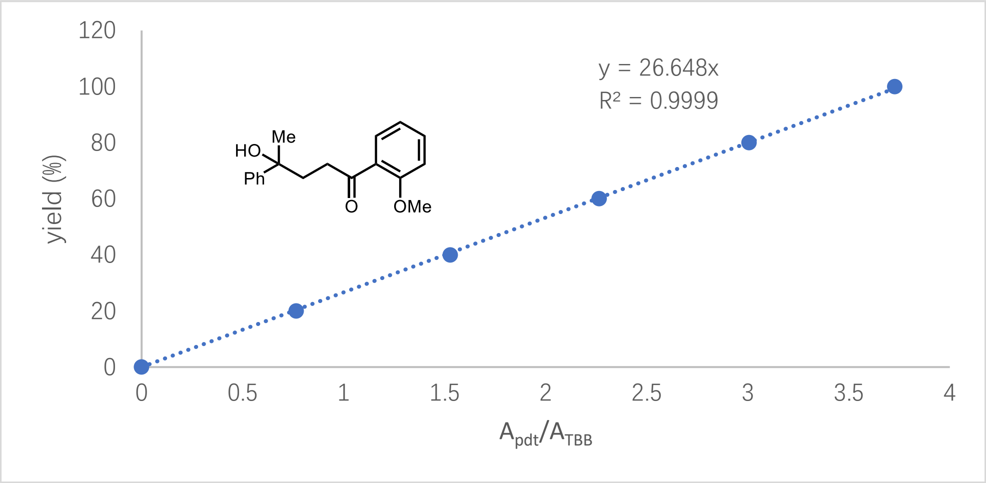
Enantioselectivity: 91:9 er. Chiral HPLC method: IC-H column, 210 nm, 4% isopropanol/hexanes, flow rate 1.0 mL/min, room temperature, t_R (major) = 23.77 min, t_R (minor) = 32.23 min.



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	23.905	MM	5246.7	130.1	0.6723	50.029	1.257
2	32.239	MM	5240.6	116.2	0.7519	49.971	0.999



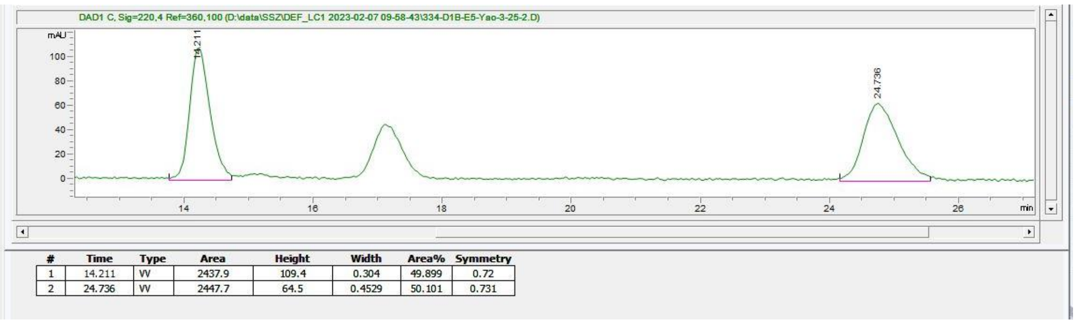
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	23.767	MM	20064.1	484.7	0.6899	91.105	0.885
2	32.229	MM	1959	44.2	0.7389	8.895	0.776



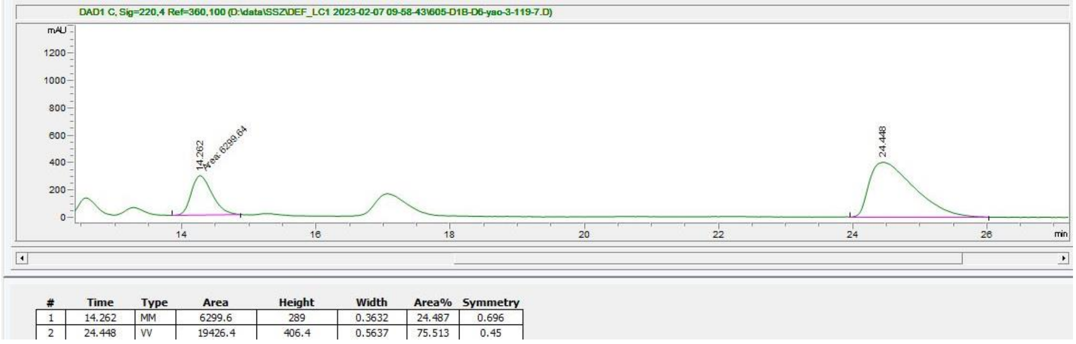
Enzymatic reaction was conducted according to the general procedure for hydroxylation reaction in vials using prop-1-en-2-ylbenzene (**1a)** and 2-bromo-1-(2-methoxyphenyl)ethan-1-one (**2j)** as the starting materials.

Yield: 71%.

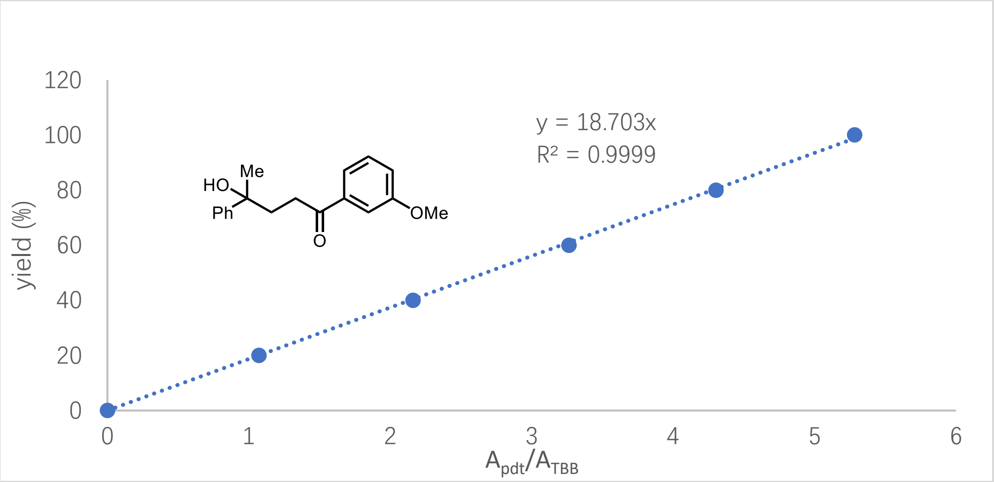
Enantioselectivity: 76:24 er. Chiral HPLC method: OJ-H column, 220 nm, 15% isopropanol/hexanes, flow rate 1.0 mL/min, room temperature, t_R (major) = 24.45 min, t_R (minor) = 14.26 min.


DAD1 C, Sig=220,4 Ref=360,100 (D:\data\SSZ\DEF_LC1 2023-02-07 09-58-43\334-D1B-E5-Yao-3-25-2.D)

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	14.211	VV	2437.9	109.4	0.304	49.899	0.72
2	24.736	VV	2447.7	64.5	0.4529	50.101	0.731


DAD1 C, Sig=220,4 Ref=360,100 (D:\data\SSZ\DEF_LC1 2023-02-07 09-58-43\605-D1B-D6-yao-3-119-7.D)

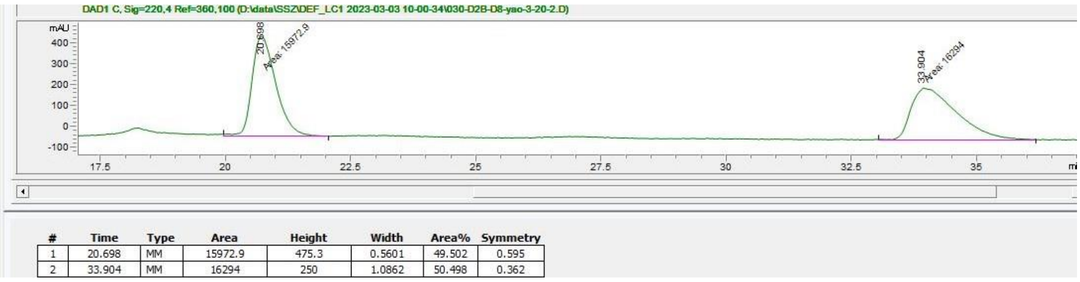
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	14.262	MM	6299.6	289	0.3632	24.487	0.696
2	24.448	VV	19426.4	406.4	0.5637	75.513	0.45



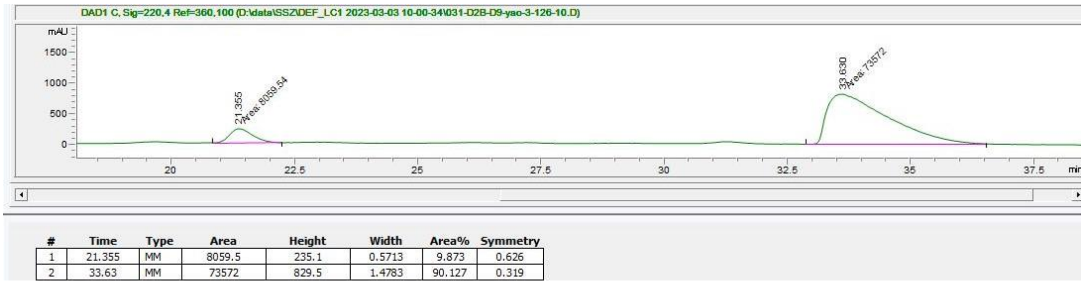
Enzymatic reaction was conducted according to the general procedure for hydroxylation reaction in vials using prop-1-en-2-ylbenzene (**1a)** and 2-bromo-1-(3-methoxyphenyl)ethan-1-one (**2k)** as the starting materials.

Yield: 49%.

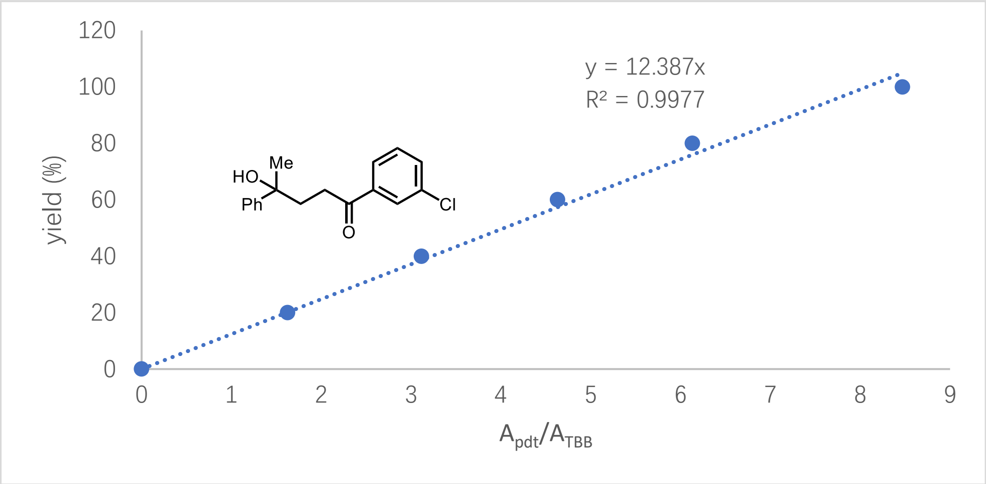
Enantioselectivity: 90:10 er. Chiral HPLC method: OJ-H column, 220 nm, 10% isopropanol/hexanes, flow rate 1.0 mL/min, room temperature, t_R (major) = 33.63 min, t_R (minor) = 21.36 min.


DAD1 C, Sig=220,4 Ref=360,100 (D:\data\SSZ\DEF_LC1 2023-03-03 10-00-34\030-D2B-D8-yao-3-20-2.D)

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	20.698	MM	15972.9	475.3	0.5601	49.502	0.595
2	33.904	MM	16294	250	1.0862	50.498	0.362


DAD1 C, Sig=220,4 Ref=360,100 (D:\data\SSZ\DEF_LC1 2023-03-03 10-00-34\031-D2B-D9-yao-3-126-10.D)

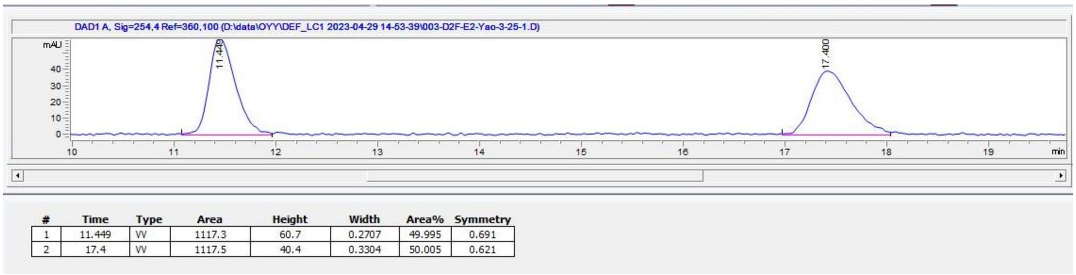
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	21.355	MM	8059.5	235.1	0.5713	9.873	0.626
2	33.63	MM	73572	829.5	1.4783	90.127	0.319



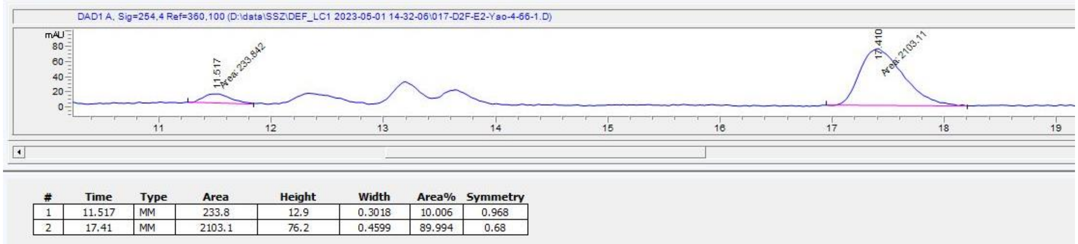
Enzymatic reaction was conducted according to the general procedure for hydroxylation reaction in vials using prop-1-en-2-ylbenzene (**1a**) and 2-bromo-1-(3-chlorophenyl)ethan-1-one (**2l**) as the starting materials.

Yield: 25%.

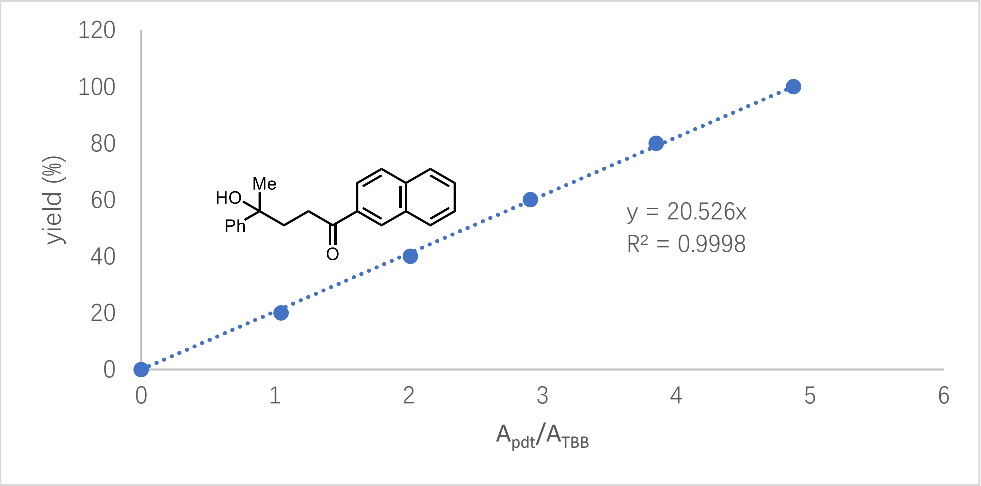
Enantioselectivity: 90:10 er. Chiral HPLC method: OJ-H column, 254 nm, 10% isopropanol/hexanes, flow rate 1.0 mL/min, room temperature, t_R (major) =17.41 min, t_R (minor) = 11.52 min.



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	11.449	VV	1117.3	60.7	0.2707	49.995	0.691
2	17.4	VV	1117.5	40.4	0.3304	50.005	0.621



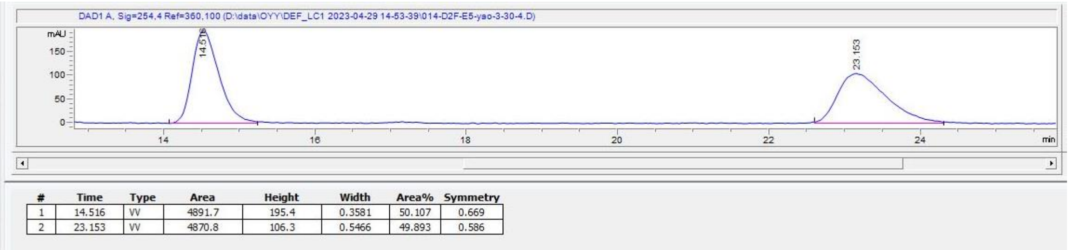
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	11.517	MM	233.8	12.9	0.3018	10.006	0.968
2	17.41	MM	2103.1	76.2	0.4599	89.994	0.68



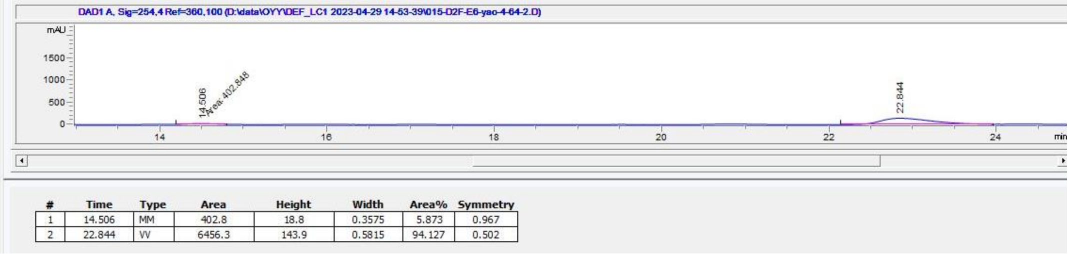
Enzymatic reaction was conducted according to the general procedure for hydroxylation reaction in vials using prop-1-en-2-ylbenzene (**1a)** and 2-bromo-1-(naphthalen-2-yl)ethan-1-one (**2m)** as the starting materials.

Yield: 26% (1.5 mol% S34Q).

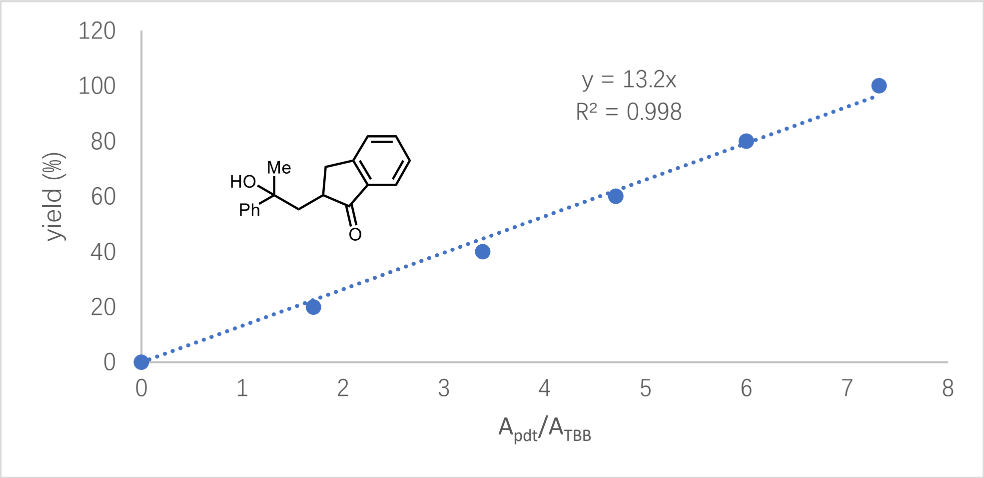
Enantioselectivity: 94:6 er. Chiral HPLC method: OJ-H column, 254 nm, 20% isopropanol/hexanes, flow rate 1.0 mL/min, room temperature, t_R (major) = 22.84 min, t_R (minor) = 14.51 min.


DAD1 A, Sig=254,4 Ref=360,100 (D:\data\OYY\DEF_LC1 2023-04-29 14-53-39\014-D2F-E5-yao-3-30-4.D)

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	14.516	VV	4891.7	195.4	0.3581	50.107	0.669
2	23.153	VV	4870.8	106.3	0.5466	49.893	0.586


DAD1 A, Sig=254,4 Ref=360,100 (D:\data\OYY\DEF_LC1 2023-04-29 14-53-39\015-D2F-E6-yao-4-64-2.D)

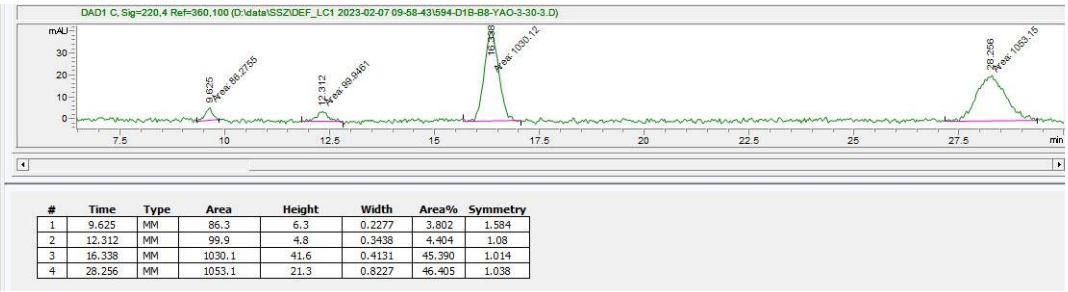
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	14.506	MM	402.8	18.8	0.3575	5.873	0.967
2	22.844	VV	6456.3	143.9	0.5815	94.127	0.502



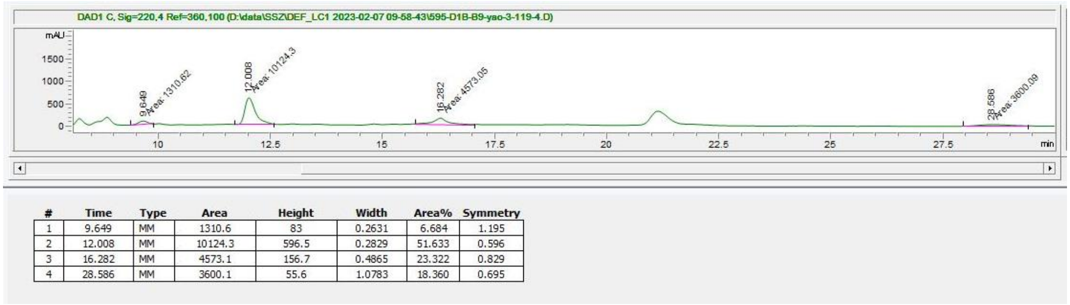
Enzymatic reaction was conducted according to the general procedure for hydroxylation reaction in vials using prop-1-en-2-ylbenzene (**1a)** and 2-(2-bromoacetyl)-2,3-dihydro-1H-inden-1-one **(2n)** as the starting materials.

Yield: 15%, d.r. 1.4:1 based on the HPLC ratio.

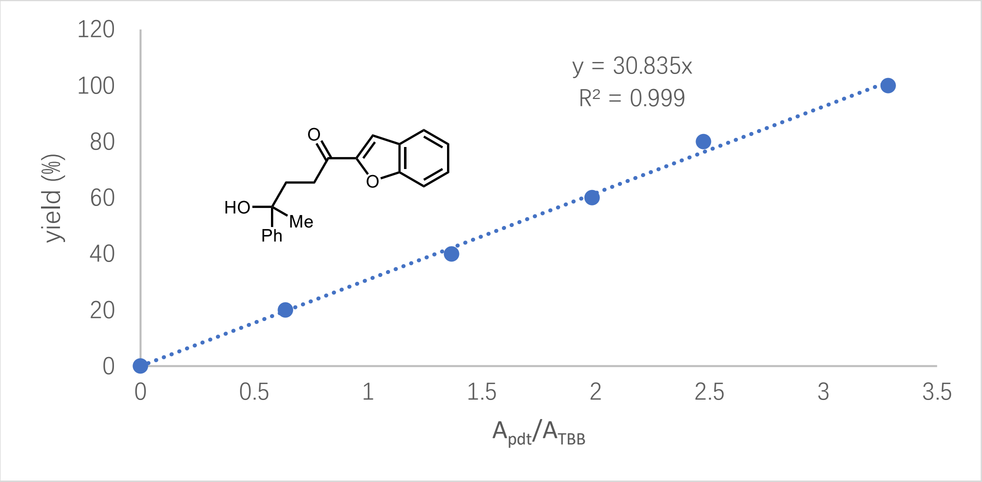
Enantioselectivity: 89:11 er and 56:44 er. Chiral HPLC method: AS-H column, 220 nm, 7% isopropanol/hexanes, flow rate 1.0 mL/min, room temperature, major isomer: t_R (major) = 12.01 min, t_R (minor) = 9.65 min. Minor isomer: t_R(major) = 16.28 min, t_R (minor) = 28.59 min.



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	9.625	MM	86.3	6.3	0.2277	3.802	1.584
2	12.312	MM	99.9	4.8	0.3438	4.404	1.08
3	16.338	MM	1030.1	41.6	0.4131	45.390	1.014
4	28.256	MM	1053.1	21.3	0.8227	46.405	1.038



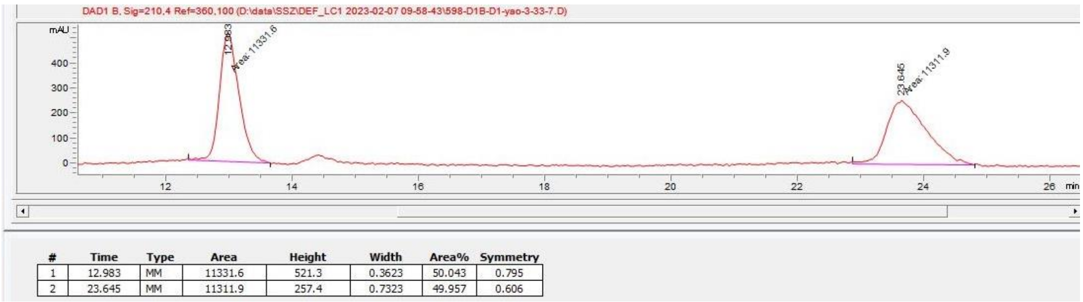
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	9.649	MM	1310.6	83	0.2631	6.684	1.195
2	12.008	MM	10124.3	596.5	0.2829	51.633	0.596
3	16.282	MM	4573.1	156.7	0.4865	23.322	0.829
4	28.586	MM	3600.1	55.6	1.0783	18.360	0.695



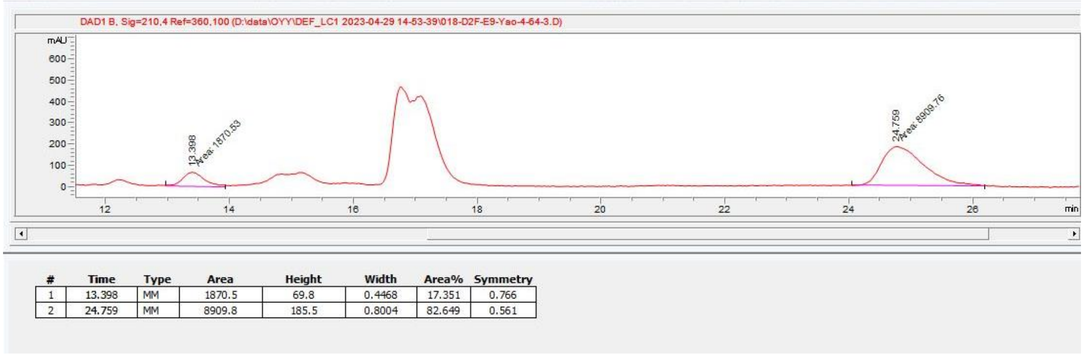
Enzymatic reaction was conducted according to the general procedure for hydroxylation reaction in vials using prop-1-en-2-ylbenzene (**1a)** and 1-(benzofuran-2-yl)-2-bromoethan-1-one (**2o)** as the starting materials.

Yield: 22% (1.5 mol% S34Q).

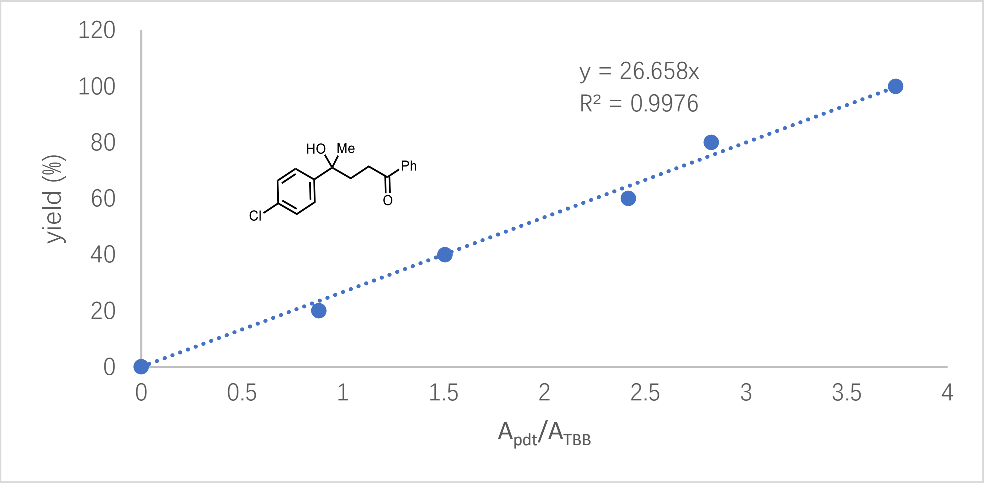
Enantioselectivity: 83:17 er. Chiral HPLC method: OJ-H column, 210 nm, 20% isopropanol/hexanes, flow rate 1.0 mL/min, room temperature, t_R (major) = 24.76 min, t_R (minor) = 13.40 min.


DAD1 B, Sig=210,4 Ref=360,100 (D:\data\SSZ\DEF_LC1 2023-02-07 09-58-43\598-D1B-D1-yao-3-33-7.D)

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	12.983	MM	11331.6	521.3	0.3623	50.043	0.795
2	23.645	MM	11311.9	257.4	0.7323	49.957	0.606


DAD1 B, Sig=210,4 Ref=360,100 (D:\data\OYY\DEF_LC1 2023-04-29 14-53-39\018-D2F-E9-Yao-4-64-3.D)

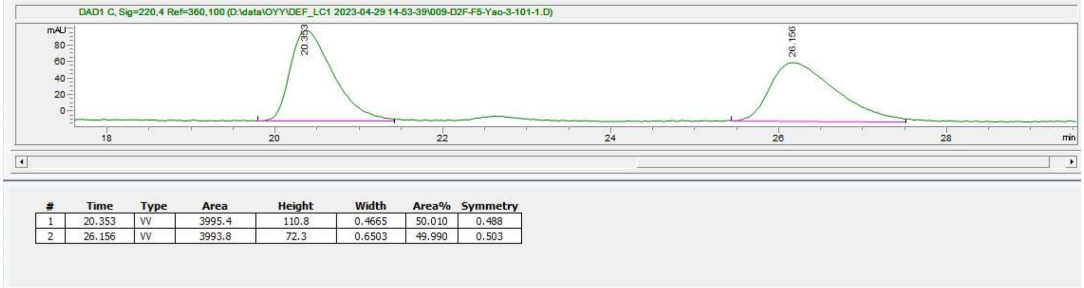
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	13.398	MM	1870.5	69.8	0.4468	17.351	0.766
2	24.759	MM	8909.8	185.5	0.8004	82.649	0.561



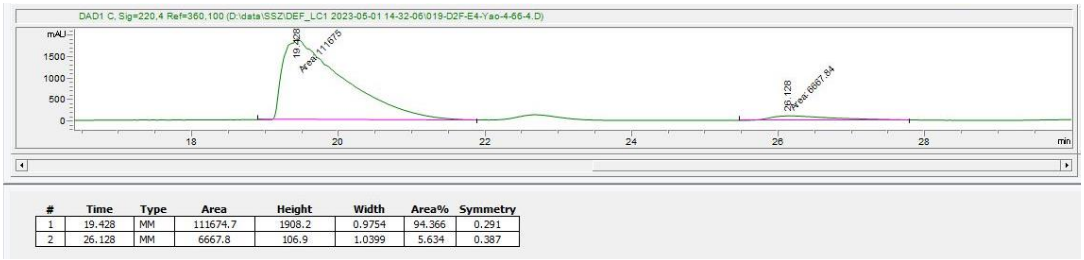
Enzymatic reaction was conducted according to the general procedure for hydroxylation reaction in vials using 1-chloro-4-(prop-1-en-2-yl)benzene (**1b**) and 2-bromo-1-phenylethan-1-one (**2a**) as the starting materials.

Yield: 70% (1.5 mol% S34Q).

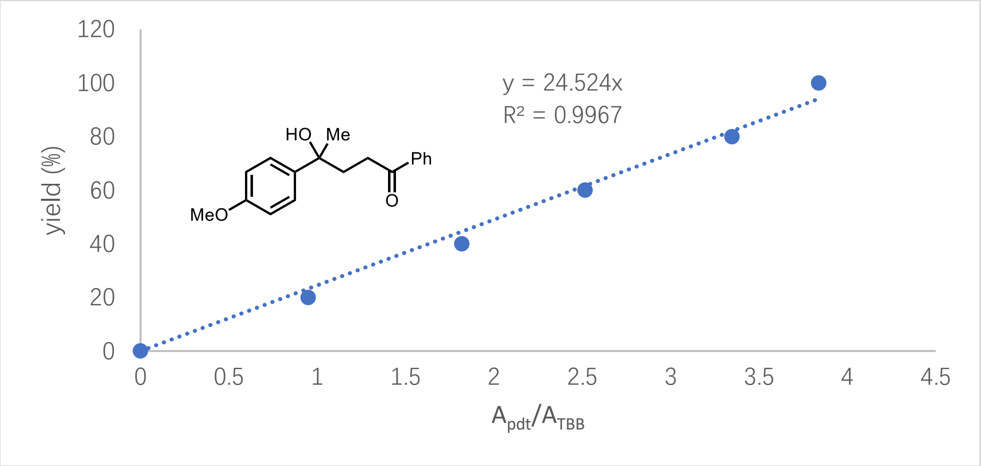
Enantioselectivity: 94:6 er. Chiral HPLC method: OJ-H column, 220 nm, 10% isopropanol/hexanes, flow rate 1.0 mL/min, room temperature, t_R (major) = 19.43 min, t_R (minor) = 26.13 min.



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	20.353	VV	3995.4	110.8	0.4665	50.010	0.488
2	26.156	VV	3993.8	72.3	0.6503	49.990	0.503



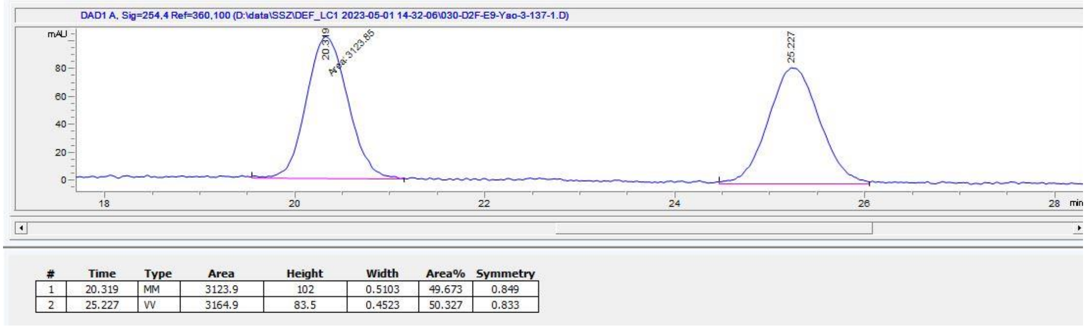
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	19.428	MM	111674.7	1908.2	0.9754	94.366	0.291
2	26.128	MM	6667.8	106.9	1.0399	5.634	0.387



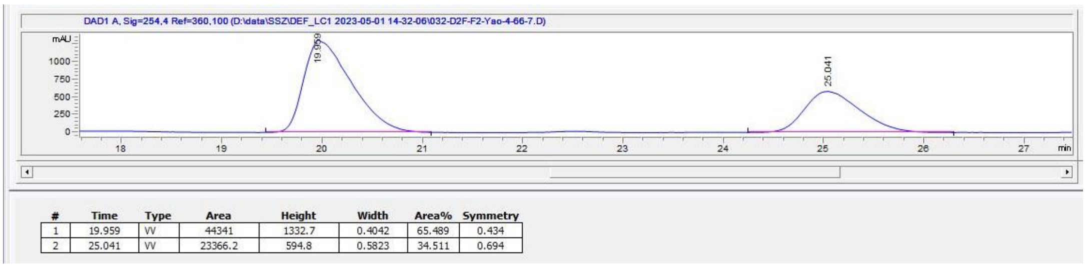
Enzymatic reaction was conducted according to the general procedure for hydroxylation reaction in vials using 1-methoxy-4-(prop-1-en-2-yl)benzene (**1c)** and 2-bromo-1-phenylethan-1-one (**2a)** as the starting materials.

Yield: 76%.

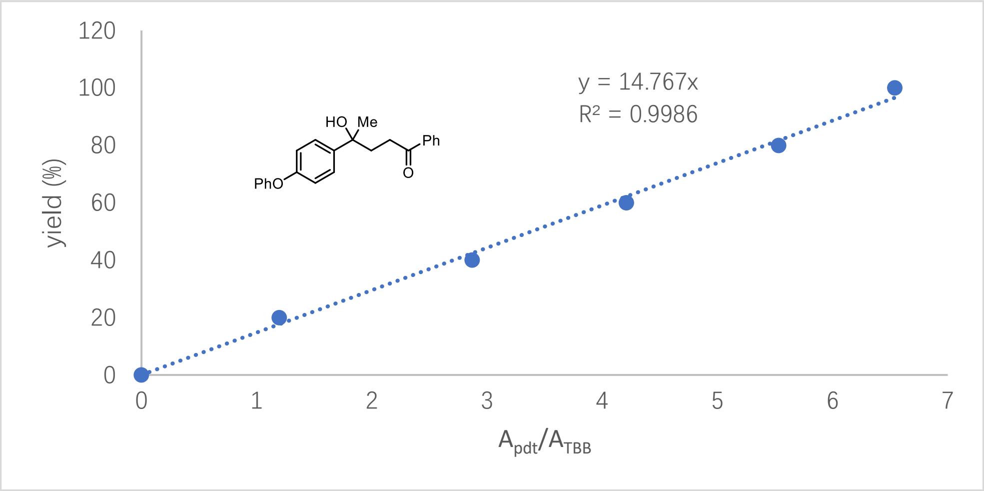
Enantioselectivity: 65:35 er. Chiral HPLC method: IC-H column, 254 nm, 4% isopropanol/hexanes, flow rate 1.0 mL/min, room temperature, t_R (major) = 19.96 min, t_R (minor) = 25.04 min.


DAD1 A, Sig=254,4 Ref=360,100 (D:\data\SSZ\DEF_LC1 2023-05-01 14-32-06\030-D2F-E9-Yao-3-137-1.D)

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	20.319	MM	3123.9	102	0.5103	49.673	0.849
2	25.227	VV	3164.9	83.5	0.4523	50.327	0.833


DAD1 A, Sig=254,4 Ref=360,100 (D:\data\SSZ\DEF_LC1 2023-05-01 14-32-06\032-D2F-F2-Yao-4-66-7.D)

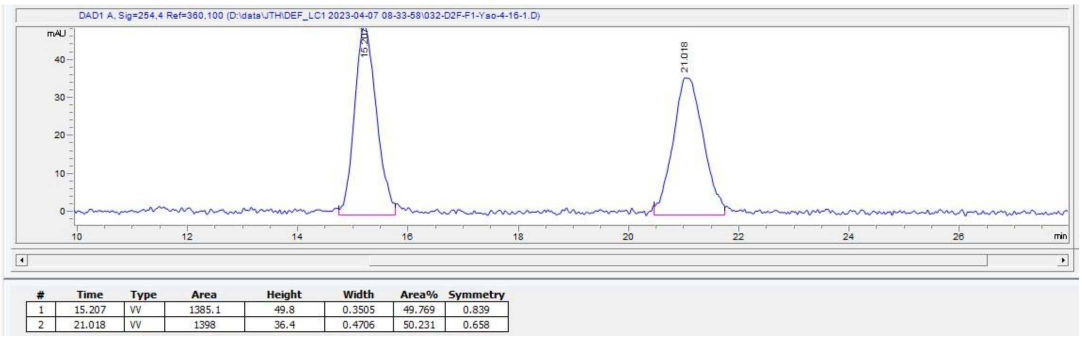
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	19.959	VV	44341	1332.7	0.4042	65.489	0.434
2	25.041	VV	23366.2	594.8	0.5823	34.511	0.694



Enzymatic reaction was conducted according to the general procedure for hydroxylation reaction in vials using 1-phenoxy-4-(prop-1-en-2-yl)benzene (**1d)** and 2-bromo-1-phenylethan-1-one (**2a)** as the starting materials.

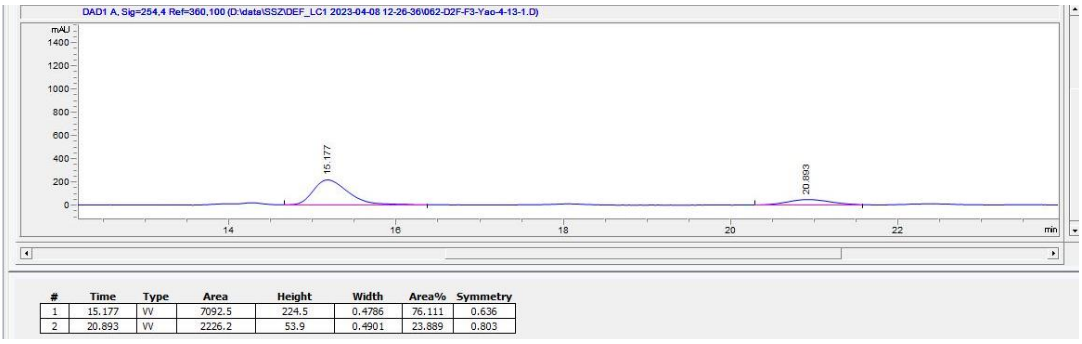
Yield: 36%.

Enantioselectivity: 76:24 er. Chiral HPLC method: AS-H column, 254 nm, 10% isopropanol/hexanes, flow rate 1.0 mL/min, room temperature, t_R (major) = 15.18 min, t_R (minor) = 20.89 min.



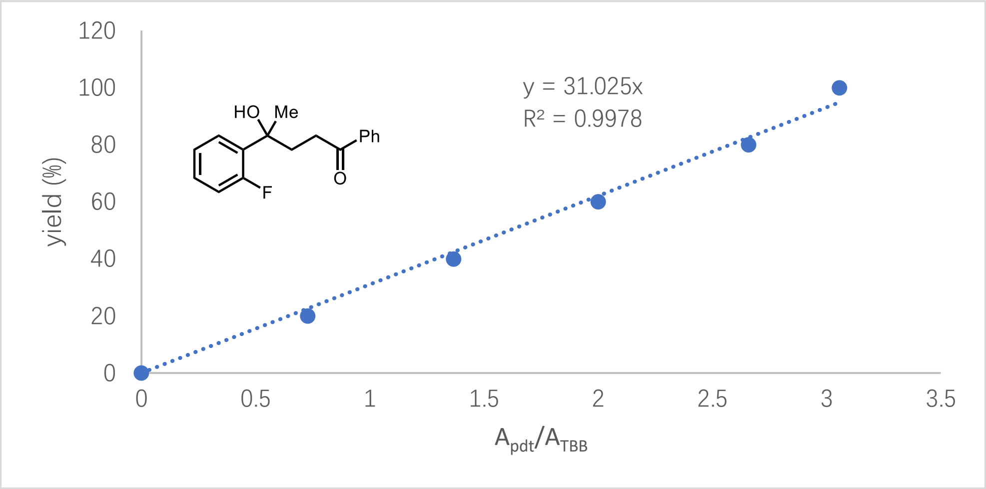
DAD1 A, Sig=254,4 Ref=360,100 (D:\data\JTH\DEF_LC1 2023-04-07 08-33-58\032-D2F-F1-Yao-4-16-1.D)

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	15.207	VV	1385.1	49.8	0.3505	49.769	0.839
2	21.018	VV	1398	36.4	0.4706	50.231	0.658



DAD1 A, Sig=254,4 Ref=360,100 (D:\data\SSZ\DEF_LC1 2023-04-08 12-26-36\062-D2F-F3-Yao-4-13-1.D)

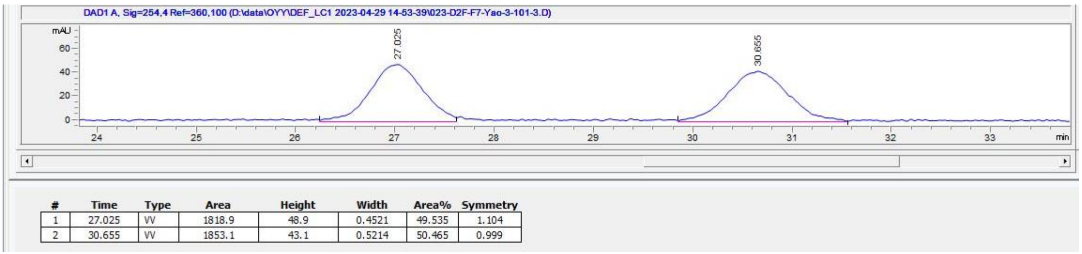
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	15.177	VV	7092.5	224.5	0.4786	76.111	0.636
2	20.893	VV	2226.2	53.9	0.4901	23.889	0.803



Enzymatic reaction was conducted according to the general procedure for hydroxylation reaction in vials using 1-fluoro-2-(prop-1-en-2-yl)benzene (**1e**) and 2-bromo-1-phenylethan-1-one (**2a**) as the starting materials.

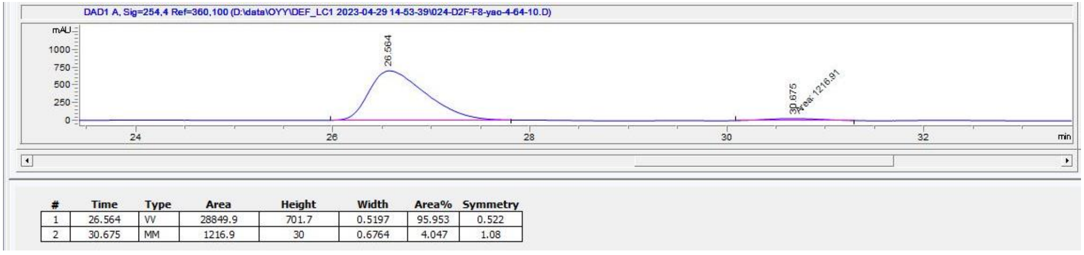
Yields: 39%.

Enantioselectivity: 96:4 er. Chiral HPLC method: IC-H column, 254 nm, 2% isopropanol/hexanes, flow rate 1.0 mL/min, room temperature, t_R (major) = 26.56 min, t_R (minor) = 30.68 min.



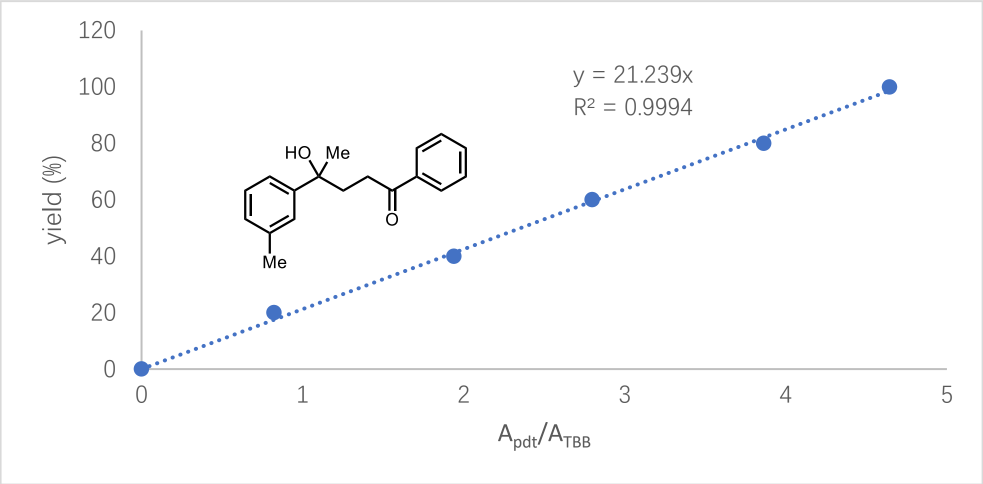
DAD1 A, Sig=254,4 Ref=360,100 (D:\data\OYY\DEF_LC1 2023-04-29 14-53-39\023-D2F-F7-Yao-3-101-3.D)

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	27.025	VV	1818.9	48.9	0.4521	49.535	1.104
2	30.655	VV	1853.1	43.1	0.5214	50.465	0.999



DAD1 A, Sig=254,4 Ref=360,100 (D:\data\OYY\DEF_LC1 2023-04-29 14-53-39\024-D2F-F8-yao-4-64-10.D)

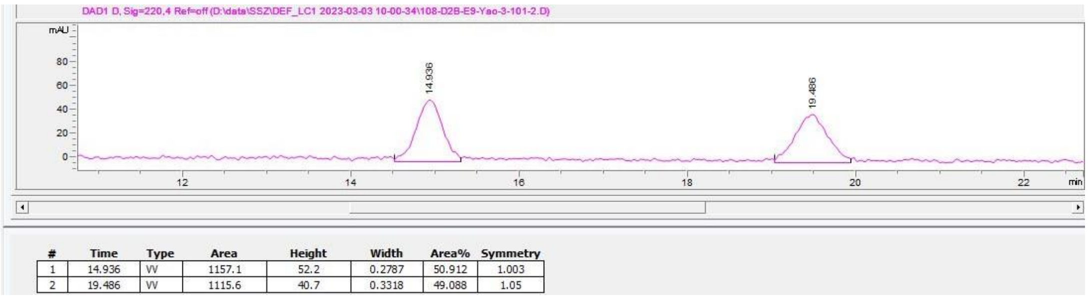
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	26.564	VV	28849.9	701.7	0.5197	95.953	0.522
2	30.675	MM	1216.9	30	0.6764	4.047	1.08



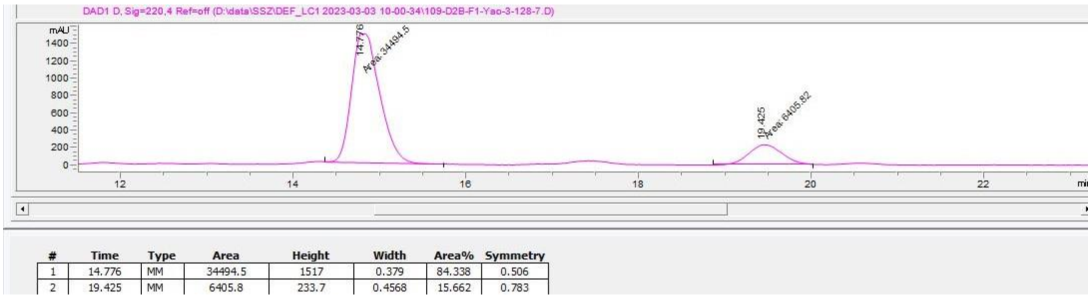
Enzymatic reaction was conducted according to the general procedure for hydroxylation reaction in vials using 1-methyl-3-(prop-1-en-2-yl)benzene (**1f**) and 2-bromo-1-phenylethan-1-one (**2a**) as the starting materials.

Yields: 80%.

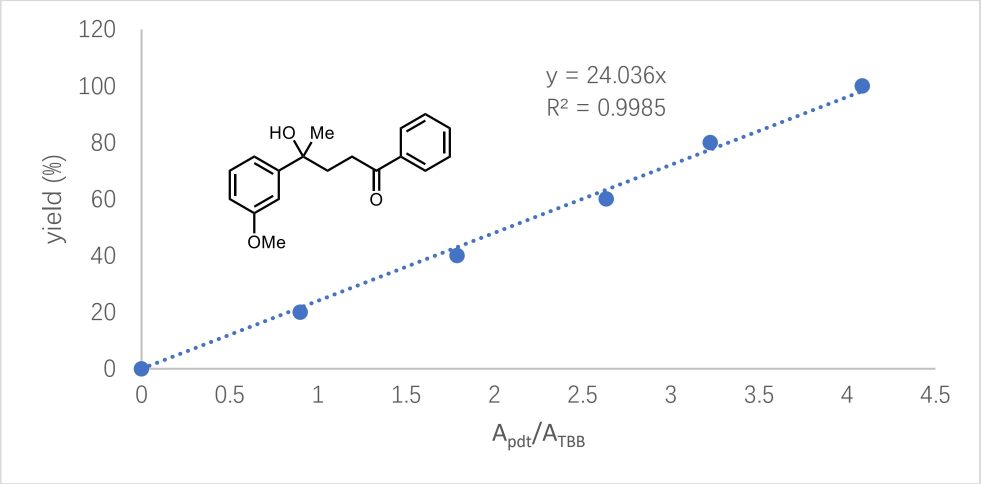
Enantioselectivity: 84:16 er. Chiral HPLC method: IC-H column, 220 nm, 7% isopropanol/hexanes, flow rate 1.0 mL/min, room temperature, t_R (major) = 14.78 min, t_R (minor) = 19.43 min.


DAD1 D, Sig=220,4 Ref=off (D:\data\SSZ\DEF_LC1 2023-03-03 10-00-34\108-D2B-E9-Yao-3-101-2.D)

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	14.936	VV	1157.1	52.2	0.2787	50.912	1.003
2	19.486	VV	1115.6	40.7	0.3318	49.088	1.05


DAD1 D, Sig=220,4 Ref=off (D:\data\SSZ\DEF_LC1 2023-03-03 10-00-34\109-D2B-F1-Yao-3-128-7.D)

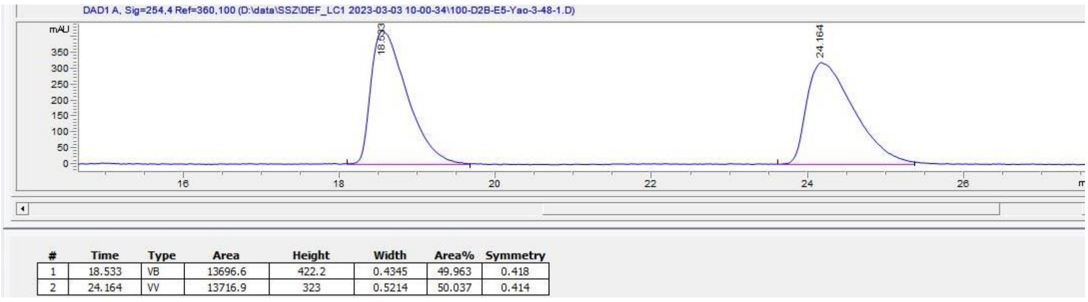
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	14.776	MM	34494.5	1517	0.379	84.338	0.506
2	19.425	MM	6405.8	233.7	0.4568	15.662	0.783



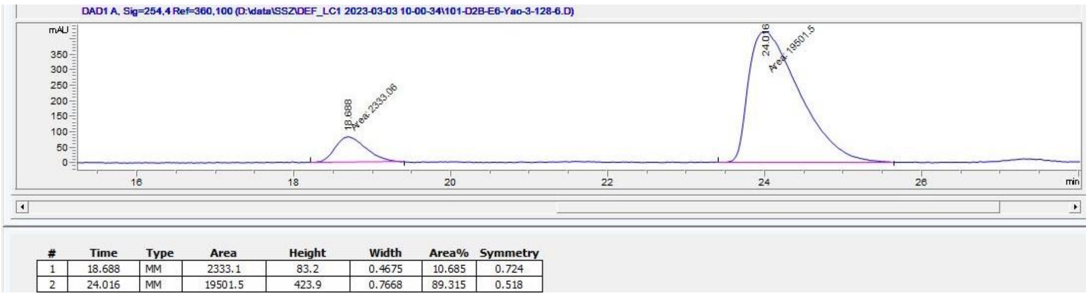
Enzymatic reaction was conducted according to the general procedure for hydroxylation reaction in vials using 1-methoxy-3-(prop-1-en-2-yl)benzene (**1g)** and 2-bromo-1-phenylethan-1-one (**2a)** as the starting materials.

Yield: 53%.

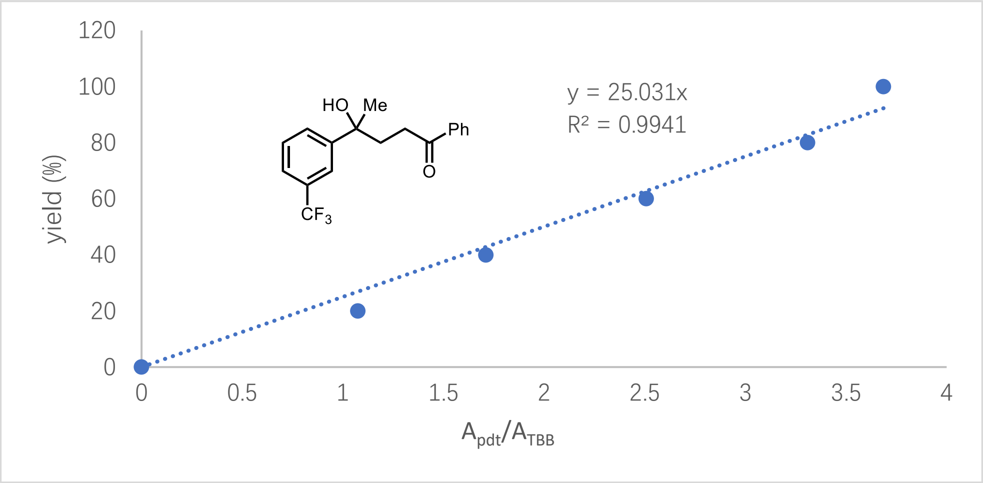
Enantioselectivity: 89:11 er. Chiral HPLC method: OJ-H column, 254 nm, 10% isopropanol/hexanes, flow rate 1.0 mL/min, room temperature, t_R (major) = 24.02 min, t_R (minor) = 18.69 min.


DAD1 A, Sig=254,4 Ref=360,100 (D:\data\SSZ\DEF_LC1 2023-03-03 10-00-34\100-D2B-E5-Yao-3-48-1.D)

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	18.533	VB	13696.6	422.2	0.4345	49.963	0.418
2	24.164	VV	13716.9	323	0.5214	50.037	0.414


DAD1 A, Sig=254,4 Ref=360,100 (D:\data\SSZ\DEF_LC1 2023-03-03 10-00-34\101-D2B-E6-Yao-3-128-6.D)

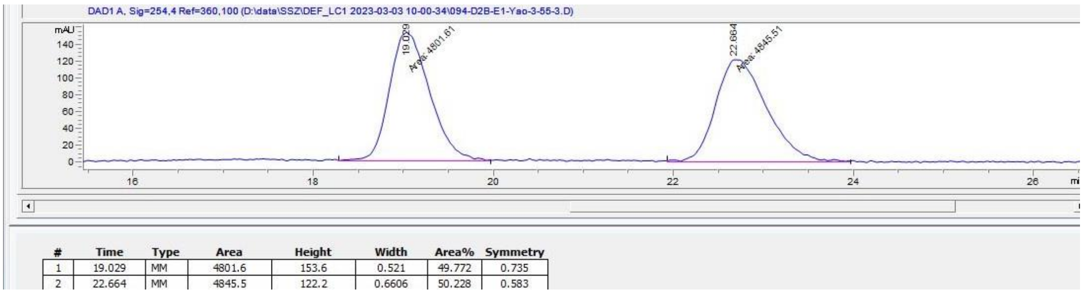
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	18.688	MM	2333.1	83.2	0.4675	10.685	0.724
2	24.016	MM	19501.5	423.9	0.7668	89.315	0.518



Enzymatic reaction was conducted according to the general procedure for hydroxylation reaction in vials using 1-(prop-1-en-2-yl)-3-(trifluoromethyl)benzene (**1h)** and 2-bromo-1-phenylethan-1-one (**2a)** as the starting materials.

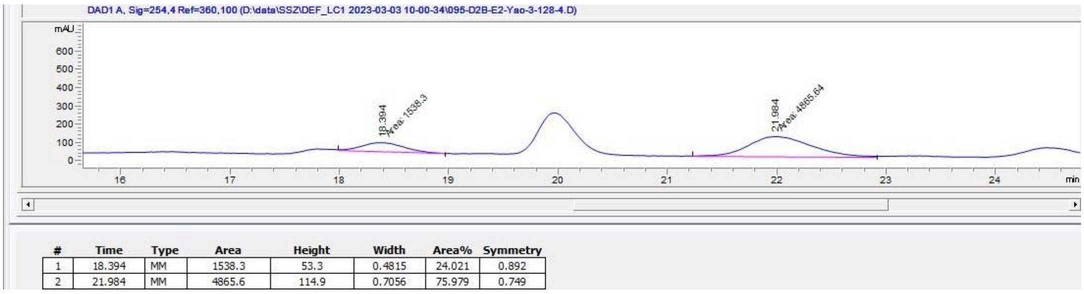
Yield: 8%.

Enantioselectivity: 76:24 er. Chiral HPLC method: AS-H column, 254 nm, 3% isopropanol/hexanes, flow rate 1.0 mL/min, room temperature, t_R (major) = 21.98 min, t_R (minor) = 18.39 min.



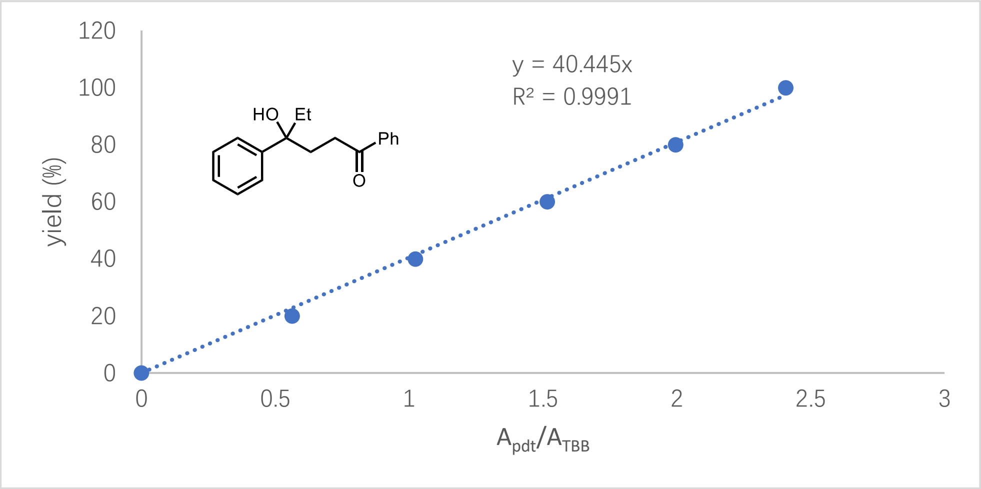
DAD1 A, Sig=254,4 Ref=360,100 (D:\data\SSZ\DEF_LC1 2023-03-03 10-00-34\094-D2B-E1-Yao-3-55-3.D)

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	19.029	MM	4801.6	153.6	0.521	49.772	0.735
2	22.664	MM	4845.5	122.2	0.6606	50.228	0.583



DAD1 A, Sig=254,4 Ref=360,100 (D:\data\SSZ\DEF_LC1 2023-03-03 10-00-34\095-D2B-E2-Yao-3-128-4.D)

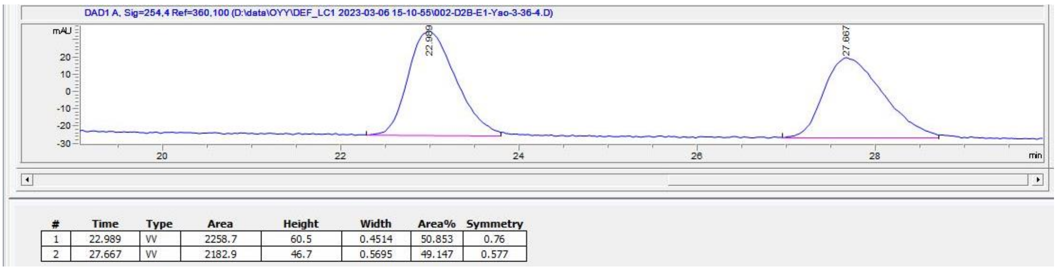
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	18.394	MM	1538.3	53.3	0.4815	24.021	0.892
2	21.984	MM	4865.6	114.9	0.7056	75.979	0.749



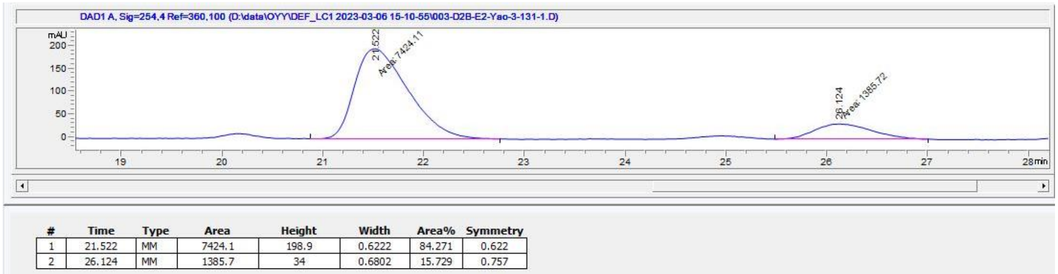
Enzymatic reaction was conducted according to the general procedure for hydroxylation reaction in vials using but-1-en-2-ylbenzene (**1i)** and 2-bromo-1-phenylethan-1-one (**2a)** as the starting materials.

Yield: 56%.

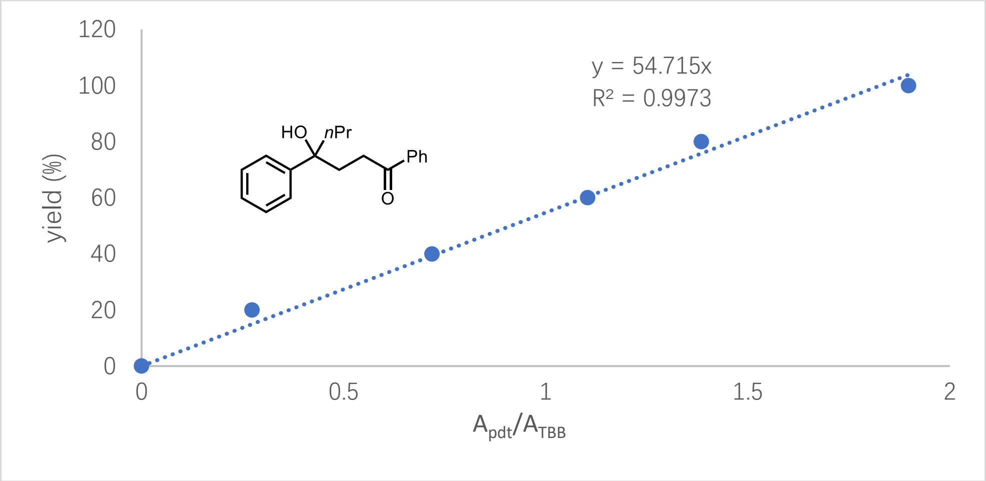
Enantioselectivity: 84:16 er. Chiral HPLC method: AS-H column, 254 nm, 3% isopropanol/hexanes, flow rate 1.0 mL/min, room temperature, t_R (major) = 21.52 min, t_R (minor) = 26.12 min.


DAD1 A, Sig=254,4 Ref=360,100 (D:\data\OYY\DEF_LC1 2023-03-06 15-10-55\002-D2B-E1-Yao-3-36-4.D)

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	22.989	VV	2258.7	60.5	0.4514	50.853	0.76
2	27.667	VV	2182.9	46.7	0.5695	49.147	0.577


DAD1 A, Sig=254,4 Ref=360,100 (D:\data\OYY\DEF_LC1 2023-03-06 15-10-55\003-D2B-E2-Yao-3-131-1.D)

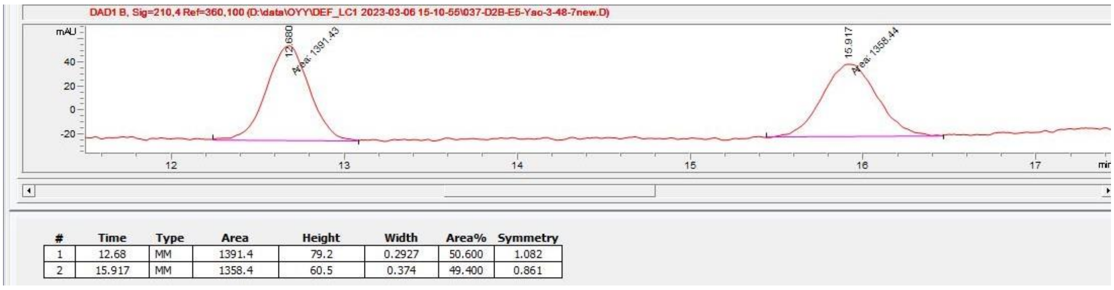
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	21.522	MM	7424.1	198.9	0.6222	84.271	0.622
2	26.124	MM	1385.7	34	0.6802	15.729	0.757



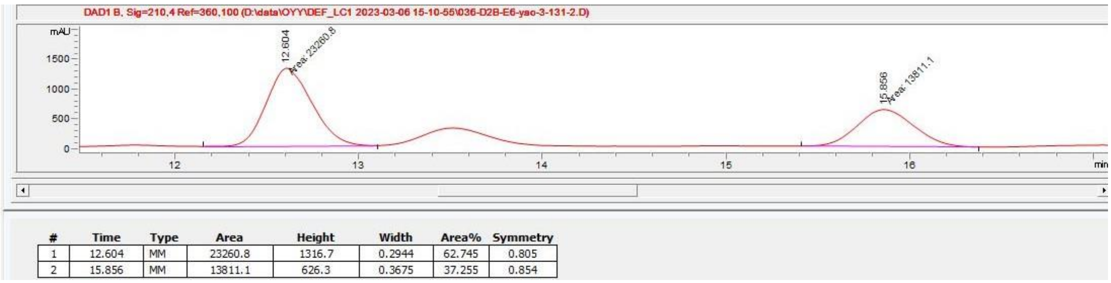
Enzymatic reaction was conducted according to the general procedure for hydroxylation reaction in vials using pent-1-en-2-ylbenzene (**1j**) and 2-bromo-1-phenylethan-1-one (**2a**) as the starting materials.

Yield: 33%.

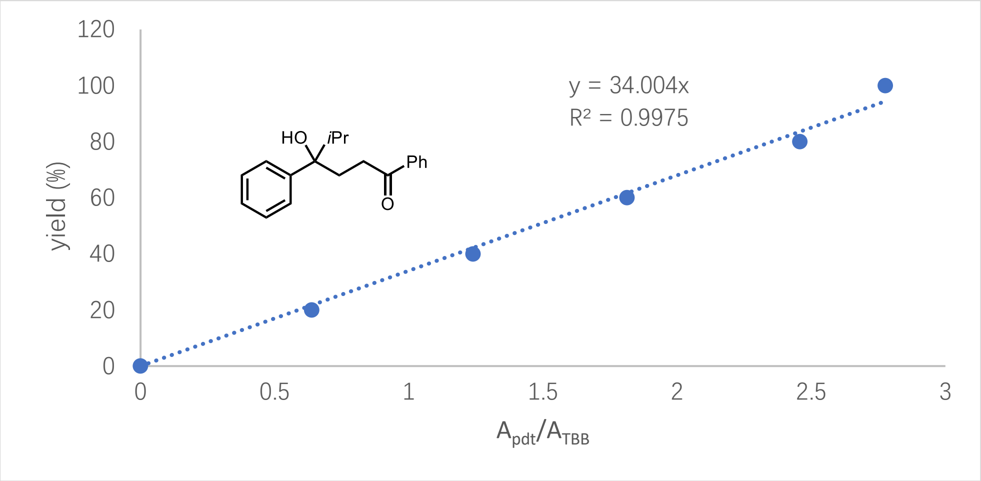
Enantioselectivity: 63:37 er. Chiral HPLC method: IC-H column, 210 nm, 5% isopropanol/hexanes, flow rate 1.0 mL/min, room temperature, t_R (major) = 12.60 min, t_R (minor) = 15.86 min.


DAD1 B, Sig=210,4 Ref=360,100 (D:\data\OYY\DEF_LC1 2023-03-06 15-10-55\037-D2B-E5-Yao-3-48-7new.D)

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	12.68	MM	1391.4	79.2	0.2927	50.600	1.082
2	15.917	MM	1358.4	60.5	0.374	49.400	0.861


DAD1 B, Sig=210,4 Ref=360,100 (D:\data\OYY\DEF_LC1 2023-03-06 15-10-55\036-D2B-E6-yao-3-131-2.D)

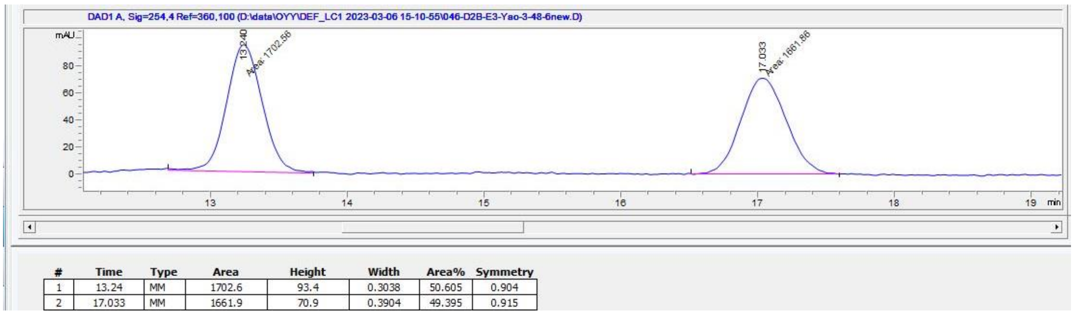
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	12.604	MM	23260.8	1316.7	0.2944	62.745	0.805
2	15.856	MM	13811.1	626.3	0.3675	37.255	0.854



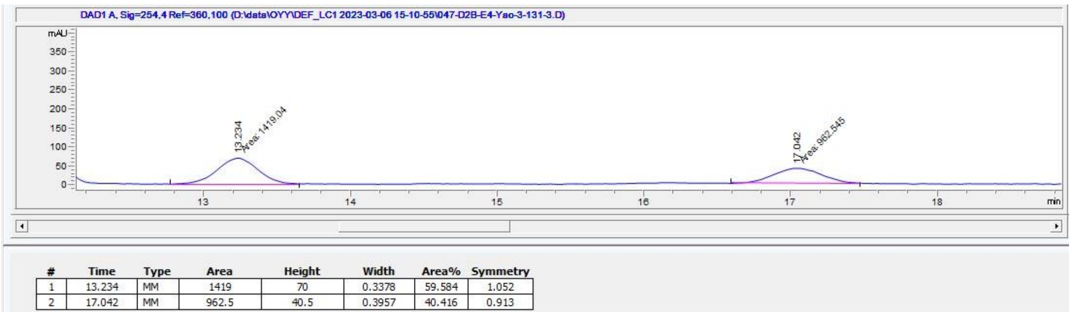
Enzymatic reaction was conducted according to the general procedure for hydroxylation reaction in vials using (3-methylbut-1-en-2-yl)benzene (**1k**) and 2-bromo-1-phenylethan-1-one (**2a**) as the starting materials.

Yield: 25%.

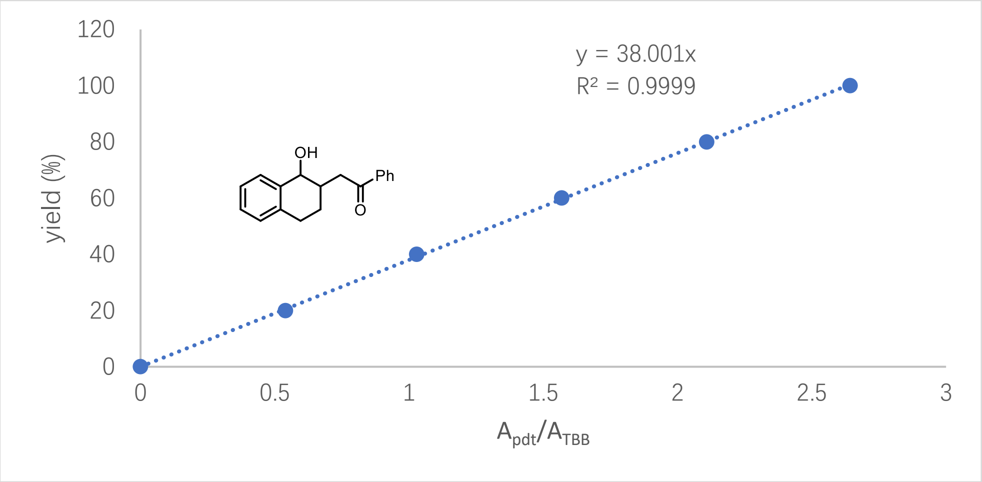
Enantioselectivity: 60:40 er. Chiral HPLC method: IC-H column, 254 nm, 2% isopropanol/hexanes, flow rate 1.0 mL/min, room temperature, t_R (major) = 13.23 min, t_R (minor) = 17.04 min.


DAD1 A, Sig=254,4 Ref=360,100 (D:\data\OYY\DEF_LC1 2023-03-06 15-10-55\046-D2B-E3-Yao-3-48-6new.D)

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	13.24	MM	1702.6	93.4	0.3038	50.605	0.904
2	17.033	MM	1661.9	70.9	0.3904	49.395	0.915


DAD1 A, Sig=254,4 Ref=360,100 (D:\data\OYY\DEF_LC1 2023-03-06 15-10-55\047-D2B-E4-Yao-3-131-3.D)

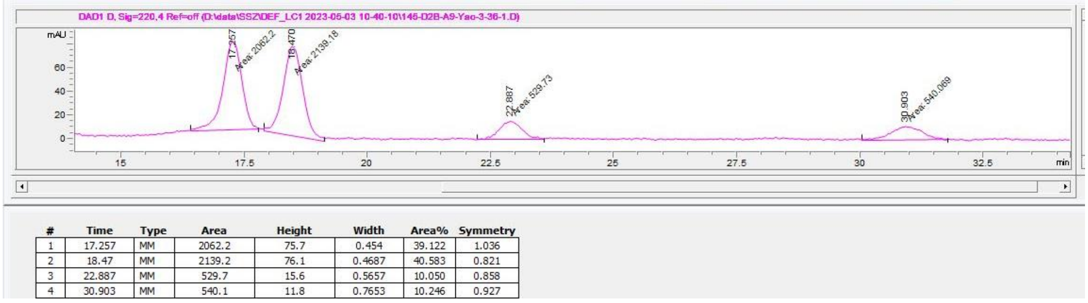
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	13.234	MM	1419	70	0.3378	59.584	1.052
2	17.042	MM	962.5	40.5	0.3957	40.416	0.913



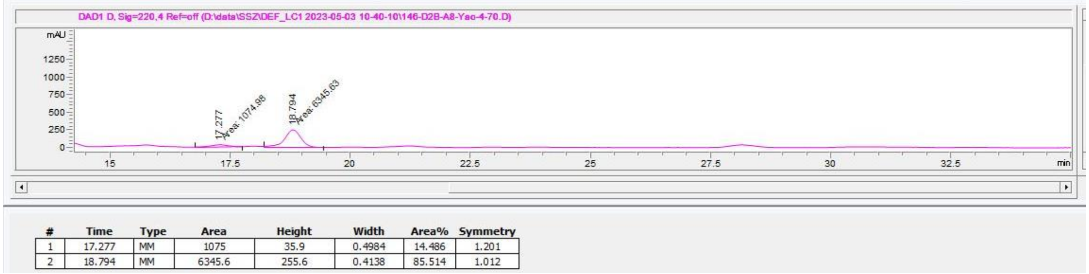
Enzymatic reaction was conducted according to the general procedure for hydroxylation reaction in vials using 1,2-dihydronaphthalene (**1l)** and 2-bromo-1-phenylethan-1-one (**2a)** as the starting materials.

Yield: 36%, d.r. > 20:1, and the major isomer is determined to be *cis* as confirmed by crude NMR.

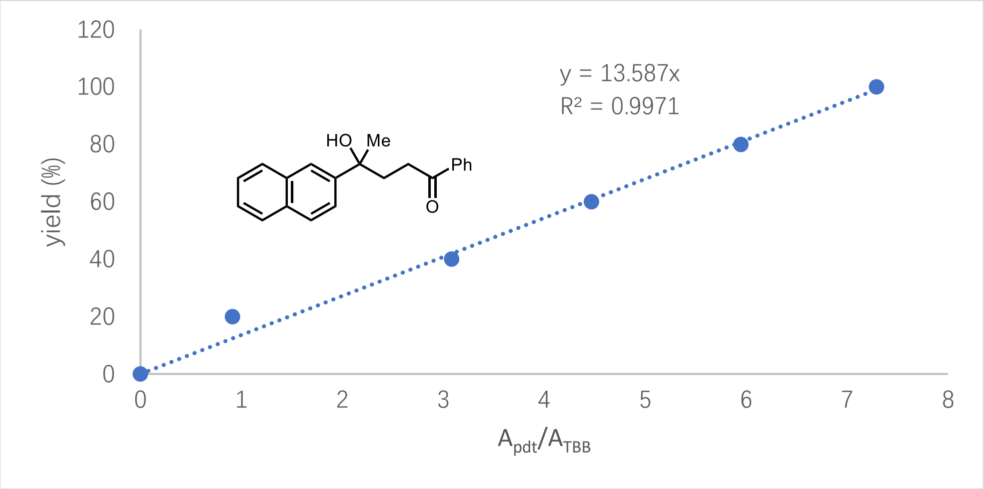
Enantioselectivity: 86:14 er. Chiral HPLC method: IC-H column, 220 nm, 7% isopropanol/hexanes, flow rate 1.0 mL/min, room temperature, t_R (major) = 18.79 min, t_R (minor) = 17.28 min.



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	17.257	MM	2062.2	75.7	0.454	39.122	1.036
2	18.47	MM	2139.2	76.1	0.4687	40.583	0.821
3	22.887	MM	529.7	15.6	0.5657	10.050	0.858
4	30.903	MM	540.1	11.8	0.7653	10.246	0.927



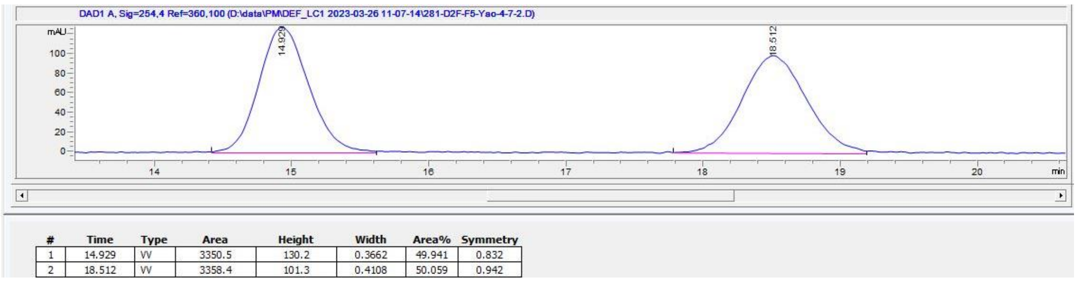
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	17.277	MM	1075	35.9	0.4984	14.486	1.201
2	18.794	MM	6345.6	255.6	0.4138	85.514	1.012



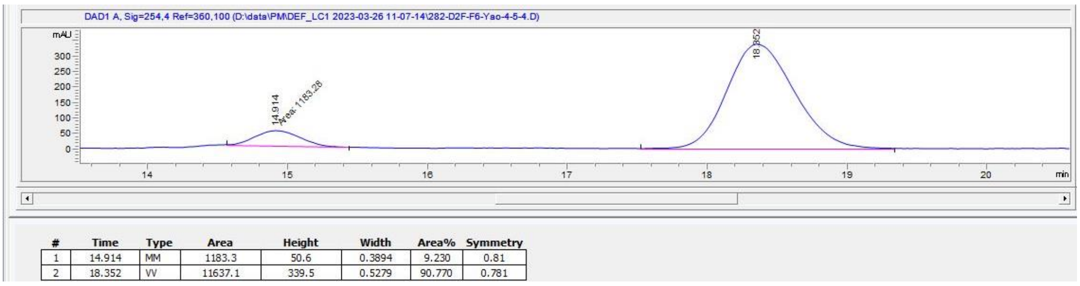
Enzymatic reaction was conducted according to the general procedure for hydroxylation reaction in vials using 2-(prop-1-en-2-yl)naphthalene (**1m**) and 2-bromo-1-phenylethan-1-one (**2a**) as the starting materials.

Yield: 52%.

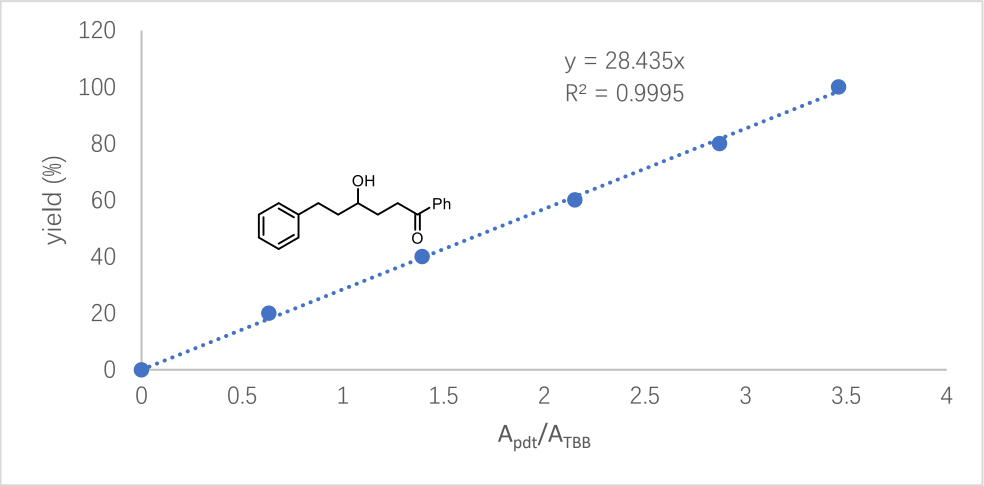
Enantioselectivity: 91:9 er. Chiral HPLC method: AS-H column, 254 nm, 10% isopropanol/hexanes, flow rate 1.0 mL/min, room temperature, t_R (major) = 18.35 min, t_R (minor) = 14.91 min.


DAD1 A, Sig=254,4 Ref=360,100 (D:\data\PM\DEF_LC1 2023-03-26 11-07-14\281-D2F-F5-Yao-4-7-2.D)

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	14.929	VV	3350.5	130.2	0.3662	49.941	0.832
2	18.512	VV	3358.4	101.3	0.4108	50.059	0.942


DAD1 A, Sig=254,4 Ref=360,100 (D:\data\PM\DEF_LC1 2023-03-26 11-07-14\282-D2F-F6-Yao-4-5-4.D)

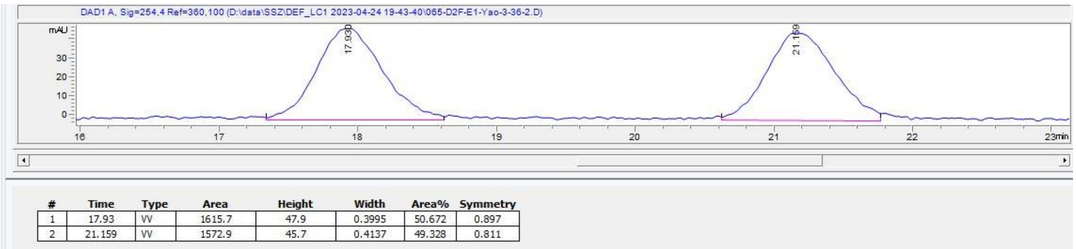
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	14.914	MM	1183.3	50.6	0.3894	9.230	0.81
2	18.352	VV	11637.1	339.5	0.5279	90.770	0.781



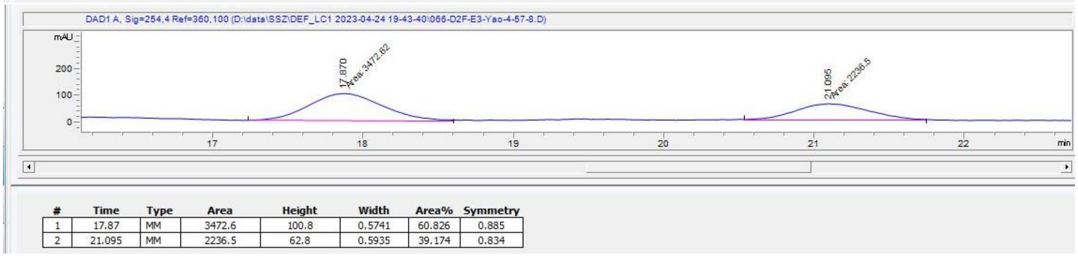
Enzymatic reaction was conducted according to the general procedure for hydroxylation reaction in vials using but-3-en-1-ylbenzene (**1n)** and 2-bromo-1-phenylethan-1-one (**2a)** as the starting materials.

Yield: 18%.

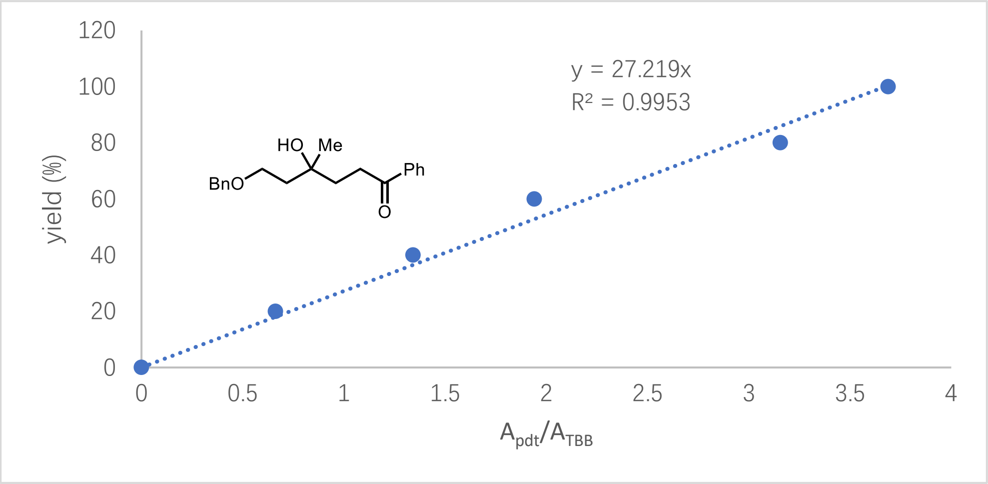
Enantioselectivity: 61:39 er. Chiral HPLC method: AS-H column, 254 nm, 7% isopropanol/hexanes, flow rate 1.0 mL/min, room temperature, t_R (major) = 17.87 min, t_R (minor) = 21.10 min.



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	17.93	VV	1615.7	47.9	0.3995	50.672	0.897
2	21.159	VV	1572.9	45.7	0.4137	49.328	0.811



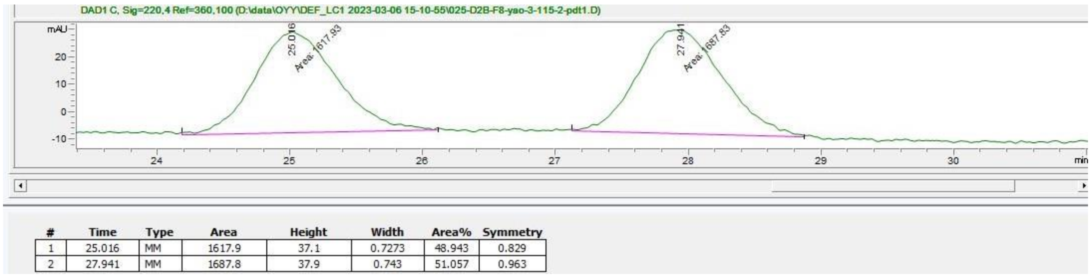
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	17.87	MM	3472.6	100.8	0.5741	60.826	0.885
2	21.095	MM	2236.5	62.8	0.5935	39.174	0.834



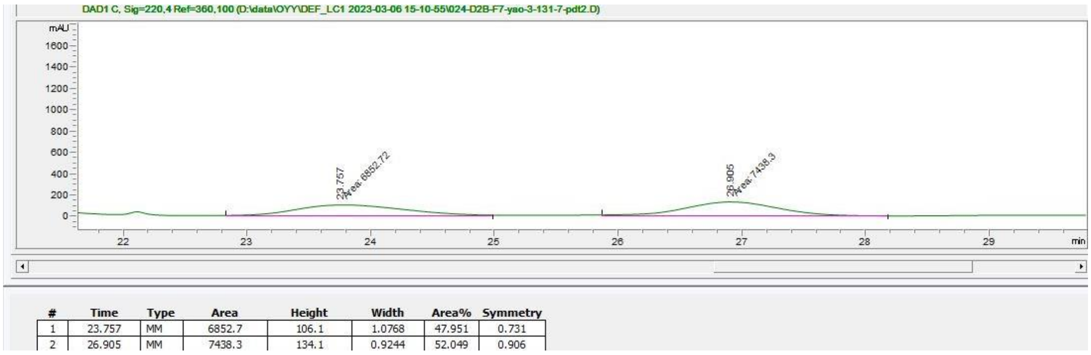
Enzymatic reaction was conducted according to the general procedure for hydroxylation reaction in vials using (((3-methylbut-3-en-1-yl)oxy)methyl)benzene (**1o)** and 2-bromo-1-phenylethan-1-one (**2a)** as the starting materials.

Yield: 40%.

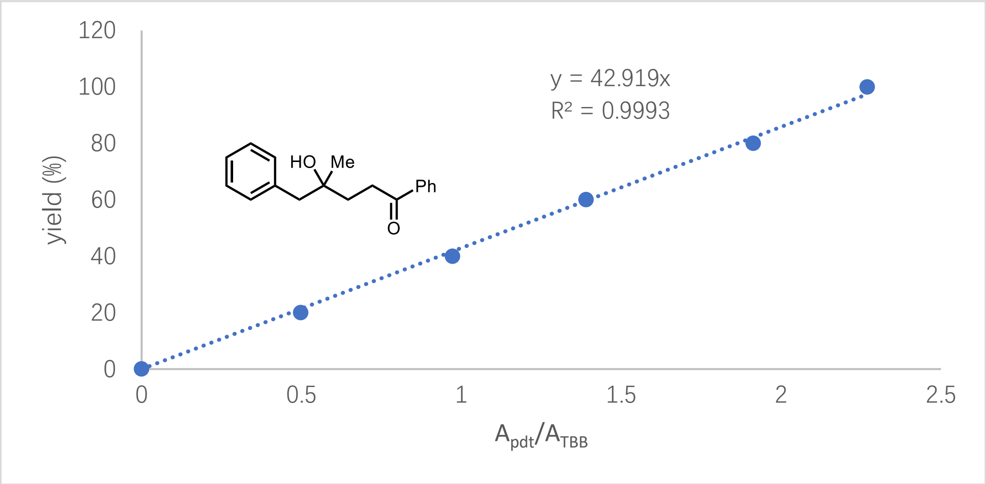
Enantioselectivity: 52:48 er. Chiral HPLC method: AS-H column, 220 nm, 5% isopropanol/hexanes, flow rate 1.0 mL/min, room temperature, t_R (major) = 26.91 min, t_R (minor) =23.76 min.


DAD1 C, Sig=220,4 Ref=360,100 (D:\data\OYY\DEF_LC1 2023-03-06 15-10-55\025-D2B-F8-yao-3-115-2-pdt1.D)

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	25.016	MM	1617.9	37.1	0.7273	48.943	0.829
2	27.941	MM	1687.8	37.9	0.743	51.057	0.963


DAD1 C, Sig=220,4 Ref=360,100 (D:\data\OYY\DEF_LC1 2023-03-06 15-10-55\024-D2B-F7-yao-3-131-7-pdt2.D)

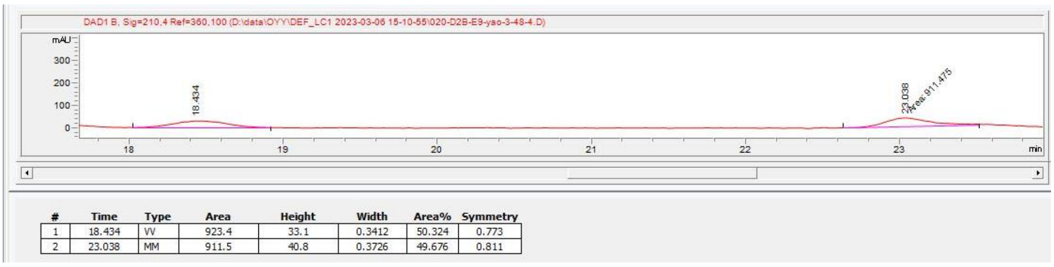
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	23.757	MM	6852.7	106.1	1.0768	47.951	0.731
2	26.905	MM	7438.3	134.1	0.9244	52.049	0.906



Enzymatic reaction was conducted according to the general procedure for hydroxylation reaction in vials using (2-methylallyl)benzene (**1p**) and 2-bromo-1-phenylethan-1-one (**2a**) as the starting materials.

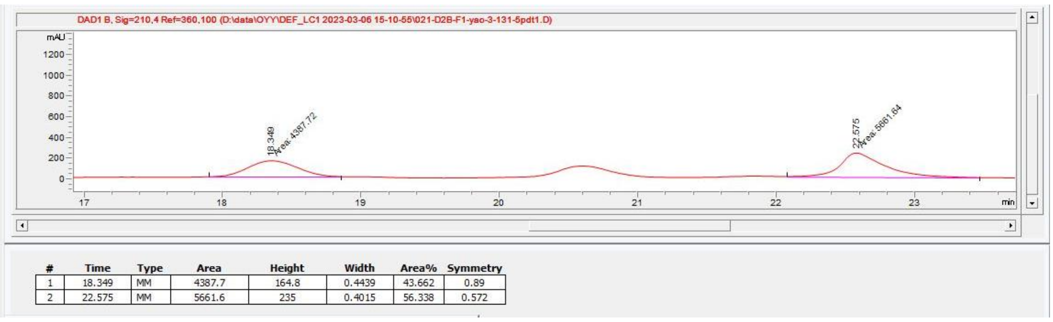
Yield: 41%.

Enantioselectivity: 56:44 er. Chiral HPLC method: AS-H column, 210 nm, 5% isopropanol/hexanes, flow rate 1.0 mL/min, room temperature, t_R (major) = 22.58 min, t_R (minor) = 18.35 min.



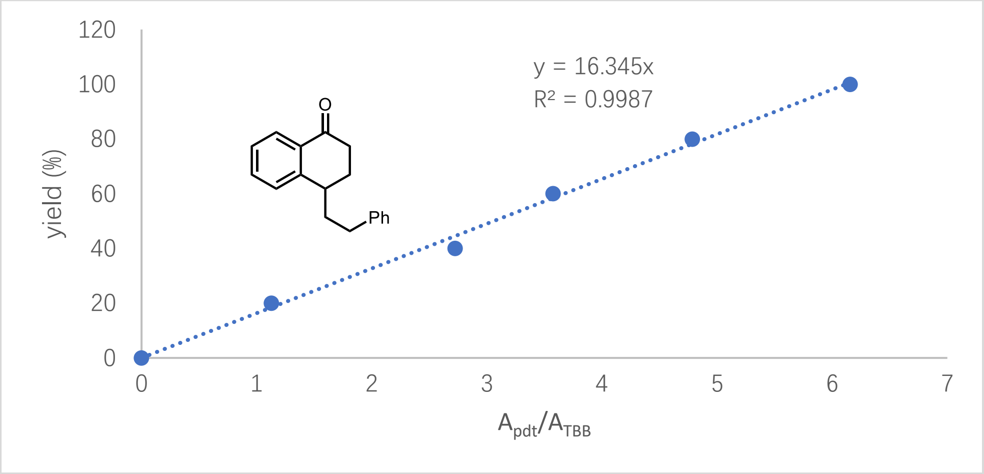
DAD1 B, Sig=210,4 Ref=360,100 (D:\data\OYY\DEF_LC1 2023-03-06 15-10-55\020-D2B-E9-yao-3-48-4.D)

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	18.434	VV	923.4	33.1	0.3412	50.324	0.773
2	23.038	MM	911.5	40.8	0.3726	49.676	0.811



DAD1 B, Sig=210,4 Ref=360,100 (D:\data\OYY\DEF_LC1 2023-03-06 15-10-55\021-D2B-F1-yao-3-131-5pdt1.D)

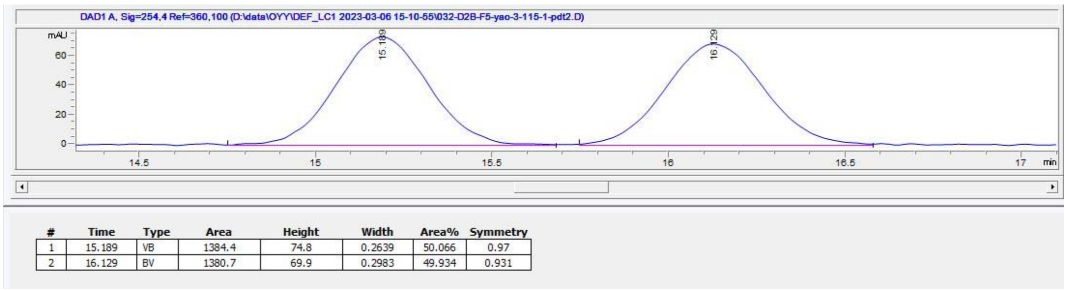
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	18.349	MM	4387.7	164.8	0.4439	43.662	0.89
2	22.575	MM	5661.6	235	0.4015	56.338	0.572



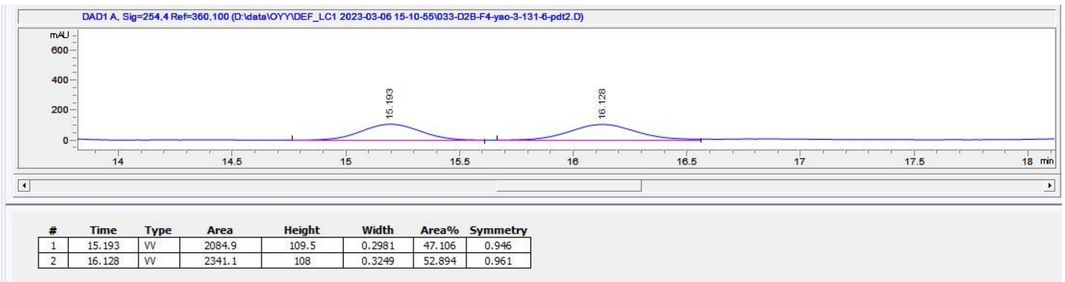
Enzymatic reaction was conducted according to the general procedure for hydroxylation reaction in vials using but-3-en-1-ylbenzene (**1n)** and 2-bromo-1-phenylethan-1-one (**2a)** as the starting materials.

Yield: 15%.

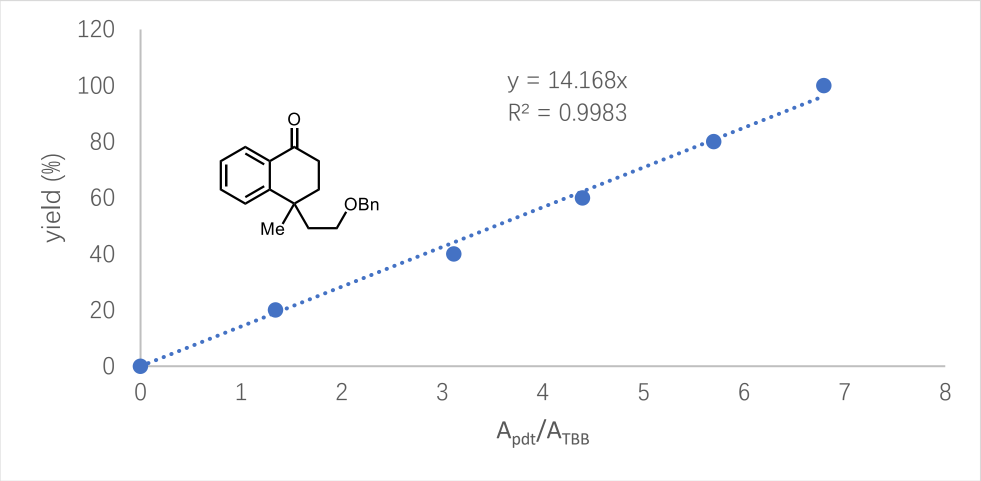
Enantioselectivity: 53:47 er. Chiral HPLC method: AS-H column, 254 nm, 5% isopropanol/hexanes, flow rate 1.0 mL/min, room temperature, t_R (major) = 16.13 min, t_R (minor) = 15.19 min.


DAD1 A, Sig=254,4 Ref=360,100 (D:\data\OYY\DEF_LC1 2023-03-06 15-10-55\032-D2B-F5-yao-3-115-1-pdt2.D)

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	15.189	VB	1384.4	74.8	0.2639	50.066	0.97
2	16.129	BV	1380.7	69.9	0.2983	49.934	0.931


DAD1 A, Sig=254,4 Ref=360,100 (D:\data\OYY\DEF_LC1 2023-03-06 15-10-55\033-D2B-F4-yao-3-131-6-pdt2.D)

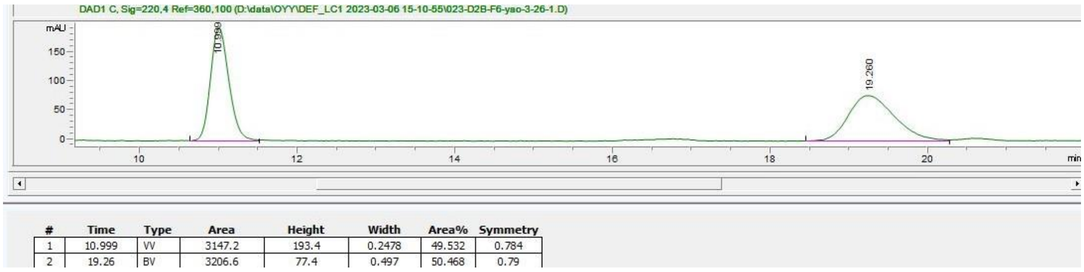
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	15.193	VV	2084.9	109.5	0.2981	47.106	0.946
2	16.128	VV	2341.1	108	0.3249	52.894	0.961



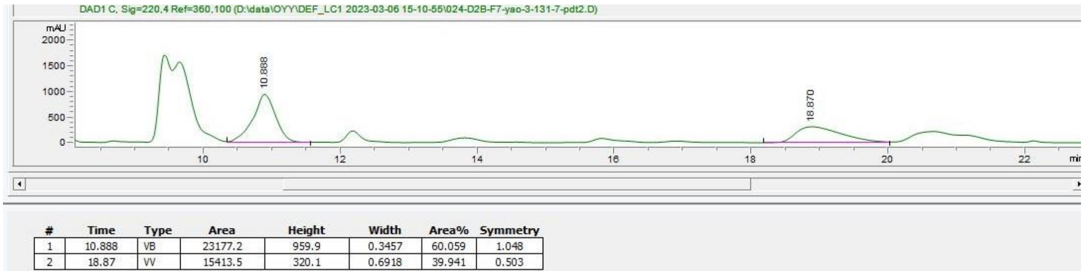
Enzymatic reaction was conducted according to the general procedure for hydroxylation reaction in vials using (((3-methylbut-3-en-1-yl)oxy)methyl)benzene (**1o)** and 2-bromo-1-phenylethan-1-one (**2a)** as the starting materials.

Yield: 19%.

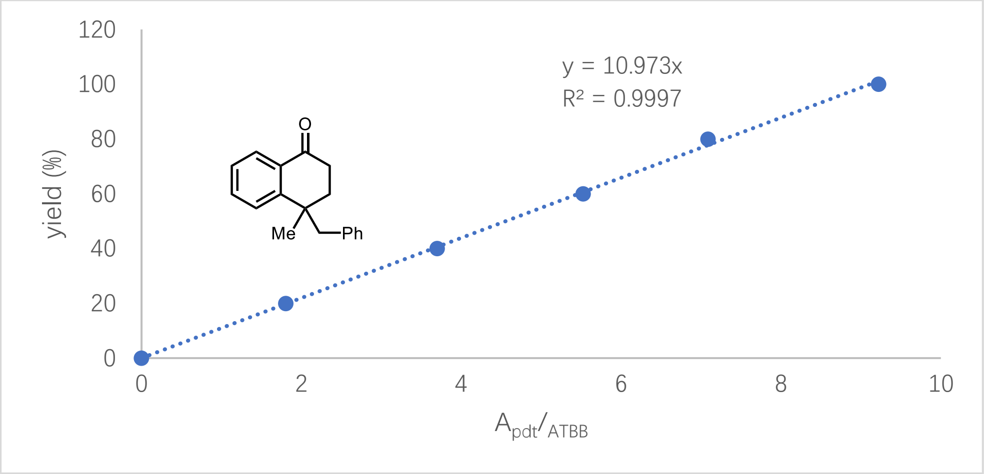
Enantioselectivity: 60:40 er. Chiral HPLC method: AS-H column, 220 nm, 5% isopropanol/hexanes, flow rate 1.0 mL/min, room temperature, t_R (major) =10.89 min, t_R (minor) = 18.87 min.


DAD1 C, Sig=220,4 Ref=360,100 (D:\data\OYY\DEF_LC1 2023-03-06 15-10-55\023-D2B-F6-yao-3-26-1.D)

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	10.999	VV	3147.2	193.4	0.2478	49.532	0.784
2	19.26	BV	3206.6	77.4	0.497	50.468	0.79


DAD1 C, Sig=220,4 Ref=360,100 (D:\data\OYY\DEF_LC1 2023-03-06 15-10-55\024-D2B-F7-yao-3-131-7-pdt2.D)

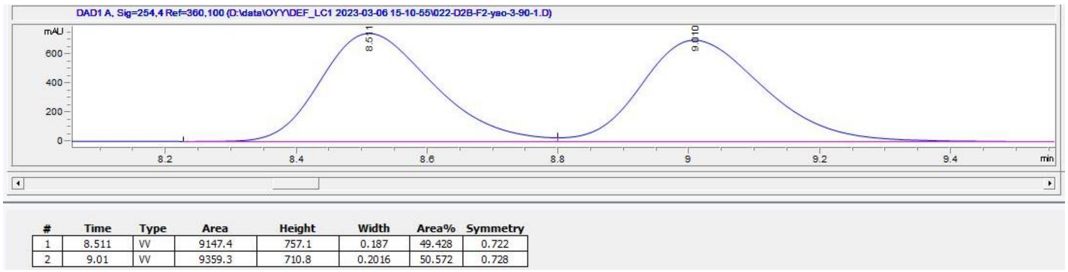
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	10.888	VB	23177.2	959.9	0.3457	60.059	1.048
2	18.87	VV	15413.5	320.1	0.6918	39.941	0.503



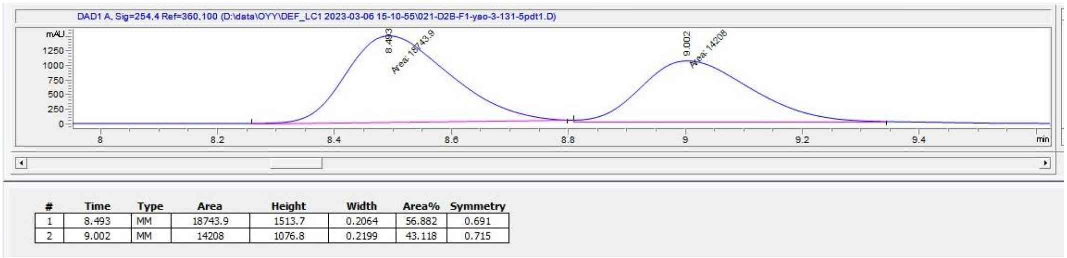
Enzymatic reaction was conducted according to the general procedure for hydroxylation reaction in vials using (2-methylallyl)benzene (**1p)** and 2-bromo-1-phenylethan-1-one (**2a)** as the starting materials.

Yield: 30%.

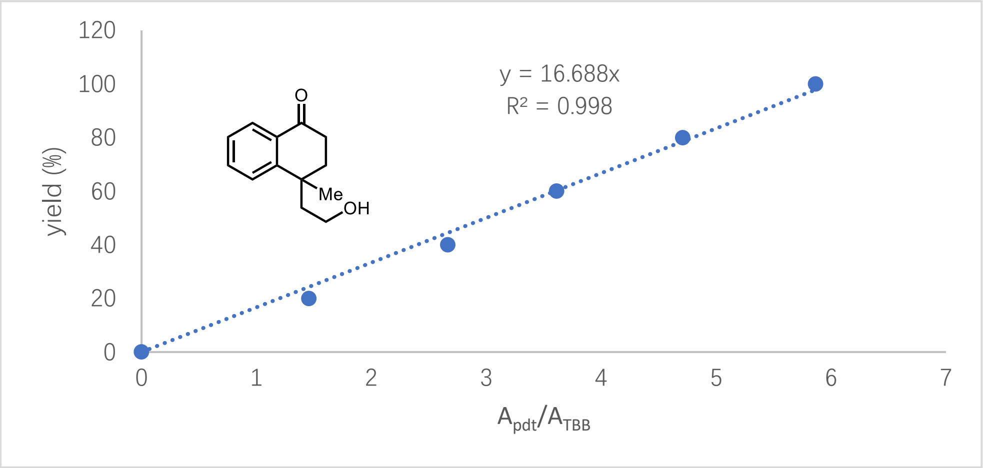
Enantioselectivity: 57:43 er. Chiral HPLC method: AS-H column, 254 nm, 5% isopropanol/hexanes, flow rate 1.0 mL/min, room temperature, t_R (major) = 8.49 min, t_R (minor) = 9.00 min.



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	8.511	VV	9147.4	757.1	0.187	49.428	0.722
2	9.01	VV	9359.3	710.8	0.2016	50.572	0.728



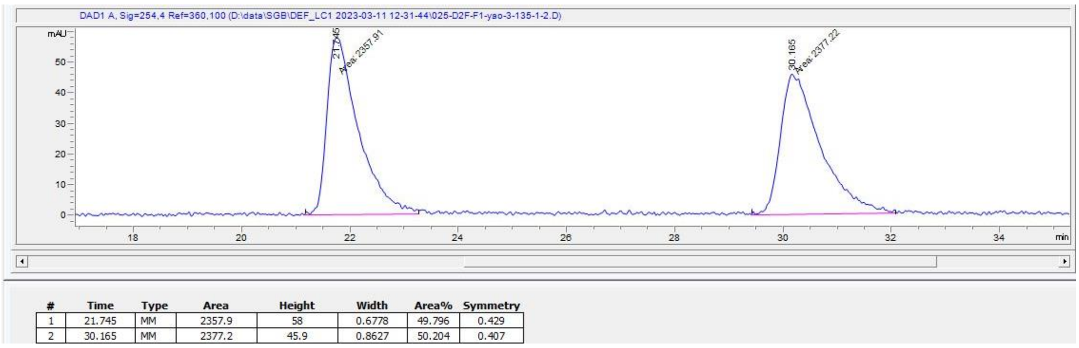
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	8.493	MM	18743.9	1513.7	0.2064	56.882	0.691
2	9.002	MM	14208	1076.8	0.2199	43.118	0.715



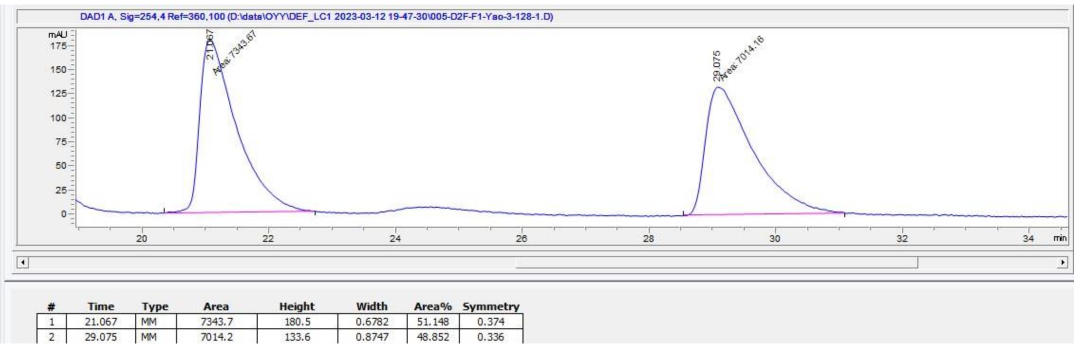
Enzymatic reaction was conducted according to the general procedure for hydroxylation reaction in vials using 3-methylbut-3-en-1-ol (**1q)** and 2-bromo-1-phenylethan-1-one (**2a)** as the starting materials.

Yield: 40%.

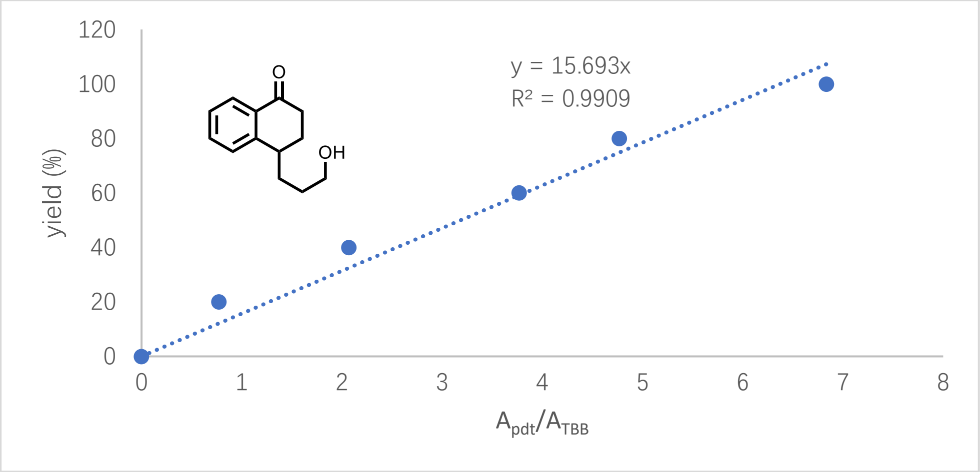
Enantioselectivity: 51:49 er. Chiral HPLC method: IB-H column, 254 nm, 5% isopropanol/hexanes, flow rate 1.0 mL/min, room temperature, t_R (major) = 21.07 min, t_R (minor) = 29.08 min.



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	21.745	MM	2357.9	58	0.6778	49.796	0.429
2	30.165	MM	2377.2	45.9	0.8627	50.204	0.407



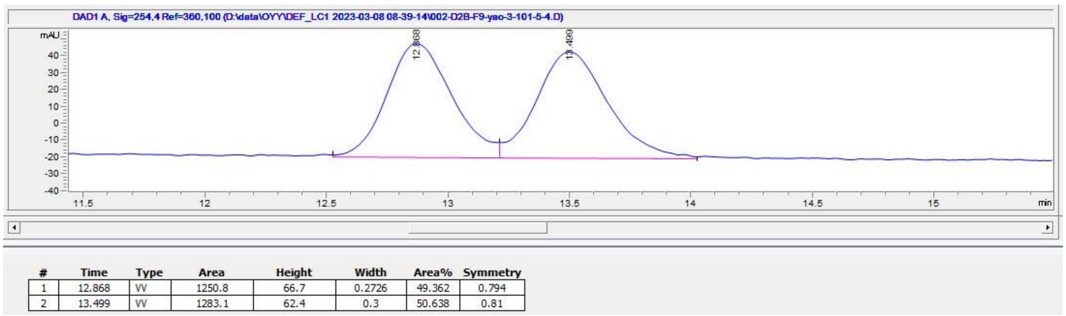
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	21.067	MM	7343.7	180.5	0.6782	51.148	0.374
2	29.075	MM	7014.2	133.6	0.8747	48.852	0.336



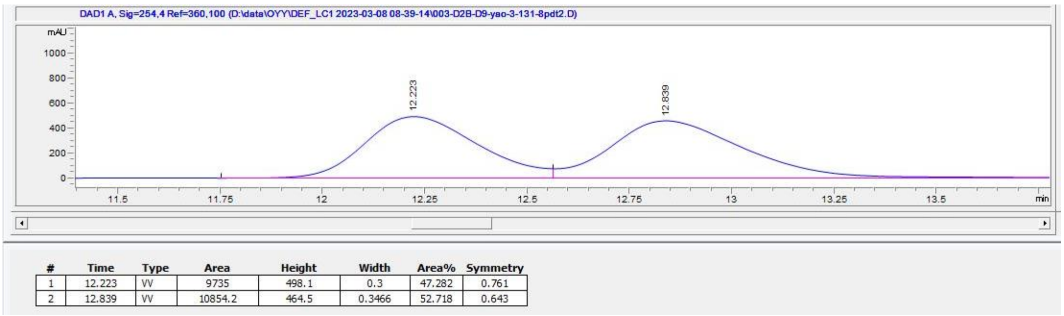
Enzymatic reaction was conducted according to the general procedure for hydroxylation reaction in vials using 3-methylbut-3-en-1-ol (**1r**) and 2-bromo-1-phenylethan-1-one (**2a**) as the starting materials.

Yield: 19%.

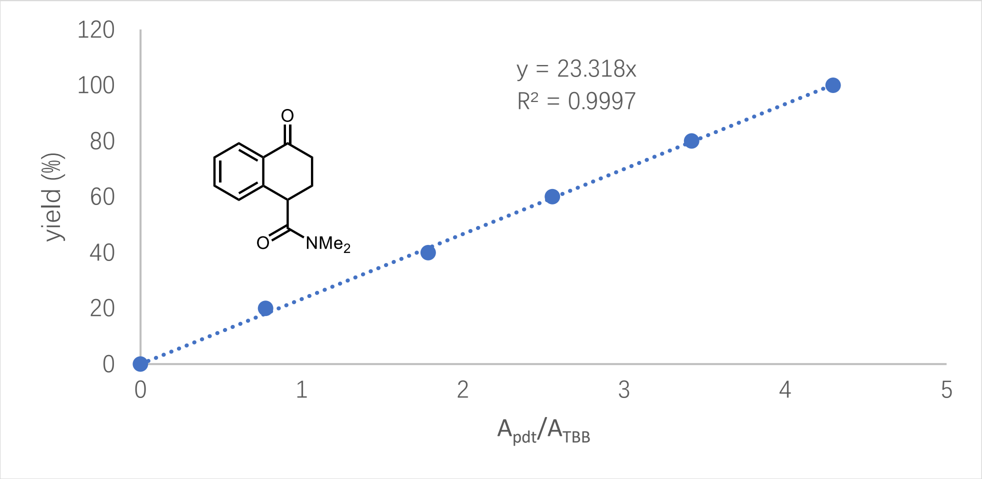
Enantioselectivity: 53:47 er. Chiral HPLC method: IA-H column, 254 nm, 10% isopropanol/hexanes, flow rate 1.0 mL/min, room temperature, t_R (major) = 12.84 min, t_R (minor) = 12.22 min.


DAD1 A, Sig=254,4 Ref=360,100 (D:\data\OYY\DEF_LC1 2023-03-08 08-39-14\002-D2B-F9-yao-3-101-5-4.D)

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	12.868	VV	1250.8	66.7	0.2726	49.362	0.794
2	13.499	VV	1283.1	62.4	0.3	50.638	0.81


DAD1 A, Sig=254,4 Ref=360,100 (D:\data\OYY\DEF_LC1 2023-03-08 08-39-14\003-D2B-D9-yao-3-131-8pdt2.D)

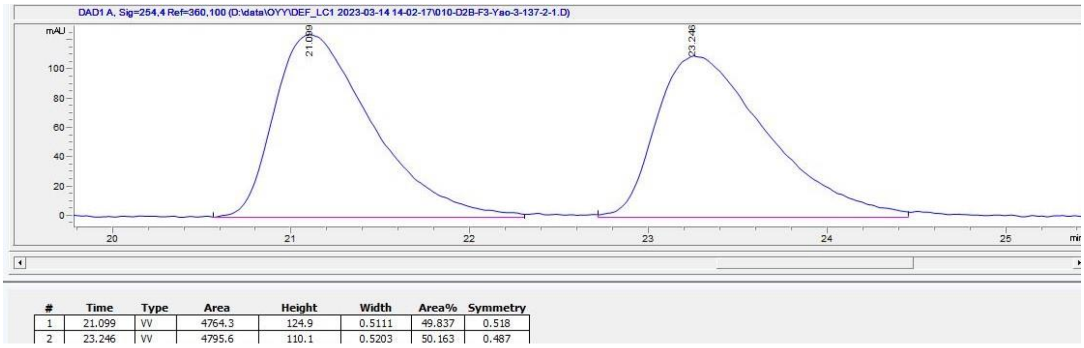
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	12.223	VV	9735	498.1	0.3	47.282	0.761
2	12.839	VV	10854.2	464.5	0.3466	52.718	0.643



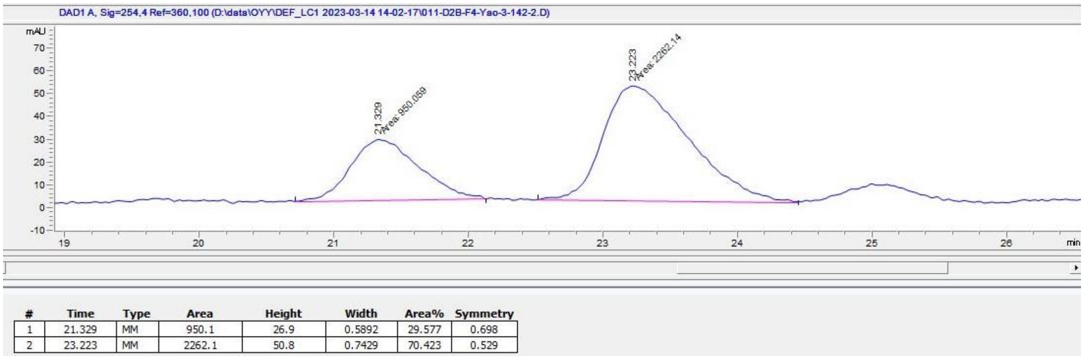
Enzymatic reaction was conducted according to the general procedure for hydroxylation reaction in vials using *N,N*-dimethylacrylamide (**1s)** and 2-bromo-1-phenylethan-1-one (**2a)** as the starting materials.

Yield: 14%.

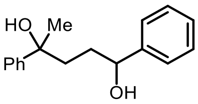
Enantioselectivity: 70:30 er. Chiral HPLC method: OJ-H column, 254 nm, 15% isopropanol/hexanes, flow rate 1.0 mL/min, room temperature, t_R (major) = 23.22 min, t_R (minor) = 21.33 min.


DAD1 A, Sig=254,4 Ref=360,100 (D:\data\OYY\DEF_LC1 2023-03-14 14-02-17\010-D2B-F3-Yao-3-137-2-1.D)

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	21.099	VV	4764.3	124.9	0.5111	49.837	0.518
2	23.246	VV	4795.6	110.1	0.5203	50.163	0.487


DAD1 A, Sig=254,4 Ref=360,100 (D:\data\OYY\DEF_LC1 2023-03-14 14-02-17\011-D2B-F4-Yao-3-142-2.D)

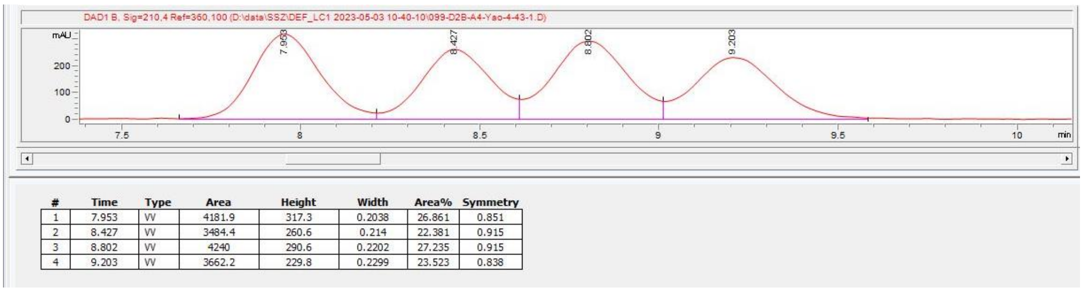
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	21.329	MM	950.1	26.9	0.5892	29.577	0.698
2	23.223	MM	2262.1	50.8	0.7429	70.423	0.529



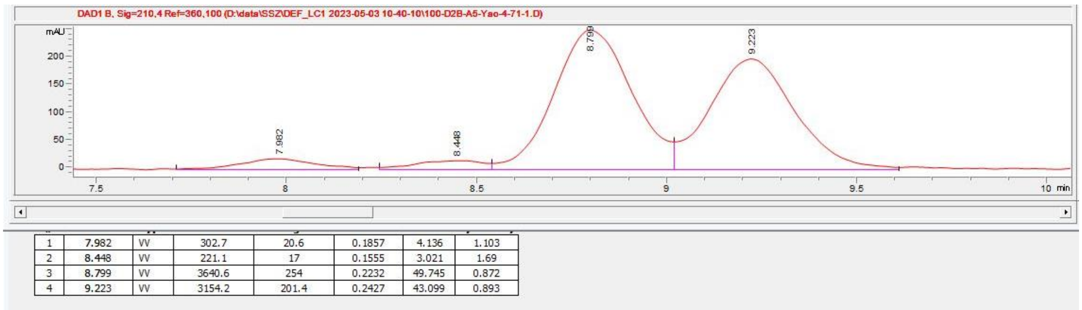
Product **rac-34** was prepared using **rac-4** according to the General procedure I for the product derivatization. Enzymatic product **34** was prepared using **4** according to the same method.

Yields: isolated, quant., d.r 1.2:1.

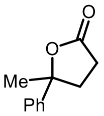
Enantioselectivity: 92:8 er, 93:7 er. Chiral HPLC method: AS-H column, 210 nm, 10% isopropanol/hexanes, flow rate 1.0 mL/min, room temperature, isomer 1: t_R (major) = 8.80 min, t_R (minor) = 7.98 min, isomer 2: t_R (major) = 9.22 min, t_R (minor) = 8.45 min.



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.953	VV	4181.9	317.3	0.2038	26.861	0.851
2	8.427	VV	3484.4	260.6	0.214	22.381	0.915
3	8.802	VV	4240	290.6	0.2202	27.235	0.915
4	9.203	VV	3662.2	229.8	0.2299	23.523	0.838



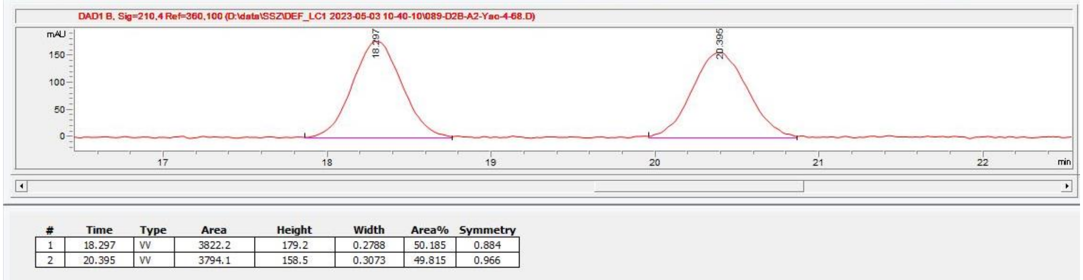
1	7.982	VV	302.7	20.6	0.1857	4.136	1.103
2	8.448	VV	221.1	17	0.1555	3.021	1.69
3	8.799	VV	3640.6	254	0.2232	49.745	0.872
4	9.223	VV	3154.2	201.4	0.2427	43.099	0.893



Product **rac-35** was prepared using **rac-4** according to the General procedure II for the product derivatization. Enzymatic product **35** was prepared using **4** according to the same method.

Yields: isolated, 60%.

Enantioselectivity: 93:7 er. Chiral HPLC method: IC-H column, 210 nm, 10% isopropanol/hexanes, flow rate 1.0 mL/min, room temperature, t_R (major) = 18.35 min, t_R (minor) = 20.45 min.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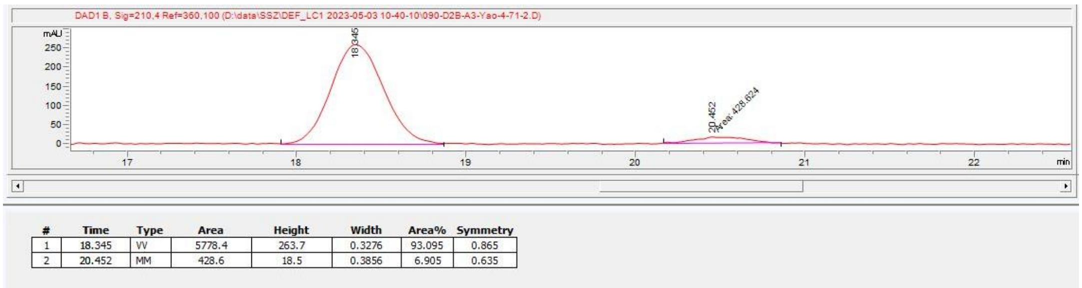
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	18.297	VV	3822.2	179.2	0.2788	50.185	0.884
2	20.395	VV	3794.1	158.5	0.3073	49.815	0.966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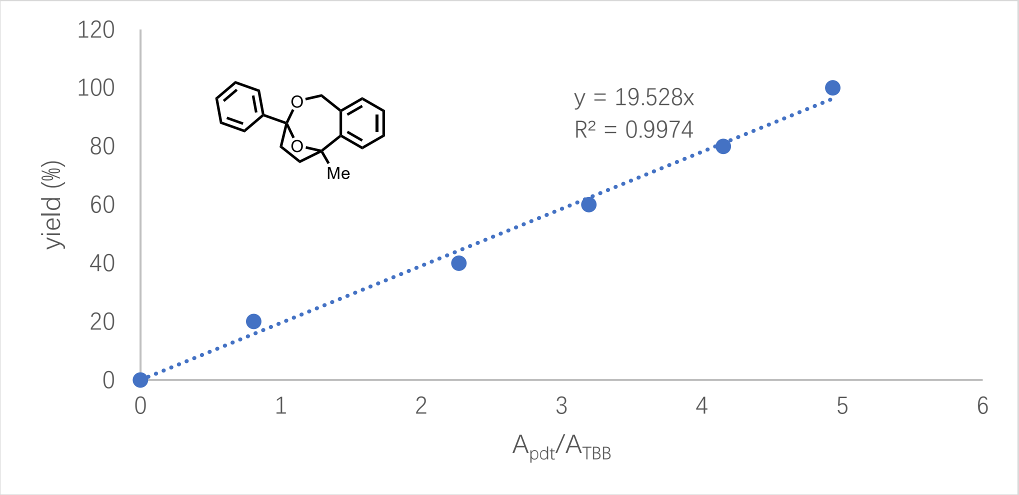
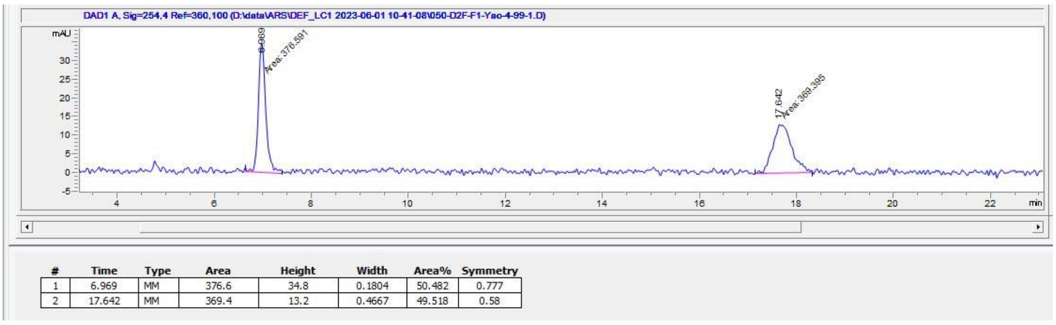
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	18.345	VV	5778.4	263.7	0.3276	93.095	0.865
2	20.452	MM	428.6	18.5	0.3856	6.905	0.635



Enzymatic reaction was conducted according to the general procedure for hydroxylation reaction in vials using (2-(prop-1-en-2-yl)phenyl)methanol **(36)** and 2-bromo-1-phenylethan-1-one **(2a)** as the starting materials.

Yield: 65%.

Enantioselectivity: 59:41 er. Chiral HPLC method: IA-H column, 254 nm, 2% isopropanol/hexanes, flow rate 1.0 mL/min, room temperature, t_R (major) = 7.05 min, t_R (minor) = 18.04 min.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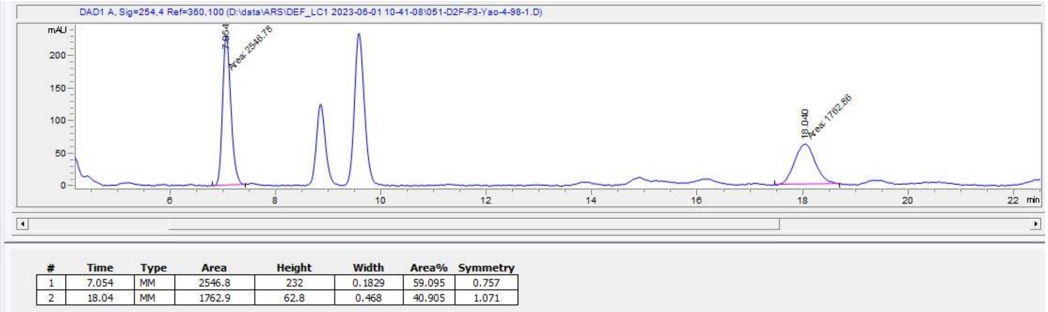
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	6.969	MM	376.6	34.8	0.1804	50.482	0.777
2	17.642	MM	369.4	13.2	0.4667	49.518	0.58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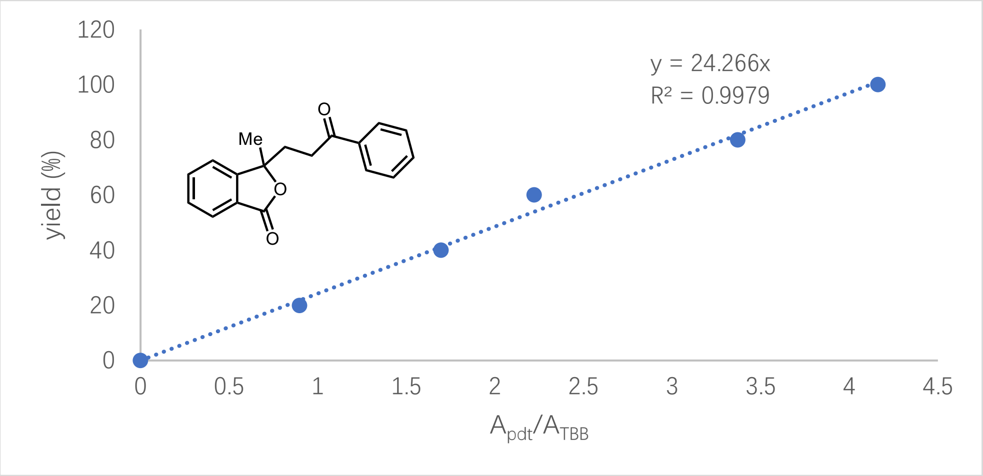
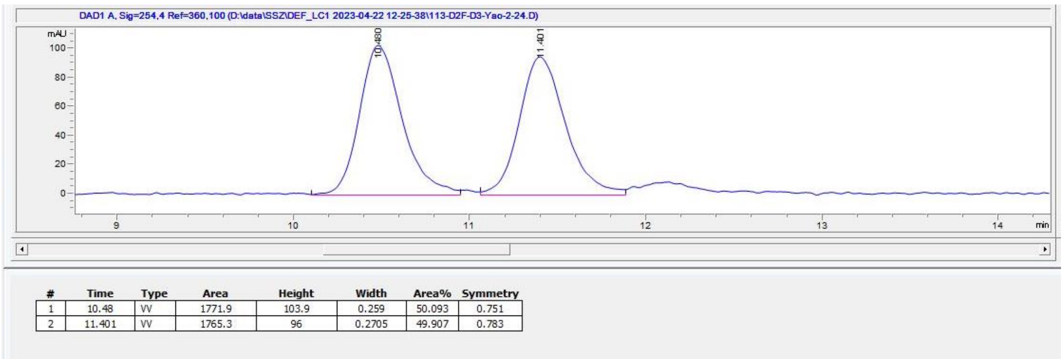
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.054	MM	2546.8	232	0.1829	59.095	0.757
2	18.04	MM	1762.9	62.8	0.468	40.905	1.071



Enzymatic reaction was conducted according to the general procedure for hydroxylation reaction in vials using 2-(prop-1-en-2-yl)benzoic acid (**38**) and 2-bromo-1-phenylethan-1-one (**2a**) as the starting materials.

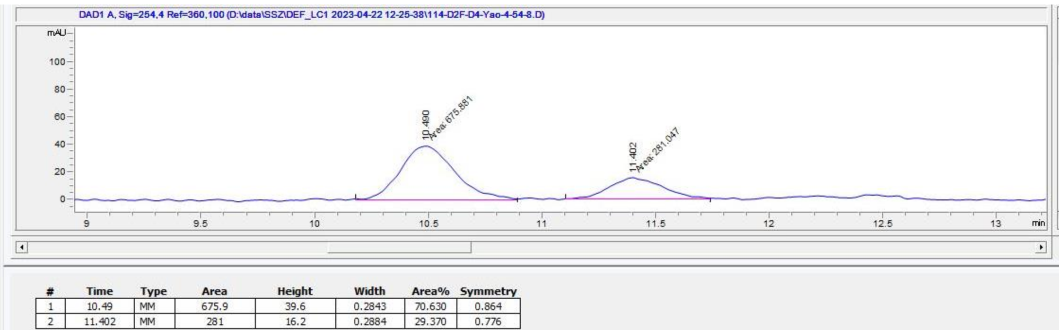
Yield: 21%.

Enantioselectivity: 71:29 er. Chiral HPLC method: IA-H column, 254 nm, 13% isopropanol/hexanes, flow rate 1.0 mL/min, room temperature, t_R (major) = 10.49 min, t_R (minor) = 11.40 min.



DAD1 A, Sig=254,4 Ref=360,100 (D:\data\SSZ\DEF_LC1 2023-04-22 12-25-38\113-D2F-D3-Yao-2-24.D)

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	10.48	VV	1771.9	103.9	0.259	50.093	0.751
2	11.401	VV	1765.3	96	0.2705	49.907	0.783



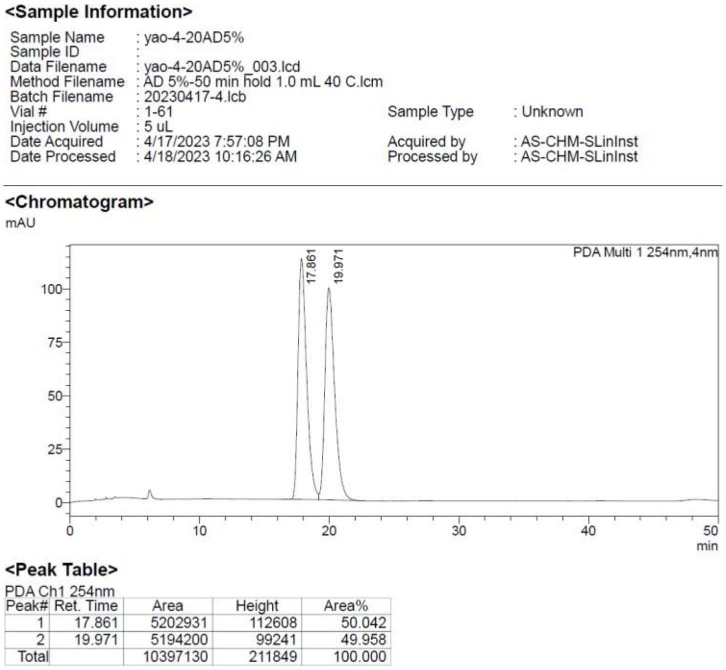
DAD1 A, Sig=254,4 Ref=360,100 (D:\data\SSZ\DEF_LC1 2023-04-22 12-25-38\114-D2F-D4-Yao-4-54-8.D)

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	10.49	MM	675.9	39.6	0.2843	70.630	0.864
2	11.402	MM	281	16.2	0.2884	29.370	0.776

Absolute configuration determination

Absolute configuration of product **8** was assigned to be *S* by using the same HPLC column AD-H according to the reported data[17]. The absolute configuration of the rest of products can be deduced to be *S*.

Enantioselectivity: 94:6 er. Chiral HPLC method: AD-H column, 254 nm, 5% isopropanol/hexanes, flow rate 1.0 mL/min, room temperature, t_R (major) = 19.99 min, t_R (minor) = 17.91 min.



<Sample Information>

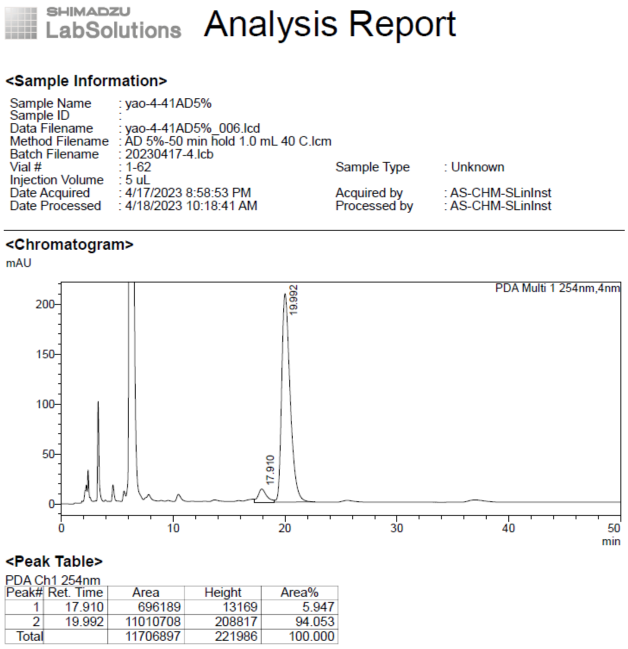
Sample Name : yao-4-20AD5%
Sample ID :
Data Filename : yao-4-20AD5%_003.lcd
Method Filename : AD 5%-50 min hold 1.0 mL 40 C.lcm
Batch Filename : 20230417-4.lcb
Vial # : 1-61
Sample Type : Unknown
Injection Volume : 5 uL
Date Acquired : 4/17/2023 7:57:08 PM
Acquired by : AS-CHM-SLinInst
Date Processed : 4/18/2023 10:16:26 AM
Processed by : AS-CHM-SLinInst

<Chromatogram>

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	17.861	5202931	112608	50.042
2	19.971	5194200	99241	49.958
Total		10397130	211849	100.000



SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name : yao-4-41AD5%
Sample ID :
Data Filename : yao-4-41AD5%_006.lcd
Method Filename : AD 5%-50 min hold 1.0 mL 40 C.lcm
Batch Filename : 20230417-4.lcb
Vial # : 1-62
Sample Type : Unknown
Injection Volume : 5 uL
Date Acquired : 4/17/2023 8:58:53 PM
Acquired by : AS-CHM-SLinInst
Date Processed : 4/18/2023 10:18:41 AM
Processed by : AS-CHM-SLinInst

<Chromatogram>

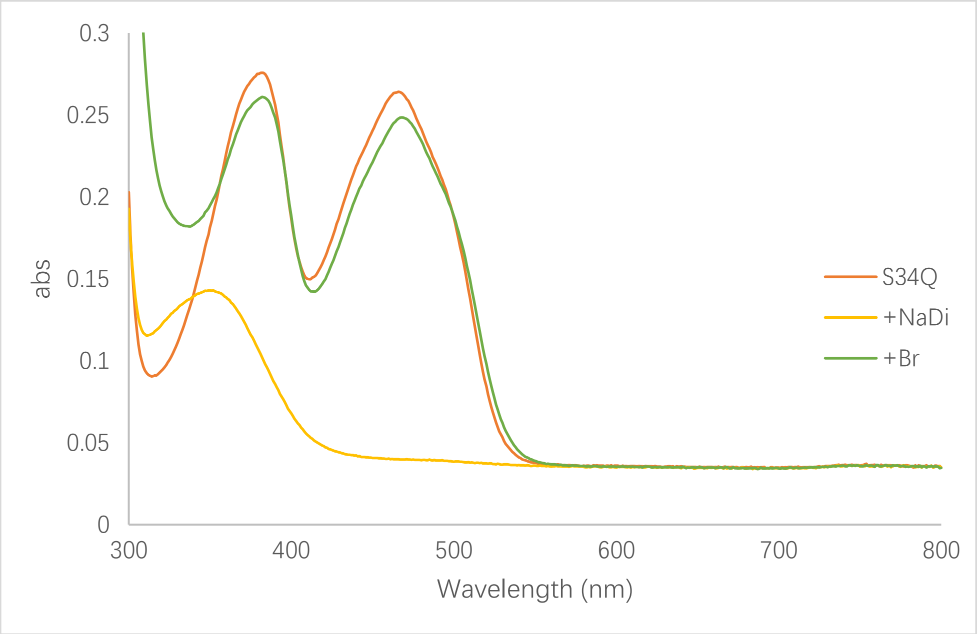
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	17.910	696189	13169	5.947
2	19.992	11010708	208817	94.053
Total		11706897	221986	100.000

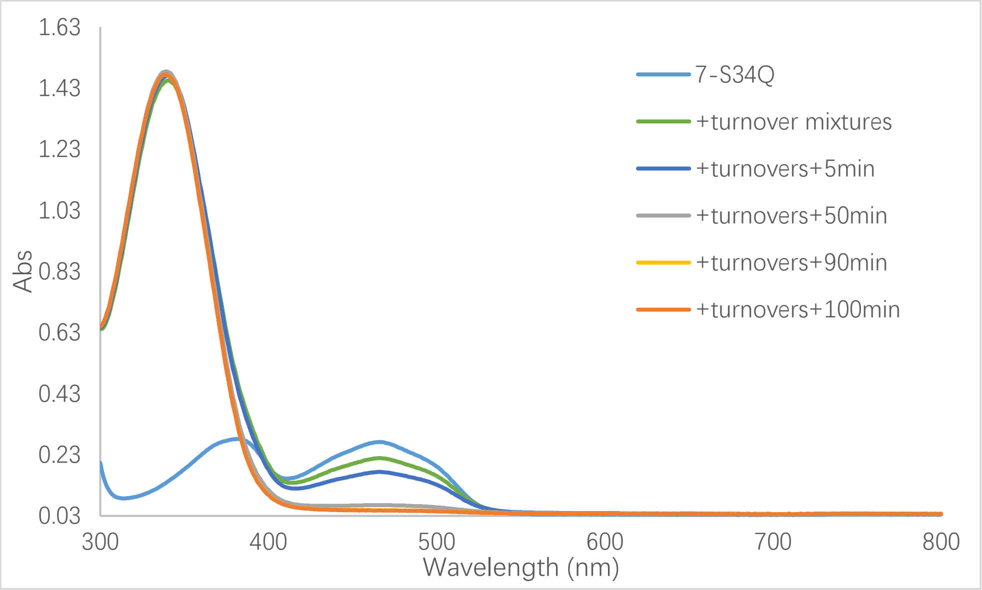
UV-Vis experiment

A blank solution of degassed Tris buffer (100 mM, pH .0) was prepared and used to obtain a baseline spectrum. A 50 µM solution of enzyme was prepared by mixing MorB-B3 (mutant S34Q, 100 nmol, 1 equiv) with degassed Tris buffer (the total volume is 800 uL) in an anaerobic chamber and a spectrum was taken of the oxidized MorB-B3. The oxidized FMN cofactor was reduced by titration with sodium dithionite (5 mg/mL) in Tris buffer (100 mM, pH 8.0). Following filtration through a syringe filter, a spectrum of the reduced MorB-B3 (FMNhq) was obtained. To detect the presence of a charge transfer-complex, 15 µmol of bromoacetophenone dissolved in THF (50 uL, 9 mg/150 µL) was added to the reduced MorB-B3 solution and filtered through a syringe filter. Upon addition of bromoacetophenone, two peaks at 350 nm and 450 nm showed up, which belong to the features of oxidized FMN. Due to the fast ground-state electron transfer, no CT state was observed between the reduced MorB-B3 and bromoacetophenone.



Turnover reduction of FMN_{ox} to FMN_{hq}

A blank solution of degassed Tris buffer (100 mM, pH 8.0) was prepared and used to obtain a baseline spectrum. A 50 µM solution of enzyme was prepared by mixing MorB-B3 (100 nmol, 1 equiv) with degassed Tris buffer (the total volume is 800 uL) in an anaerobic chamber and a spectrum was taken of the oxidized MorB-B3. The oxidized FMN cofactor was reduced by cofactor regeneration mix ($NADP^+$, 5 equiv, GDH, 0.12 mg, and glucose, 100 equiv.), as monitored by UV-Vis. FMNox was fully reduced to FMNhq in 50 min.

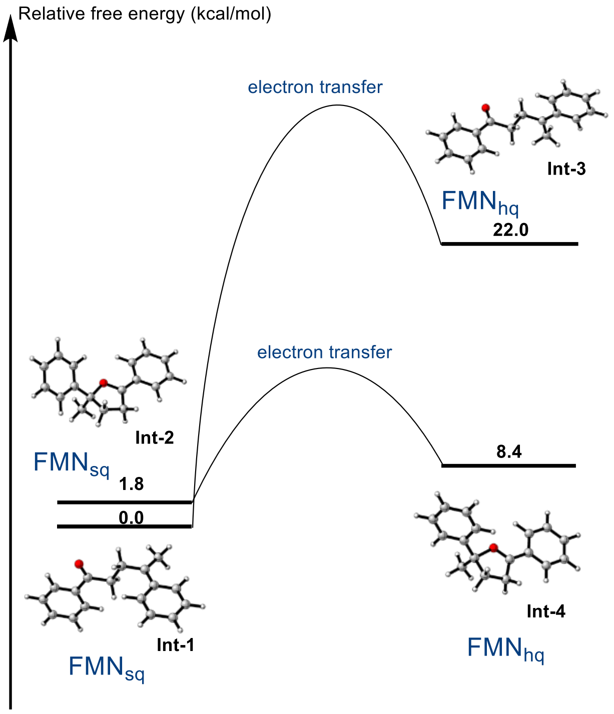


Density functional theory (DFT) calculations

All DFT computations were carried out using the Gaussian 16, Revision C.01 program[21] and the and the ωB97XD functional[22]. All structures were optimized at the ωB97X-D/6-31G(d,p) level of theory[22]. Higher level of theory single point calculations were performed at the ωB97X-D/6-31G(d,p) level of theory with polarizable continuum model (IEFPCM) in water[23-25]. Computed structures were illustrated with CYLview20[26]. Simplified model of FMNsq and FMN were used as previous computational works[27,28].

Thermal energy diagram of radical oxidation step

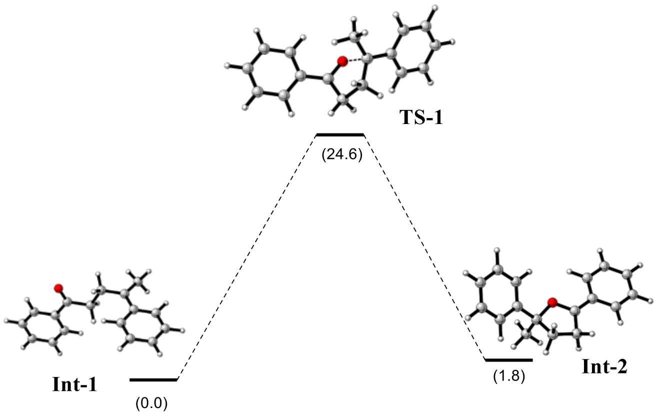
We performed the DFT calculation to compare the changes in Gibbs free energy during the radical oxidation step. Two radical intermediates were proposed for this step, and both of them are endothermic. The oxidation of the linear radical intermediate exhibited a ΔG as high as 22.0 kcal/mol, a value too high to be likely at room temperature. However, the oxidation of the cyclic intermediate showed a ΔG of only 6.6 kcal/mol, a value that suggests feasibility at room temperature (**Supplementary Figure 5**).



Supplementary Figure 5. Thermal energy changes during radical oxidation step

Pathway to radical intermediate 2 (Int-2)

The transformation from **Int-1** to **Int-2** typically involves a straightforward intramolecular cyclization. However, we discovered that the energy barrier to reach the transition state (**TS-1**) is 24.6 kcal/mol, a value slightly above what is usually achievable at room temperature (**Supplementary Figure 5**). We hypothesize that the larger enzyme pocket of MorB may help the preorganization of the molecular skeleton, facilitating the cyclization from **Int-1** to **Int-2**. In contrast, other EREDs, such as NCR and GluER-T36A, possess narrower pockets, creating conditions less conducive to the radical cyclization step, and instead favoring the reductive coupling product.

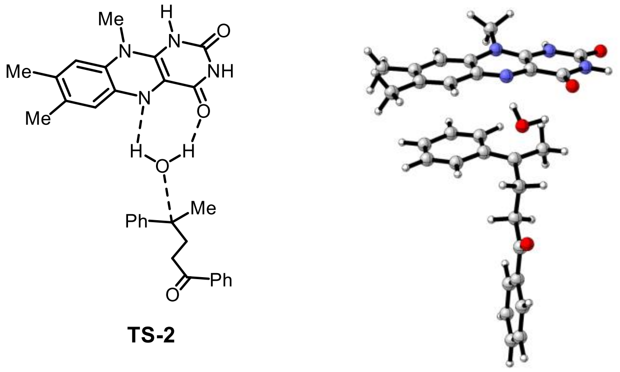


Supplementary Figure 6. Pathway to **Int-2**

Possible FMN-mediated hydroxylation step

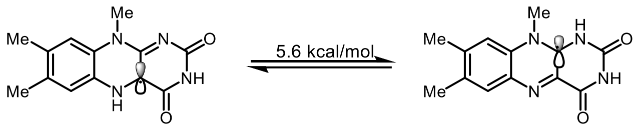
Though the nucleophilic attack of a cation by H_2O is a common mechanism of hydroxylation in SN1 reactions, the hydroxylation product could also be directly obtained from a linear radical intermediate.

We hypothesize that FMNsq could facilitate the coordination of H_2O and the linear radical intermediate, simultaneously breaking the O-H bond of H_2O and forming the C-O bond of the product. Concurrently, FMNsq would be reduced to FMNhq. We performed DFT calculation to find the transition state of the direct hydroxylation step (**Supplementary Figure 7**).


TS-2

Supplementary Figure 7. Transition state of FMN-mediated hydroxylation

We assumed that FMN mediated the interaction between H_2O and the radical intermediate, thus the N-5 atom of FMN should interact with H_2O. Consequently, the original N-5 hydrogen atom would need to be repositioned to another amide nitrogen atom, which we designate as FMN$_{sq}$′. The energy difference between FMN$_{sq}$ and FMN$_{sq}$′ is only 5.6 kcal/mol. This energy gap should allow transformation between these two states at room temperature (**Supplementary Figure 8**).

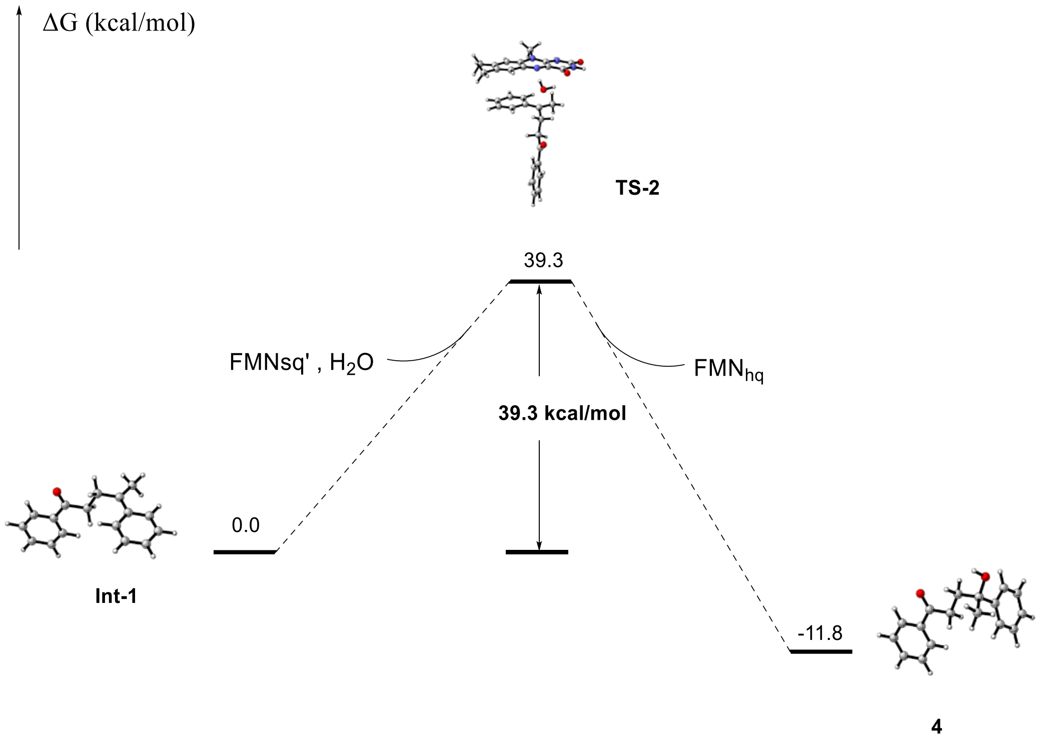


FMN$_{sq}$

FMN$_{sq}$'

Supplementary Figure 8. Interconversion of FMN$_{sq}$ and FMN$_{sq}$′

However, the activation energy barrier for direct FMN$_{sq}$ mediated hydroxylation step is 39.3 kcal/mol, which is not feasible at room temperature (**Supplementary Figure 9**).

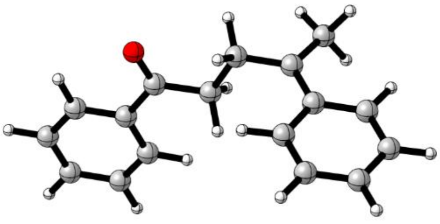


Supplementary Figure 9. Direct FMN-mediated hydroxylation.

Molecular coordinates of calculated structures

Note: energies reported below are in units of hartrees

Int-1 (Liner Radical)



Electronic Energy: -733.26464566

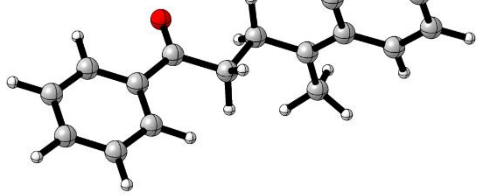
Thermal correction to Gibbs Free Energy: 0.24737200

C	-2.90949400	0.22292500	0.03238300
C	-2.62401400	-0.77928100	-0.93290800
C	-4.97599800	-0.98734000	0.53632500
C	-3.48466500	-1.84227200	-1.14724100
H	-1.71323200	-0.72081500	-1.51902300
C	-4.66818700	-1.95868500	-0.41695900
H	-5.89493400	-1.06354500	1.10975000
H	-3.23250100	-2.59048800	-1.89257800
H	-5.34046600	-2.79268900	-0.58902500
C	-4.12017500	0.07783400	0.76038400
H	-4.38885500	0.81905700	1.50521700
C	-2.02674700	1.31991900	0.27190200
C	-2.31360800	2.30689400	1.36666500
H	-1.48720400	3.01211800	1.48503100
H	-3.21785600	2.89522200	1.15916200
H	-2.47362900	1.81648100	2.33518400
C	-0.74487600	1.48092400	-0.49450000
H	-0.85515900	1.18550200	-1.54173900
H	-0.45226600	2.53499800	-0.51743700
C	0.39773500	0.66975200	0.13177900
H	0.12757700	-0.39322100	0.17312200
H	0.55643500	0.97589600	1.17407800
C	2.91126100	0.07114900	-0.12099400
C	2.87307200	-0.75817000	1.00355000
C	4.11293600	0.22319300	-0.81917400
C	4.02000000	-1.42433200	1.42214300
H	1.95075000	-0.89174800	1.55924300
C	5.25738400	-0.44135500	-0.40102000
H	4.12203900	0.87040200	-1.68946100
C	5.21194700	-1.26654400	0.72109300
H	3.98289300	-2.06710000	2.29559000
H	6.18638800	-0.31809700	-0.94817100
H	6.10621100	-1.78718500	1.04898300
C	1.70811100	0.81471500	-0.62198300
O	1.78446300	1.51740700	-1.61207500

Int-3 (Liner Cation)

Electronic Energy: -733.09346812

Thermal correction to Gibbs Free Energy: 0.24936800

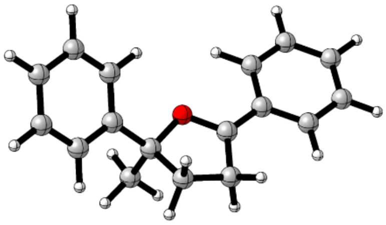


C	2.92114600	0.20866200	-0.05232800
C	4.13814600	0.20050600	-0.79088200
C	3.61403200	-1.85554800	1.03920000
C	5.06755500	-0.80042100	-0.60411100
H	4.35753300	0.99356400	-1.49517000
C	4.80358200	-1.82969300	0.30498800
H	3.42462300	-2.65994600	1.74002700
H	5.99691200	-0.79212300	-1.16117700
H	5.53454700	-2.61976900	0.44417000
C	2.68826000	-0.84717700	0.87479000
H	1.77313000	-0.87512100	1.45374400
C	1.96761200	1.24024000	-0.22816600
C	2.14101400	2.31823300	-1.23598000
H	2.67966100	2.01742600	-2.13332600
H	1.17741900	2.74970600	-1.51315800
H	2.71298200	3.12422400	-0.75181500
C	0.72828500	1.32204300	0.57727100
H	0.83079500	0.91084000	1.58084500
H	0.42451900	2.36680000	0.68825400
C	-0.40301000	0.57213300	-0.16373500
H	-0.14612800	-0.48330600	-0.30723100
H	-0.57770200	0.99364300	-1.15964100
C	-2.92418700	0.04018800	0.13798300
C	-2.95404000	-0.65427400	-1.07705200
C	-4.09249900	0.15071100	0.90155200
C	-4.13756500	-1.22997200	-1.52089400
H	-2.06177500	-0.75403500	-1.68734400
C	-5.27286800	-0.42493600	0.45473000
H	-4.05293000	0.69241800	1.84002400
C	-5.29573800	-1.11504400	-0.75573600
H	-4.15855100	-1.76734900	-2.46260600
H	-6.17637700	-0.33660500	1.04788400
H	-6.21935400	-1.56462800	-1.10485100
C	-1.69277400	0.67717200	0.66745500
O	-1.66262600	1.27091600	1.72585800

Int-2 (Cyclic Radical)

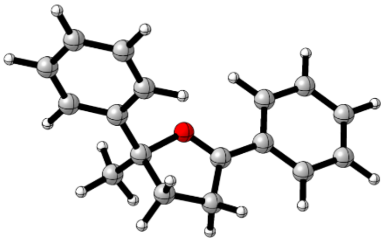
Electronic Energy: -733.26676648

Thermal correction to Gibbs Free Energy: 0.25240700



C	-2.31353300	0.00663200	0.09422500
C	-2.23804100	-1.37145500	-0.09788300
C	-4.69898200	-0.09183000	-0.31254200
C	-3.38533700	-2.10390000	-0.39245900
H	-1.27634100	-1.86413400	-0.02048700
C	-4.61776800	-1.46921700	-0.50017000
H	-5.65507400	0.41496200	-0.39790400
H	-3.31201200	-3.17696500	-0.53939700
H	-5.51020000	-2.04219900	-0.73059800
C	-3.55472600	0.63914900	-0.01638000
H	-3.62935600	1.71439200	0.12420400
C	-1.08325900	0.83439500	0.41424300
C	-1.17110500	1.44000800	1.81775600
H	-0.27836100	2.03419100	2.03492100
H	-2.04947100	2.08414800	1.90950000
H	-1.24672500	0.64205000	2.55961100
C	-0.77723200	1.89487200	-0.66389000
H	-1.10725300	1.52510700	-1.63809600
H	-1.28758700	2.83962700	-0.46468200
C	0.75136800	2.00455700	-0.62375300
H	1.08544900	2.80260800	0.05420200
H	1.17950300	2.22277100	-1.60702700
C	2.41803100	0.05064700	-0.07921500
C	3.55550700	0.72587000	-0.59490600
C	2.60807000	-1.24500700	0.47040400
C	4.80441900	0.13127300	-0.56390500
H	3.44462800	1.72082400	-1.01552100
C	3.86437400	-1.82250900	0.49196200
H	1.75252200	-1.77291200	0.87631000
C	4.97376700	-1.14584000	-0.02332600
H	5.66021400	0.66677400	-0.96410100
H	3.98745000	-2.81436800	0.91688700
H	5.95590600	-1.60614500	-0.00198400
C	1.14653300	0.65252900	-0.11440900
O	0.07427400	-0.02147000	0.38370600

Int-4 (Cyclic Cation)

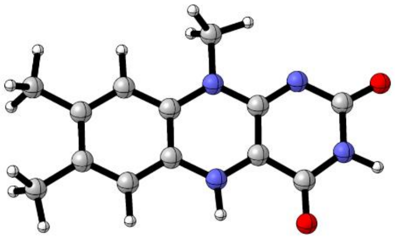


Electronic Energy: -733.12226784

Thermal correction to Gibbs Free Energy: 0.25652900

C	-2.29274400	0.10348700	0.05827600
C	-2.16299100	-0.87711900	-0.93202800
C	-4.50042600	-0.74172300	0.56053000
C	-3.18672300	-1.78351000	-1.16740800
H	-1.25121800	-0.94725000	-1.51957900
C	-4.36187700	-1.71422200	-0.42199000
H	-5.41258600	-0.68215100	1.14386700
H	-3.07009700	-2.54270600	-1.93296000
H	-5.16577300	-2.41789500	-0.60843300
C	-3.46833400	0.16031700	0.80584400
H	-3.60055100	0.90632800	1.58093900
C	-1.16247600	1.08155000	0.27723500
C	-1.26269800	1.93867300	1.52720900
H	-0.37202500	2.56257000	1.64028700
H	-2.12489500	2.60372400	1.44552400
H	-1.37509000	1.32253300	2.42077700
C	-0.75531800	1.88773100	-0.96977400
H	-1.13131900	1.40708600	-1.87413000
H	-1.16824100	2.89594900	-0.92831800
C	0.77723800	1.87968900	-0.95521000
H	1.20414100	2.74883800	-0.43857400
H	1.23025300	1.84030300	-1.94734500
C	2.35663900	0.00383600	-0.01207800
C	3.48582700	0.50696100	-0.68819300
C	2.46894600	-1.14503500	0.79866100
C	4.70678900	-0.12886600	-0.55036500
H	3.40860200	1.39181900	-1.31096700
C	3.69319200	-1.77473100	0.92406900
H	1.59461200	-1.52646000	1.31384800
C	4.80744100	-1.26668900	0.25206400
H	5.58038900	0.25401800	-1.06462300
H	3.78788300	-2.65949800	1.54264900
H	5.76619600	-1.76412900	0.35479700
C	1.09525600	0.66515300	-0.14279800
O	0.08415900	0.22923800	0.49974700

FMNsq



Electronic Energy: -872.77629006

Thermal correction to Gibbs Free Energy: 0.21126800

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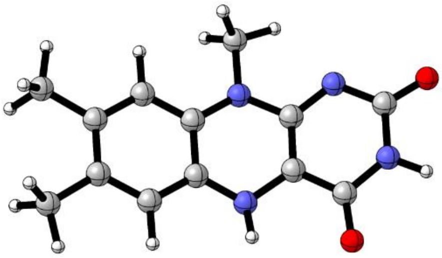
C	0.97052400	-0.61651000	-0.00000400
C	0.98496100	0.79122600	-0.00007200
C	2.19387400	1.48588200	-0.00008200
C	3.41050300	0.81935000	-0.00001200
C	-1.40143300	0.78214400	-0.00005000
C	-1.45686200	-0.63527800	-0.00000700
C	-2.62221900	1.55821400	-0.00000200
H	2.22455600	-2.36122300	0.00013900
H	2.16903400	2.57233100	-0.00015100
C	4.70834100	-1.35158500	0.00012500
H	5.31329700	-1.10739300	0.88004500
H	5.31280800	-1.10830200	-0.88039100
H	4.53630700	-2.42989400	0.00072100
C	4.70312800	1.59113700	0.00002500
H	5.30978500	1.35213300	-0.88000500
H	5.30911700	1.35311500	0.88079100
H	4.52189500	2.66801700	-0.00063500
N	-0.24775800	-1.30957000	-0.00002300
C	-0.25143800	-2.76449100	0.00002800
H	0.25303600	-3.14484900	0.89316000
H	0.25316500	-3.14490100	-0.89300900
H	-1.28961600	-3.08867500	-0.00003400
N	-2.57302000	-1.31689100	0.00004700
C	-3.77812100	-0.64630700	0.00007800
O	-4.85758900	-1.19956400	-0.00010800
N	-3.74472800	0.77010000	0.00009400
H	-4.64414500	1.23071100	0.00002900
N	-0.22510800	1.45315000	-0.00015000
O	-2.62619400	2.78555200	-0.00006600
H	-0.29437400	2.46486000	-0.00007900

FMNhq anion



Electronic Energy: -872.91296794

Thermal correction to Gibbs Free Energy: 0.20987200

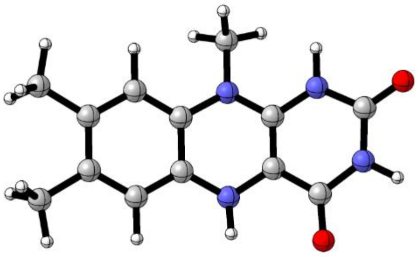
C	3.38682700	-0.59466700	0.15027000
C	2.16422100	-1.27069000	0.00642300

C	0.96191600	-0.60610400	-0.20672500
C	0.97929100	0.81123800	-0.26599200
C	2.18965200	1.47615800	-0.10066900
C	3.39796900	0.79708100	0.09764400
C	-1.41116400	0.78860100	-0.23190400
C	-1.46613500	-0.58776700	-0.17869700
C	-2.57636300	1.54588300	0.03086300
H	2.16765900	-2.35395300	0.06200100
H	2.18697300	2.56357800	-0.14239600
C	4.65944900	-1.37605500	0.36199600
H	5.15017200	-1.11259700	1.30788100
H	5.39248000	-1.19086600	-0.43399700
H	4.46137100	-2.45155000	0.38271600
C	4.68365600	1.57027200	0.25215000
H	5.41371600	1.30456500	-0.52284000
H	5.16423300	1.37190600	1.21847300
H	4.50646700	2.64732700	0.18518100
N	-0.25429200	-1.28787100	-0.38588900
C	-0.26502500	-2.72888200	-0.33627800
H	0.09358900	-3.11430100	0.63088500
H	0.37226100	-3.13996300	-1.12900200
H	-1.29619300	-3.05066900	-0.47093800
N	-2.55861200	-1.31788100	0.04721500
C	-3.73446000	-0.66211000	0.25437400
O	-4.81983400	-1.21138400	0.44903600
N	-3.68988600	0.74463400	0.25639100
H	-4.56359000	1.21505500	0.43589200
N	-0.20203000	1.47199000	-0.53822700
O	-2.63968300	2.78709800	0.06500000
H	-0.25827000	2.45190400	-0.29329700

FMNhq

Electronic Energy: -873.38683846

Thermal correction to Gibbs Free Energy: 0.22330800



C	3.36911100	-0.59878600	0.25098500
C	2.15846700	-1.27603100	0.06483100
C	0.99146600	-0.60281300	-0.26227800
C	1.00760400	0.79788700	-0.36784500
C	2.20355400	1.47124700	-0.16299700
C	3.39023700	0.79423700	0.13148800
C	-1.36592100	0.79543000	-0.31299600
C	-1.38593100	-0.55816900	-0.23987200
C	-2.52903700	1.57038600	0.01789100

H	2.14423700	-2.35525400	0.17976400
H	2.21179500	2.55482700	-0.24927900
C	4.62263400	-1.36832200	0.57866700
H	5.05108700	-1.05119400	1.53607400
H	5.39736100	-1.21832100	-0.18183300
H	4.42431400	-2.44103500	0.64285500
C	4.67057400	1.56494700	0.32328000
H	5.43678400	1.25134700	-0.39441600
H	5.08707500	1.40580500	1.32415100
H	4.51119900	2.63783000	0.19436900
N	-0.24068200	-1.28150800	-0.50072600
C	-0.26466100	-2.71254800	-0.69425000
H	-0.19194100	-3.28109800	0.24432700
H	0.57470400	-2.99598100	-1.33272000
H	-1.17855000	-2.99922600	-1.21996100
N	-2.54799700	-1.21761700	0.10622600
C	-3.73989400	-0.57431300	0.40994600
O	-4.74163100	-1.18268500	0.72713800
N	-3.66020400	0.79785300	0.32183000
H	-4.50417400	1.30424800	0.55046700
N	-0.18296700	1.45310800	-0.70869900
O	-2.57449000	2.79171200	0.02286500
H	-0.22201400	2.44568500	-0.51556800
H	-2.55915600	-2.21160700	0.27022300

H_2O

Electronic Energy: -76.44526872

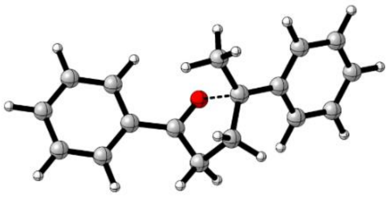
Thermal correction to Gibbs Free Energy: 0.00355900

O	0.00000000	0.11786000	0.00000000
H	0.75782400	-0.47142700	0.00000000
H	-0.75782400	-0.47144900	0.00000000

TS-1

Electronic Energy: -733.22862083

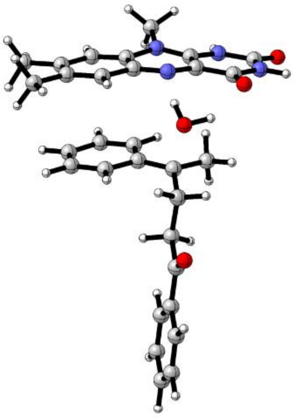
Thermal correction to Gibbs Free Energy: 0.25048300



C	-2.41333700	-0.08872700	0.28546800
C	-2.84196400	0.95278100	-0.55459900
C	-4.51754500	-1.22301700	-0.15332400
C	-4.07907700	0.90692000	-1.17951500
H	-2.18589100	1.79822700	-0.73557000
C	-4.92667000	-0.18126100	-0.97962700
H	-5.16982000	-2.07498600	0.01126200
H	-4.38361700	1.72107300	-1.82977200
H	-5.89639700	-0.21604600	-1.46555400
C	-3.27427800	-1.18080200	0.46718800
H	-2.98019300	-2.00132700	1.11273700
C	-1.09034900	-0.02777900	0.91887700
C	-0.59963600	-1.20733600	1.70812800
H	0.47369300	-1.10622500	1.89609700
H	-1.10171200	-1.26451600	2.68379600
H	-0.76226800	-2.14877800	1.17941600
C	-0.55441900	1.31489200	1.36742900
H	-1.35936500	2.04572200	1.46800900
H	-0.09026000	1.20659900	2.35223500
C	0.52983400	1.84659200	0.36199500
H	1.27921300	2.45889200	0.86718200
H	0.03420900	2.46764500	-0.39183400
C	2.44686000	0.17789500	-0.29481000
C	3.50579500	1.06419300	-0.03358300
C	2.75208400	-1.15825300	-0.61458900
C	4.82187700	0.62248700	-0.07243900
H	3.30108800	2.10641500	0.18955100
C	4.06710900	-1.59331100	-0.64651700
H	1.93192500	-1.83453700	-0.82927600

C	5.10987700	-0.70645200	-0.37488000
H	5.62840200	1.31968600	0.13235000
H	4.28550600	-2.62937000	-0.88635700
H	6.13948900	-1.04821300	-0.40440600
C	1.05171700	0.60161800	-0.28011000
O	0.11609100	-0.19036300	-0.61255500

TS-2



Electronic Energy: -76.44526872

Thermal correction to Gibbs Free Energy: 0.00355900

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C	-0.62927900	3.06943500	-0.13850600
H	-1.65999200	1.84926400	1.26781600
C	0.24934700	3.11575700	-1.22809300
H	1.47360700	1.95984200	-2.56295200
H	-1.01729400	3.99047700	0.28417800
H	0.51839900	4.06719200	-1.67441900
C	3.27316300	3.30080200	-0.09124700
C	3.80090500	2.15646800	-0.70718100
C	3.52919300	0.88704800	-0.23094100
C	2.69194000	0.69790600	0.91026400
C	2.19346400	1.86807000	1.52373200
C	2.47954300	3.14223600	1.05645700
C	2.75487700	-1.59739700	0.64473500
C	3.59136100	-1.48945700	-0.44480400
C	2.30851900	-2.92831800	1.03308700
H	4.41436300	2.28513100	-1.59407800
H	1.57326000	1.73340200	2.40452000
C	3.61104900	4.66842300	-0.62501800
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H	4.21852000	5.24200200	0.08580600
H	4.17477300	4.60076100	-1.55937400
C	1.92392000	4.34596500	1.77033700
H	2.72415800	4.98633900	2.15832000
H	1.31807800	4.96367800	1.09740300
H	1.29233300	4.04768000	2.60991200
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C	5.26026300	-0.14754200	-1.67859300

H	4.98808900	0.04829000	-2.72420700
H	5.87948600	0.67959600	-1.32410100
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C	0.43515600	0.71382000	-1.17397400
H	0.86384800	-0.19166000	-1.58781500
C	-1.01388200	-0.61674200	0.33978600
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H	0.54120000	-1.91165300	-0.42494600
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C	-2.33386700	-0.68311800	1.05714400
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C	-6.00839700	-0.03217300	-1.46676000
C	-7.31488900	-0.42008200	0.52489900
C	-7.17830800	0.15251300	-2.19571700
H	-5.05185900	0.05235600	-1.97203400
C	-8.48211600	-0.23655600	-0.20315200
H	-7.34071100	-0.64327000	1.58595100
C	-8.41491600	0.05011900	-1.56524300
H	-7.12450500	0.37664900	-3.25603300
H	-9.44593900	-0.31642400	0.28894500
H	-9.32719900	0.19405900	-2.13553100
C	-4.84398100	-0.52876500	0.74051000
O	-4.94004700	-0.75665800	1.93044100
O	-0.07240800	-0.94582400	2.47338300
H	0.10309400	-1.88846500	2.60616200
H	0.83743500	-0.65862500	2.19440700
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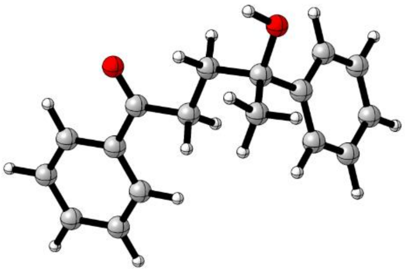
4

Electronic Energy: -809.14478852

Thermal correction to Gibbs Free Energy: 0.26548000



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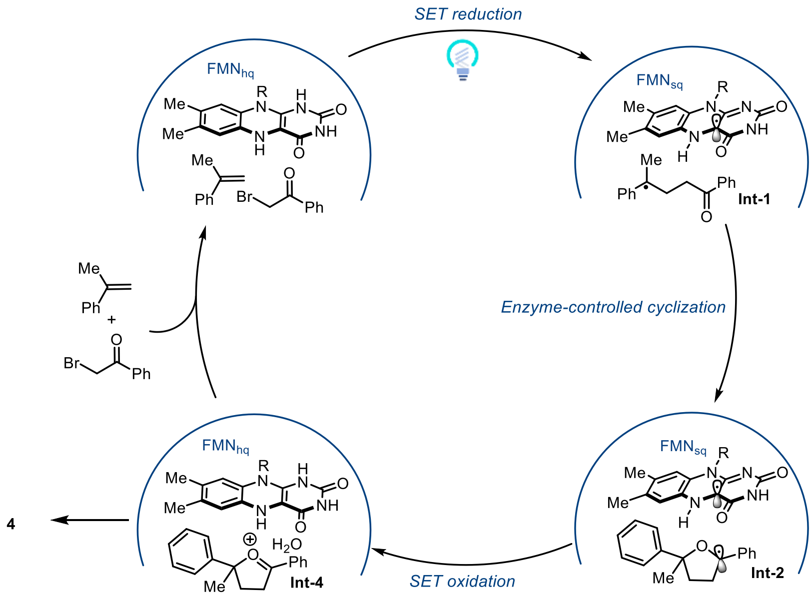
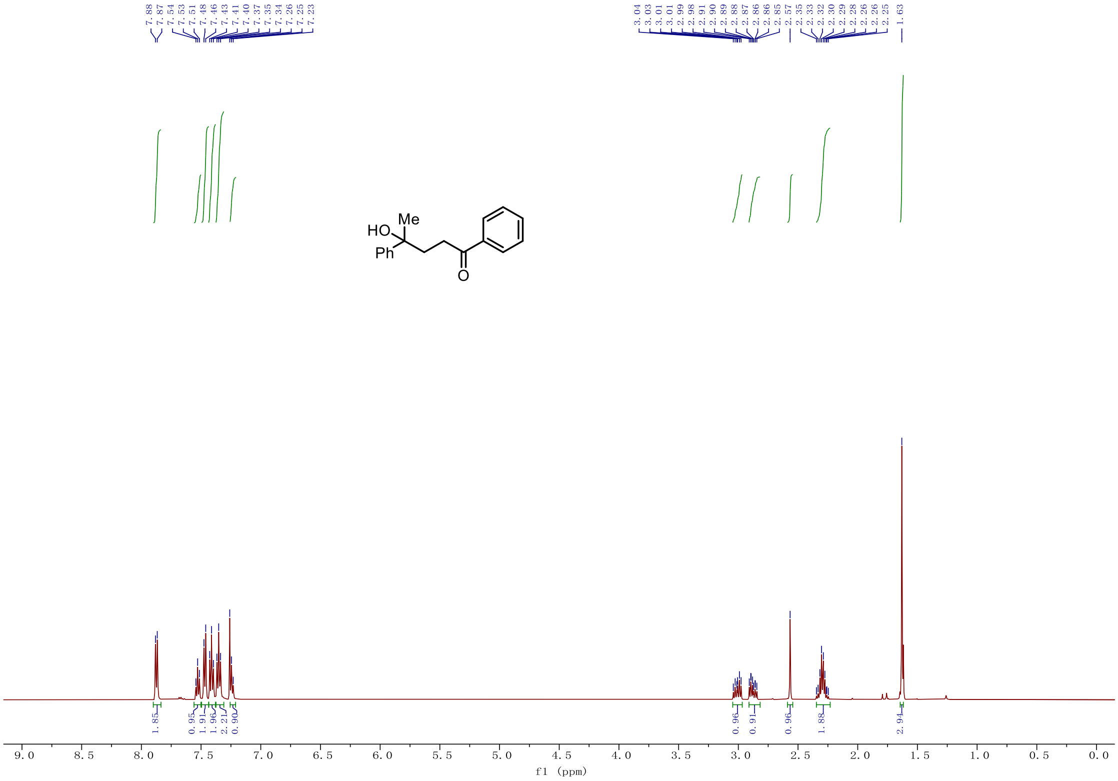
C	-3.55415000	1.63670900	-1.53467500
C	-2.72723300	2.48241600	0.55627800
H	-1.94151700	1.03204400	1.91892800
C	-3.30932500	2.71213400	-0.68511200
H	-4.01281100	1.80350500	-2.50441800
H	-2.53550600	3.31133800	1.23063600
H	-3.57333300	3.72056000	-0.98744600
C	-3.21675700	0.34515300	-1.14693700
H	-3.41830000	-0.49489500	-1.80144200
C	-2.20822700	-1.31865200	0.45789700
C	-2.20176600	-1.57580000	1.96865400
H	-1.44446800	-0.99328700	2.49983500
H	-1.98540700	-2.63322300	2.15358900
H	-3.18115300	-1.34340900	2.39253400
C	-0.83508100	-1.63389500	-0.17551700
H	-0.96231700	-1.62786800	-1.26234200
H	-0.54639700	-2.65653800	0.09867200
C	0.29167900	-0.68225400	0.20064200
H	0.05794400	0.33479100	-0.13546400
H	0.41343000	-0.61440700	1.28980700
C	2.81792600	-0.21523500	-0.14072900
C	2.73748900	0.97876500	0.58186300
C	4.05141300	-0.61891100	-0.66031600
C	3.87410200	1.75512000	0.78126000
H	1.78983200	1.31343000	0.99090700
C	5.18556900	0.15584200	-0.46086300
H	4.09352800	-1.54750000	-1.21912600
C	5.09797700	1.34468700	0.26093200
H	3.80389600	2.68149700	1.34192900
H	6.13936200	-0.16458300	-0.86736300
H	5.98412200	1.95184400	0.41719600
C	1.62844100	-1.09596400	-0.38787900
O	1.74081900	-2.11761200	-1.03862400
O	-3.17782600	-2.17737800	-0.13903200
H	-2.83882000	-3.07578900	-0.08189500

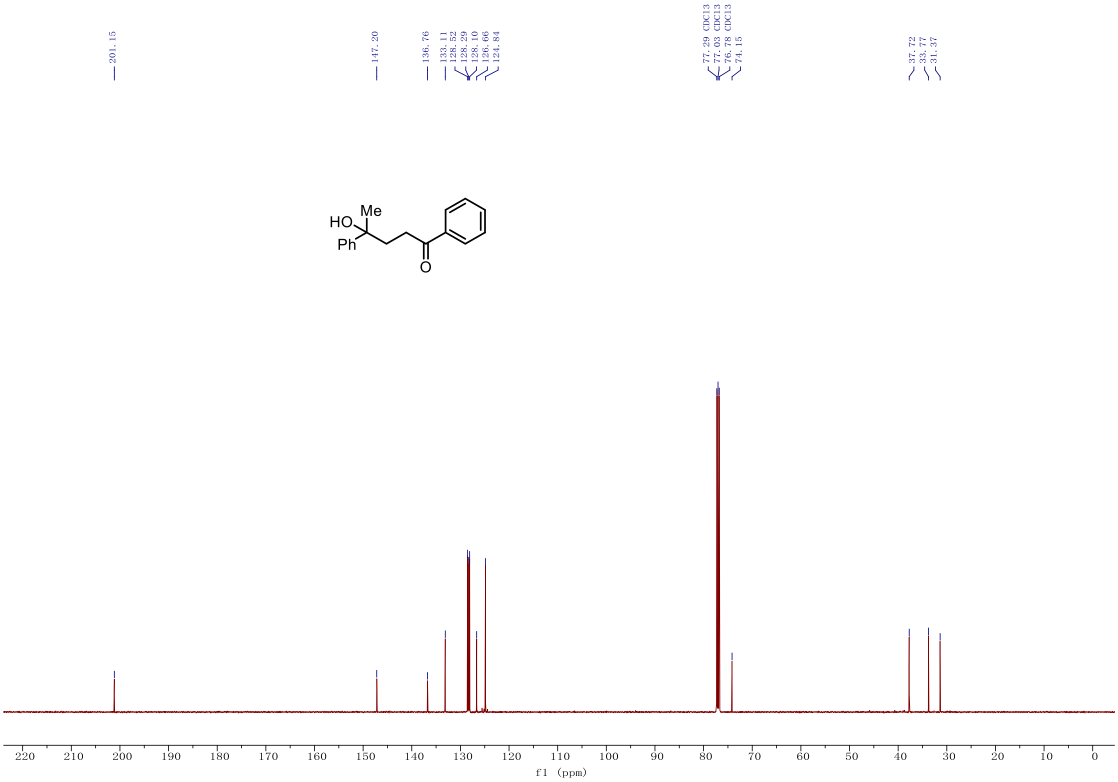
Proposed mechanism

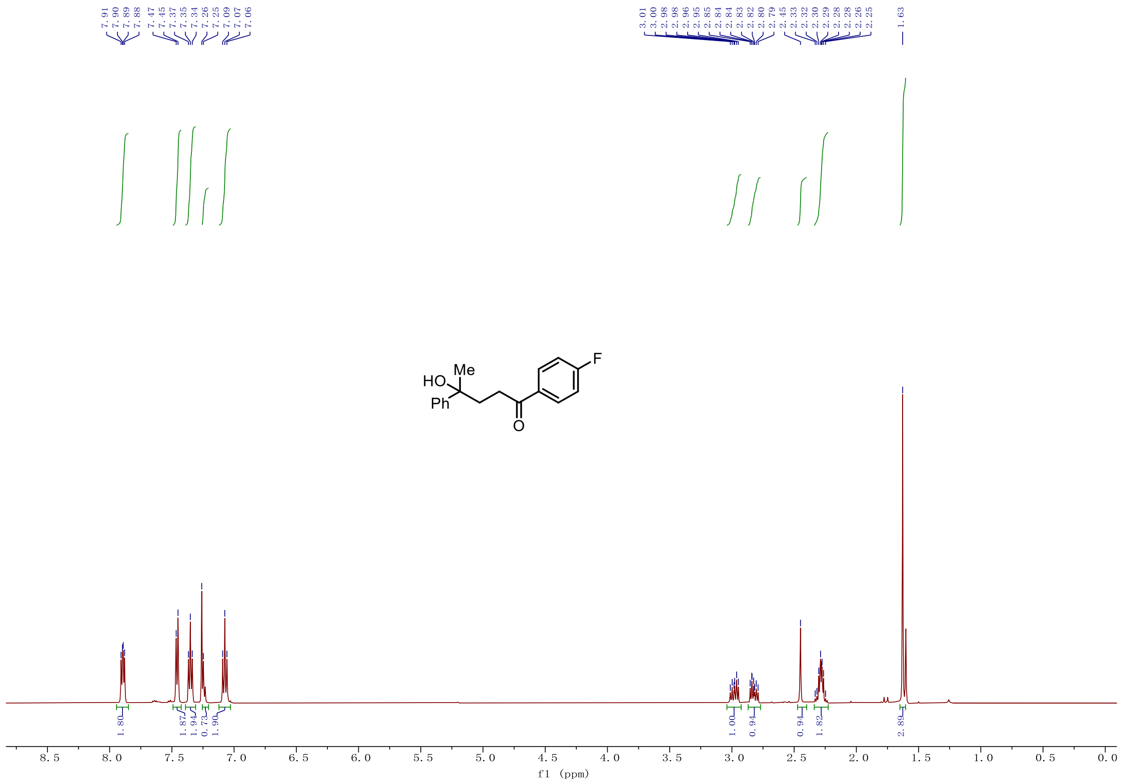


Supplementary Figure 10. Proposed mechanism for photoenzymatic carbohydroxylation.

3. NMR spectra



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7.25
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7.06
3.01
3.00
2.98
2.98
2.96
2.95
2.85
2.84
2.84
2.83
2.82
2.80
2.79
2.45
2.33
2.32
2.30
2.29
2.28
2.28
2.26
2.25
1.63
HO
Me
Ph
O
F
1.80
1.87
1.91
0.73
1.90
1.00
0.94
0.94
1.82
2.89
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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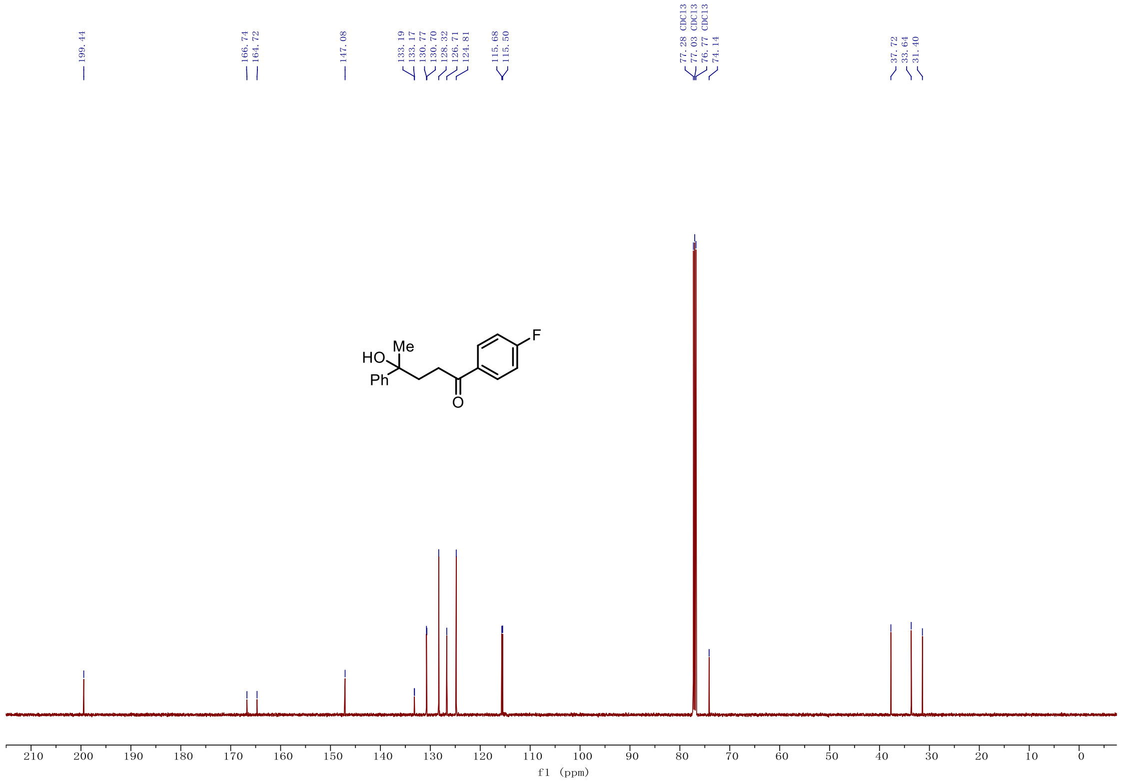
f1 (ppm)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115.50
77.28 CDCl3
77.03 CDCl3
76.77 CDCl3
74.14
37.72
33.64
31.40
HO
Me
Ph
O
F
210
200
190
180
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120
110
100
90
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50
40
30
20
10
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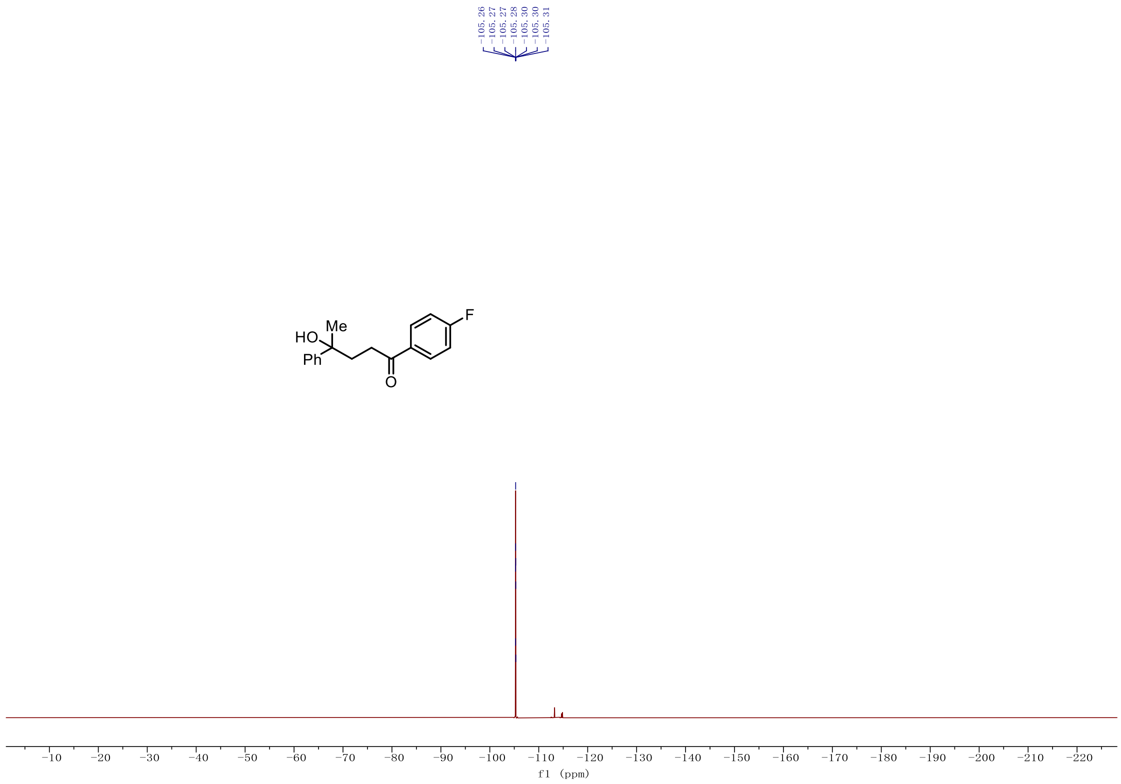
f1 (ppm)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-105.30
-105.30
-105.31
Me
HO
Ph
F
O
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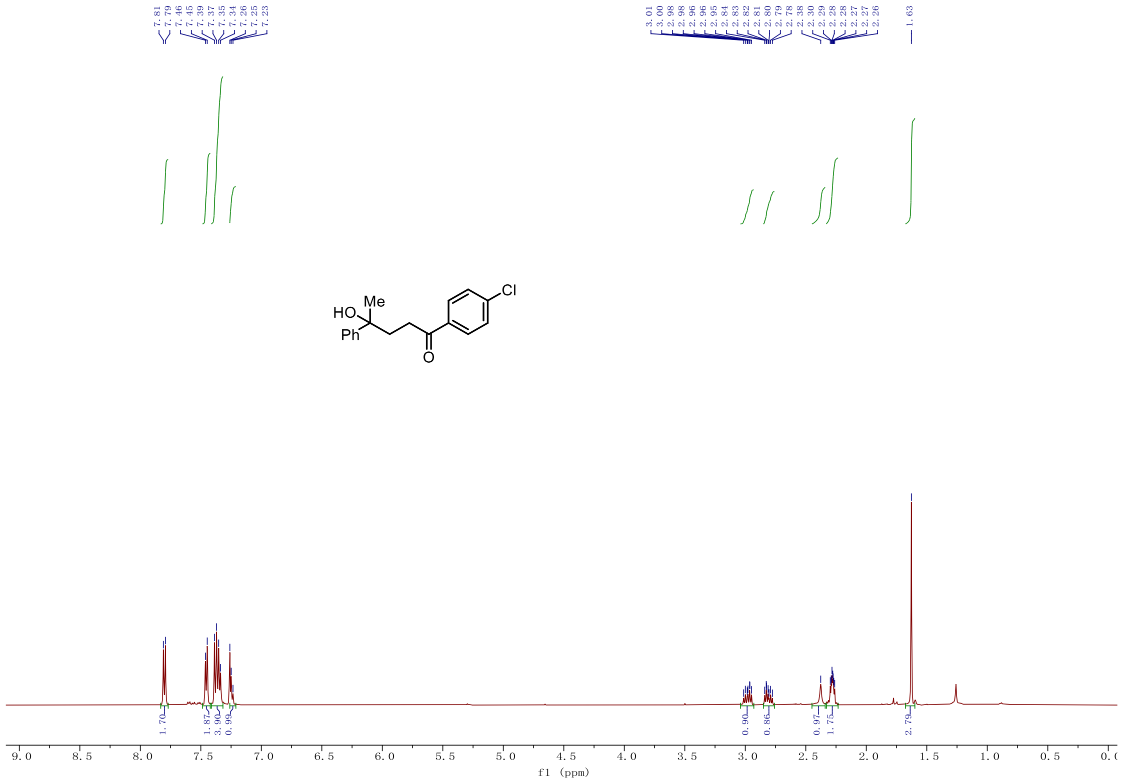
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
−220
f1 (ppm)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7.23
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2.96
2.96
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2.28
2.28
2.27
2.27
2.26
1.63
Me
HO
Ph
Cl
O
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3.00
0.99
0.90
0.86
0.97
1.75
2.79
9.0
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8.0
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7.0
6.5
6.0
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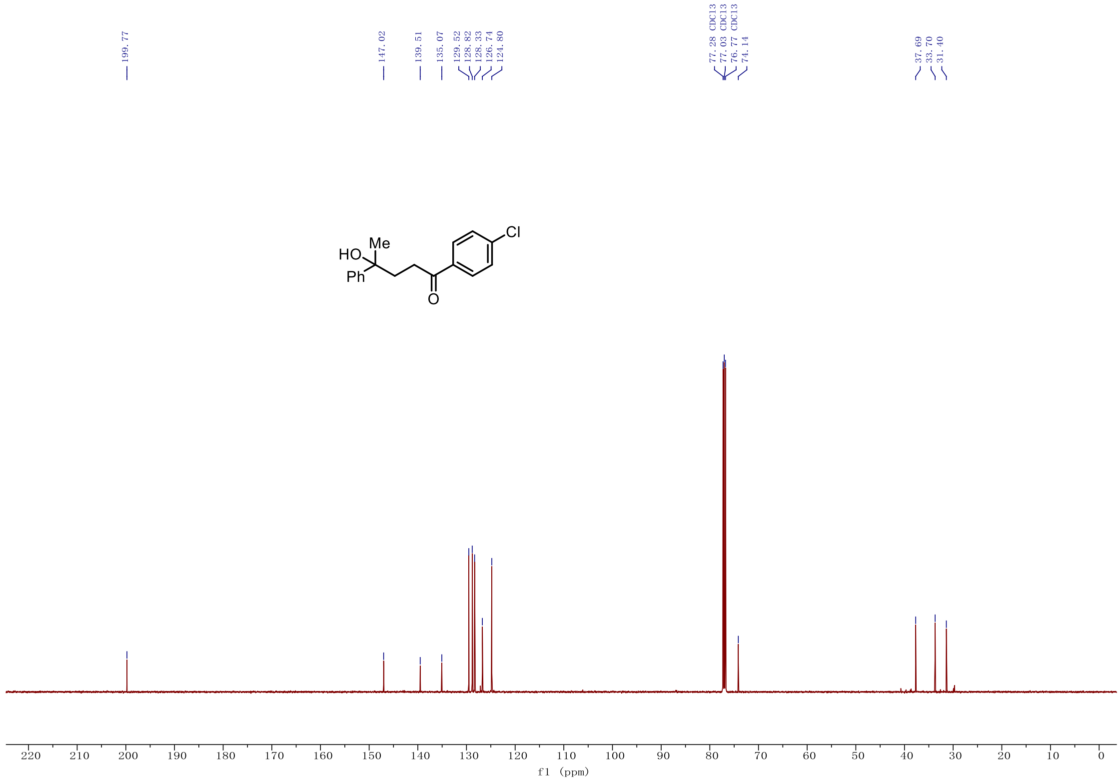
f1 (ppm)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128.82
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126.74
124.80
77.28 CDCl3
77.03 CDCl3
76.77 CDCl3
74.14
37.69
33.70
31.40
Me
HO
Ph
O
Cl
220
210
200
190
180
170
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150
140
130
120
110
100
90
80
70
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50
40
30
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10
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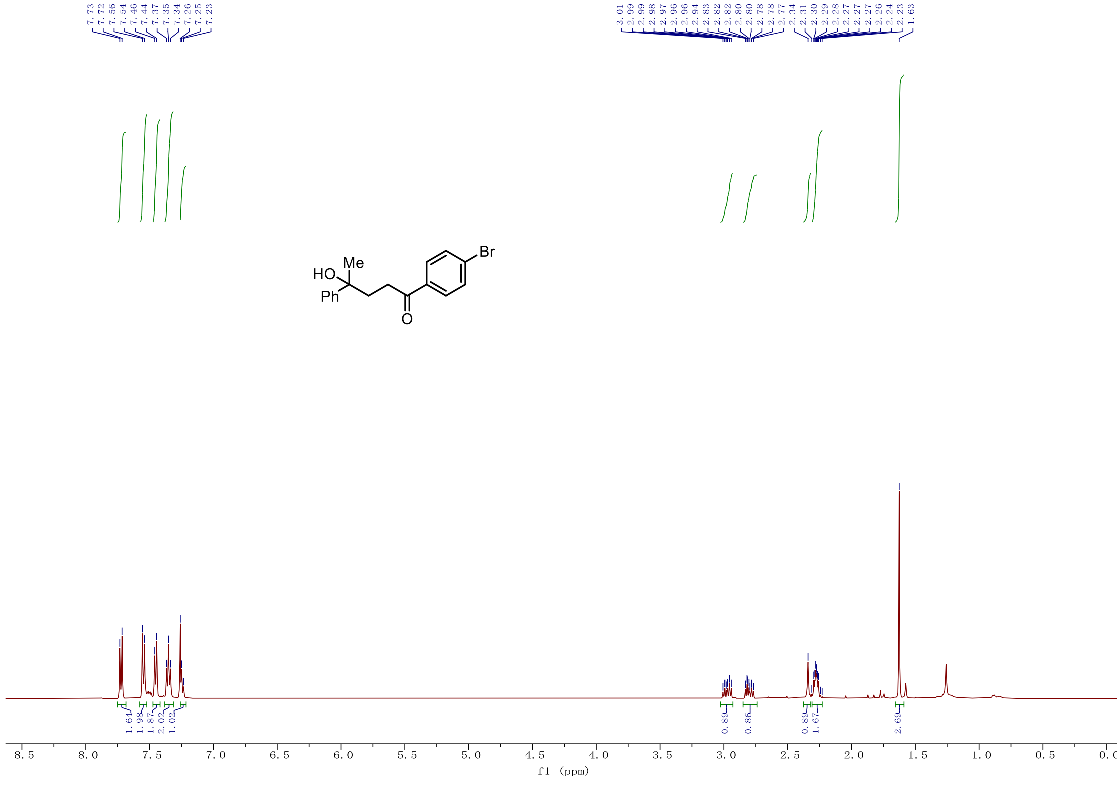
f1 (ppm)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2.98
2.97
2.96
2.96
2.94
2.83
2.82
2.82
2.80
2.80
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HO
Ph
O
Br
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0.89
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8.5
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7.0
6.5
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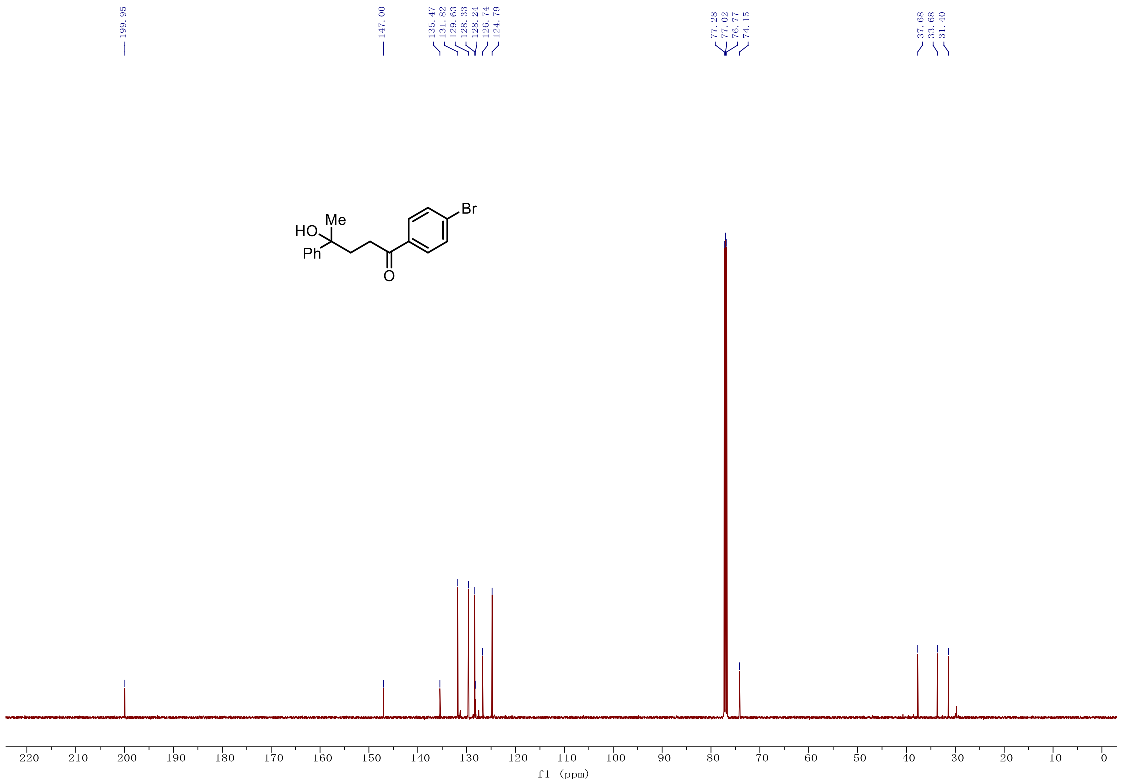
f1 (ppm)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128.24
126.74
124.79
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74.15
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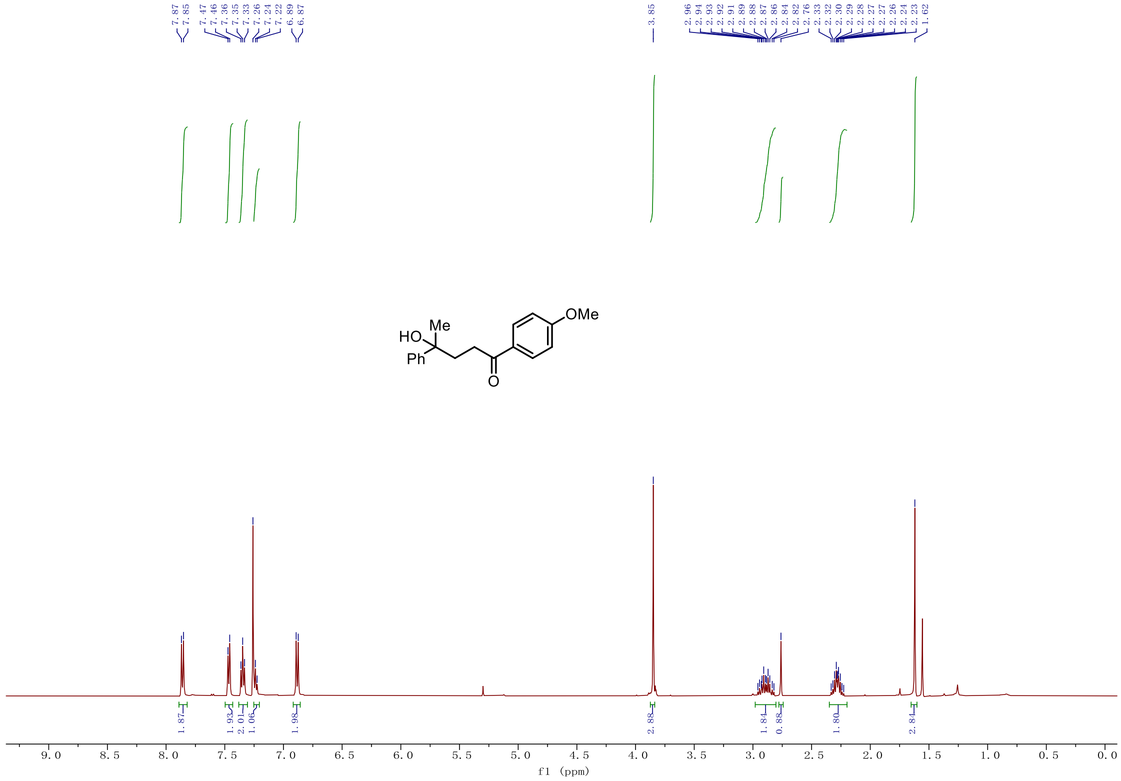
Me
HO
Ph
Br
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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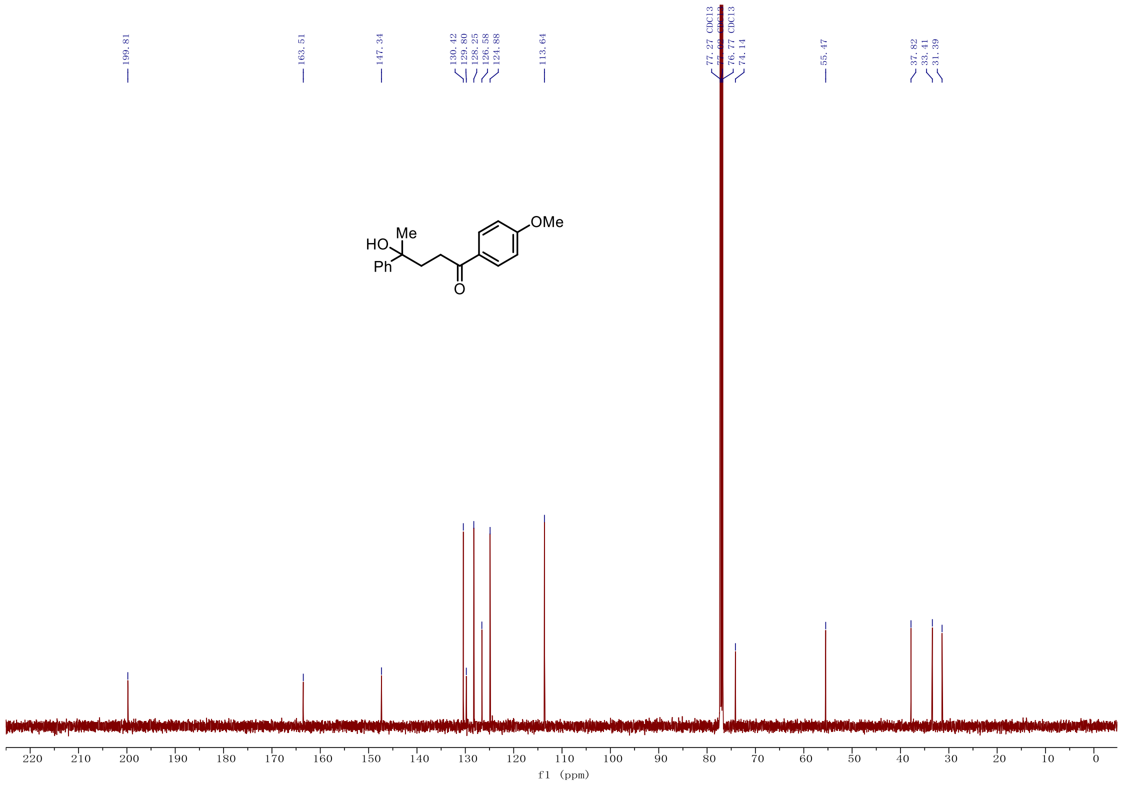
2.94
2.93
2.92
2.91
2.89
2.88
2.87
2.86
2.84
2.82
2.76
2.33
2.32
2.30
2.29
2.28
2.27
2.27
2.26
2.24
2.23
1.62
Me
HO
Ph
OMe
O
1.87
1.93
2.01
1.06
1.98
2.88
1.84
0.88
1.80
2.84
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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77.02 CDCl3
76.77 CDCl3
74.14
55.47
37.82
33.41
31.39
HO
Me
Ph
O
OMe
220
210
200
190
180
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10
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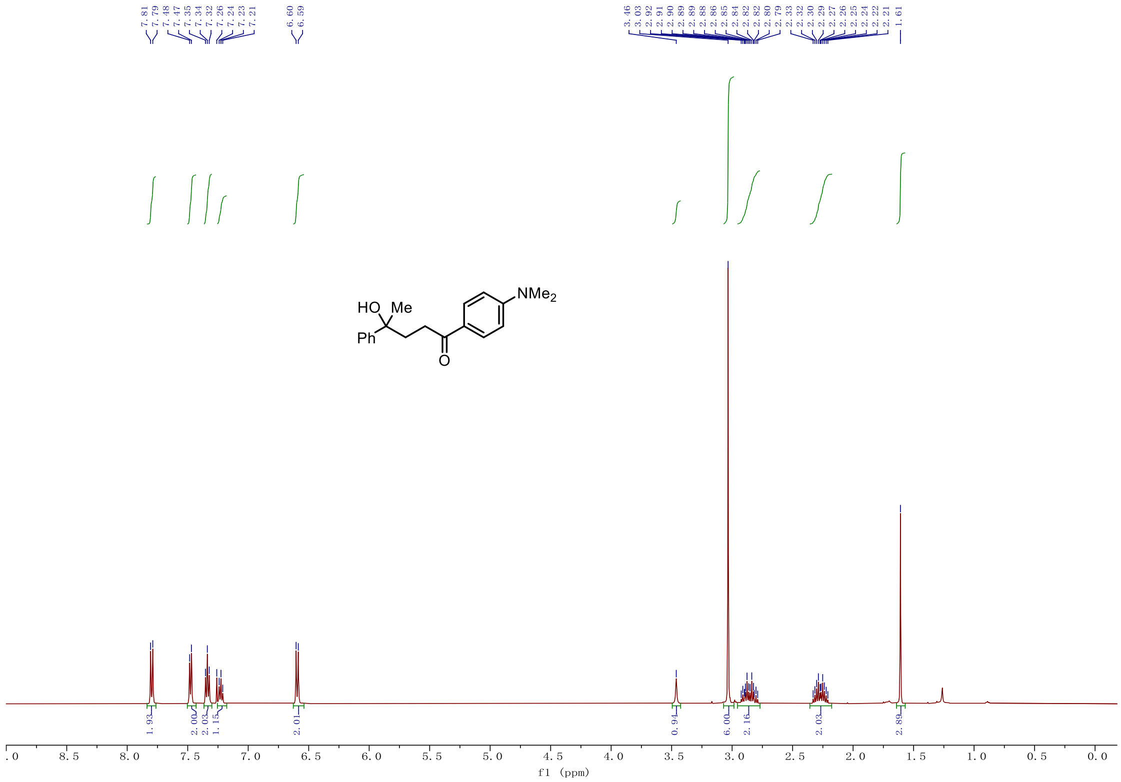
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2.21
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7.0
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6.0
5.5
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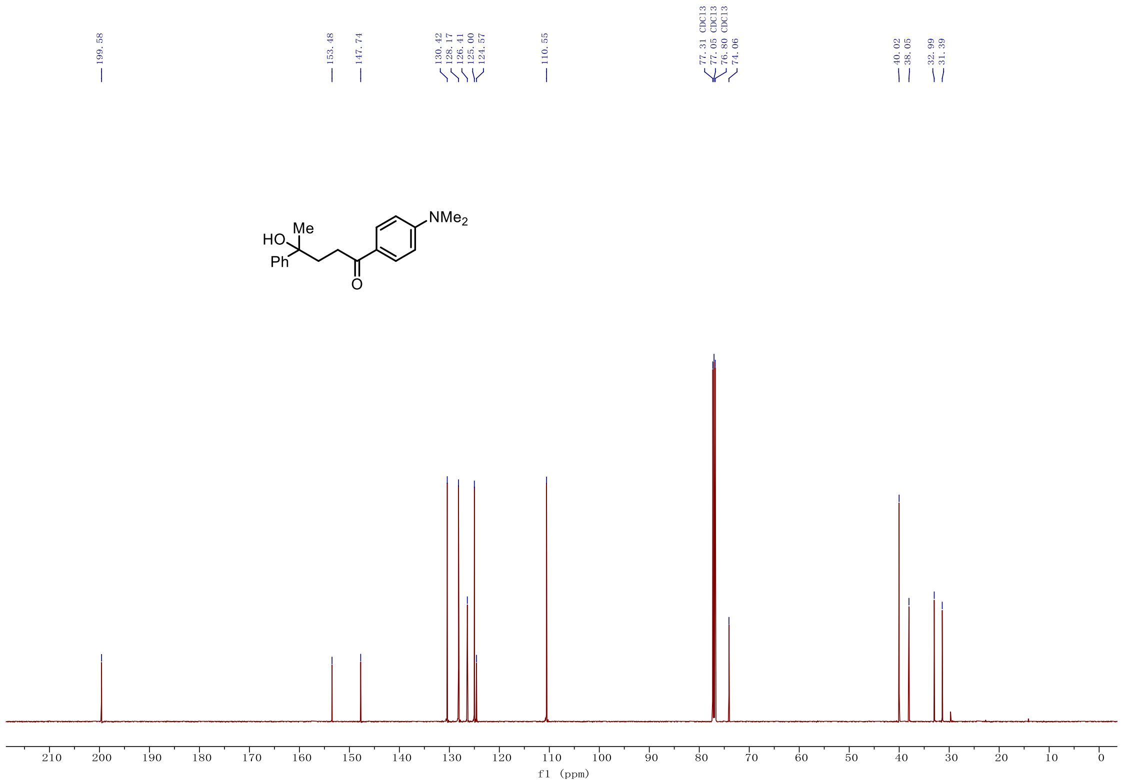
f1 (ppm)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40.02
38.05
32.99
31.39
NMe2
HO
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Ph
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180
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50
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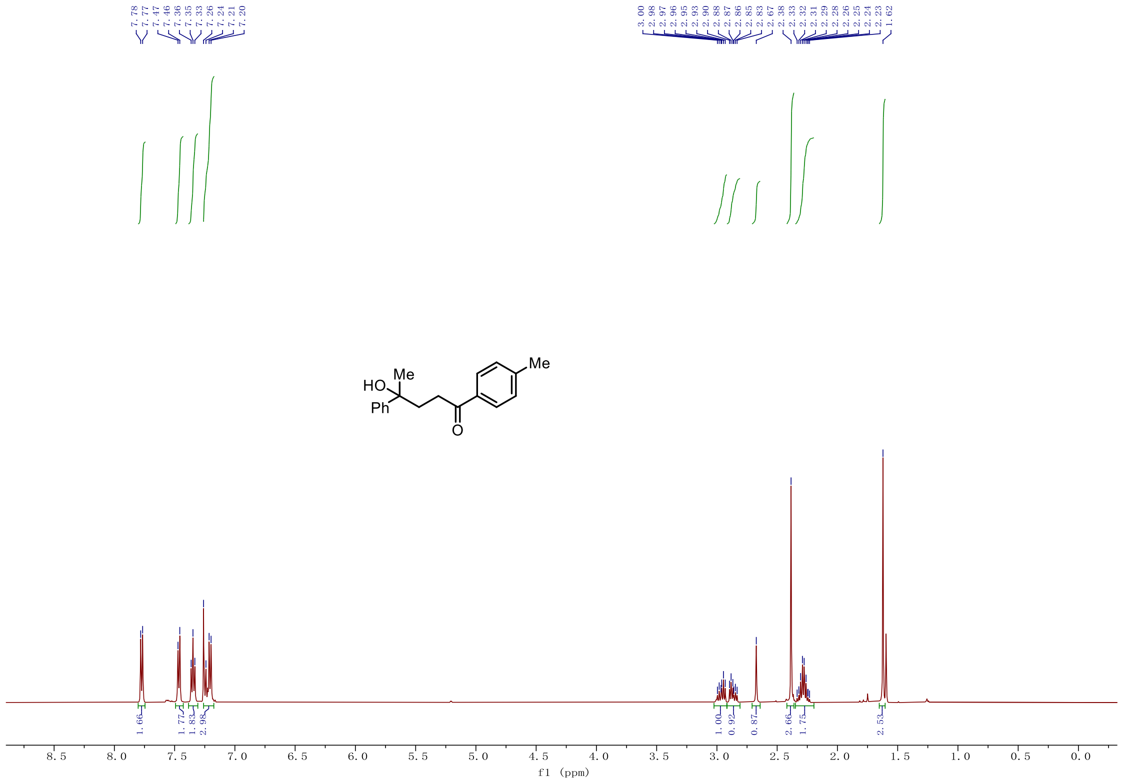
f1 (ppm)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2.90
2.88
2.87
2.86
2.85
2.83
2.67
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2.31
2.29
2.28
2.26
2.25
2.24
2.23
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Me
Ph
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0.87
2.66
1.75
2.53
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7.0
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6.0
5.5
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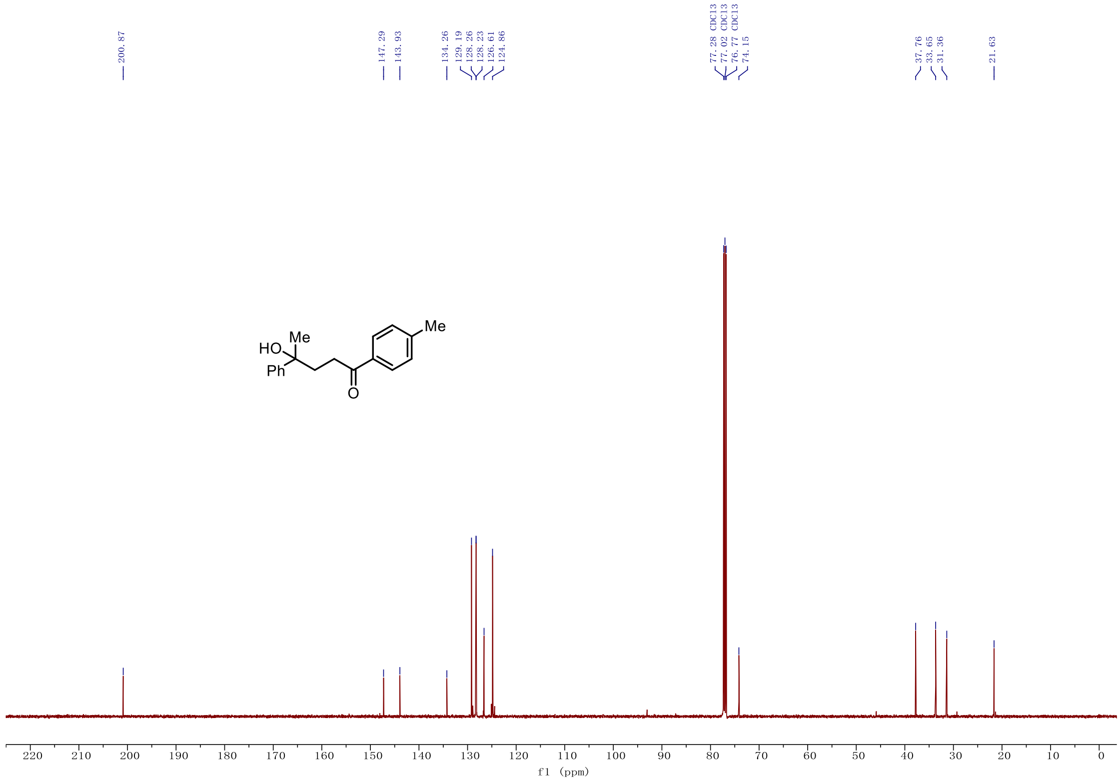
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77.02 CDCl3
76.77 CDCl3
74.15
37.76
33.65
31.86
21.63
HO
Me
Ph
O
Me
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180
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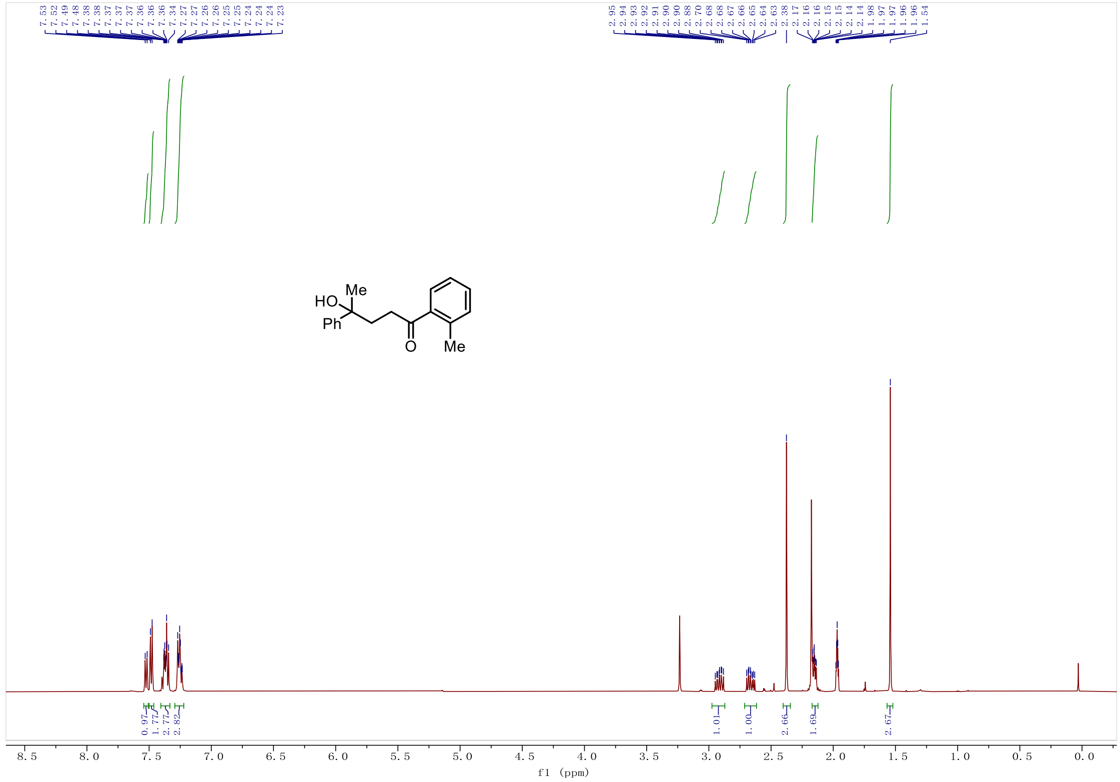
f1 (ppm)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7.25
7.24
7.24
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7.23
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2.94
2.93
2.92
2.91
2.90
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2.88
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2.68
2.67
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2.65
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2.63
2.38
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2.14
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1.97
1.96
1.96
1.54
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Ph
O
Me
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1.00
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2.67
8.5
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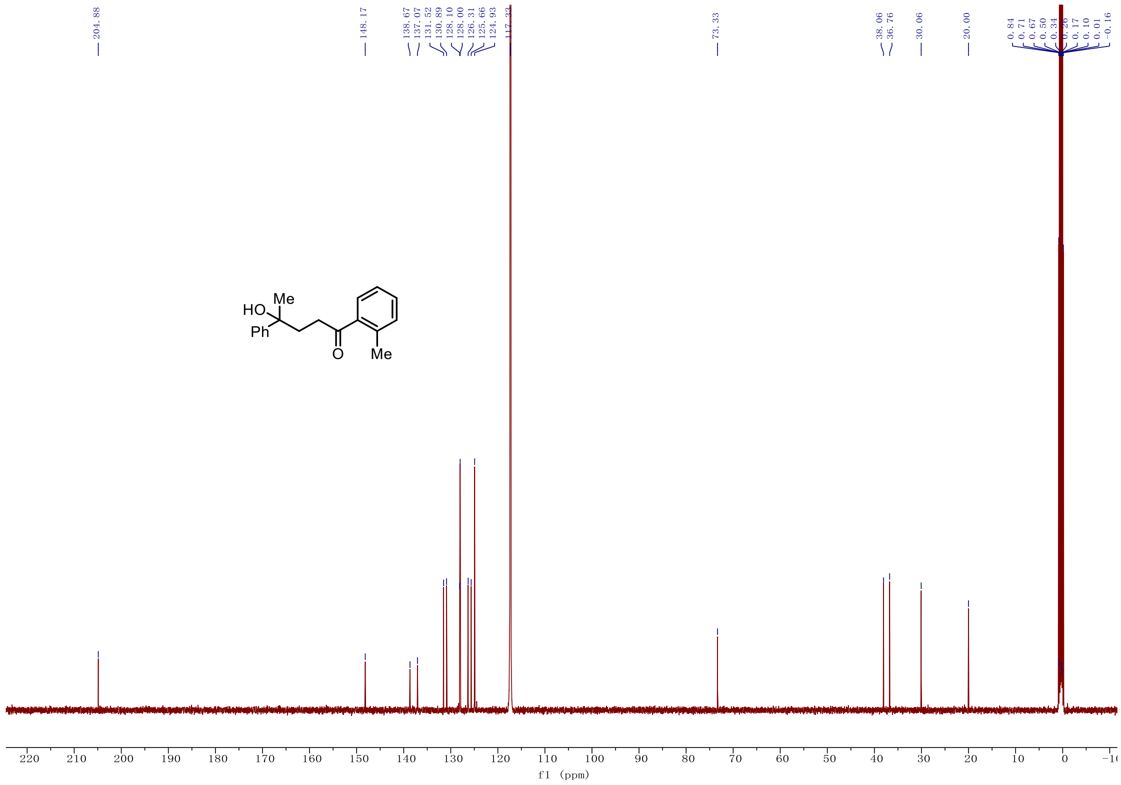
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38.06
36.76
30.06
20.00
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0.71
0.67
0.50
0.34
0.26
0.17
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HO
Me
Ph
O
Me
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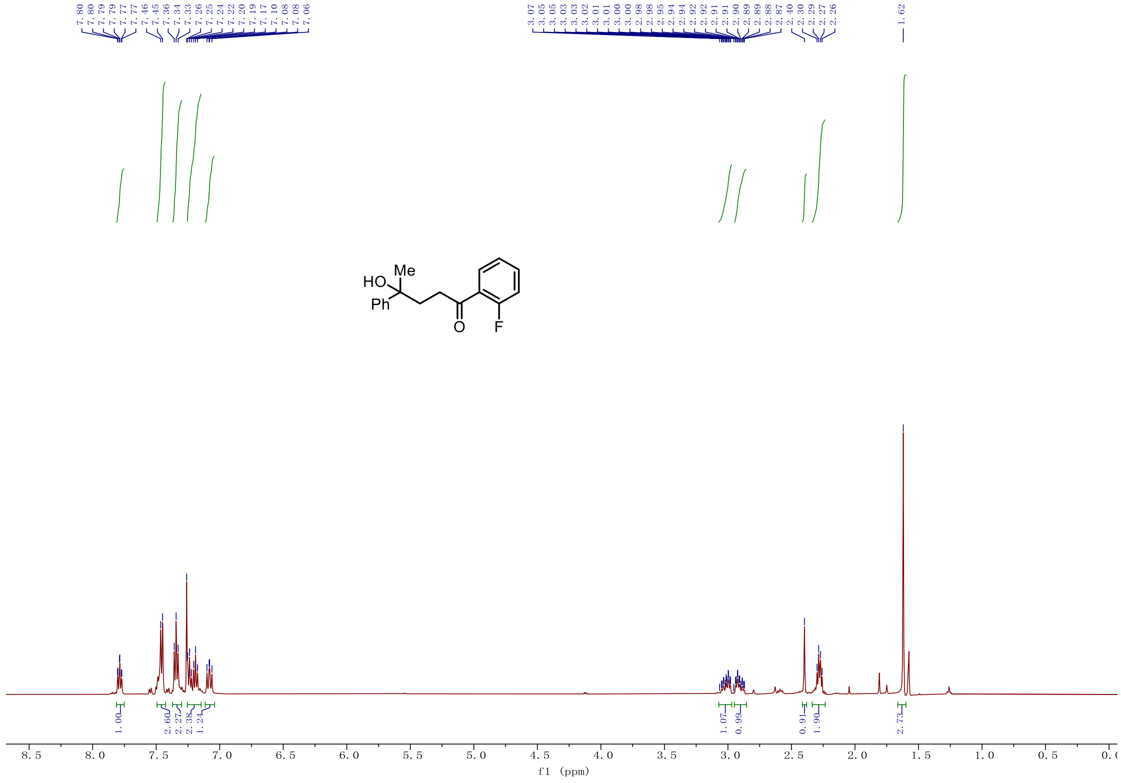
f1 (ppm)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7.17
7.10
7.08
7.08
7.06
3.07
3.05
3.05
3.03
3.02
3.01
3.01
3.00
3.00
2.98
2.95
2.94
2.94
2.92
2.92
2.91
2.91
2.90
2.89
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2.87
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2.29
2.27
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1.62
HO
Me
Ph
O
F
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2.60
2.27
2.38
1.24
1.07
0.99
0.91
1.90
2.73
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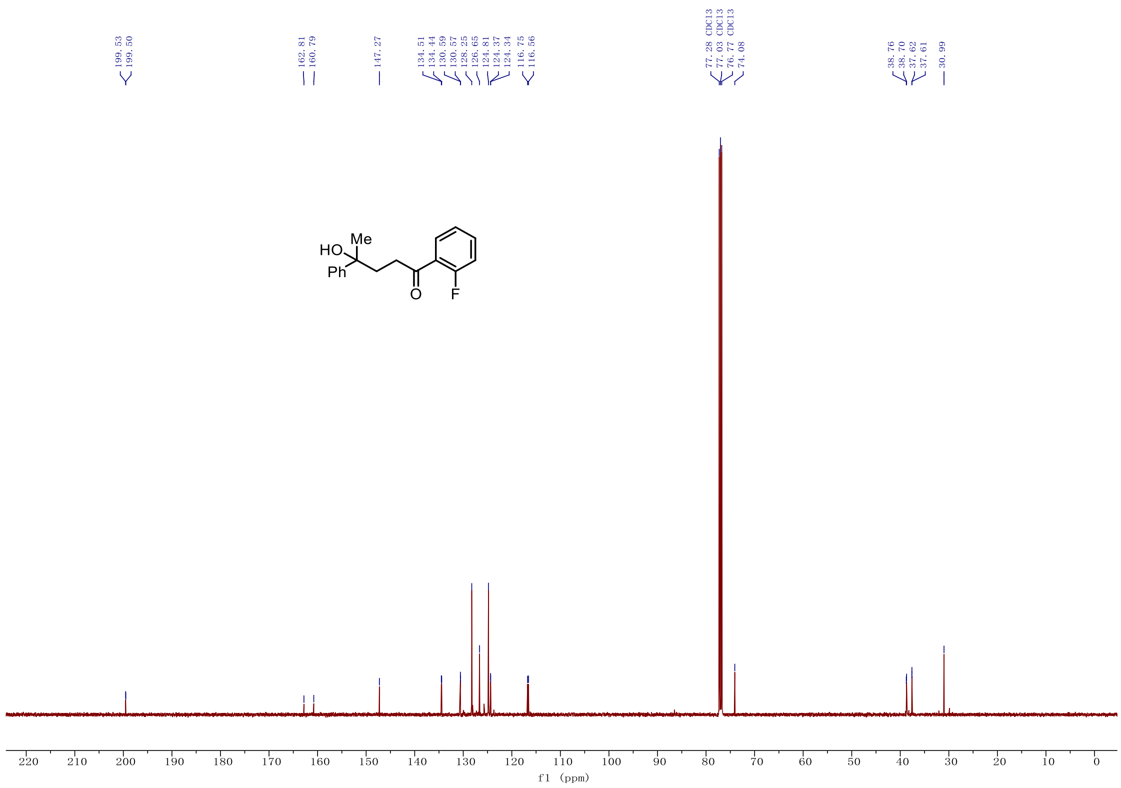
f1 (ppm)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124.34
116.75
116.56
77.28 CDCl3
77.03 CDCl3
76.77 CDCl3
74.08
38.76
38.70
37.62
37.61
30.99
Me
HO
Ph
O
F
220
210
200
190
180
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120
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90
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70
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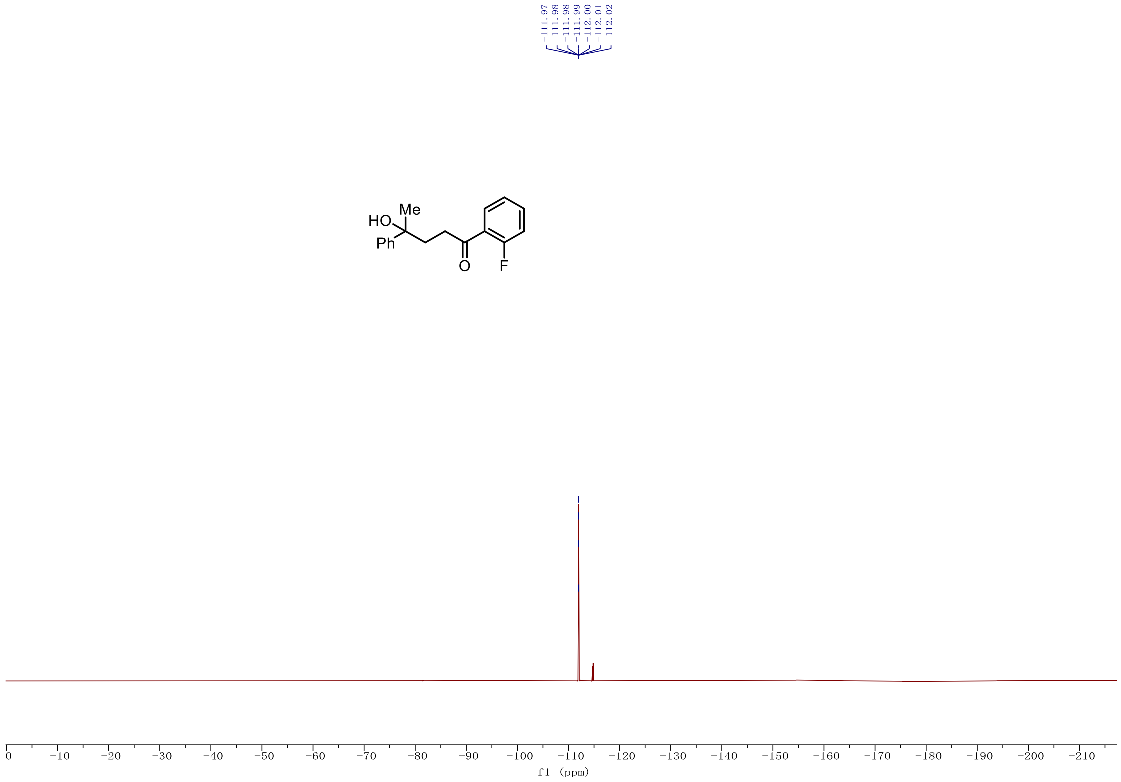
f1 (ppm)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−112.02
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HO
Ph
O
F
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−20
−30
−40
−50
−60
−70
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−120
−130
−140
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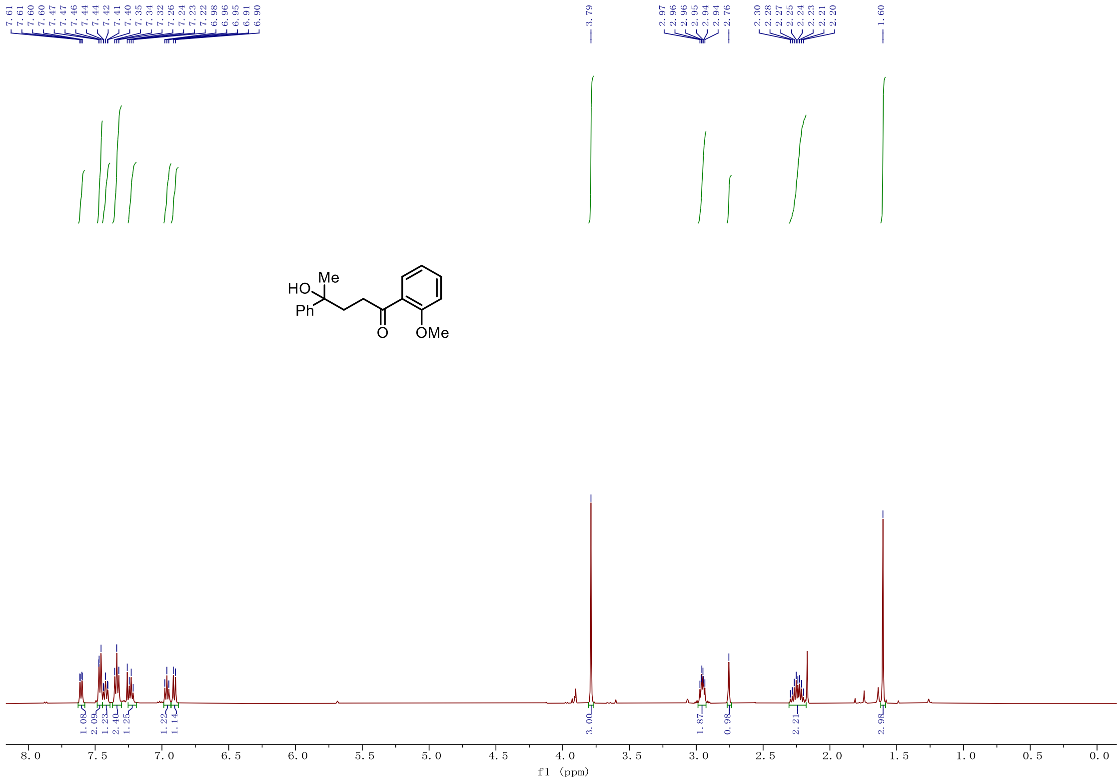
−160
−170
−180
−190
−200
−210
f1 (ppm)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7.42
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7.35
7.34
7.32
7.26
7.24
7.23
7.23
7.22
6.98
6.96
6.95
6.91
6.90
3.79
2.97
2.96
2.96
2.95
2.94
2.94
2.76
2.30
2.28
2.27
2.25
2.24
2.23
2.21
2.20
1.60
HO
Me
Ph
O
OMe
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2.09
1.23
2.40
1.25
1.22
1.14
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2.98
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7.0
6.5
6.0
5.5
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2.0
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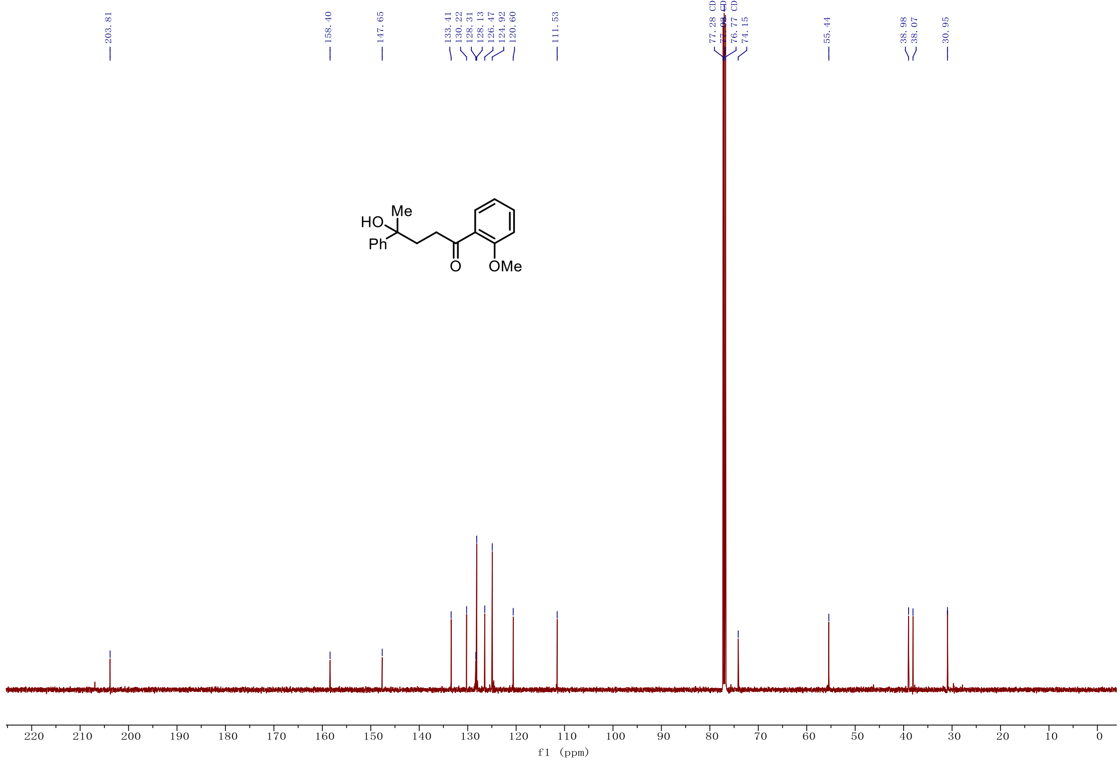
1.0
0.5
0.0
f1 (ppm)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CDCl3
76.77 CDCl3
74.15
55.44
38.98
38.07
30.95
HO
Me
Ph
O
OMe
220
210
200
190
180
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90
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10
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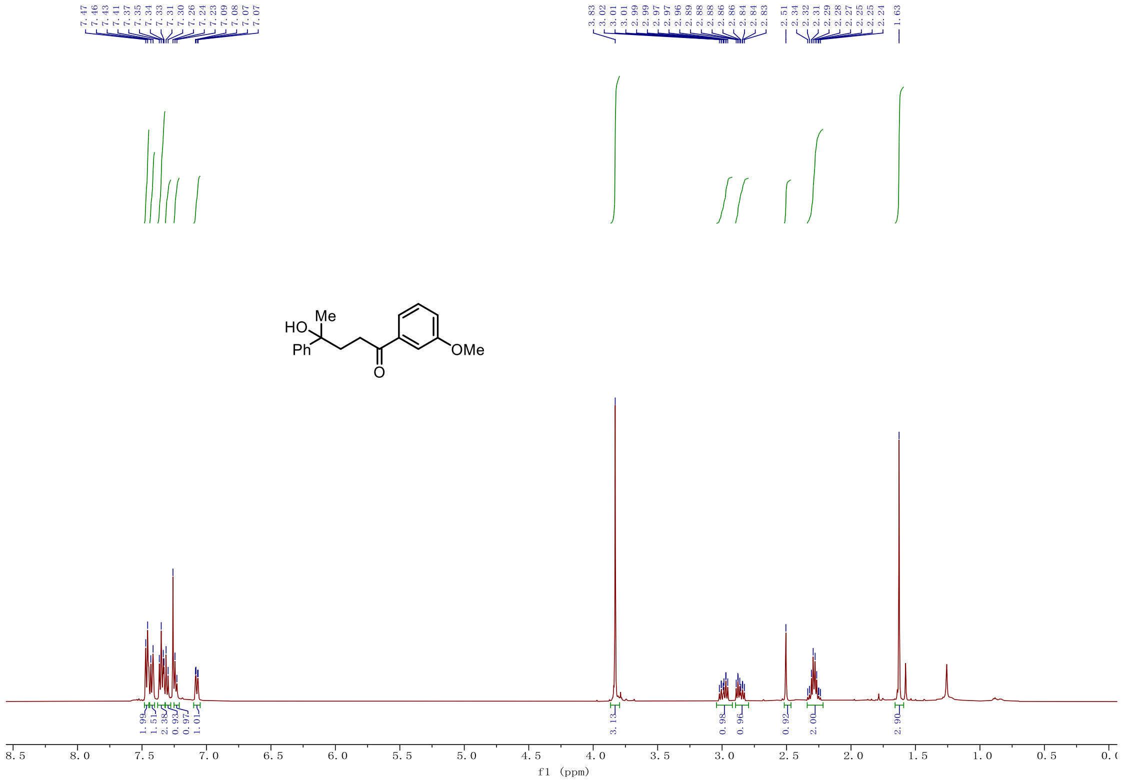
f1 (ppm)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7.23
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7.08
7.07
7.07
3.83
3.02
3.01
3.01
2.99
2.99
2.97
2.97
2.96
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2.88
2.86
2.86
2.84
2.84
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Me
Ph
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OMe
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0.92
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2.90
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6.0
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3.0
2.5
2.0
1.5
1.0
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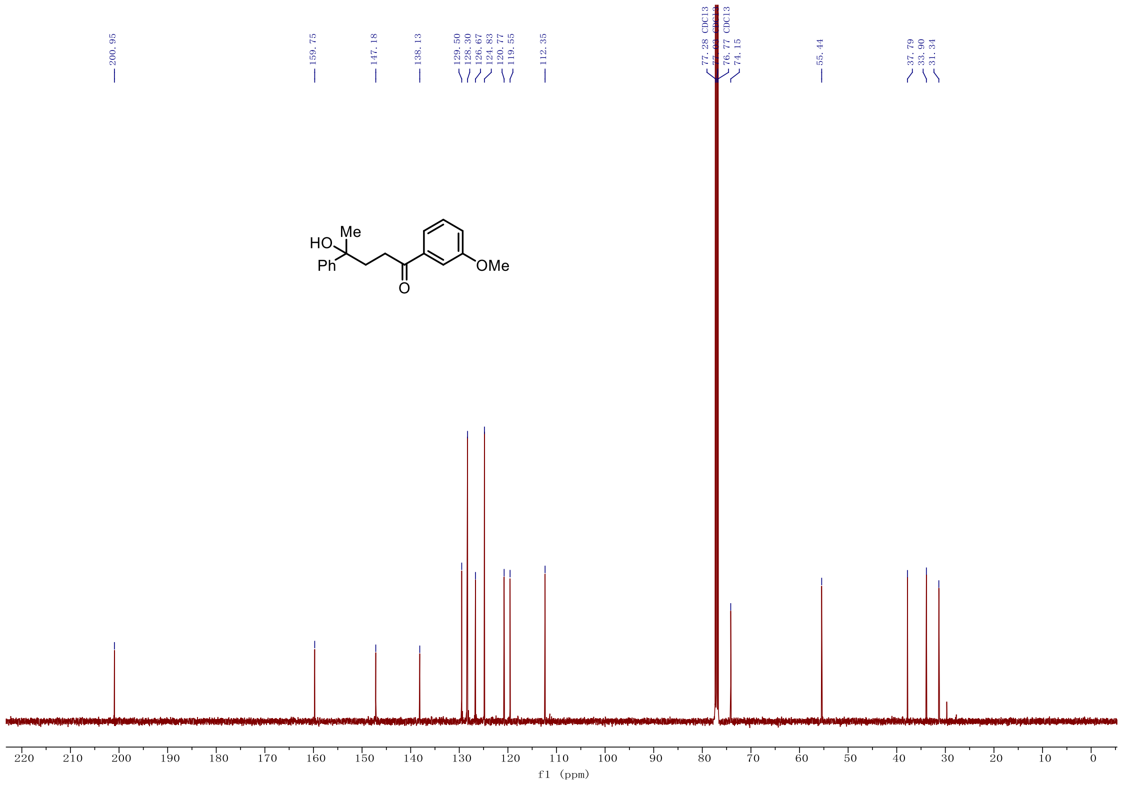
0.0
f1 (ppm)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77.02 CDCl3
76.77 CDCl3
74.15
55.44
37.79
33.90
31.34
HO
Me
Ph
O
OMe
220
210
200
190
180
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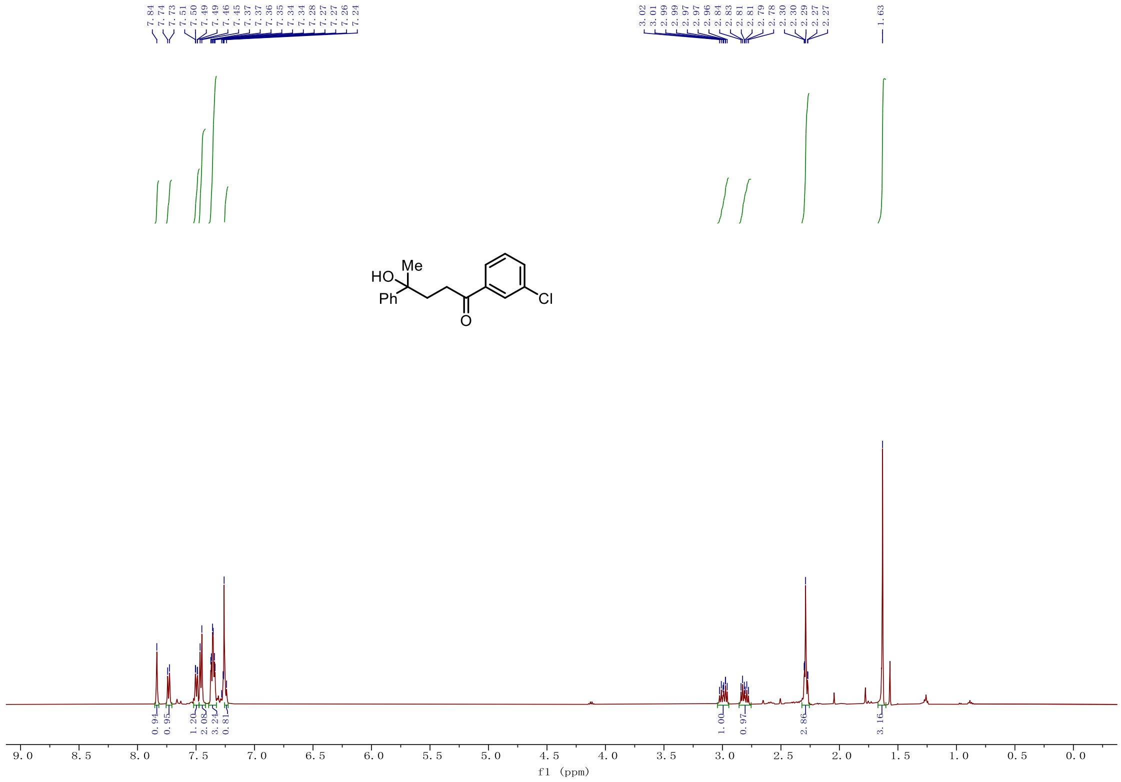
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7.28
7.27
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7.24
3.02
3.01
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2.99
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2.83
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2.27
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Me
Ph
O
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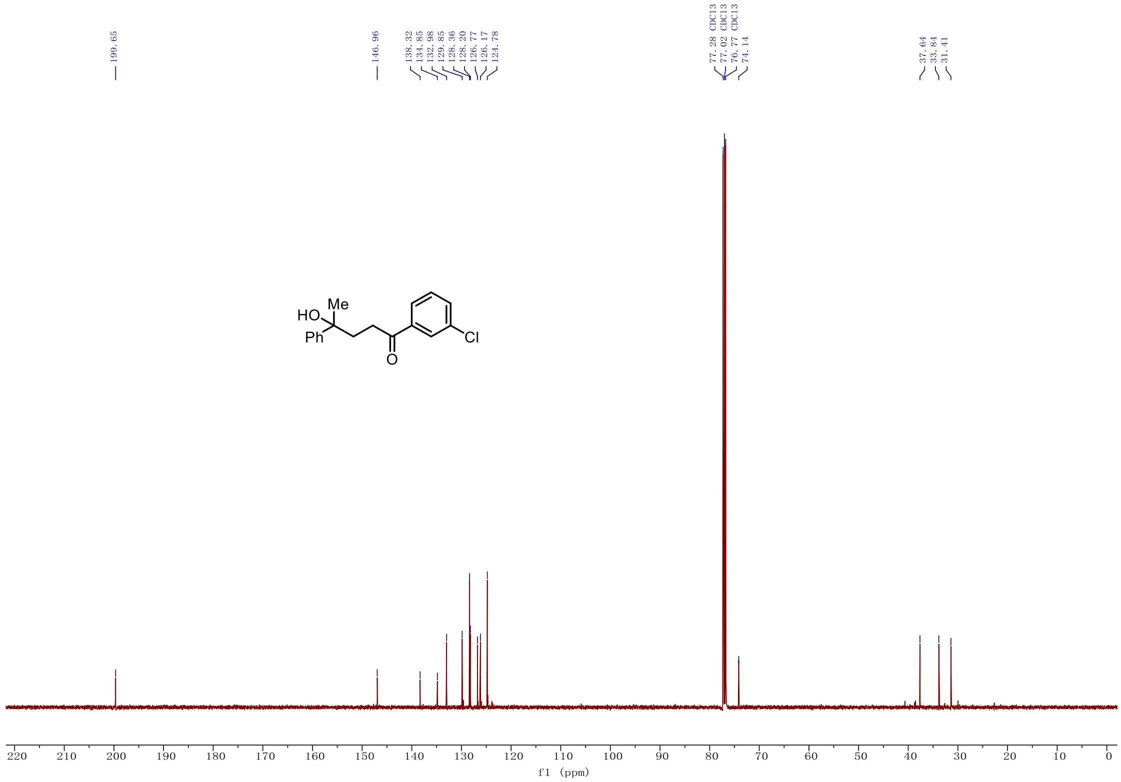
f1 (ppm)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77.02 CDCl3
76.77 CDCl3
74.14
37.64
33.84
31.41
HO
Me
Ph
O
Cl
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200
190
180
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90
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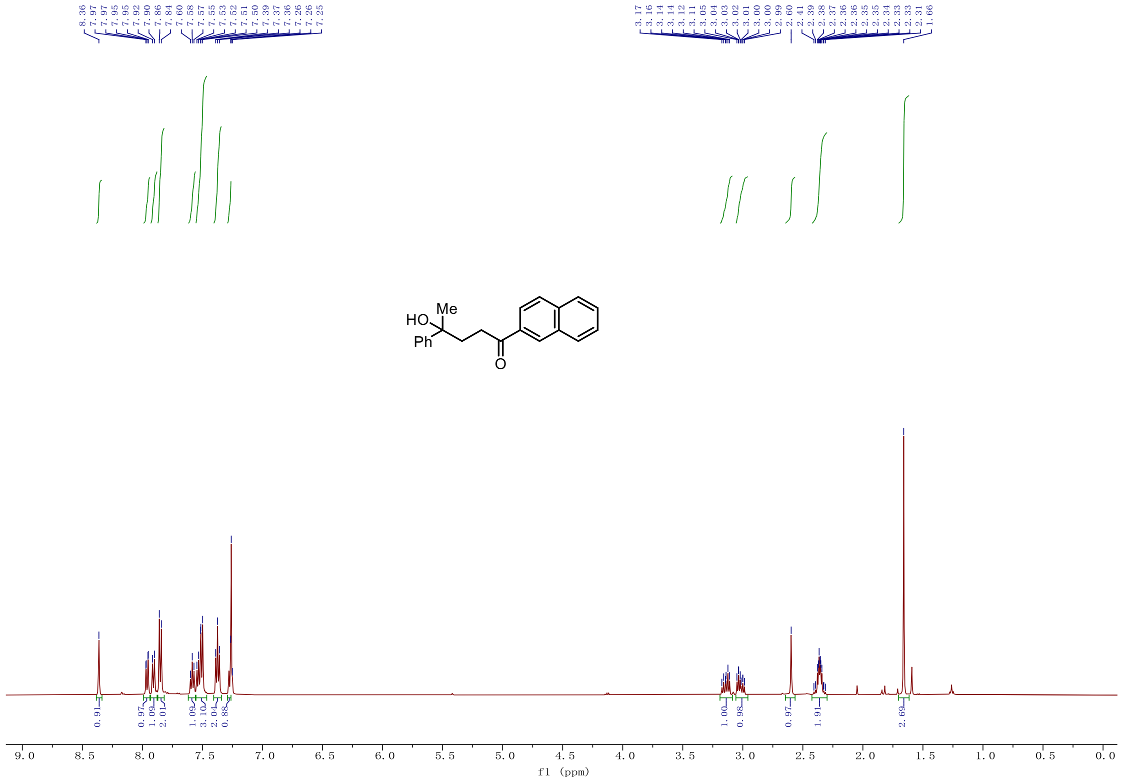
0
f1 (ppm)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7.37
7.36
7.26
7.25
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3.16
3.14
3.14
3.12
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3.05
3.04
3.03
3.02
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3.00
3.00
2.99
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2.36
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2.33
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Me
Ph
O
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6.0
5.5
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3.0
2.5
2.0
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1.0
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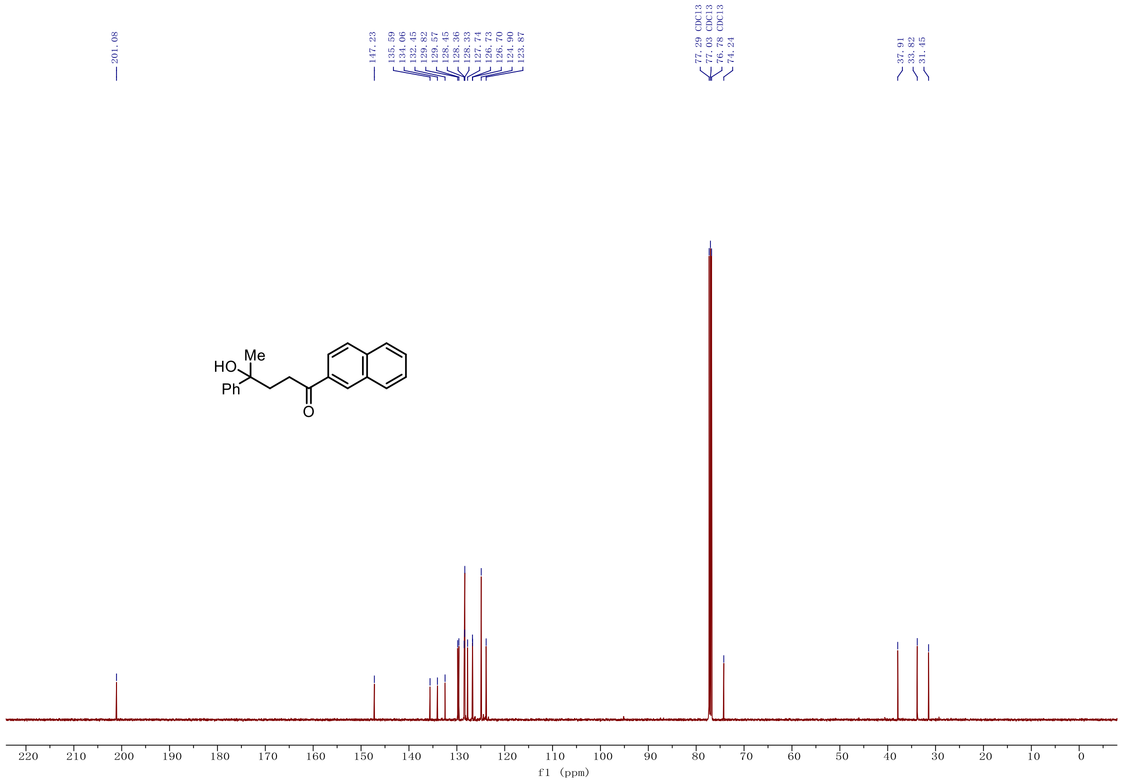
f1 (ppm)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76.78 CDCl3
74.24
37.91
33.82
31.45
HO
Me
Ph
O
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210
200
190
180
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40
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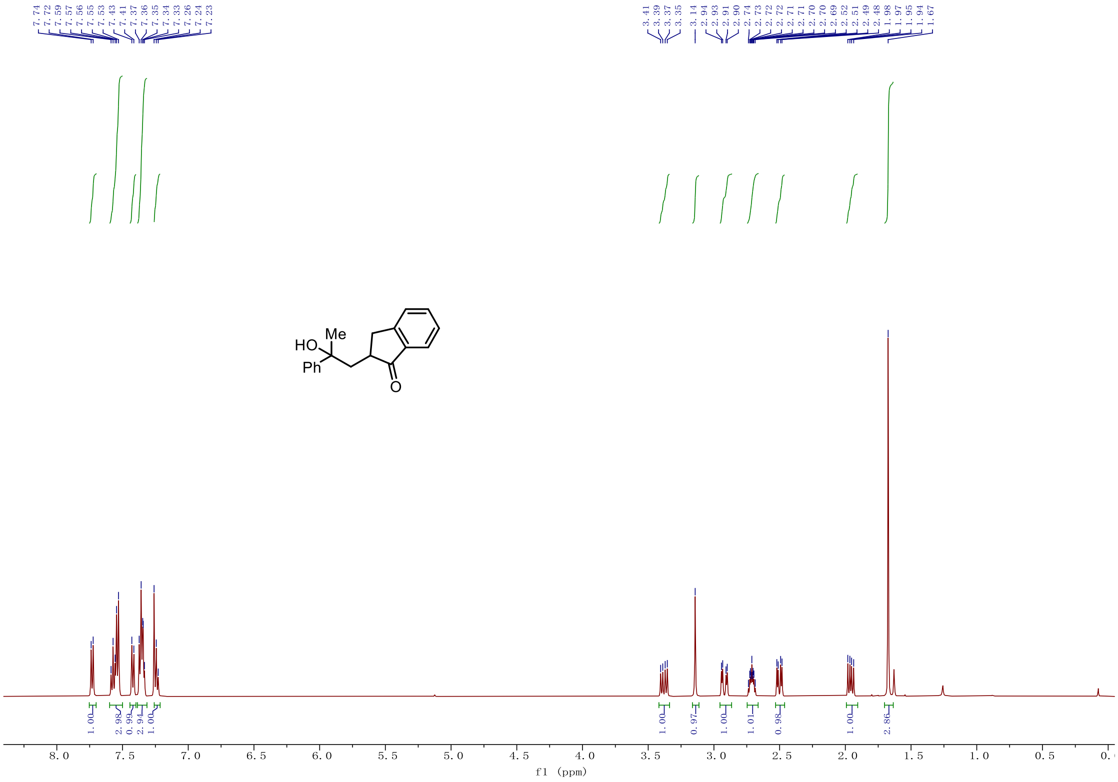
f1 (ppm)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2.90
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Ph
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6.0
5.5
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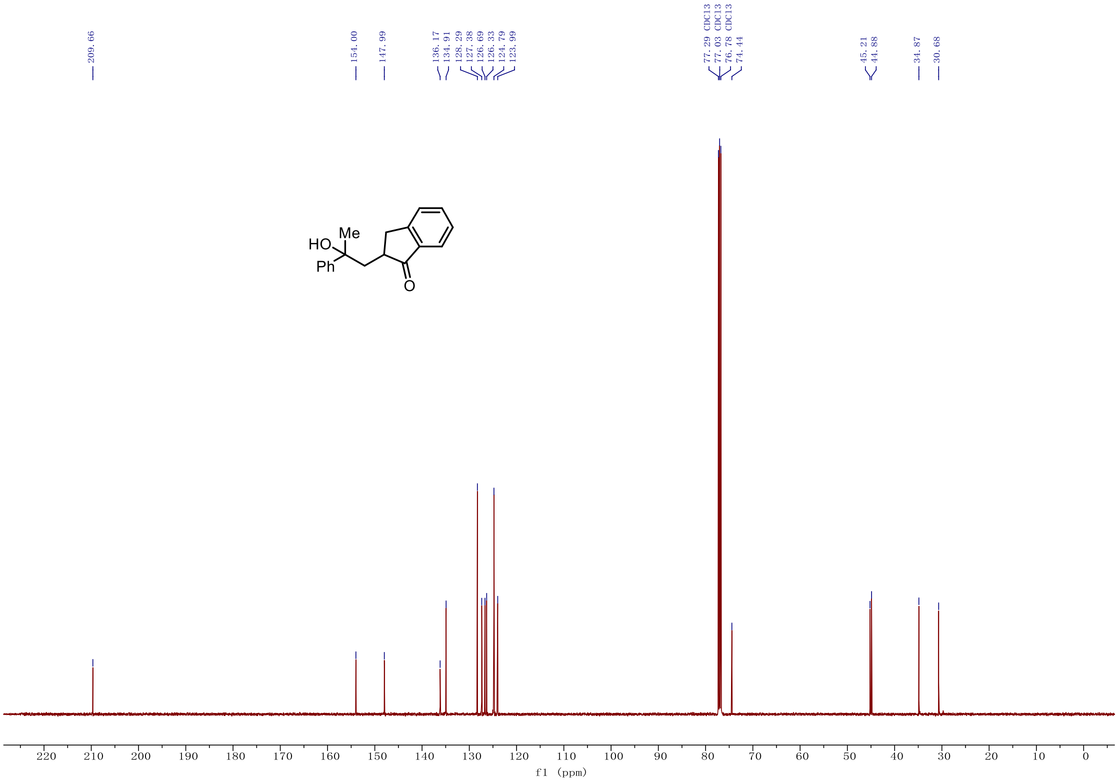
f1 (ppm)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77.03 CDCl3
76.78 CDCl3
74.44
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44.88
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30.68
HO
Me
Ph
O
220
210
200
190
180
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120
110
100
90
80
70
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50
40
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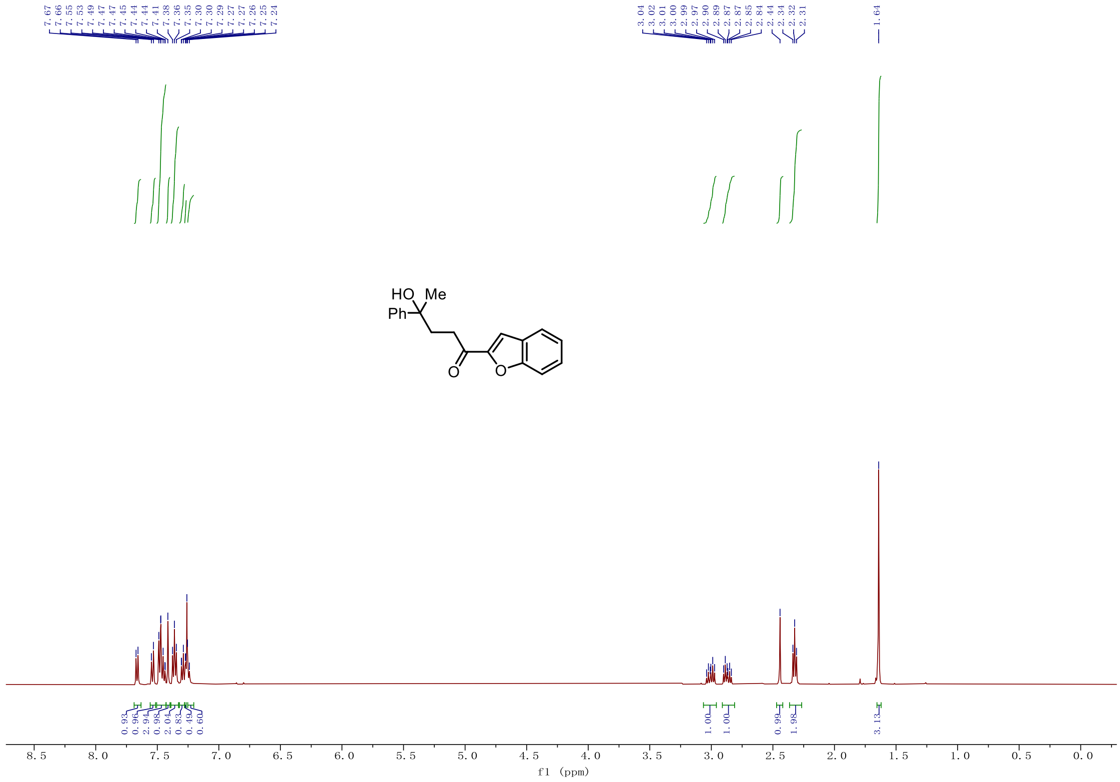
10
0
f1 (ppm)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7.26
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7.24
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3.02
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3.00
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Me
Ph
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O
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1.00
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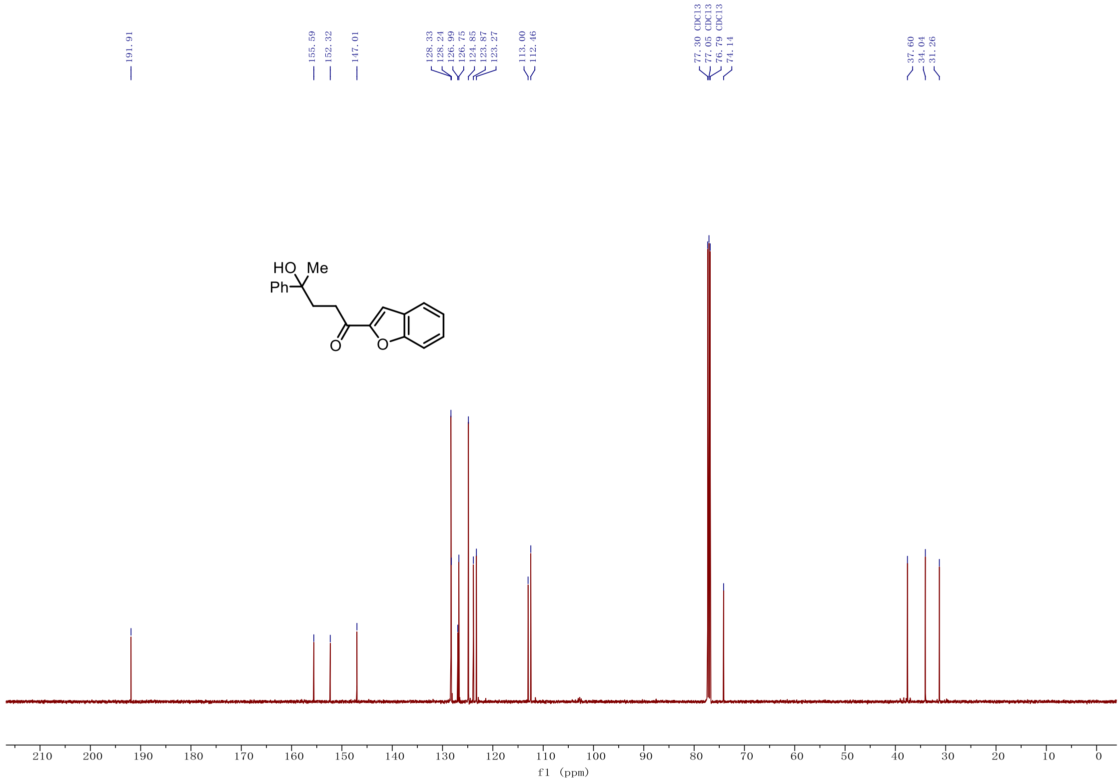
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77.05 CDCl3
76.79 CDCl3
74.14
37.60
34.04
31.26
HO
Me
Ph
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O
210
200
190
180
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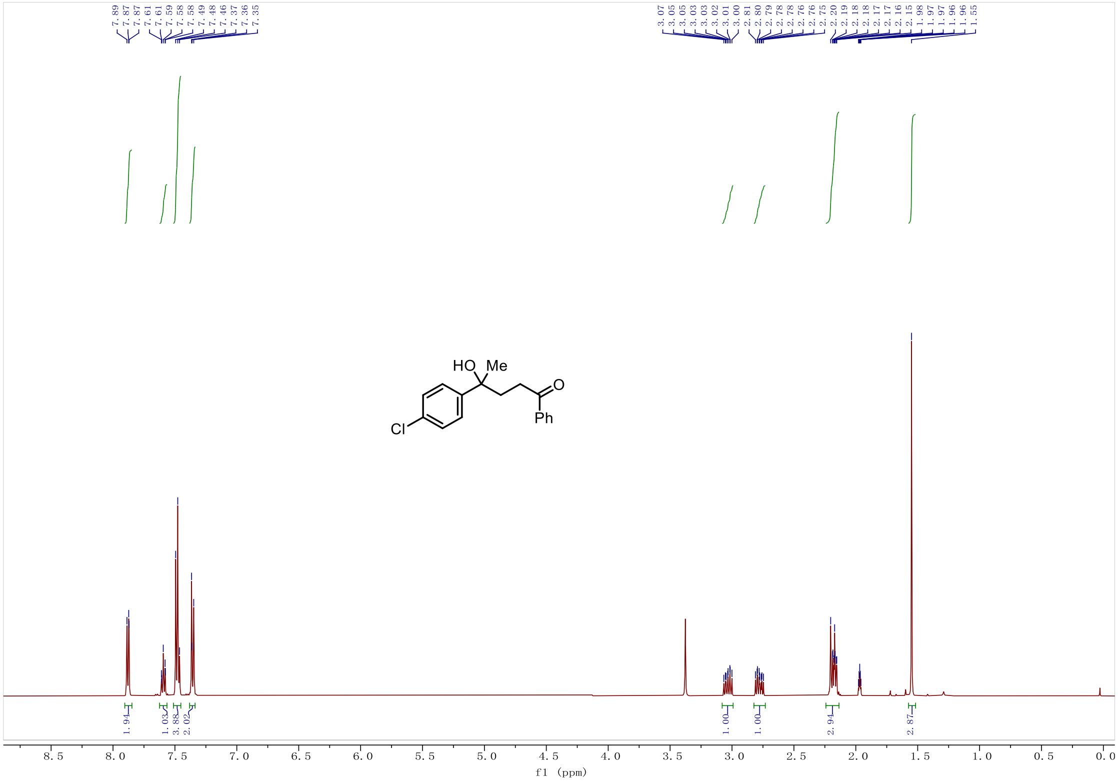
10
0
f1 (ppm)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2.78
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2.76
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2.17
2.16
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1.97
1.97
1.96
1.96
1.55
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O
Cl
Ph
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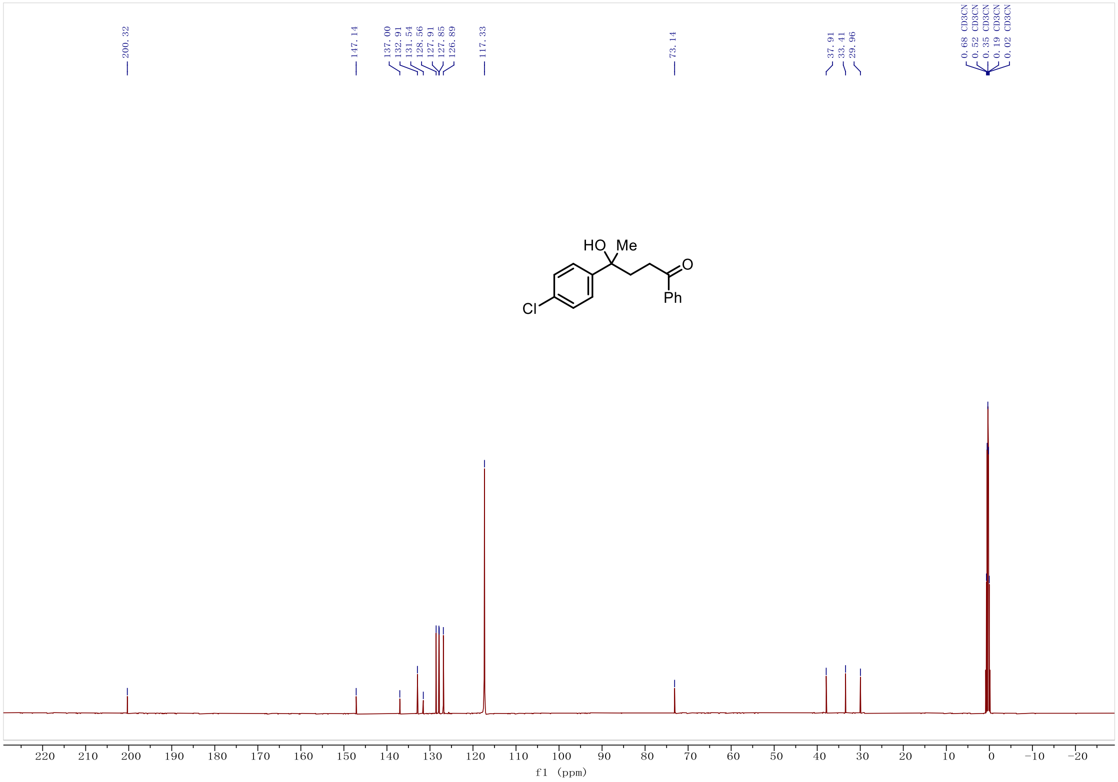
f1 (ppm)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0.52 CD3CN
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0.19 CD3CN
0.02 CD3CN
HO
Me
O
Cl
Ph
220
210
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190
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170
160
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20
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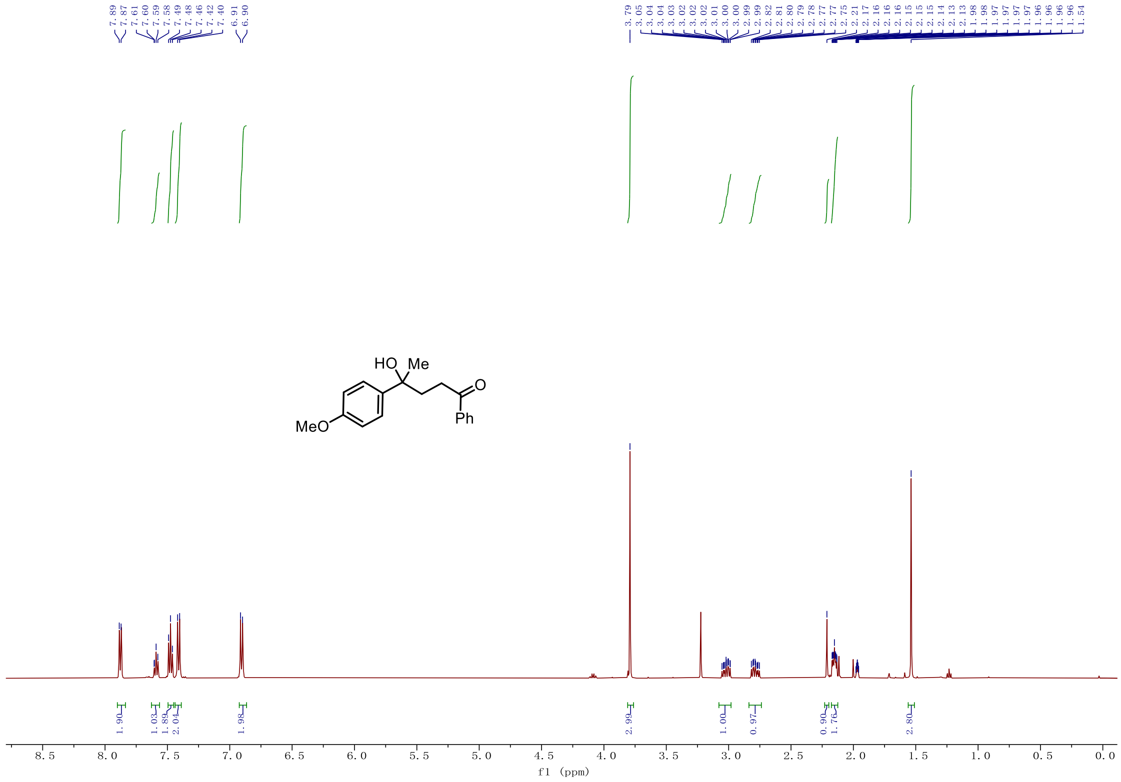
−10
−20
f1 (ppm)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3.00
2.99
2.99
2.82
2.81
2.80
2.79
2.78
2.77
2.75
2.21
2.17
2.16
2.16
2.16
2.15
2.15
2.15
2.14
2.13
2.13
1.98
1.98
1.97
1.97
1.97
1.96
1.96
1.96
1.54
HO
Me
O
Ph
MeO
1.90
1.03
1.89
2.04
1.98
2.99
1.00
0.97
0.90
1.76
2.80
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.5
3.0
2.5
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1.5
1.0
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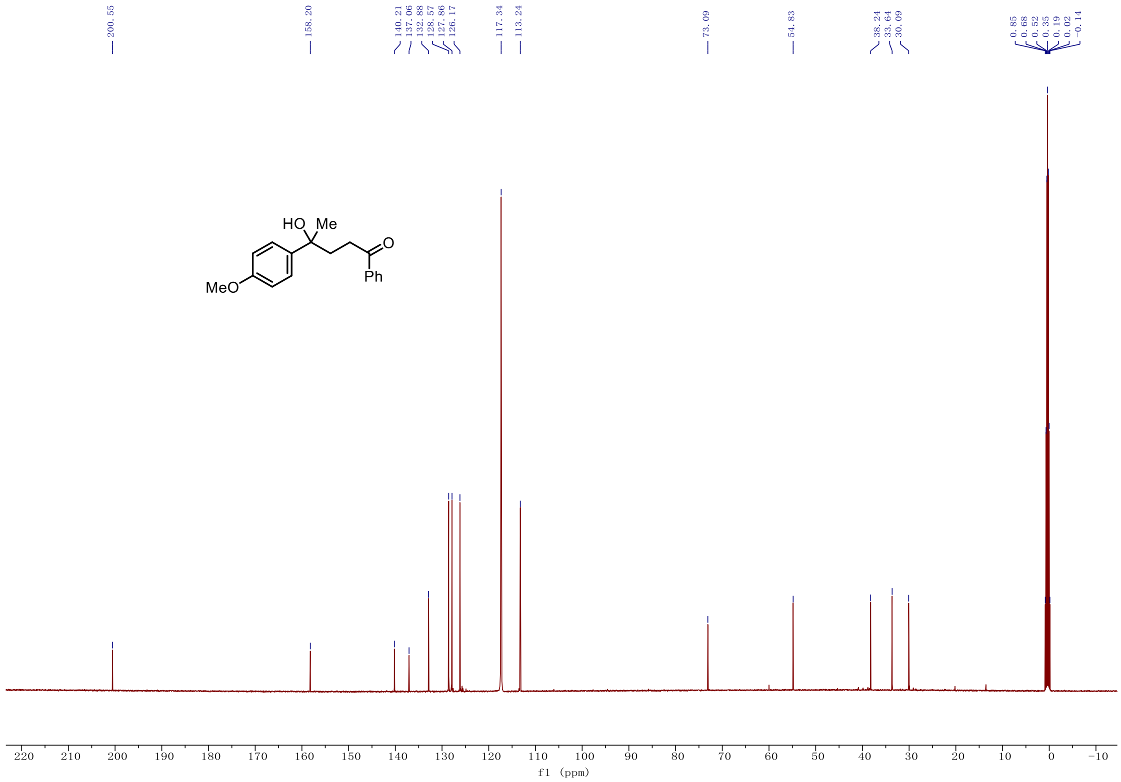
0.0
f1 (ppm)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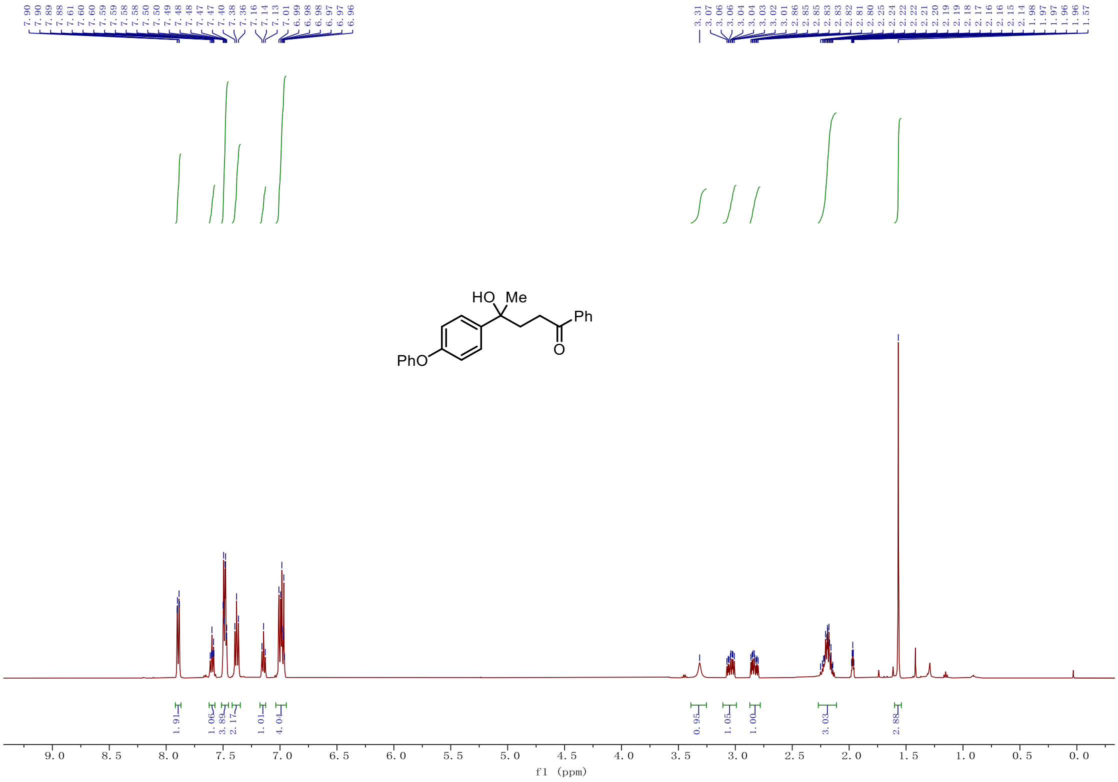
132.88
128.57
127.86
126.17
117.34
113.24
73.09
54.83
38.24
33.64
30.09
0.85
0.68
0.52
0.35
0.19
0.02
-0.14
HO
Me
O
Ph
MeO
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.90
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7.60
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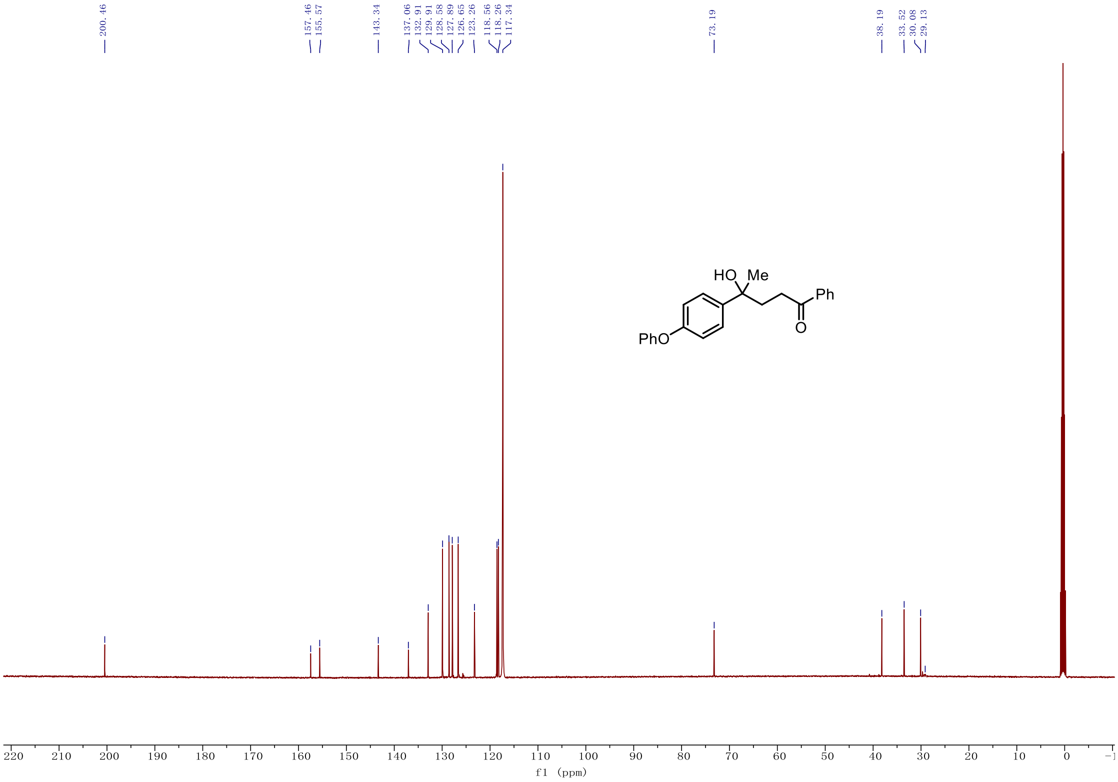
7.58
7.58
7.50
7.50
7.49
7.48
7.48
7.47
7.47
7.40
7.38
7.36
7.16
7.14
7.13
7.01
6.99
6.98
6.98
6.97
6.97
6.96
3.31
3.07
3.06
3.06
3.04
3.04
3.03
3.02
3.01
2.86
2.85
2.85
2.83
2.83
2.82
2.81
2.80
2.25
2.24
2.22
2.22
2.21
2.20
2.19
2.19
2.18
2.17
2.16
2.16
2.15
2.14
1.98
1.97
1.97
1.96
1.96
1.57
HO
Me
Ph
PhO
O
1.91
1.06
3.89
2.17
1.01
4.04
0.95
1.05
1.00
3.03
2.88
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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128.58
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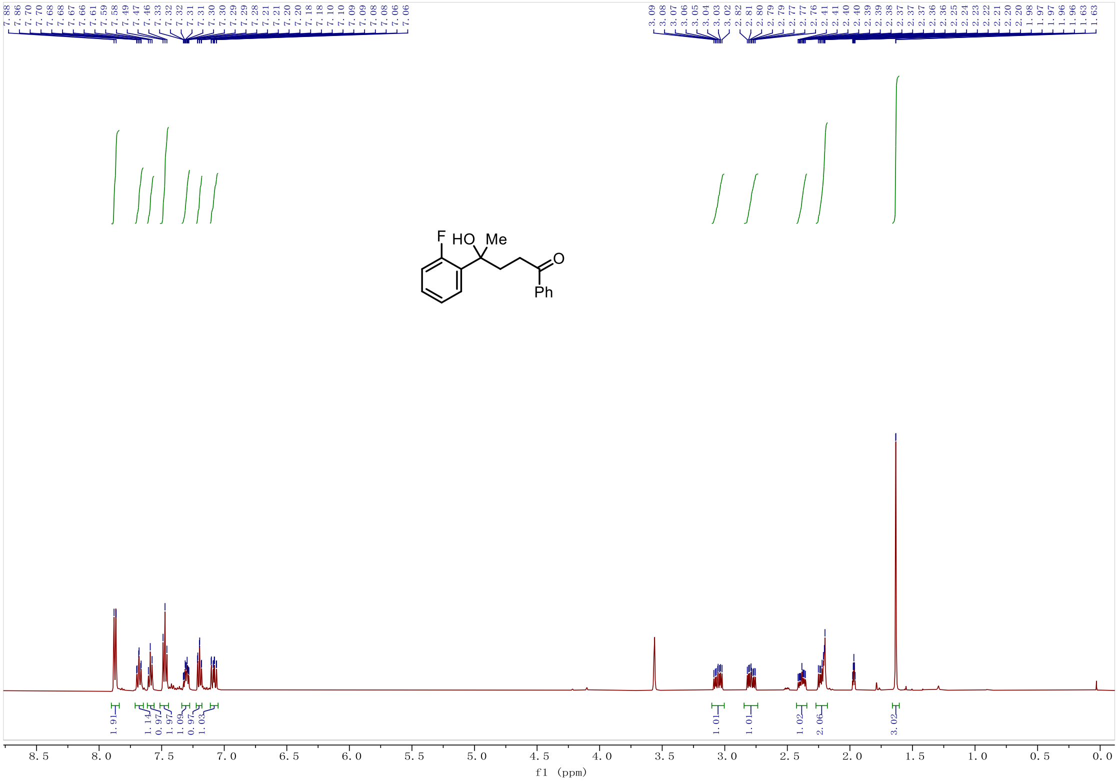
126.65
123.26
118.56
118.26
117.34
73.19
38.19
33.52
30.08
29.13
HO
Me
Ph
PhO
O
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)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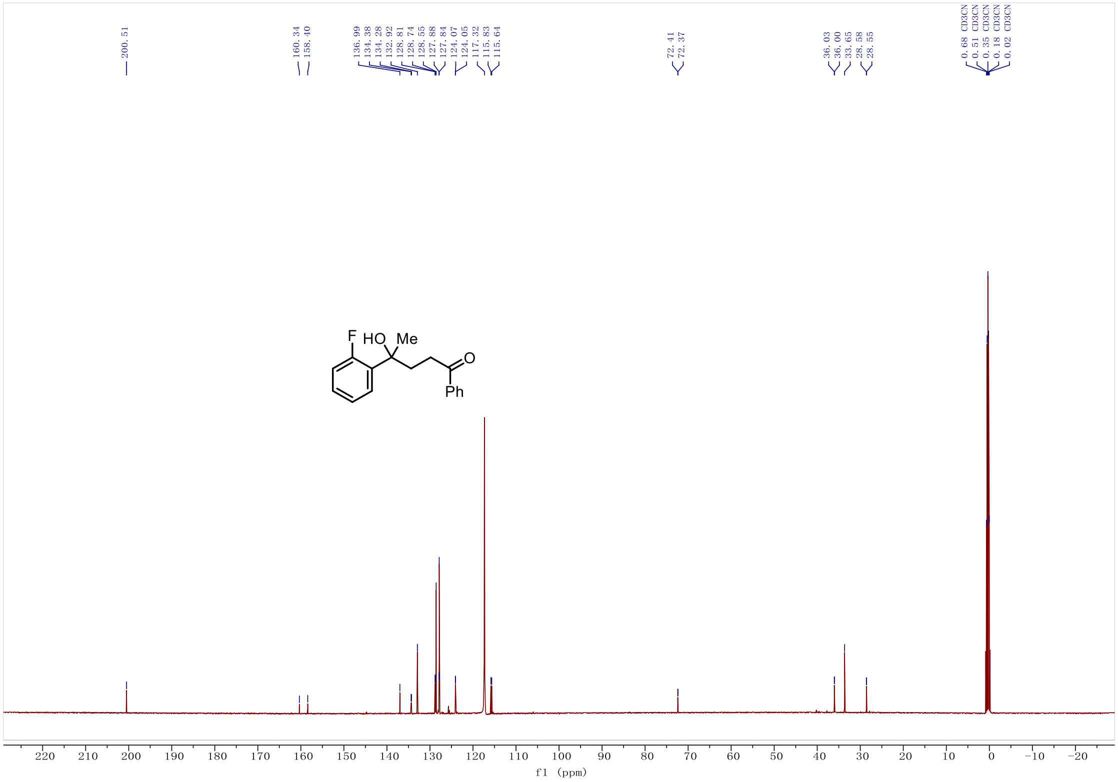
7.86
7.70
7.68
7.68
7.67
7.66
7.61
7.59
7.58
7.49
7.47
7.46
7.33
7.32
7.32
7.31
7.31
7.30
7.29
7.29
7.28
7.21
7.21
7.20
7.18
7.18
7.10
7.10
7.09
7.08
7.08
7.06
7.06
3.09
3.08
3.07
3.06
3.05
3.04
3.03
3.02
2.82
2.81
2.80
2.79
2.79
2.77
2.77
2.76
2.41
2.41
2.40
2.40
2.39
2.39
2.38
2.37
2.37
2.36
2.36
2.25
2.24
2.24
2.23
2.22
2.21
2.20
2.20
1.98
1.97
1.97
1.96
1.96
1.63
1.63
F
HO
Me
O
Ph
1.91
1.14
0.97
1.97
1.09
0.97
1.03
1.01
1.01
1.02
2.06
3.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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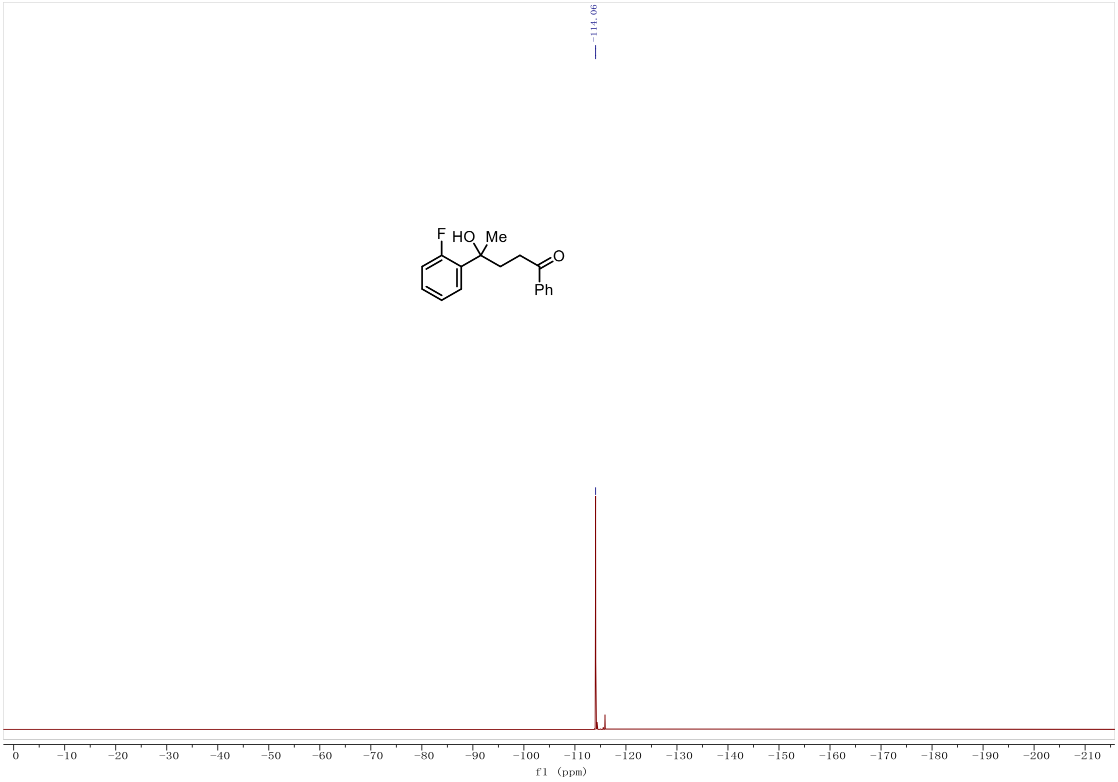
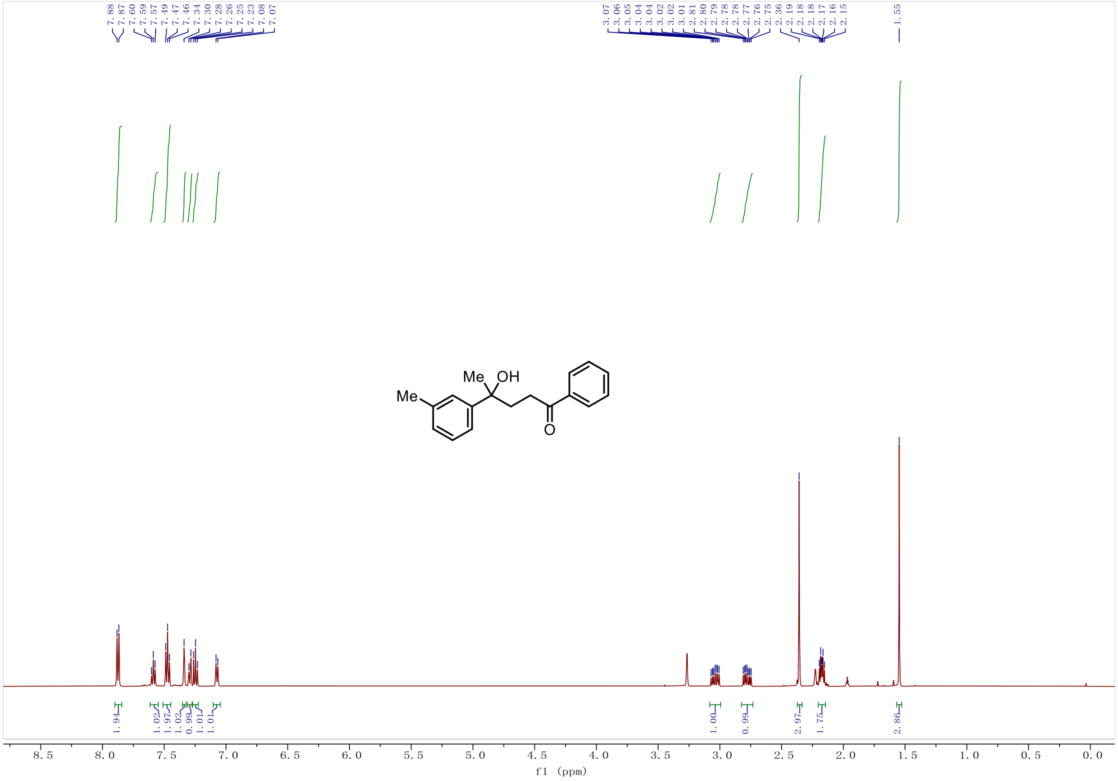
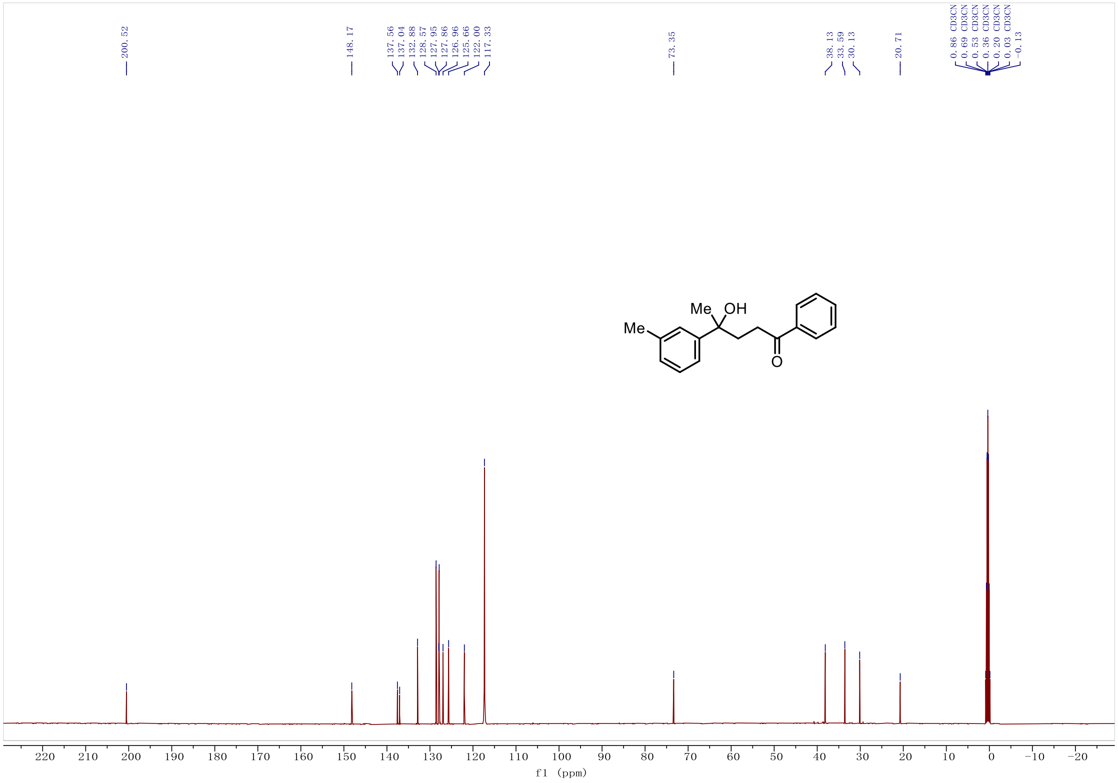
134.38
134.28
132.92
128.81
128.74
128.55
127.88
127.84
124.07
124.05
117.32
115.83
115.64
72.41
72.37
36.03
36.00
33.65
28.58
28.55
0.68 CD3CN
0.51 CD3CN
0.35 CD3CN
0.18 CD3CN
0.02 CD3CN
F
HO
Me
O
Ph
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)


−114.06
F
HO
Me
O
Ph
0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)


7.88 7.87 7.60 7.59 7.57 7.49 7.47 7.46 7.34 7.30 7.28 7.26 7.25 7.23 7.08 7.07
3.07 3.06 3.05 3.04 3.04 3.02 3.02 3.01 2.81 2.80 2.79 2.78 2.78 2.77 2.76 2.75 2.36 2.19 2.18 2.18 2.17 2.16 2.15
1.55
Me
Me
OH
O
1.94 1.02 1.97 1.02 0.99 1.01 1.01 1.00 0.99 2.97 1.75 2.86
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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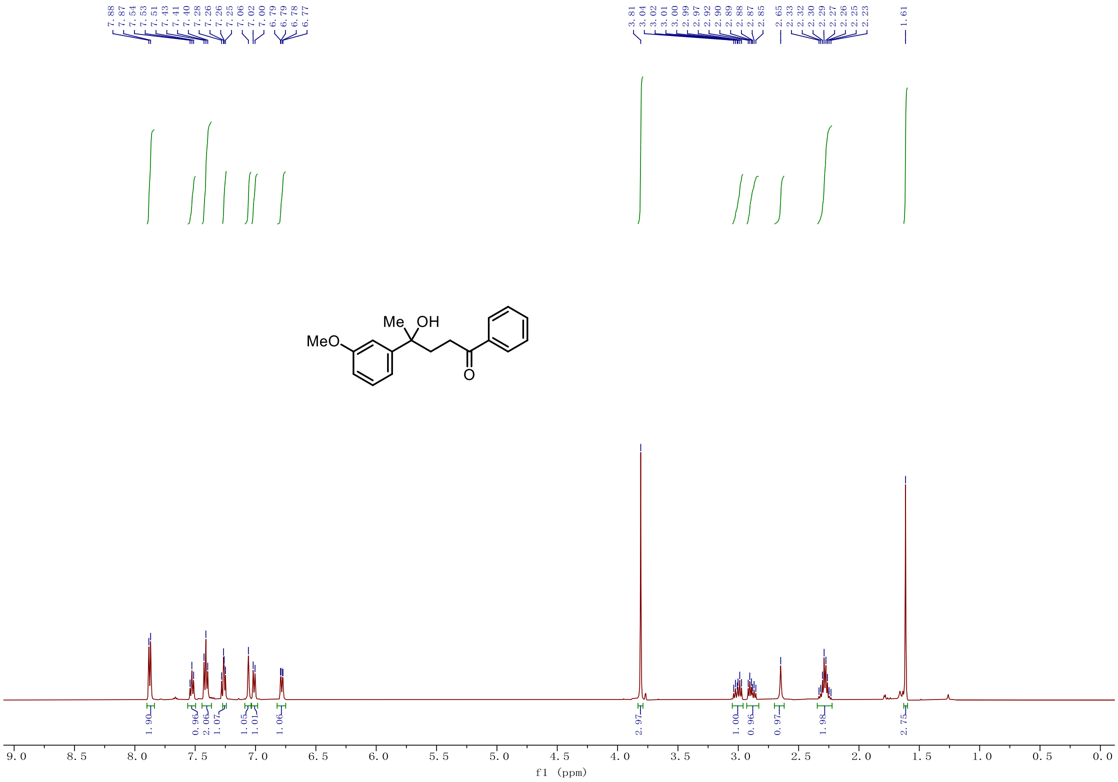
148.17
137.56
137.04
132.88
128.57
127.95
127.86
126.96
125.66
122.00
117.33
73.35
38.13
33.59
30.13
20.71
0.86 CD3CN
0.69 CD3CN
0.53 CD3CN
0.36 CD3CN
0.20 CD3CN
0.03 CD3CN
-0.13
Me
OH
Me
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)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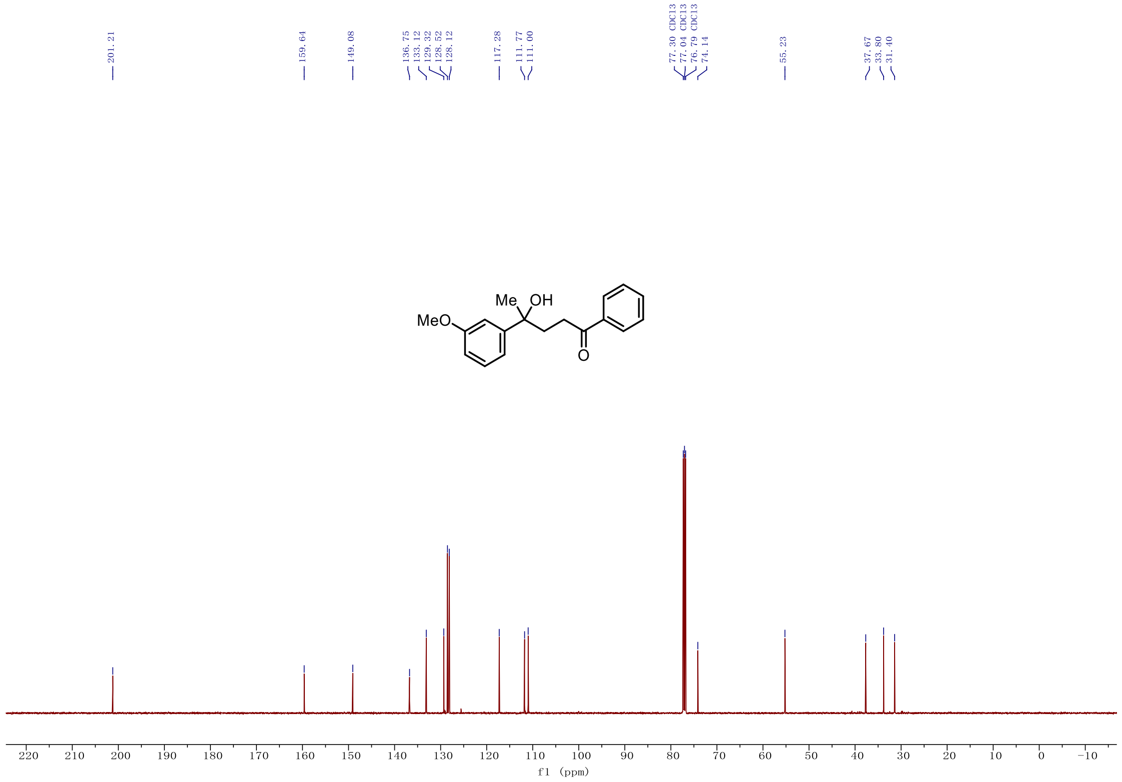
7.87
7.54
7.53
7.51
7.43
7.41
7.40
7.28
7.26
7.26
7.25
7.06
7.02
7.00
6.79
6.78
6.77
3.81
3.04
3.02
3.01
3.00
2.99
2.97
2.92
2.90
2.89
2.88
2.87
2.85
2.65
2.33
2.32
2.30
2.29
2.27
2.26
2.25
2.23
1.61
Me
OH
MeO
O
1.90
0.96
2.06
1.07
1.05
1.01
1.06
2.97
1.00
0.96
0.97
1.98
2.75
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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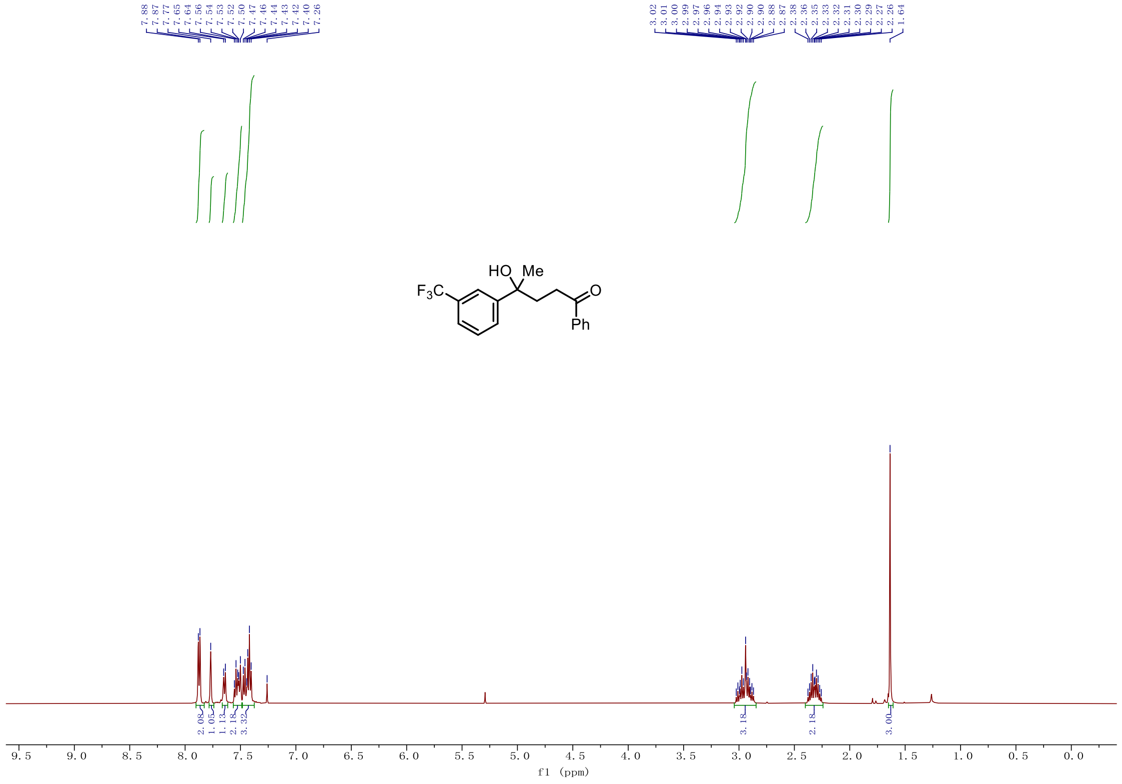
159.64
149.08
136.75
133.12
129.32
128.52
128.12
117.28
111.77
111.00
77.30 CDCl3
77.04 CDCl3
76.79 CDCl3
74.14
55.23
37.67
33.80
31.40
MeO
Me
OH
O
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.87
7.77
7.65
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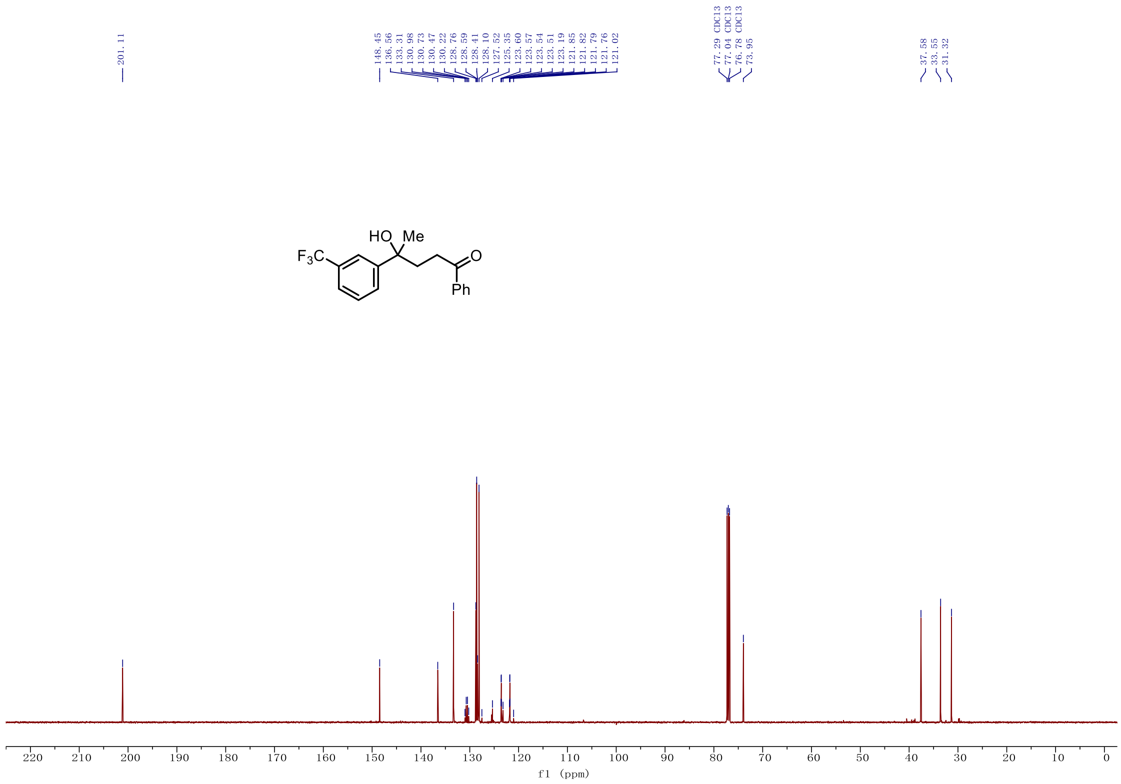
7.56
7.54
7.53
7.52
7.50
7.47
7.46
7.44
7.43
7.42
7.40
7.26
3.02
3.01
3.00
2.99
2.97
2.96
2.94
2.93
2.92
2.90
2.88
2.87
2.38
2.36
2.35
2.33
2.32
2.31
2.30
2.29
2.27
2.26
1.64
HO
Me
F3C
O
Ph
2.08
1.05
1.13
2.18
3.32
3.18
2.18
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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136.56
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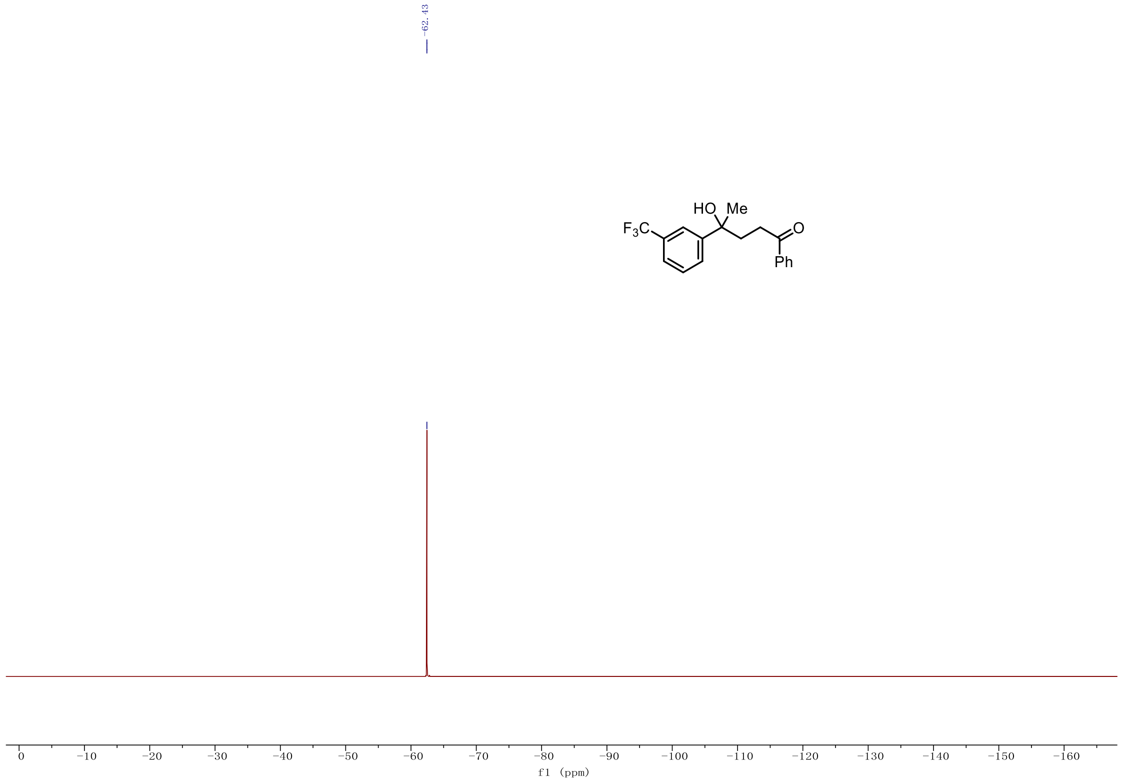
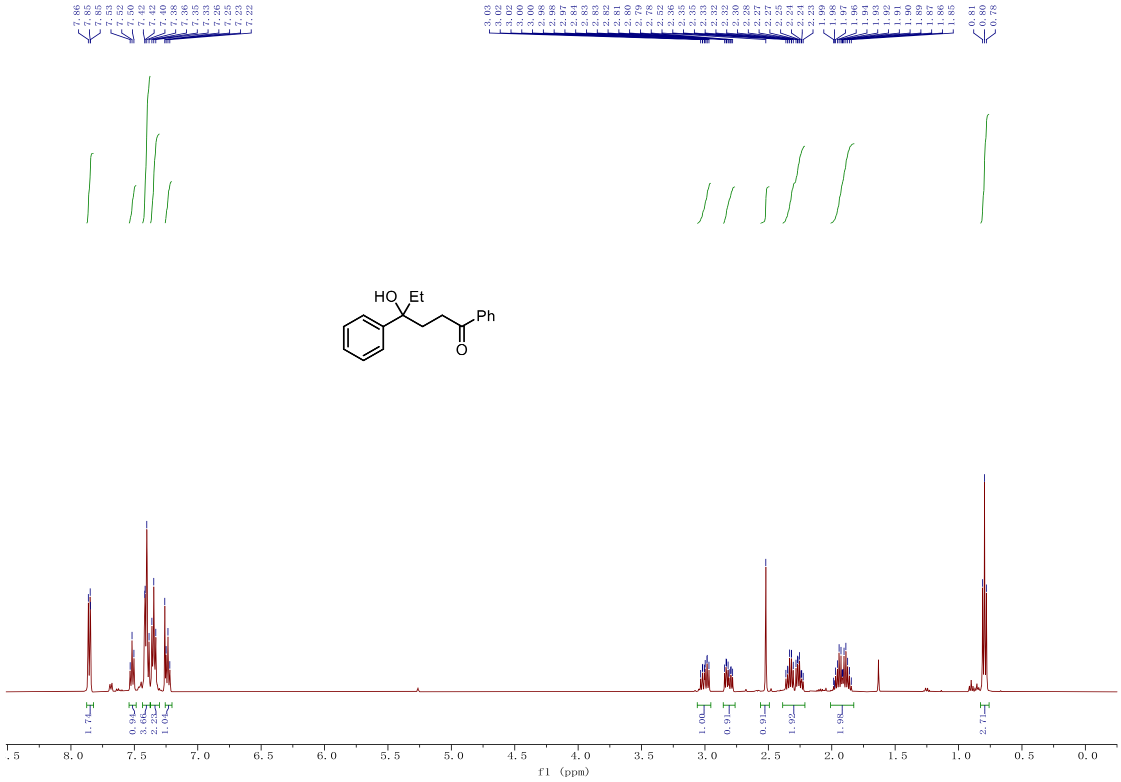
130.98
130.73
130.47
130.22
128.76
128.59
128.41
128.10
127.52
125.35
123.60
123.57
123.54
123.51
123.19
121.85
121.82
121.79
121.76
121.02
77.29 CDC13
77.04 CDC13
76.78 CDC13
73.95
37.58
33.55
31.32
HO
Me
F_3C
O
Ph
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-62.43
HO
Me
F_3C
O
Ph
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
f1 (ppm)


7.86
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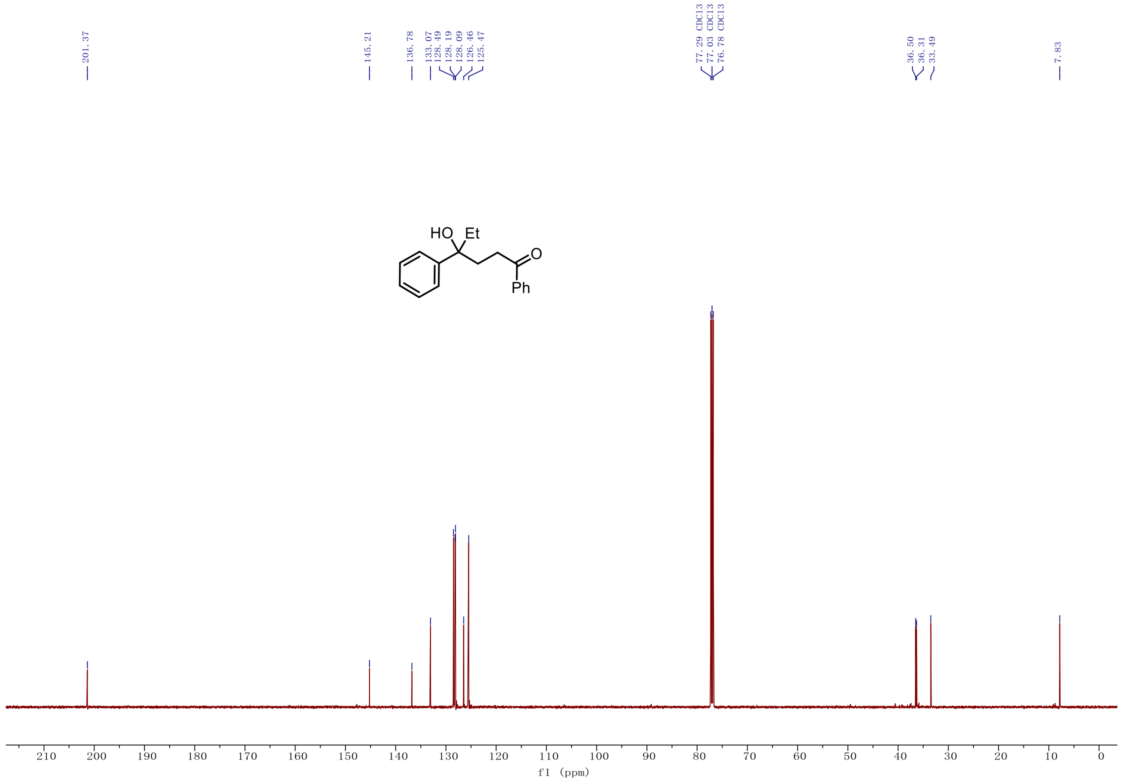
7.42
7.42
7.40
7.38
7.36
7.35
7.33
7.26
7.25
7.23
7.22
3.03
3.02
3.02
3.00
3.00
2.98
2.98
2.97
2.84
2.83
2.83
2.82
2.81
2.80
2.79
2.78
2.52
2.36
2.35
2.35
2.33
2.32
2.32
2.30
2.28
2.27
2.27
2.25
2.24
2.24
2.23
1.99
1.98
1.97
1.96
1.94
1.93
1.92
1.91
1.90
1.89
1.87
1.86
1.85
0.81
0.80
0.78
HO
Et
Ph
O
1.74
0.94
3.66
2.23
1.04
1.00
0.91
0.91
1.92
1.98
2.71
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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133.07
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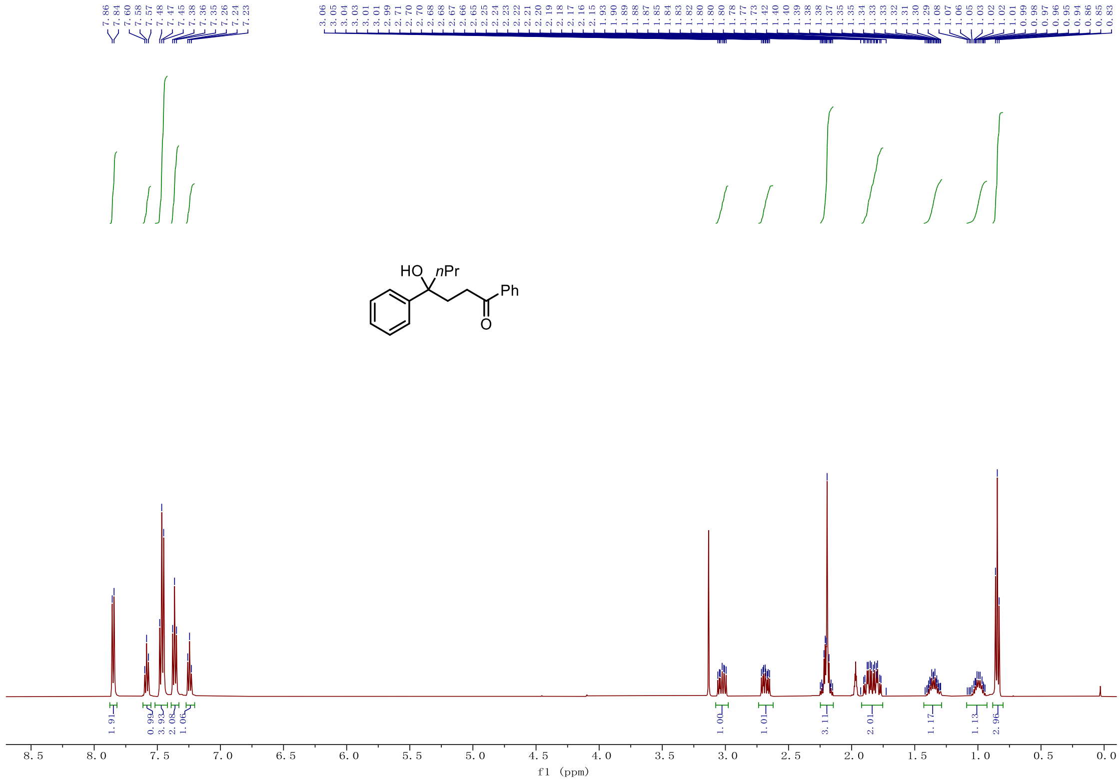
128.19
128.09
126.46
125.47
77.29 CDCl3
77.03 CDCl3
76.78 CDCl3
36.50
36.31
33.49
7.83
HO
Et
O
Ph
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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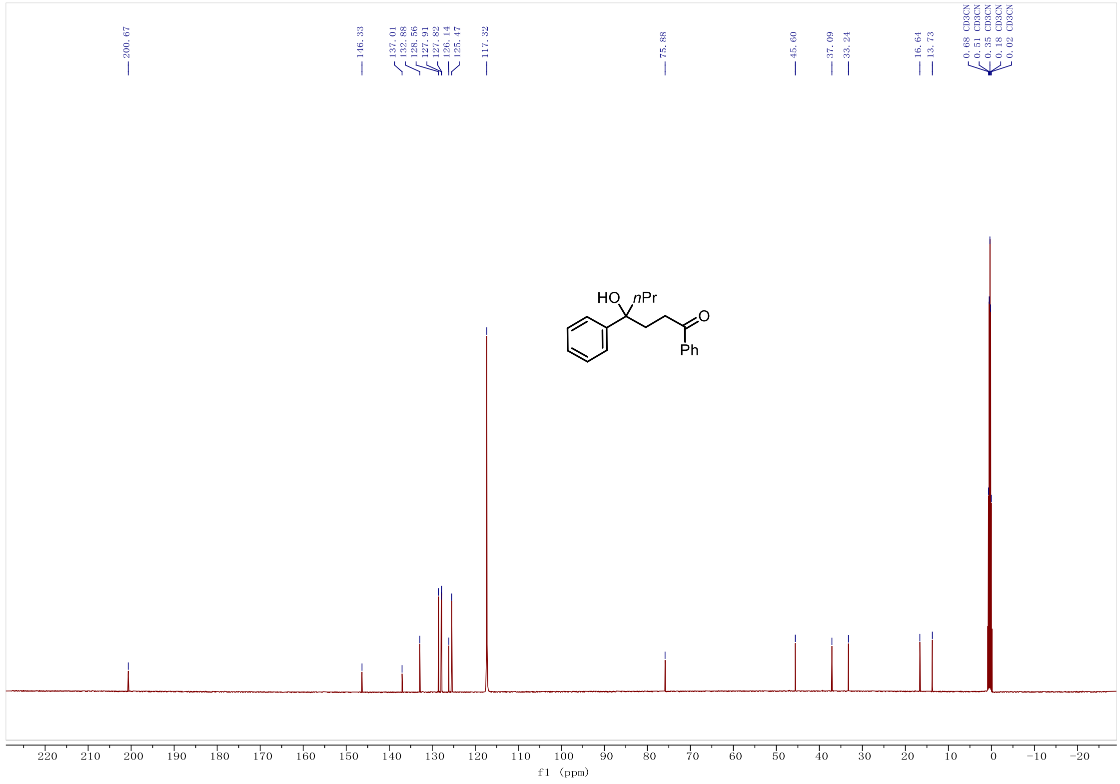
7.84
7.60
7.58
7.57
7.48
7.47
7.45
7.38
7.36
7.35
7.26
7.24
7.23
3.06
3.05
3.04
3.03
3.01
3.01
2.99
2.71
2.70
2.70
2.68
2.68
2.67
2.66
2.65
2.25
2.24
2.23
2.22
2.21
2.20
2.19
2.18
2.17
2.16
2.15
1.93
1.90
1.89
1.88
1.87
1.85
1.84
1.83
1.82
1.80
1.80
1.78
1.77
1.73
1.42
1.40
1.40
1.39
1.38
1.38
1.37
1.35
1.35
1.34
1.33
1.33
1.32
1.31
1.30
1.29
1.08
1.07
1.06
1.05
1.03
1.02
1.02
1.01
0.99
0.98
0.97
0.96
0.95
0.94
0.86
0.85
0.83
HO
nPr
Ph
O
1.91
0.99
3.93
2.08
1.06
1.00
1.01
3.11
2.01
1.17
1.13
2.96
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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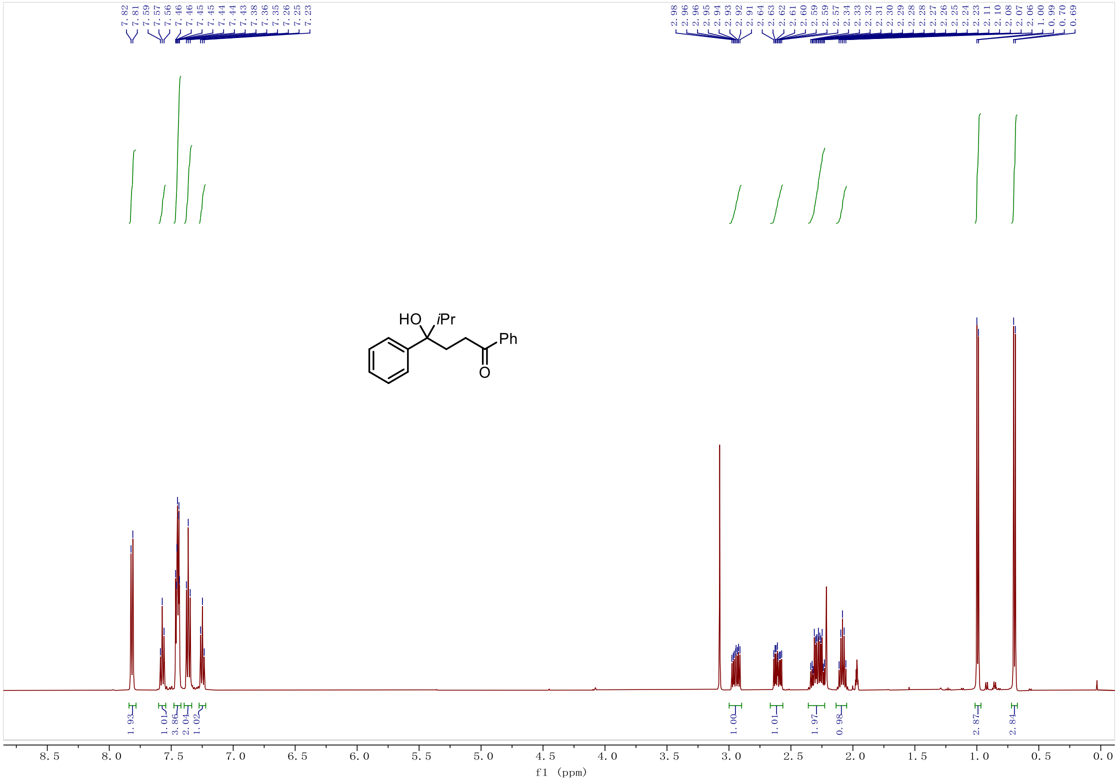
127.91
127.82
126.14
125.47
117.32
75.88
45.60
37.09
33.24
16.64
13.73
0.68 CD3CN
0.51 CD3CN
0.35 CD3CN
0.18 CD3CN
0.02 CD3CN
HO
nPr
O
Ph
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)


7.82
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7.45
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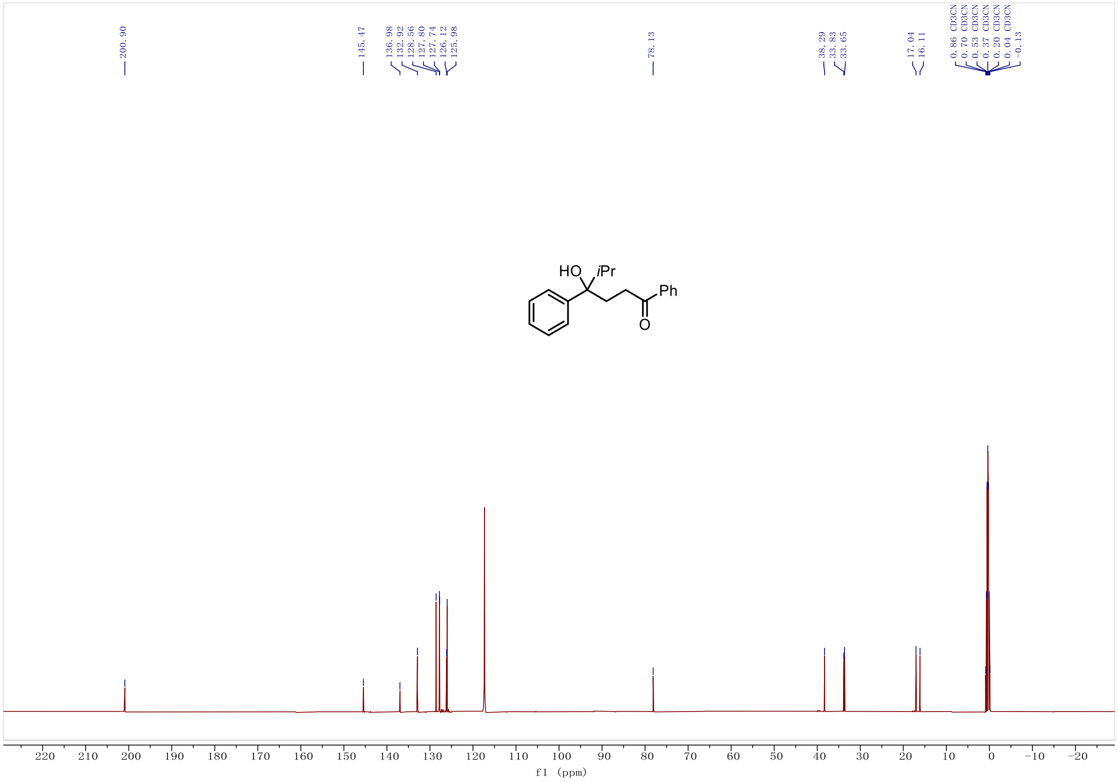
7.38
7.36
7.35
7.26
7.25
7.23
2.98
2.96
2.96
2.95
2.94
2.93
2.92
2.91
2.64
2.63
2.62
2.61
2.60
2.59
2.59
2.57
2.34
2.33
2.32
2.31
2.30
2.29
2.28
2.28
2.27
2.26
2.25
2.24
2.23
2.11
2.10
2.08
2.07
2.06
1.00
0.99
0.70
0.69
HO
iPr
Ph
O
1.93
1.01
3.86
2.04
1.02
1.00
1.01
1.97
0.98
2.87
2.81
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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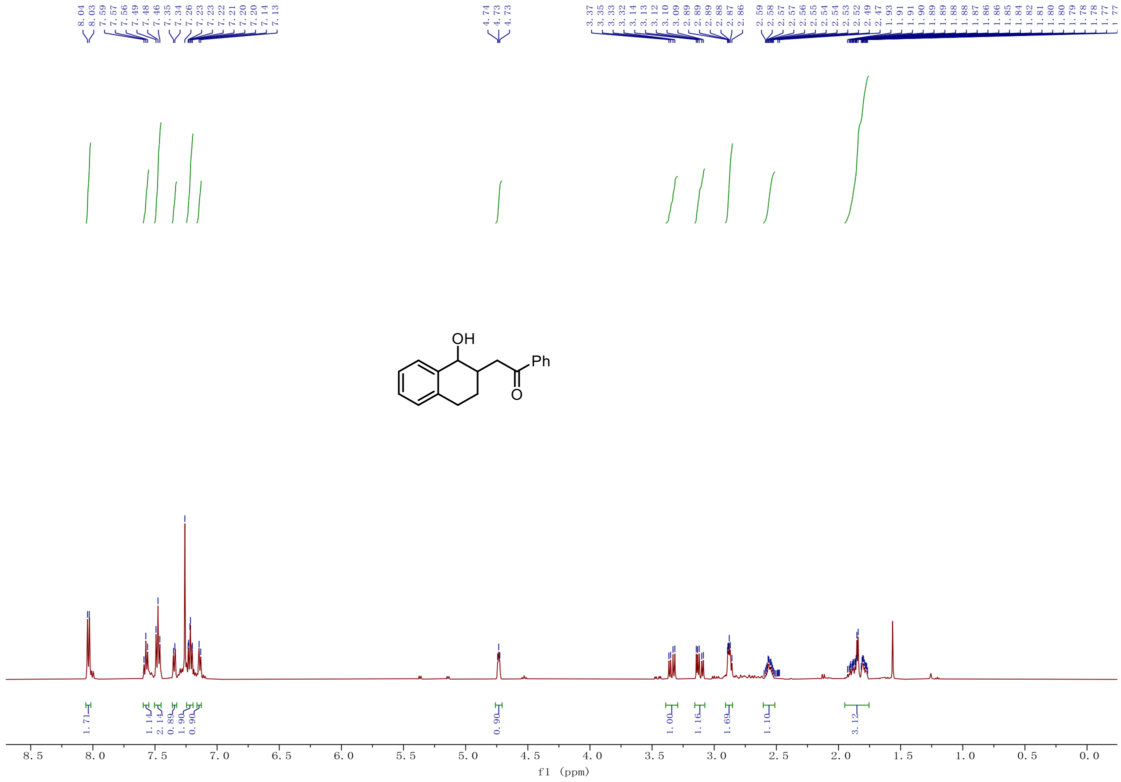
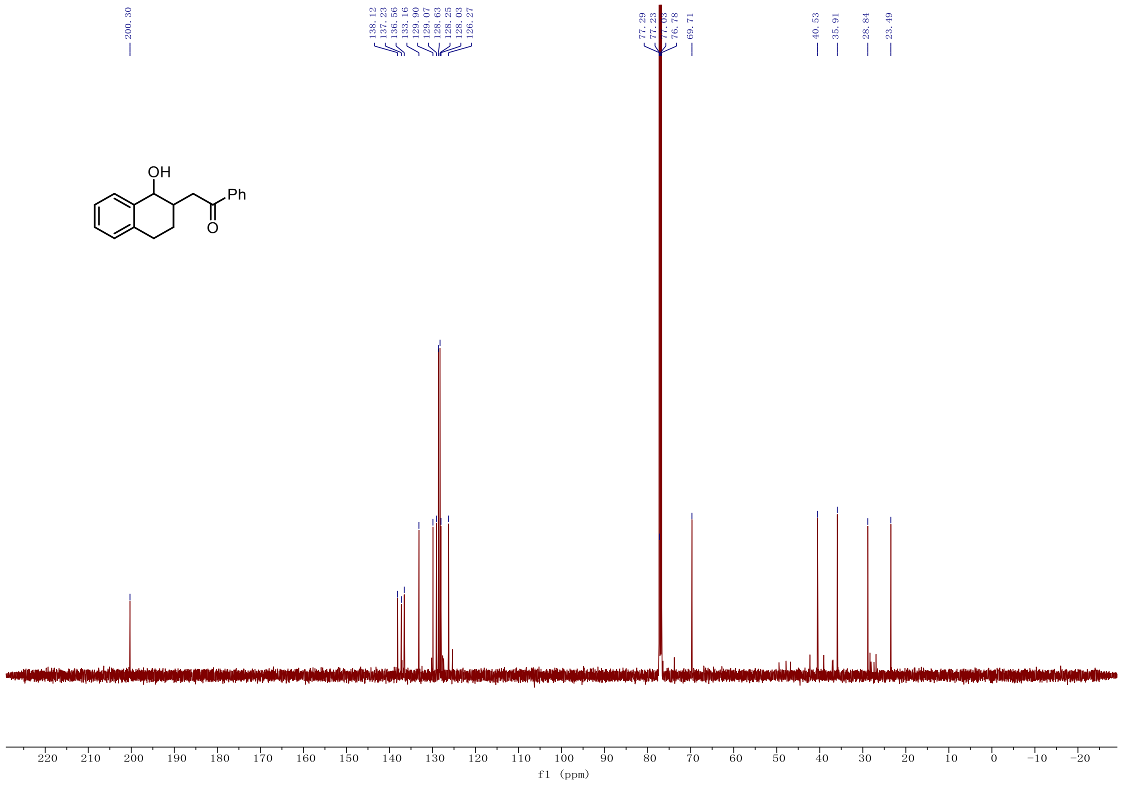
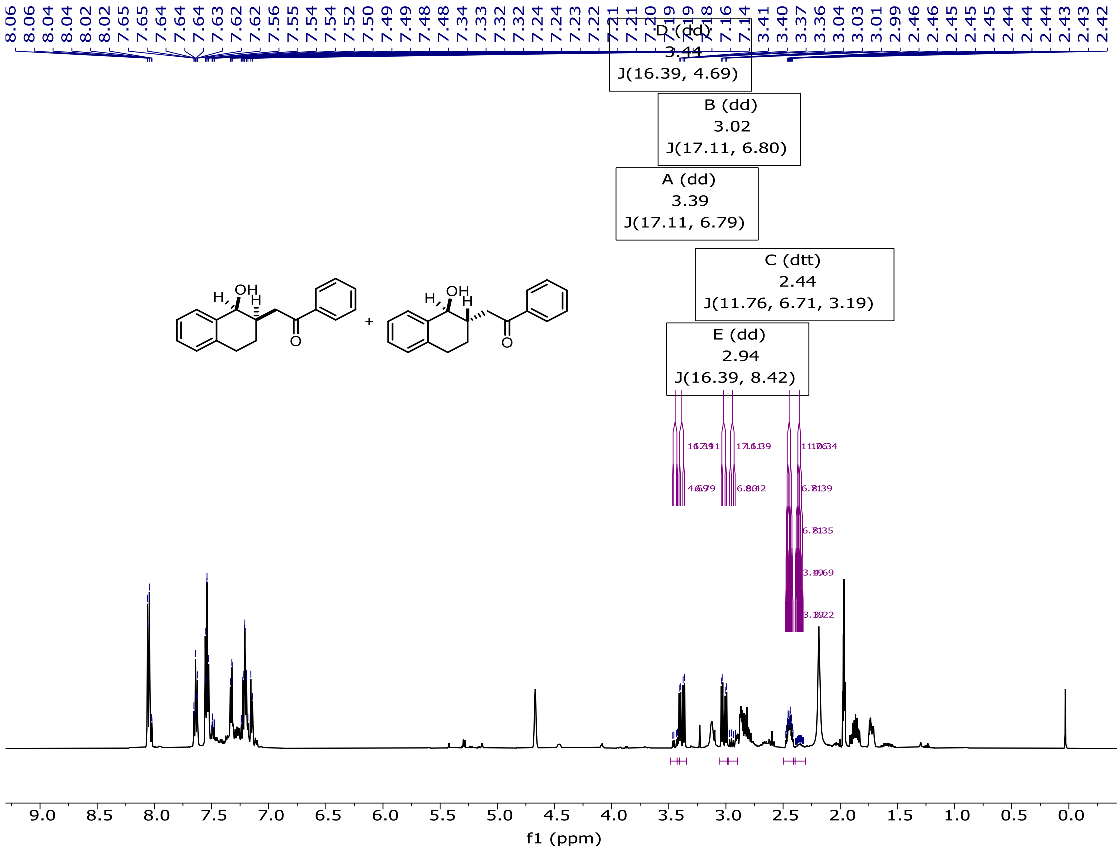
132.92
128.56
127.80
127.74
126.12
125.98
78.13
38.29
33.83
33.65
17.04
16.11
0.86 CD3CN
0.70 CD3CN
0.53 CD3CN
0.37 CD3CN
0.20 CD3CN
0.04 CD3CN
-0.13
HO
iPr
Ph
O
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)

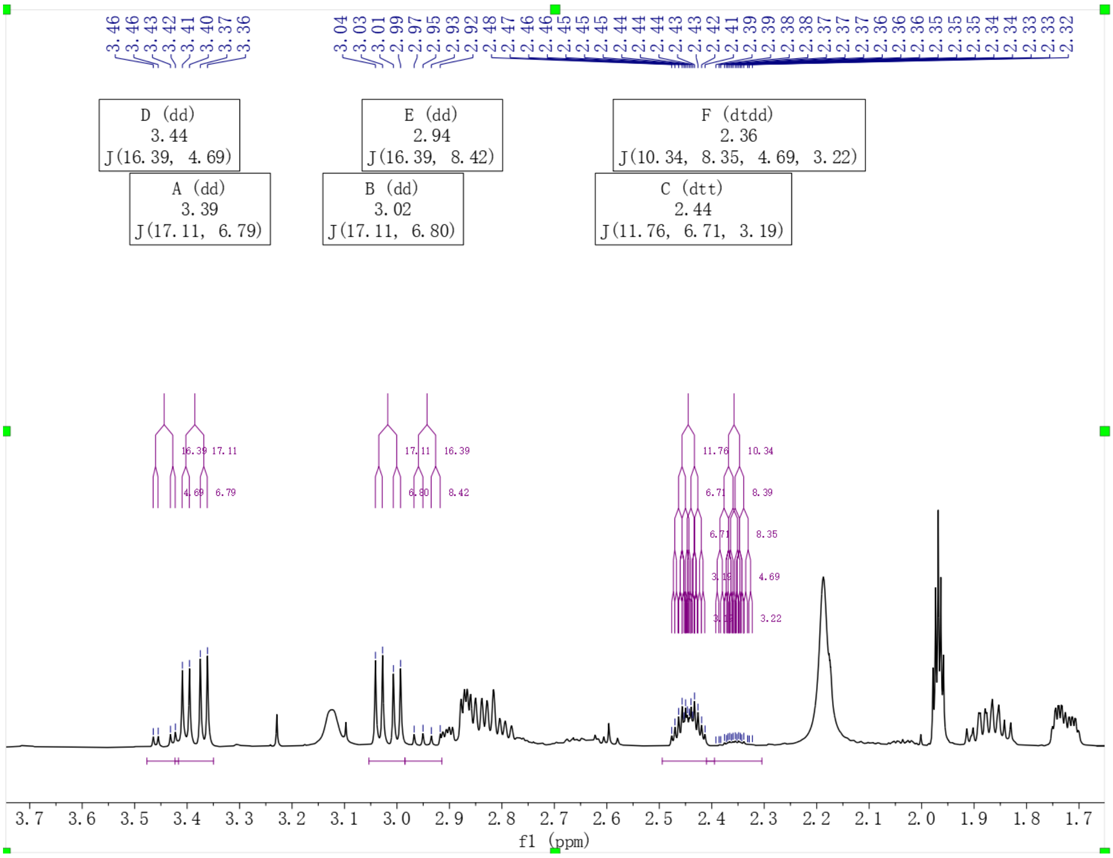




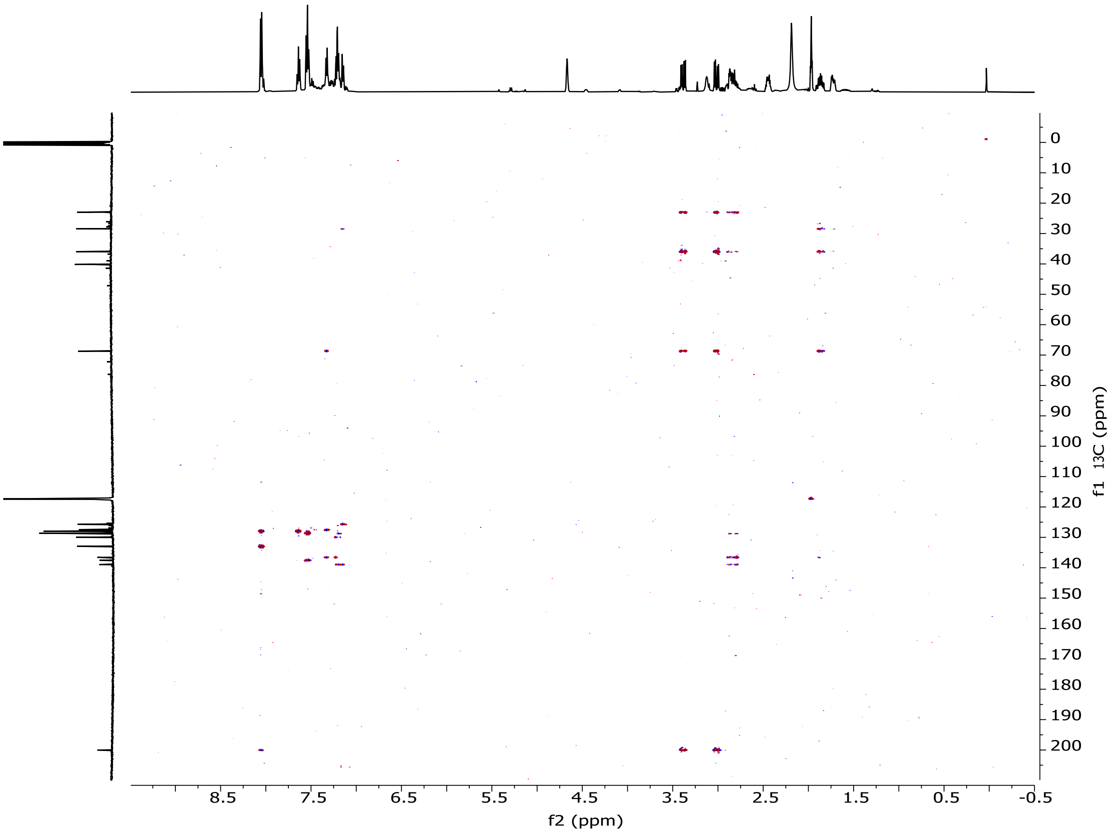
Peak assignment of rac-29

The dr of **rac-29** is 7:1 (*cis/trans*) based on the NMR.

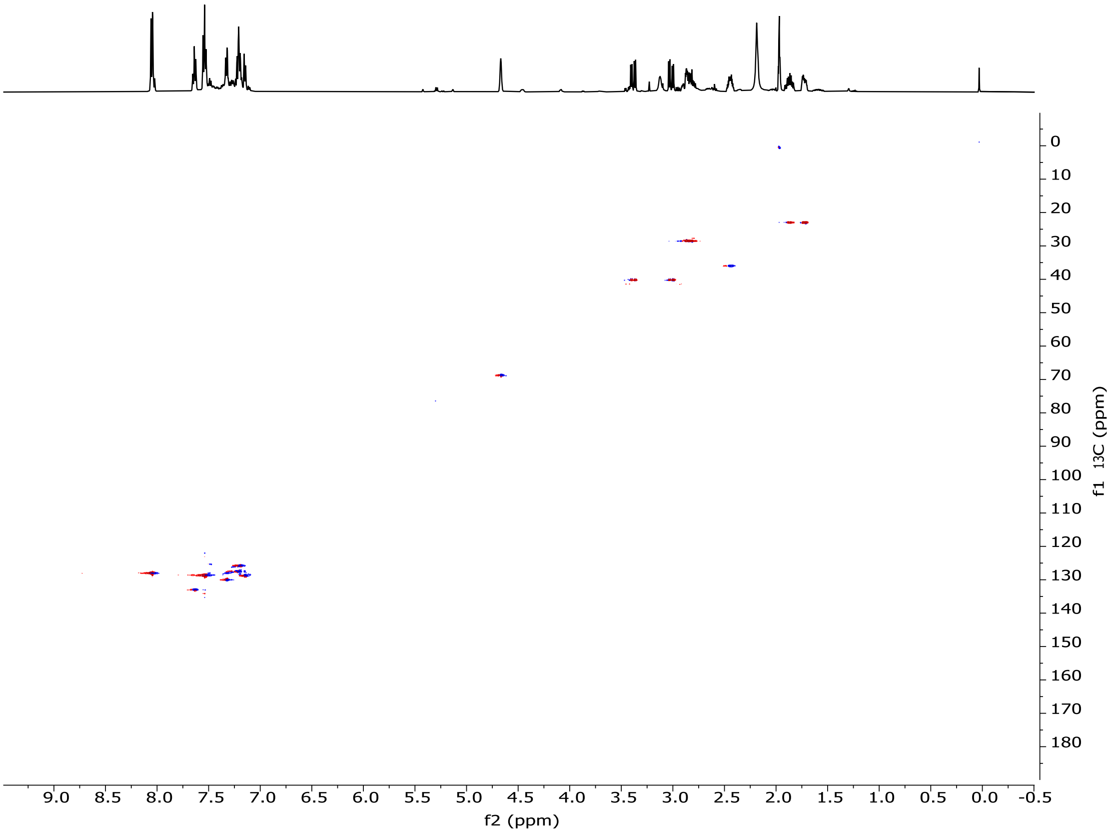




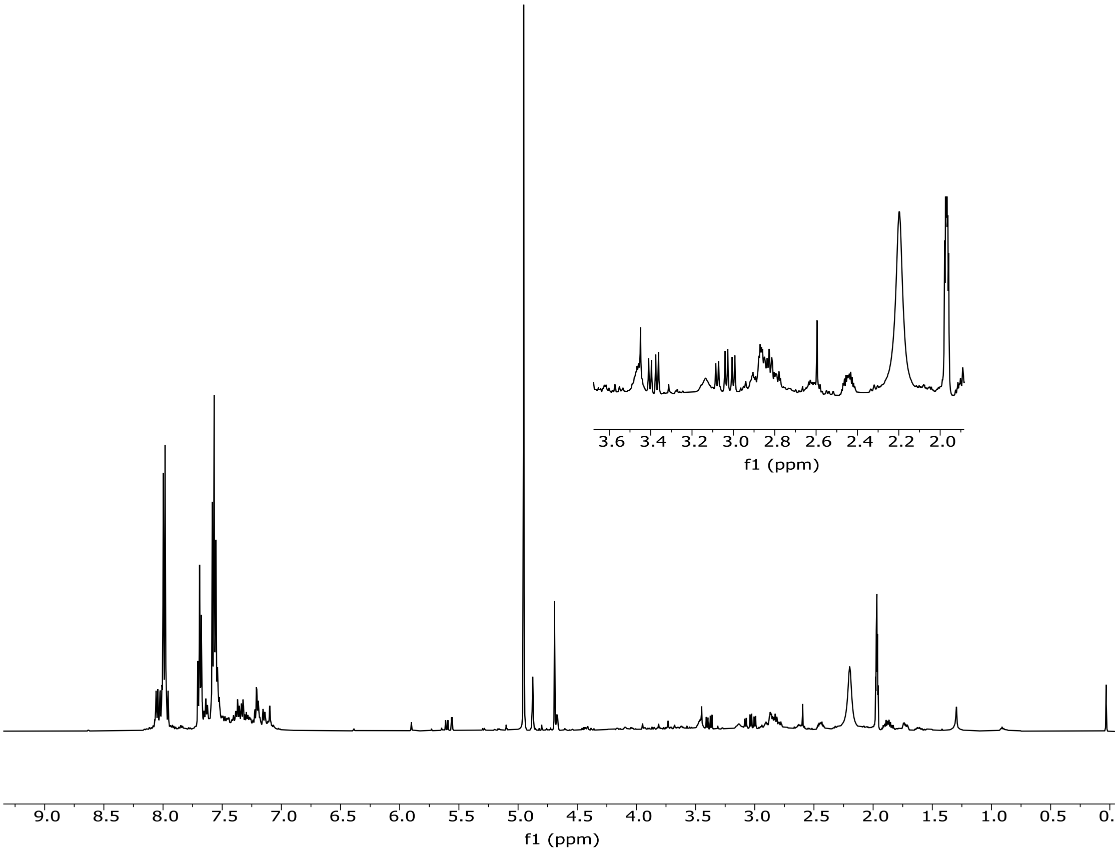
HMBC of **rac-29**



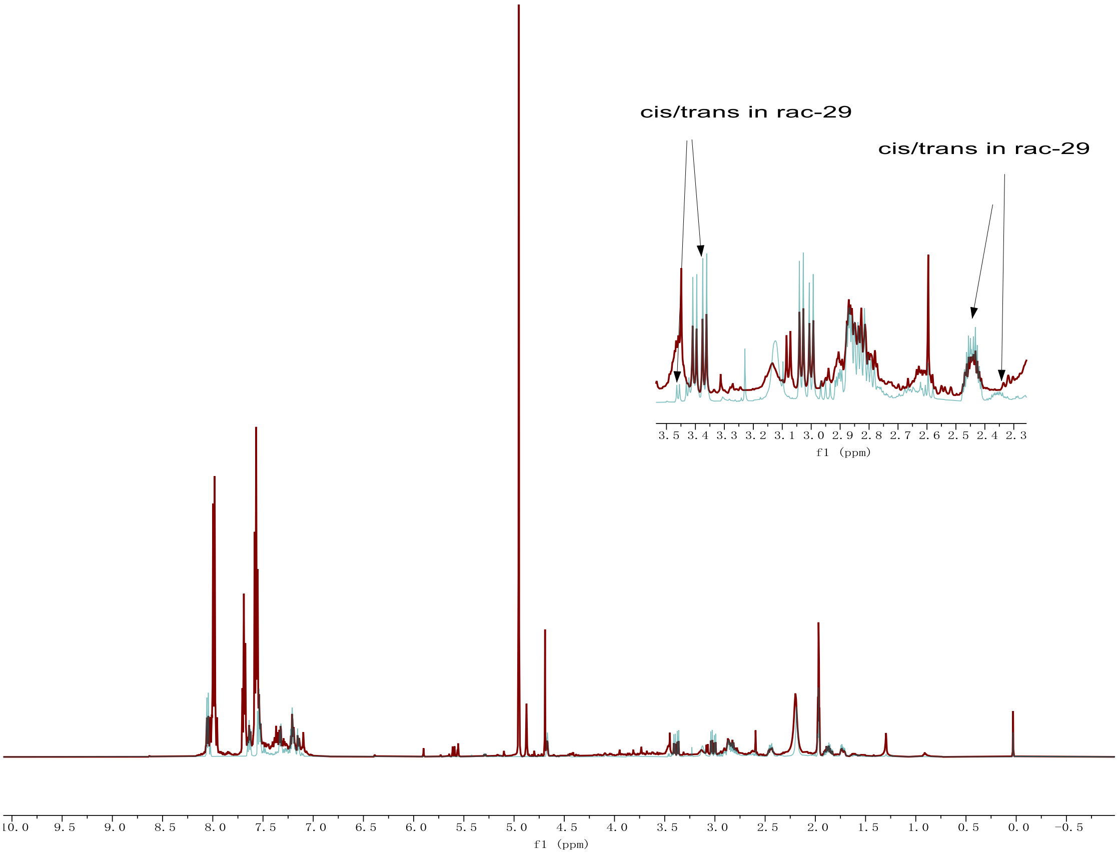
HSQC of **rac-29**

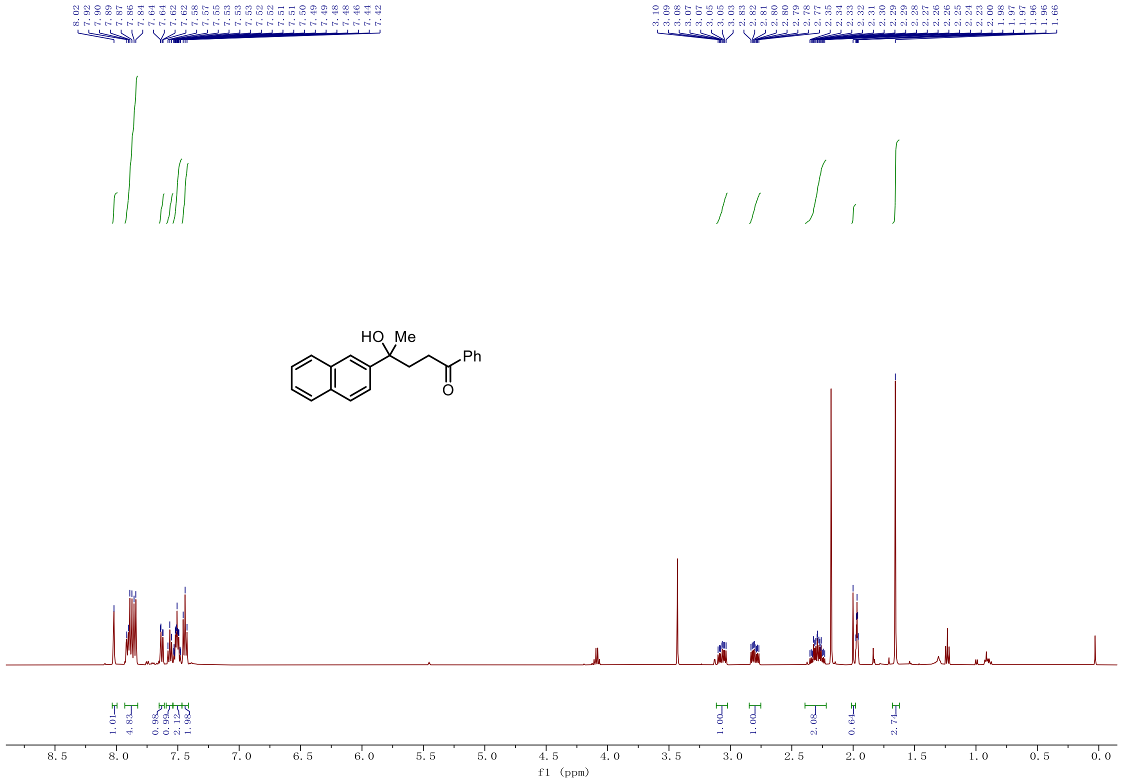


Crude NMR of enzymatic reaction for **29**. Stacked with **rac-29**, the major isomer of the enzymatic product is assigned to be *cis*. There is barely *trans*-isomer in enzymatic reaction.



Crude NMR of enzymatic reaction stacked with **rac-29:**

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7.44
7.42
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3.05
3.05
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Ph
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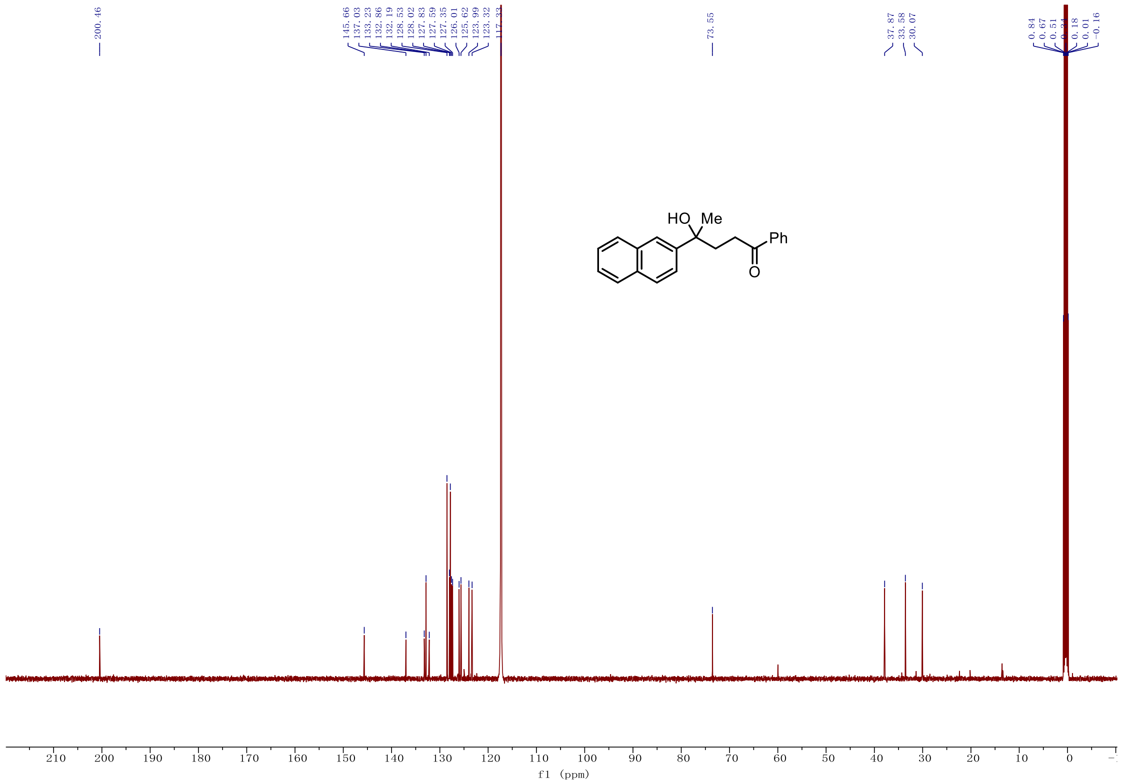
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Ph
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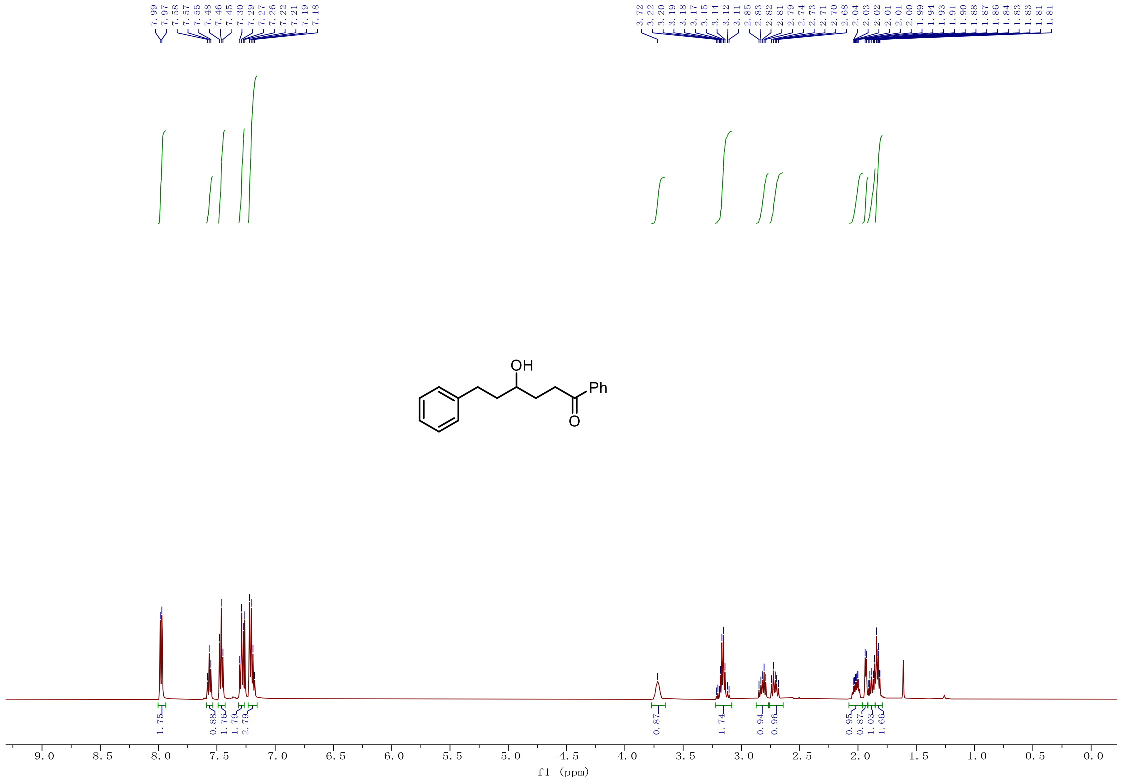
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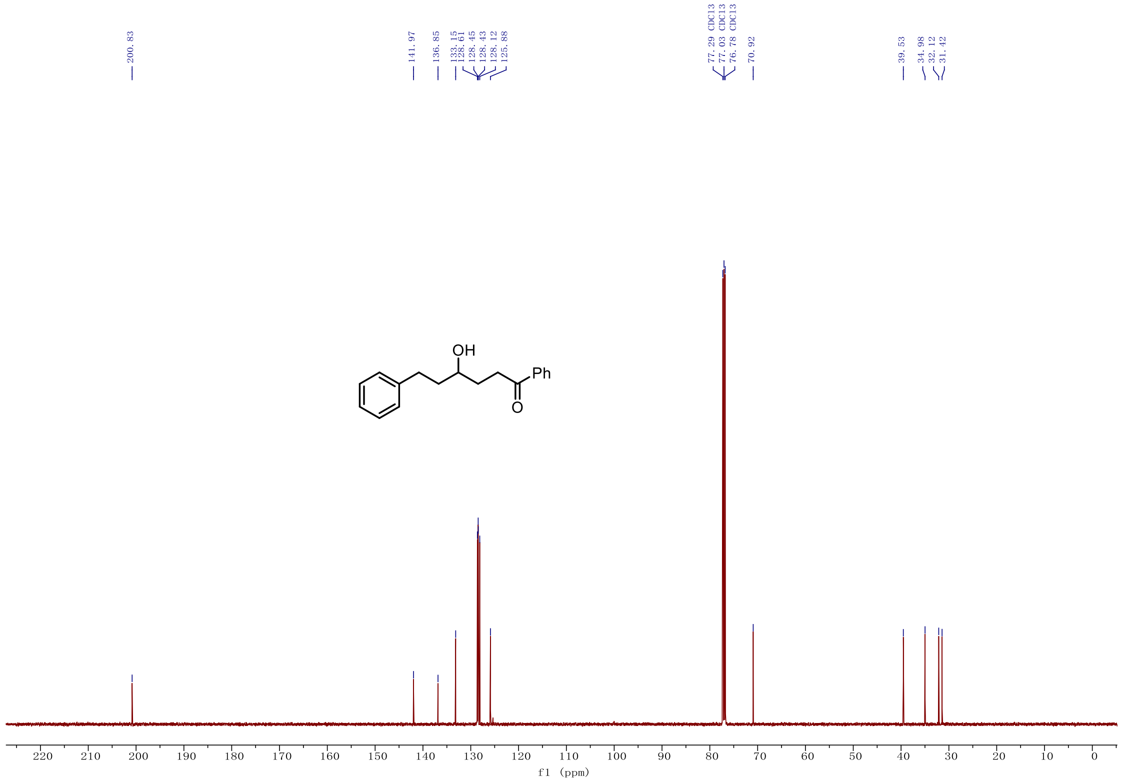
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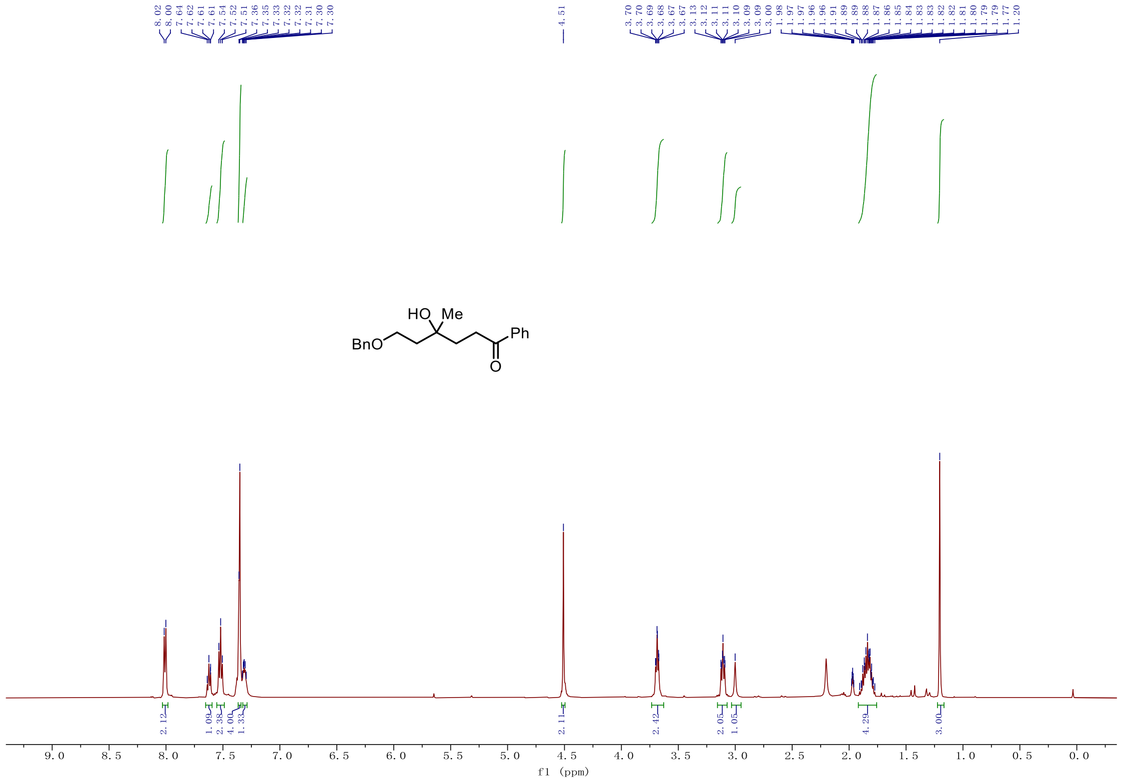
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Ph
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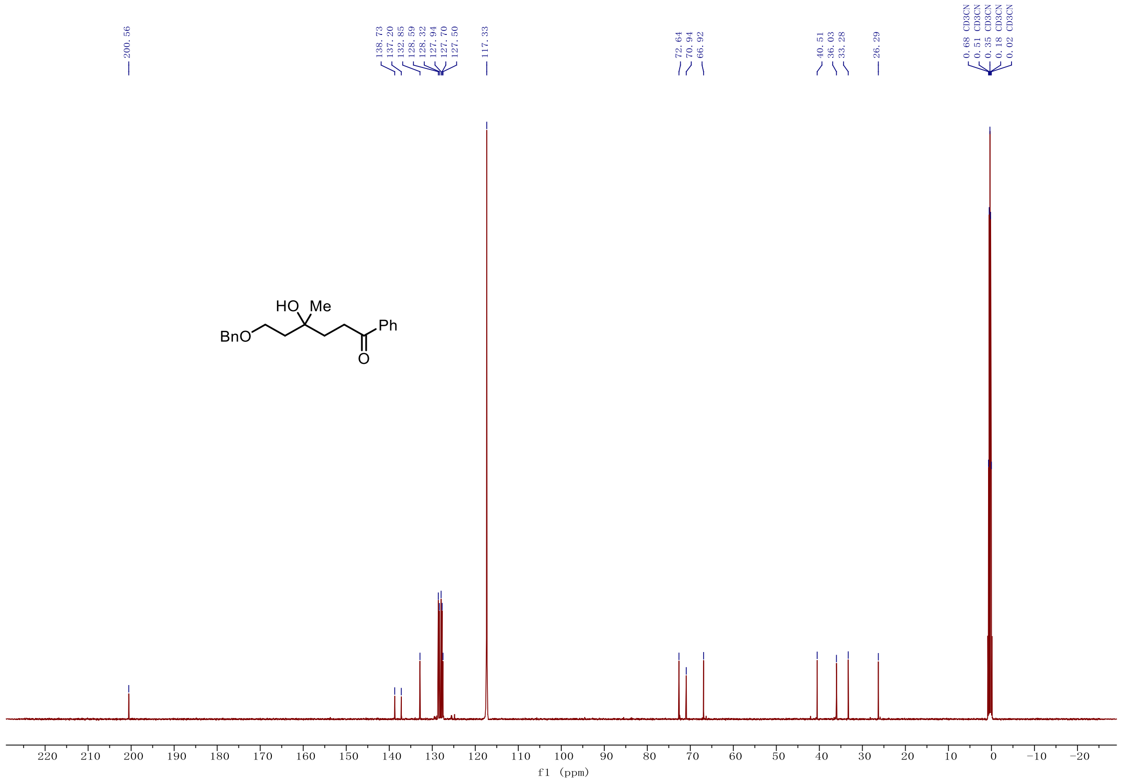
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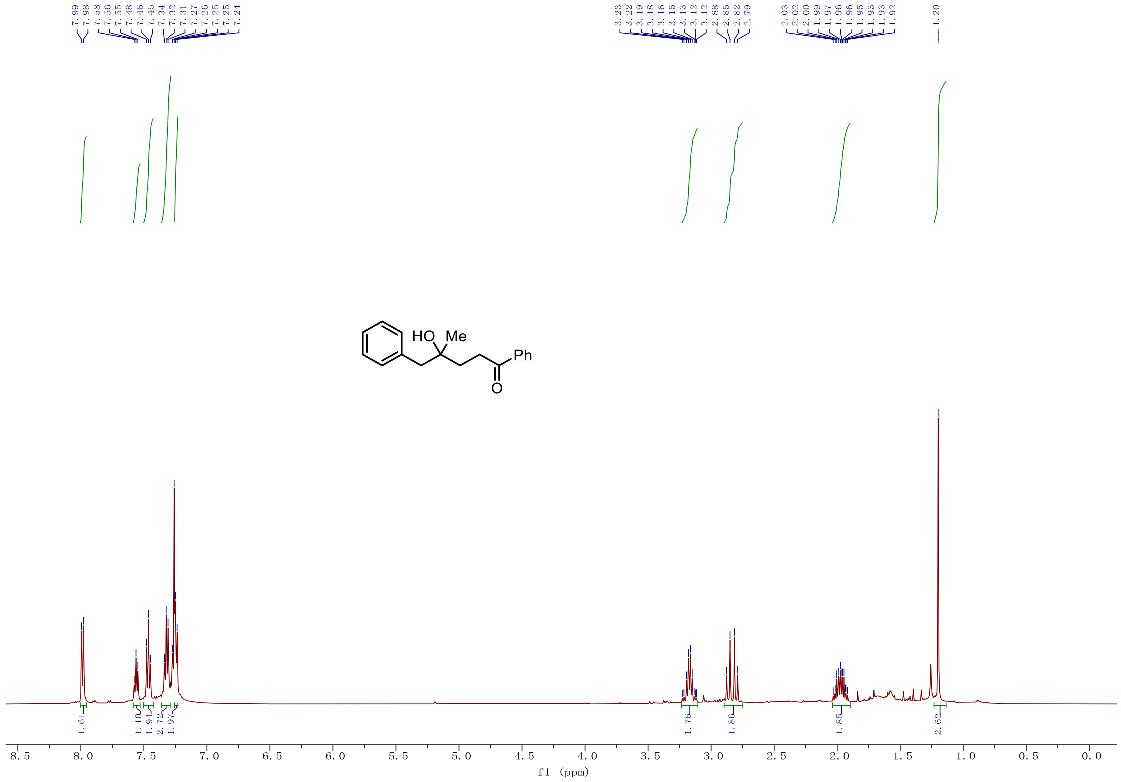
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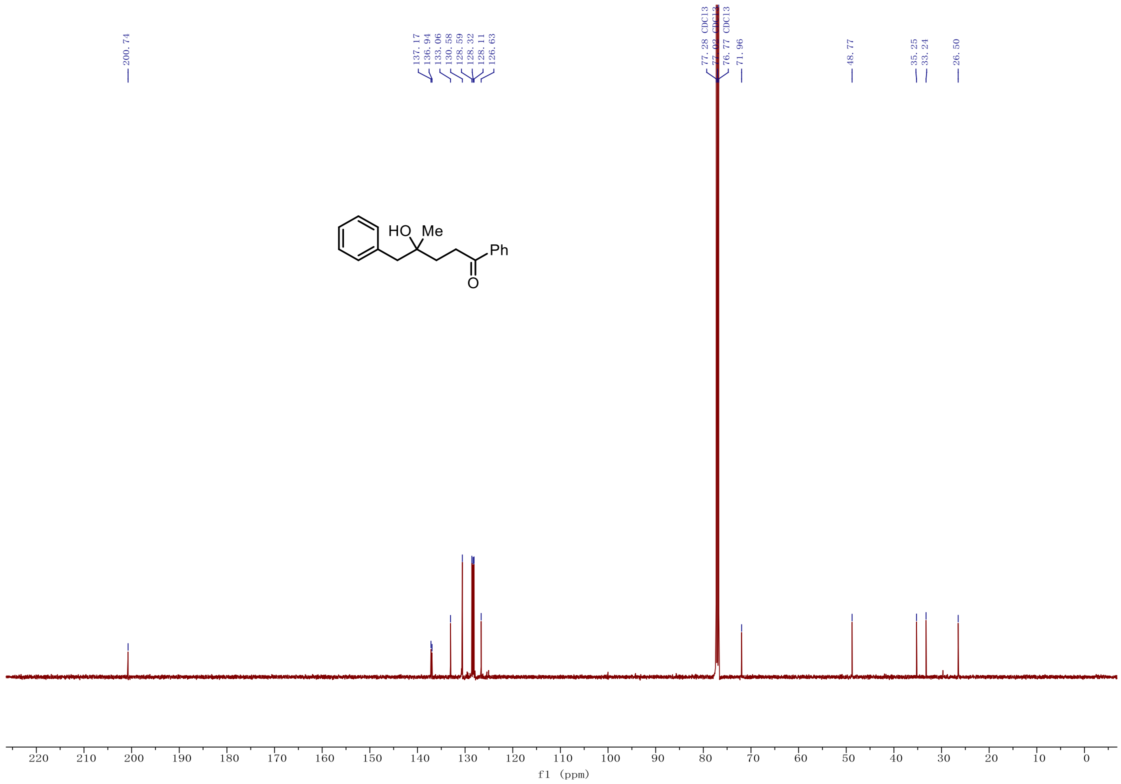
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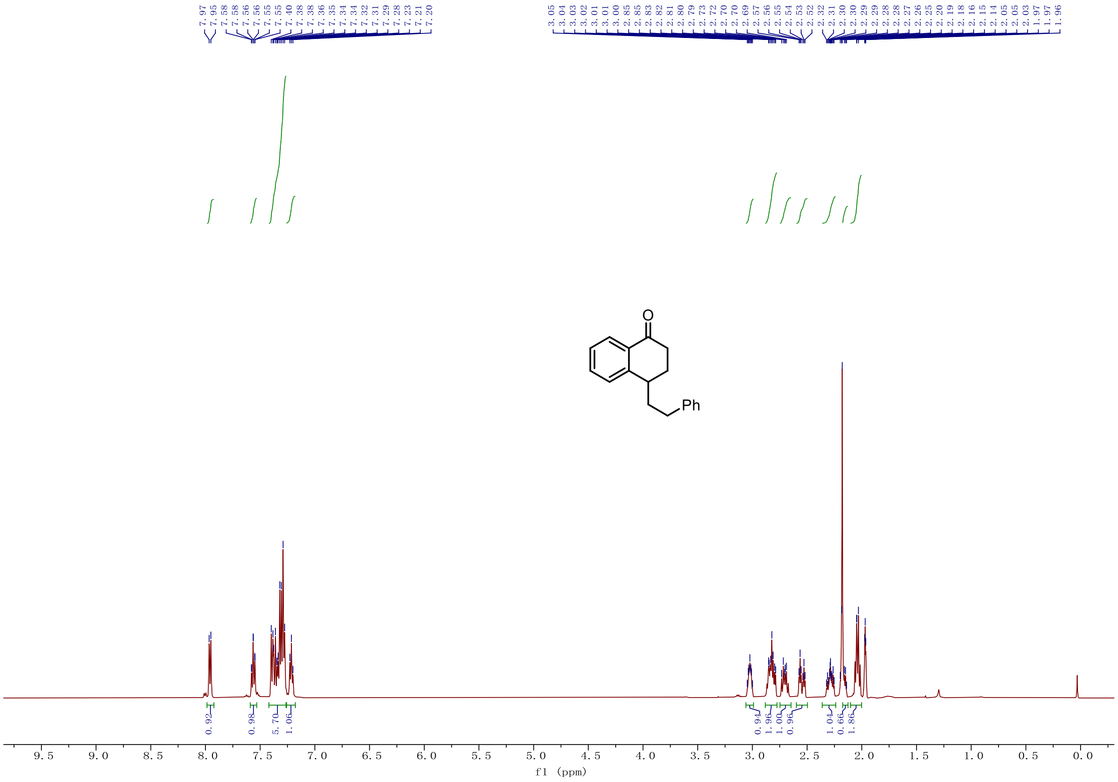
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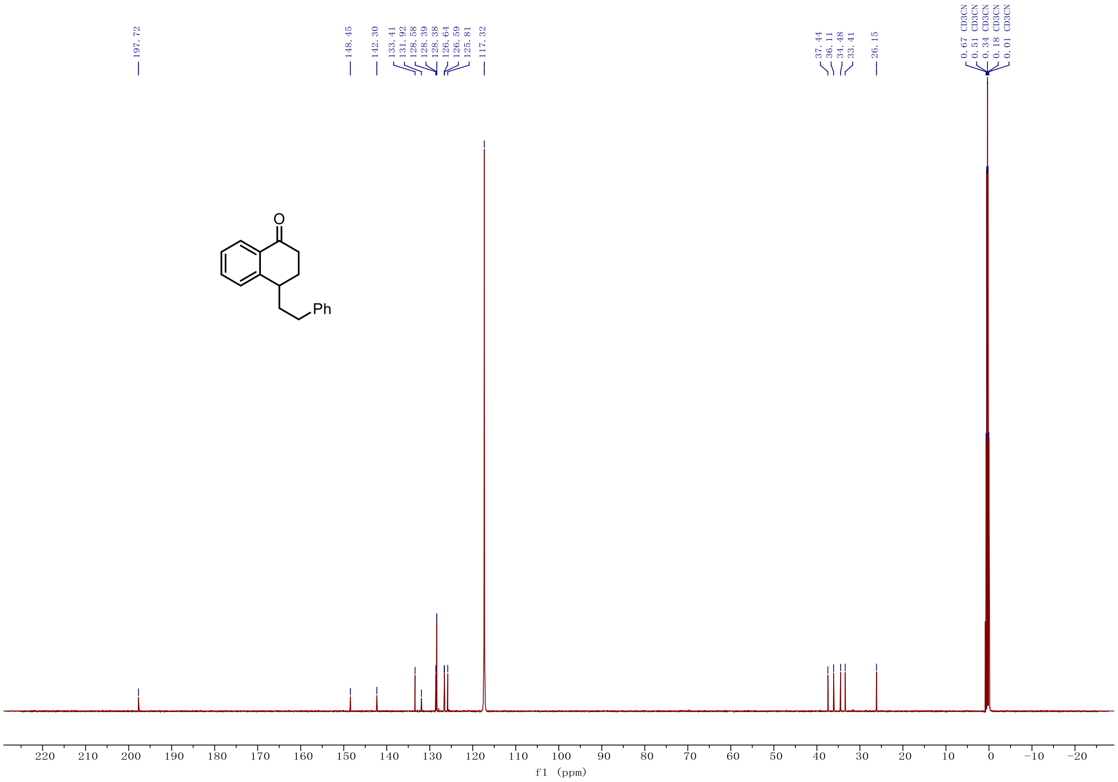
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Ph
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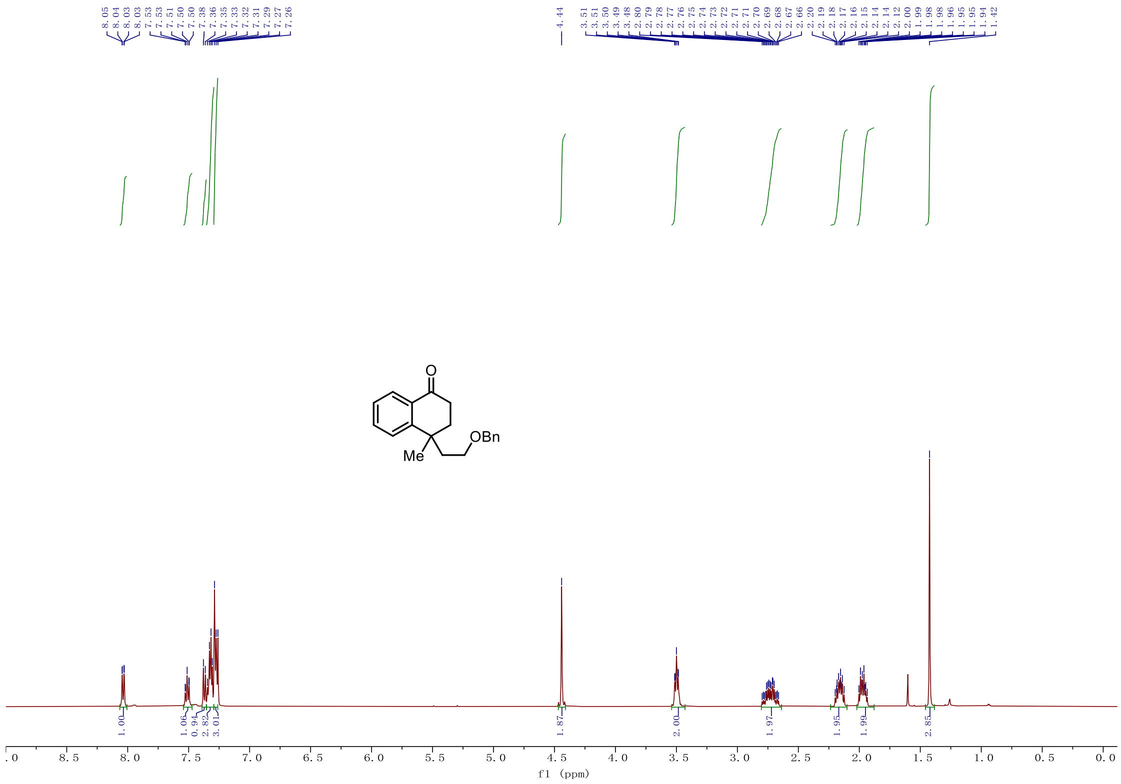
f1 (ppm)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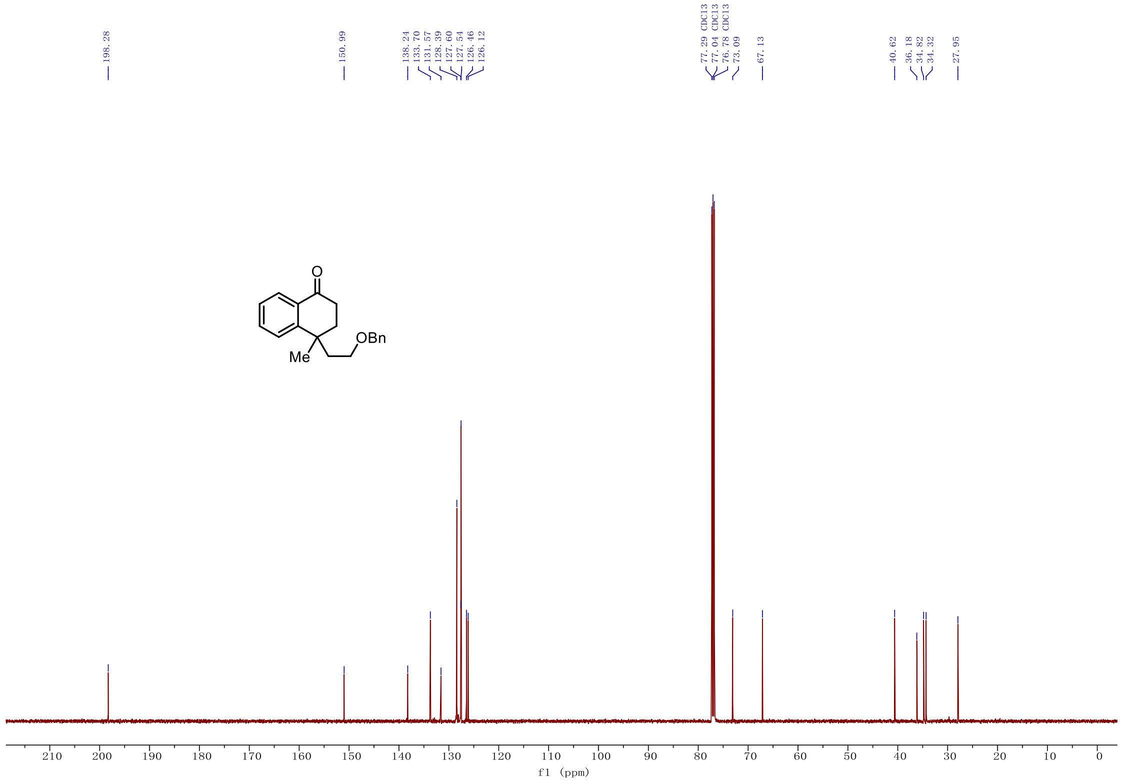
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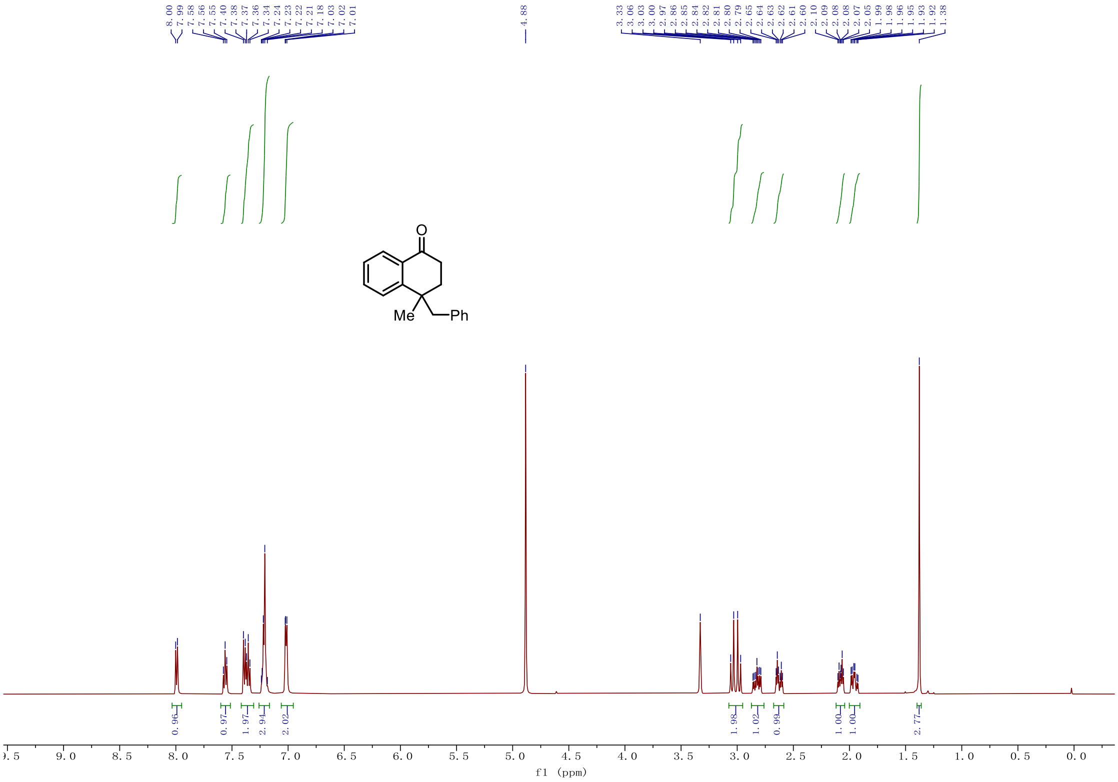
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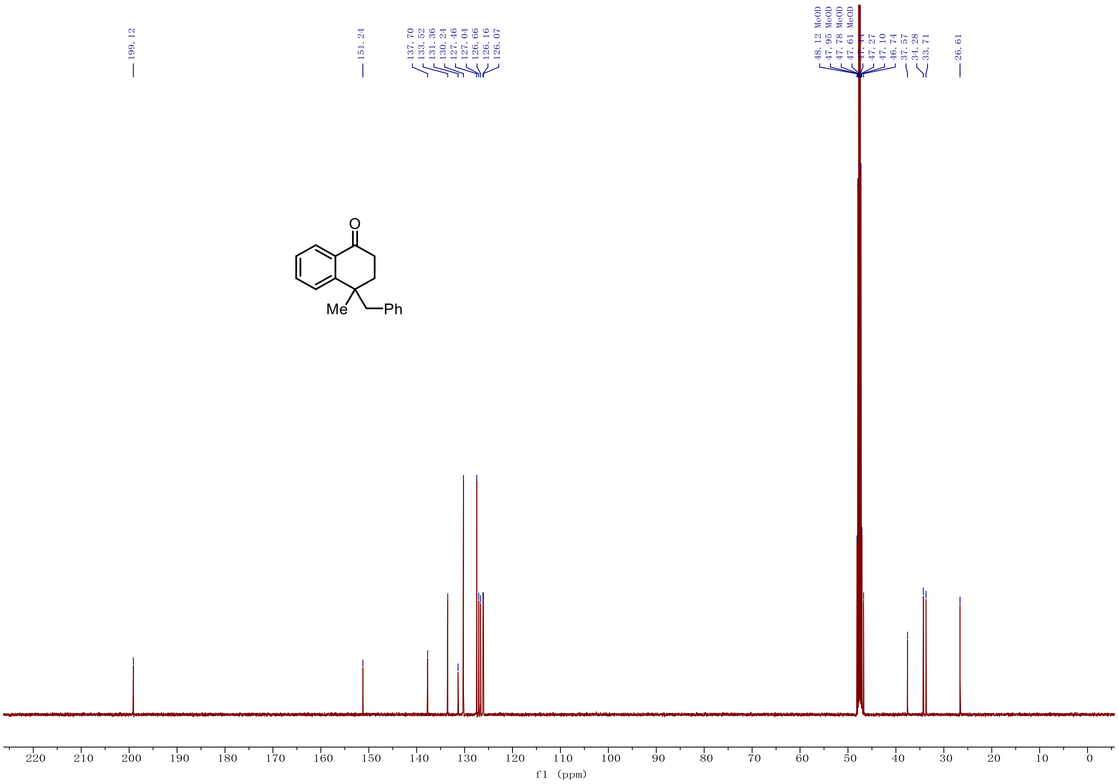
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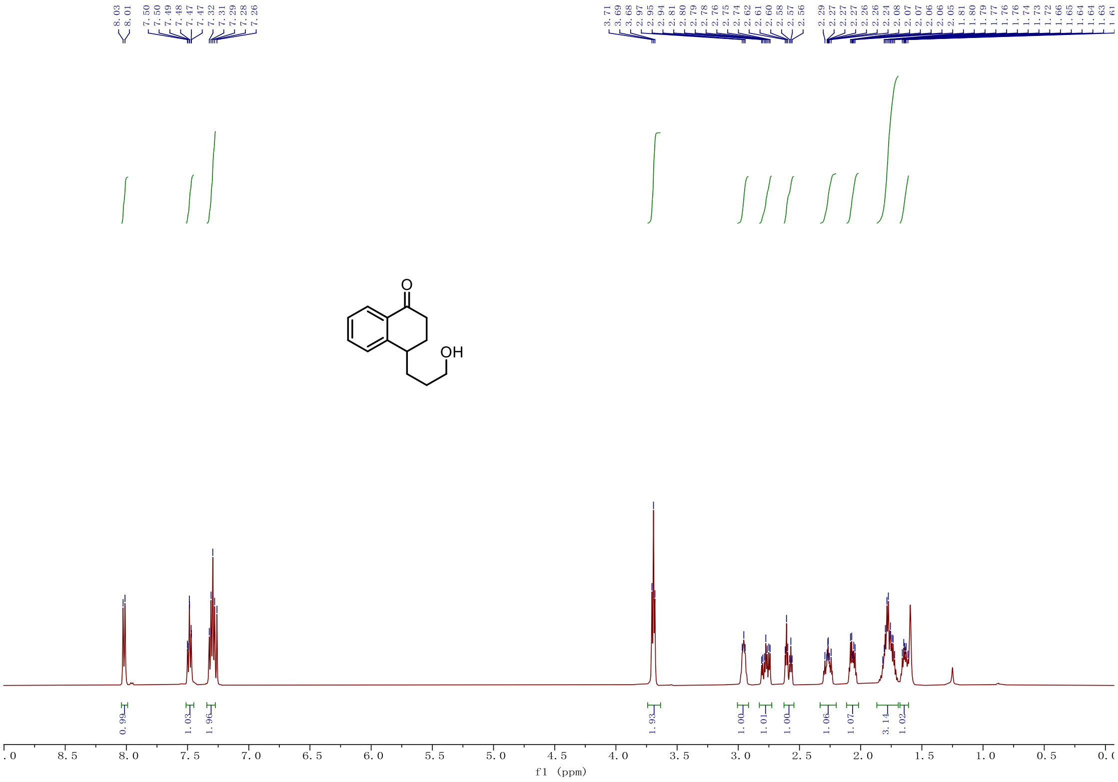
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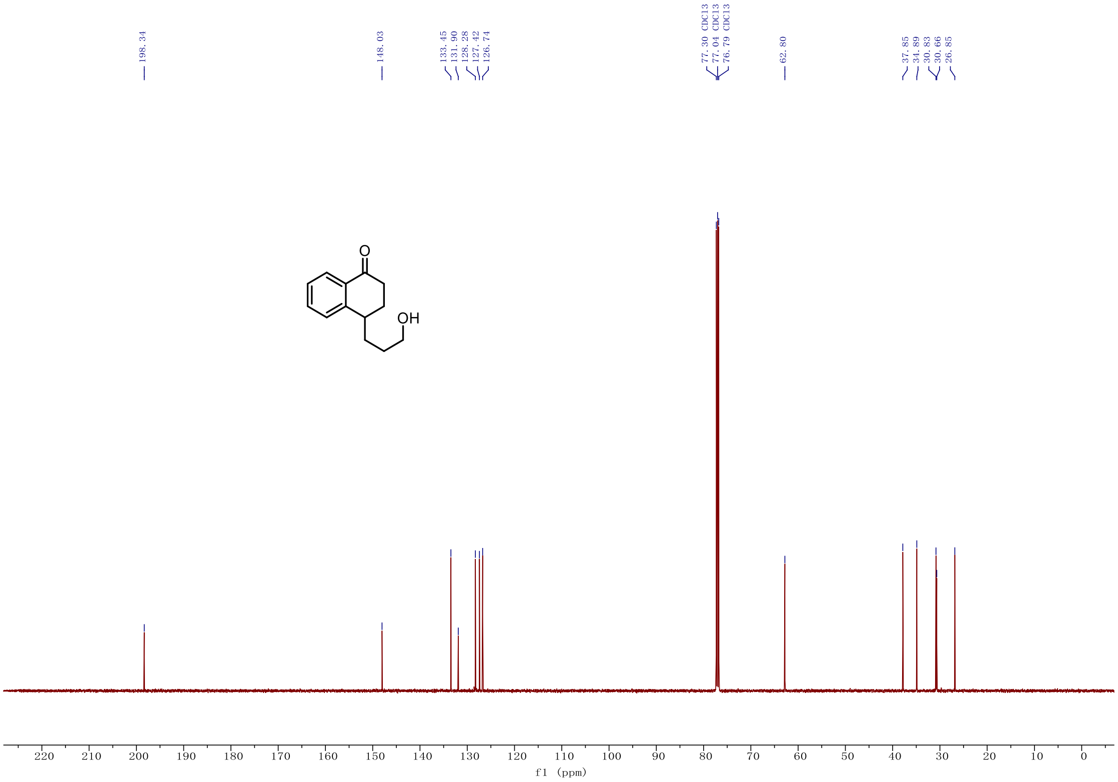
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O
OH
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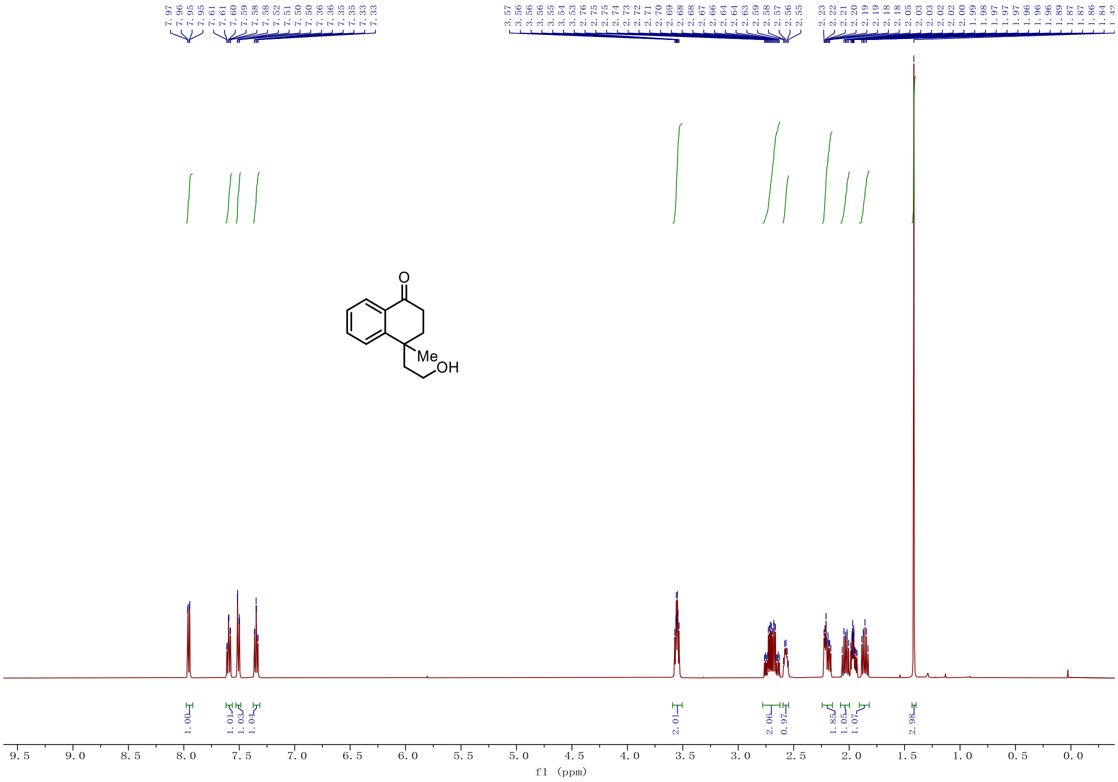
f1 (ppm)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1.89
1.87
1.87
1.86
1.84
1.42
O
Me
OH
1.00
1.01
1.03
1.04
2.01
2.06
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1.85
1.05
1.07
2.98
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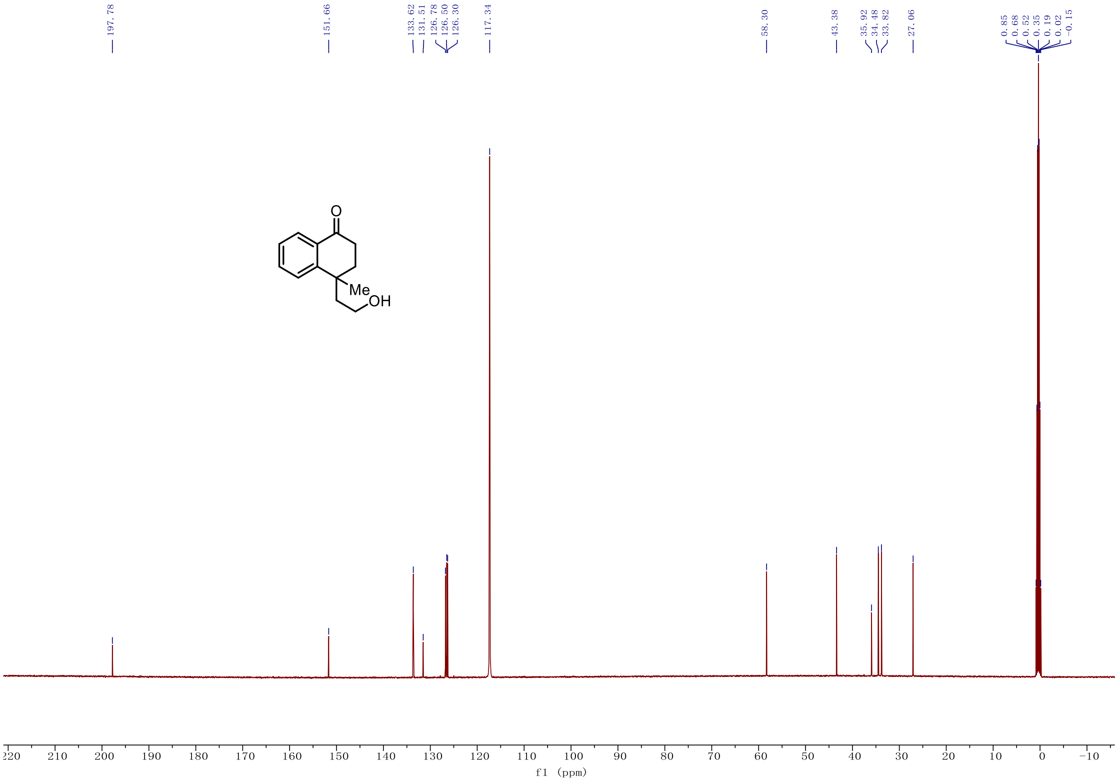
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33.82
27.06
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0.68
0.52
0.35
0.19
0.02
-0.15
O
Me
OH
220
210
200
190
180
170
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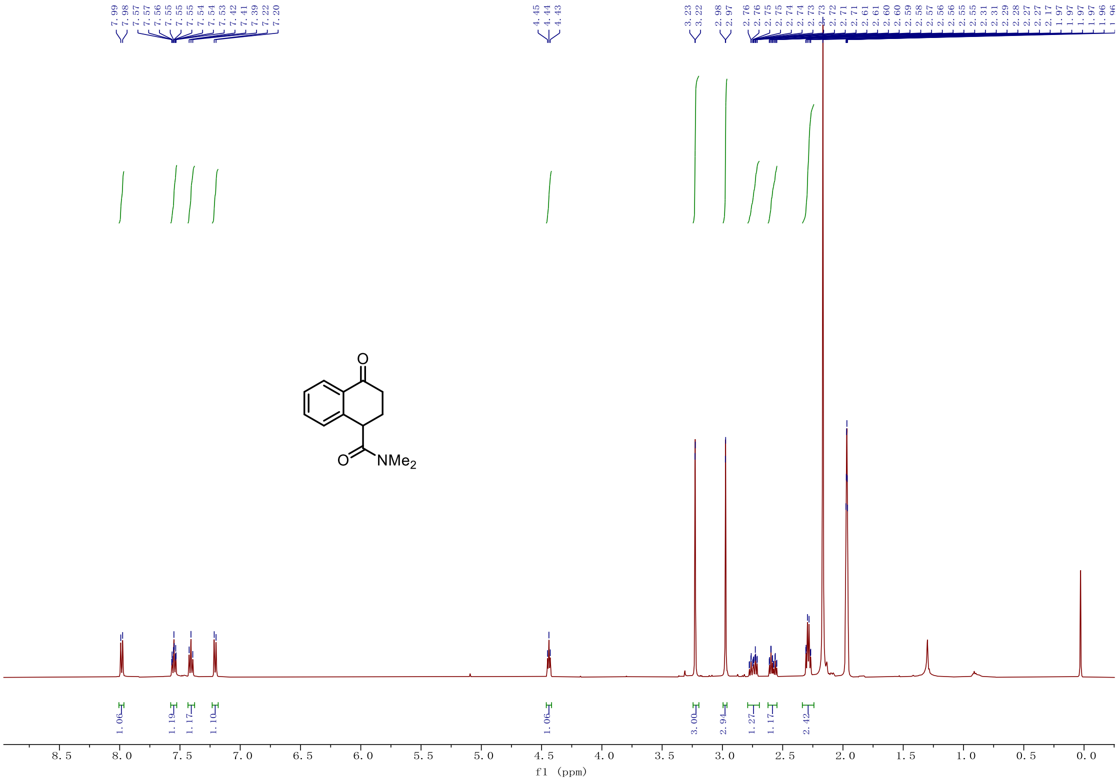
f1 (ppm)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3.23
3.22
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2.97
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2.76
2.75
2.75
2.74
2.74
2.73
2.73
2.72
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2.71
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2.61
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2.56
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2.31
2.29
2.28
2.27
2.27
2.17
1.97
1.97
1.97
1.97
1.96
O
NMe2
1.06
1.19
1.17
1.10
1.06
3.00
2.94
1.27
1.17
2.42
8.5
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7.0
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6.0
5.5
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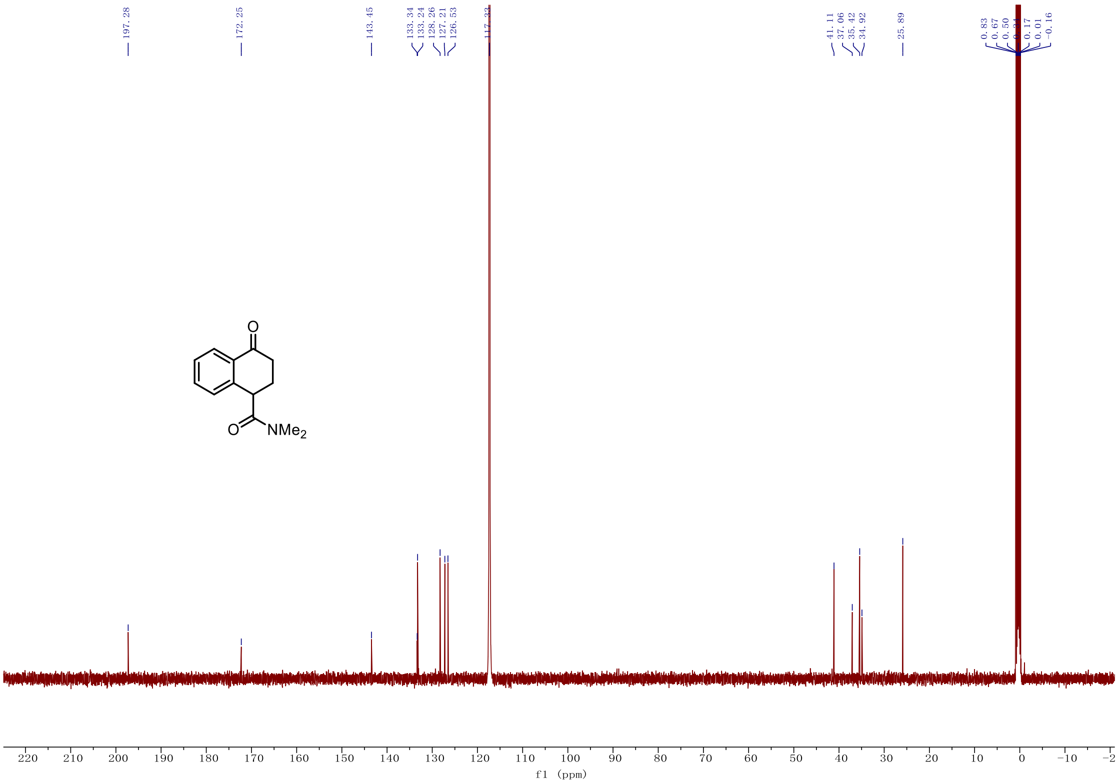
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35.42
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25.89
0.83
0.67
0.50
0.34
0.17
0.01
-0.16
O
NMe2
220
210
200
190
180
170
160
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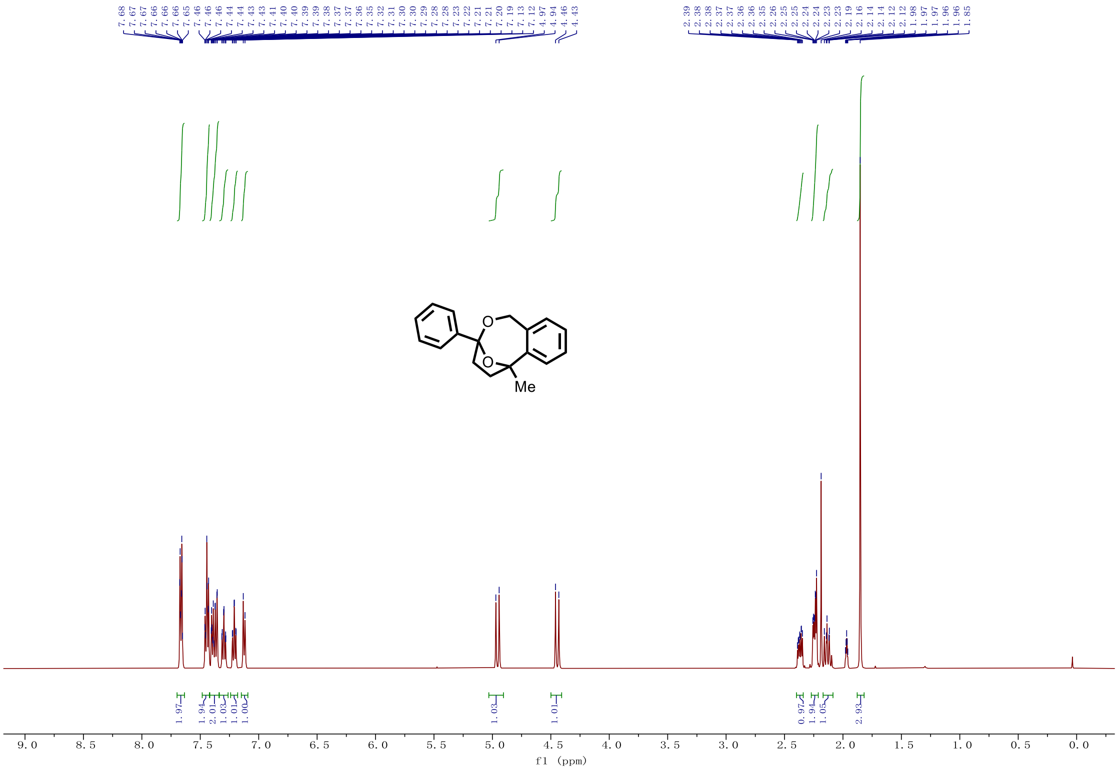
-2
f1 (ppm)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2.39 2.38 2.38 2.37 2.37 2.36 2.36 2.35 2.26 2.25 2.25 2.24 2.24 2.23 2.23 2.19 2.16 2.14 2.14 2.12 2.12 1.98 1.97 1.97 1.96 1.96 1.85
O
O
Me
1.97 1.94 2.01 1.03 1.01 1.00 1.03 1.01 0.97 1.94 1.05 2.93
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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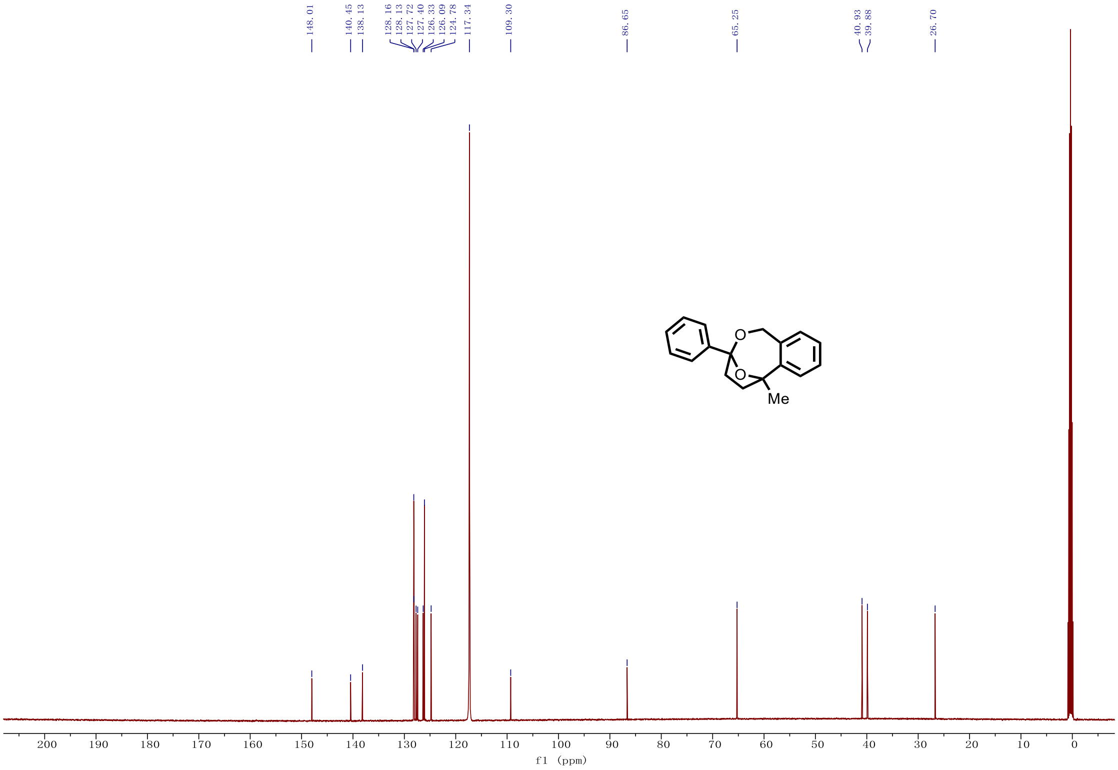
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109.30
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26.70
O
O
Me
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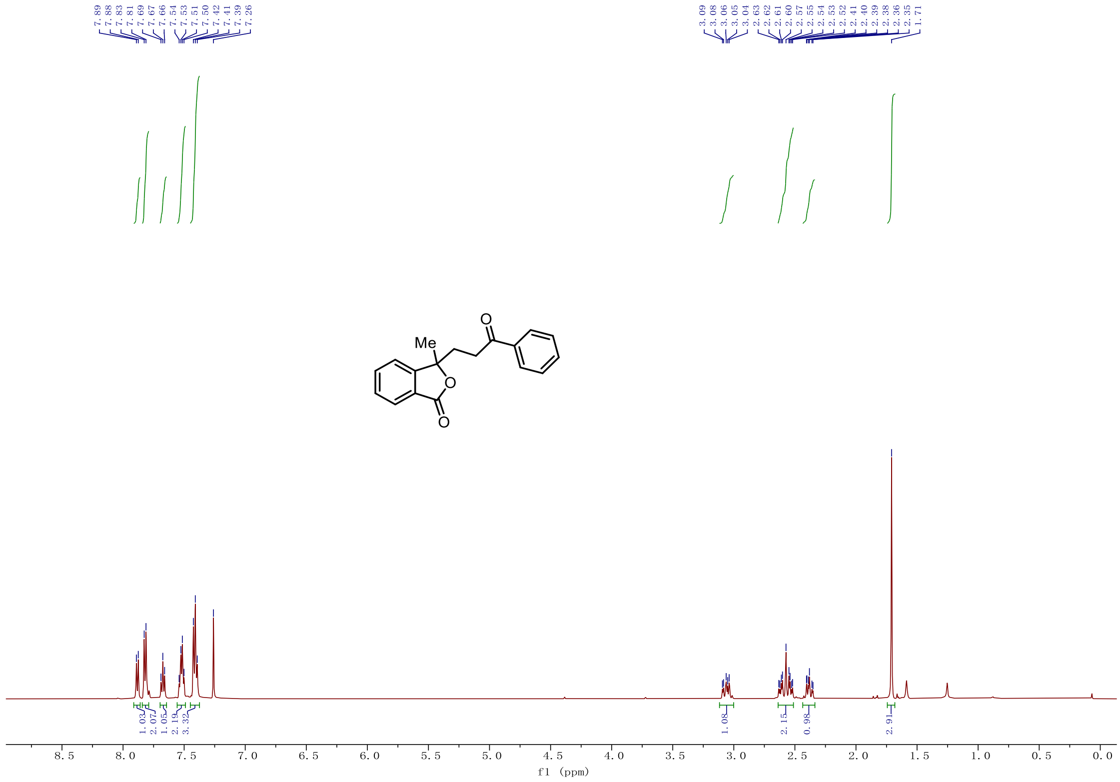
f1 (ppm)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7.51
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7.41
7.39
7.26
3.09
3.08
3.06
3.05
3.04
2.63
2.62
2.61
2.60
2.57
2.55
2.54
2.53
2.52
2.41
2.40
2.39
2.38
2.36
2.35
1.71
Me
O
O
O
1.03
2.07
1.05
2.19
3.32
1.08
2.15
0.98
2.91
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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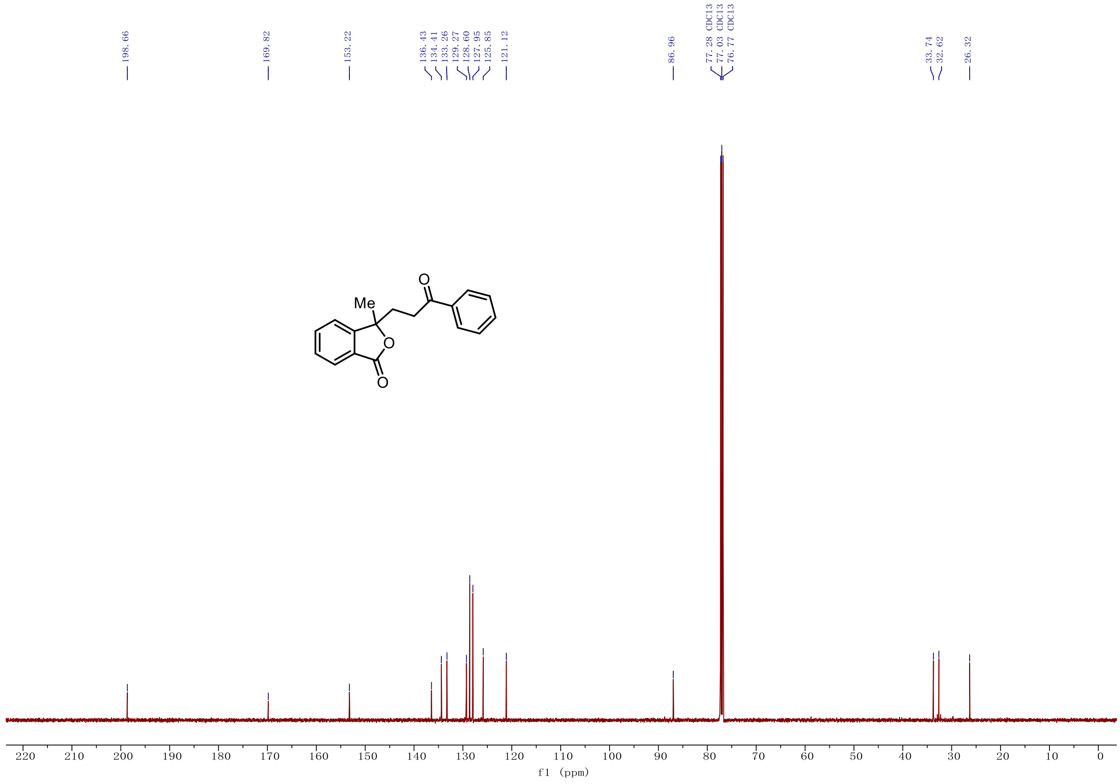
0.0
f1 (ppm)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125.85
121.12
86.96
77.28 CDCl3
77.03 CDCl3
76.77 CDCl3
33.74
32.62
26.32
Me
O
O
O
220
210
200
190
180
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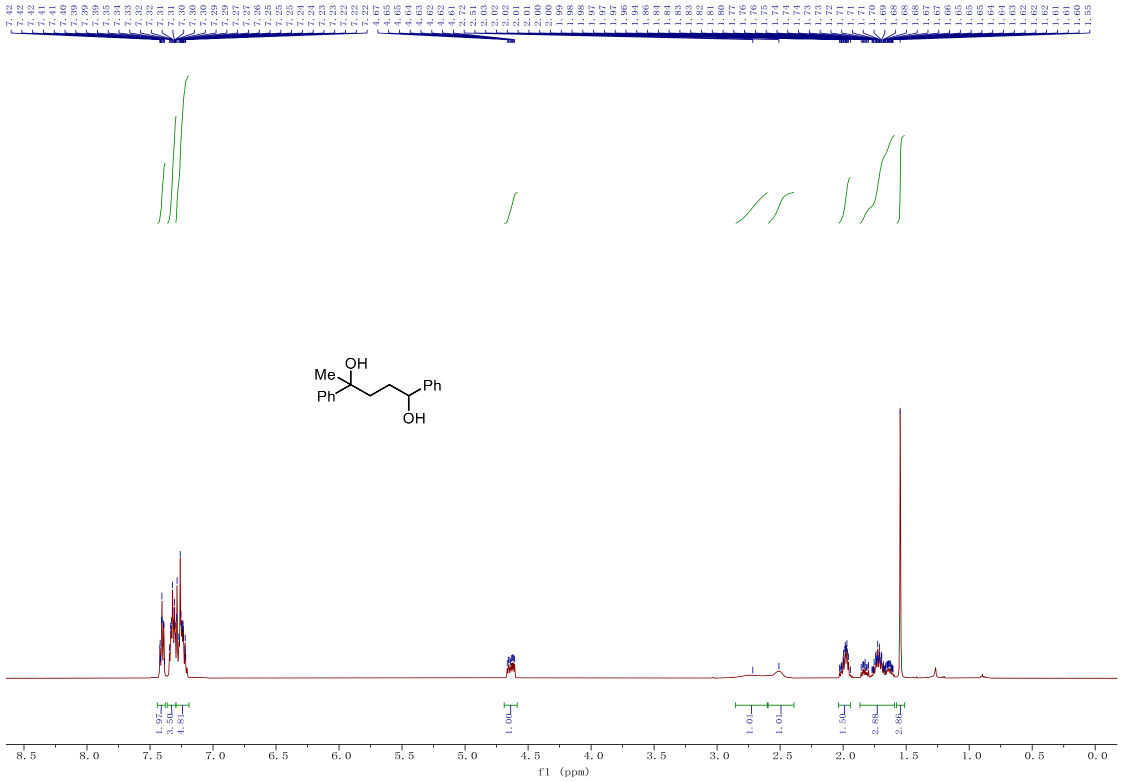
f1 (ppm)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1.83
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OH
Ph
Ph
OH
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3.50
4.81
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1.01
1.50
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2.86
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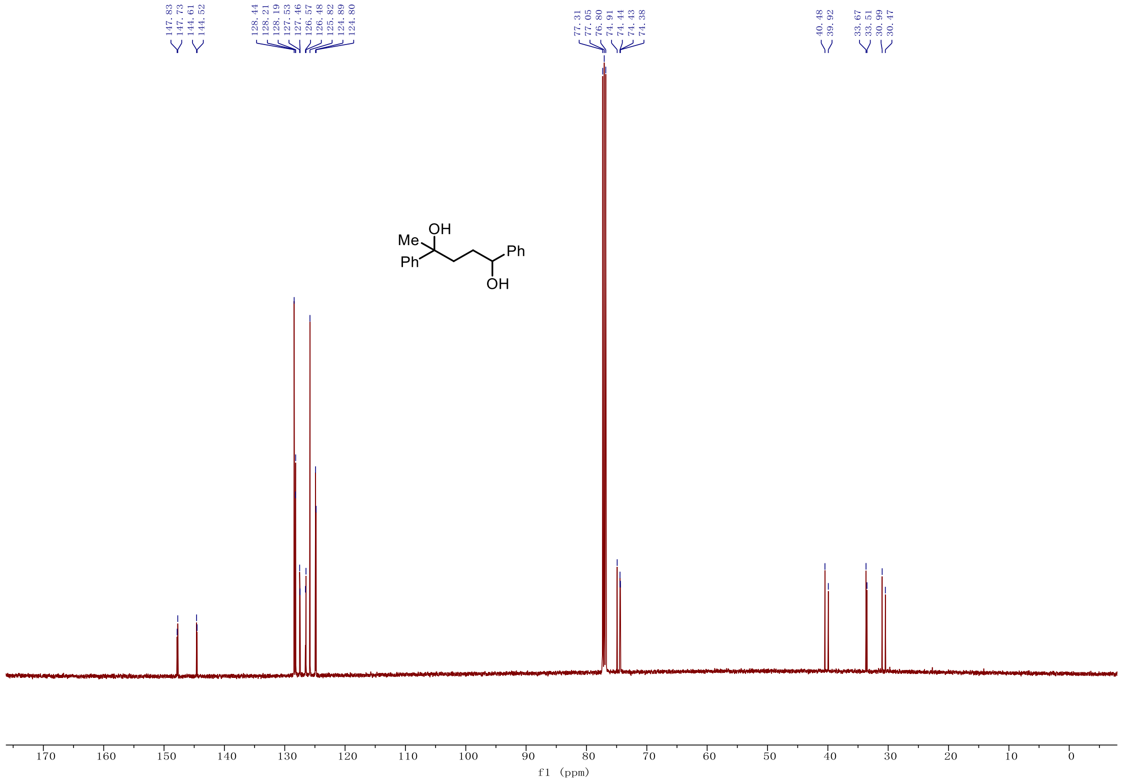
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124.80
77.31
77.05
76.80
74.91
74.44
74.43
74.38
40.48
39.92
33.67
33.51
30.99
30.47
Me
OH
Ph
Ph
OH
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150
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130
120
110
100
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70
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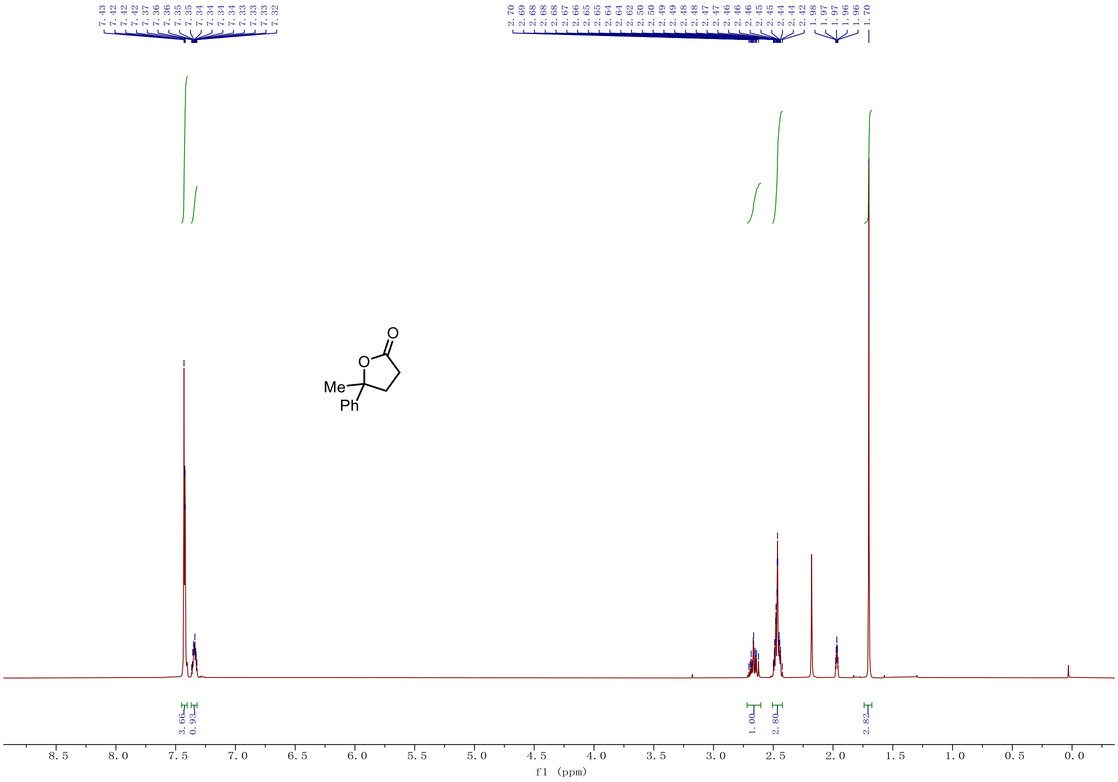
f1 (ppm)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7.33
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2.68
2.67
2.66
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2.46
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2.45
2.44
2.44
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1.97
1.97
1.96
1.96
1.70
O
O
Me
Ph
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1.00
2.80
2.82
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8.0
7.5
7.0
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6.0
5.5
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2.5
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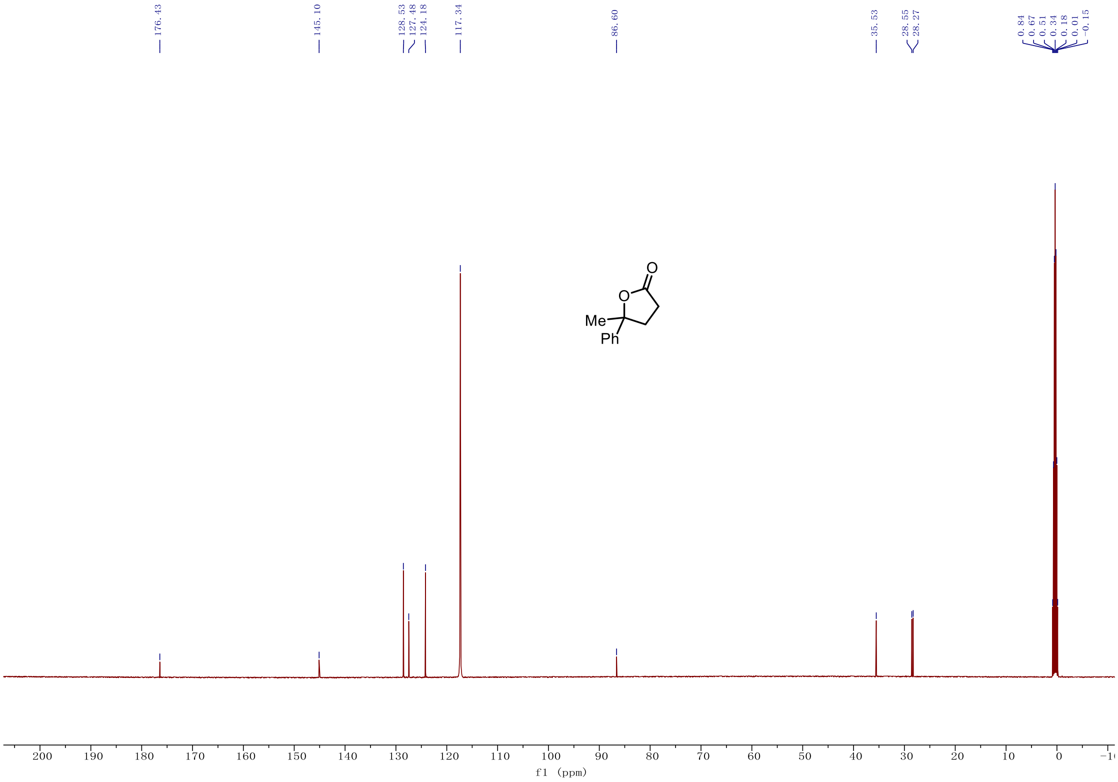
0.0
f1 (ppm)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0.18
0.01
-0.15
O
O
Me
Ph
200
190
180
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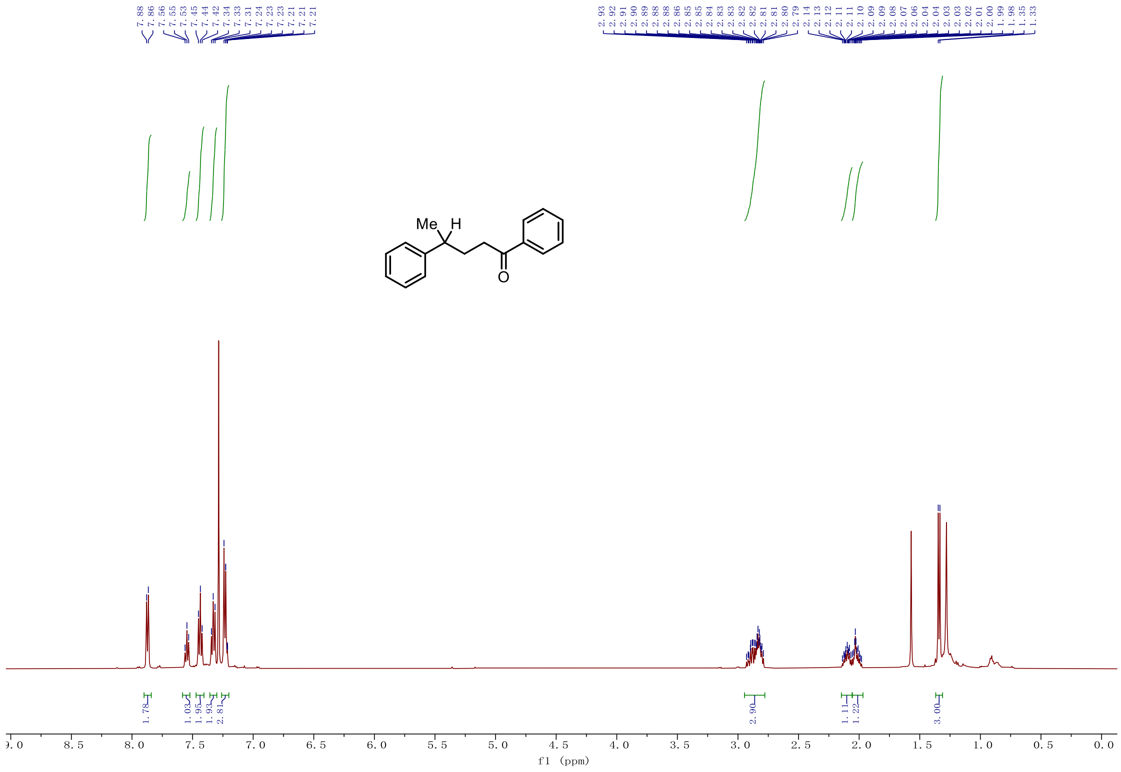
f1 (ppm)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2.85
2.85
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2.83
2.82
2.82
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2.81
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2.01
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3.5
3.0
2.5
2.0
1.5
1.0
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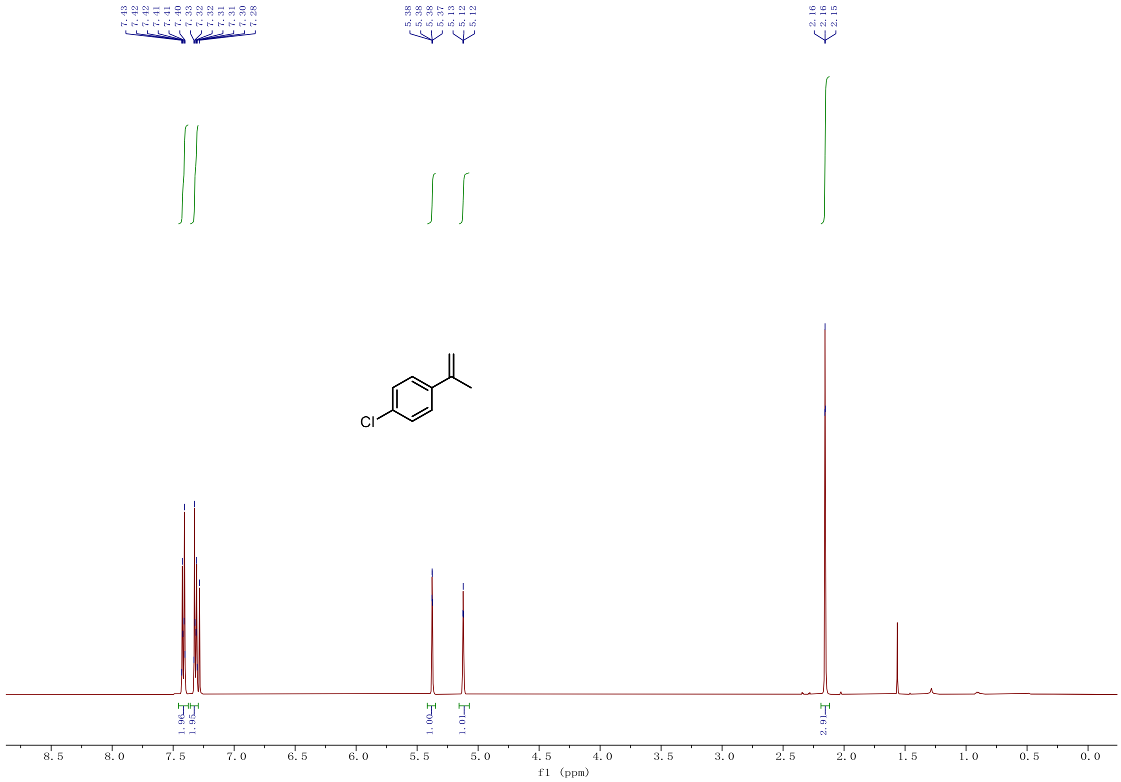
f1 (ppm)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5.38
5.38
5.37
5.13
5.12
5.12
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2.16
2.15
Cl
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1.95
1.00
1.01
2.91
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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3.0
2.5
2.0
1.5
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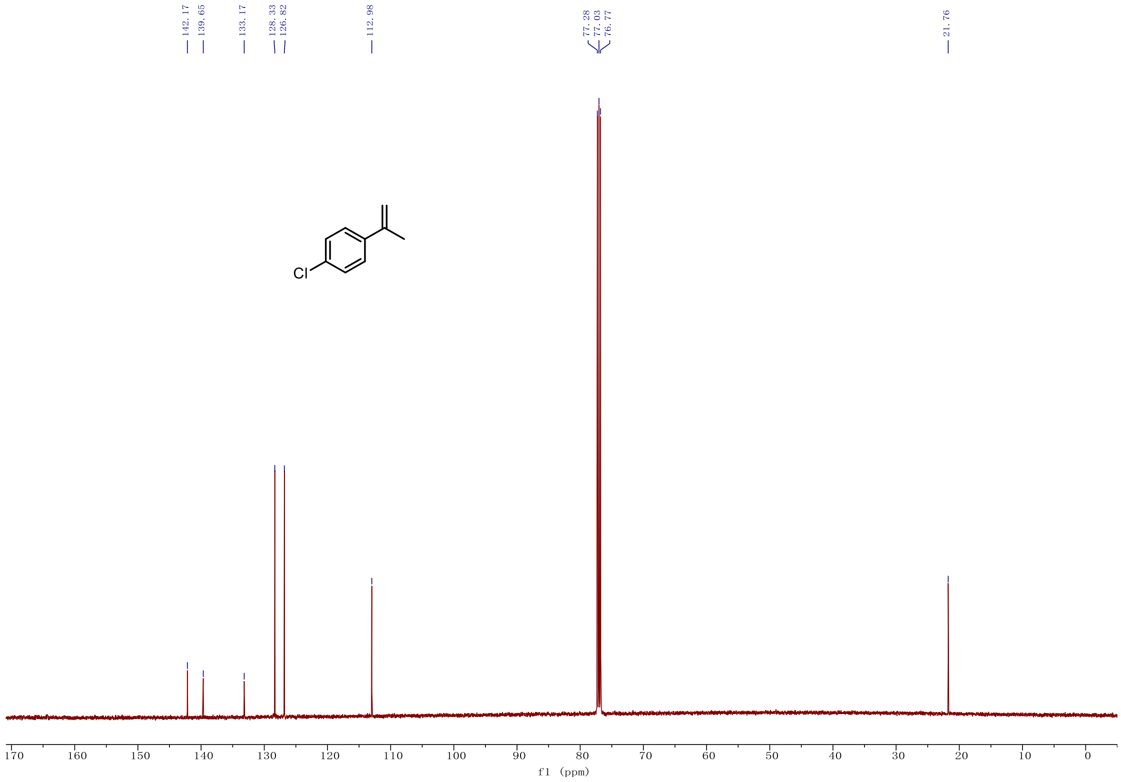
f1 (ppm)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77.03
76.77
21.76
Cl
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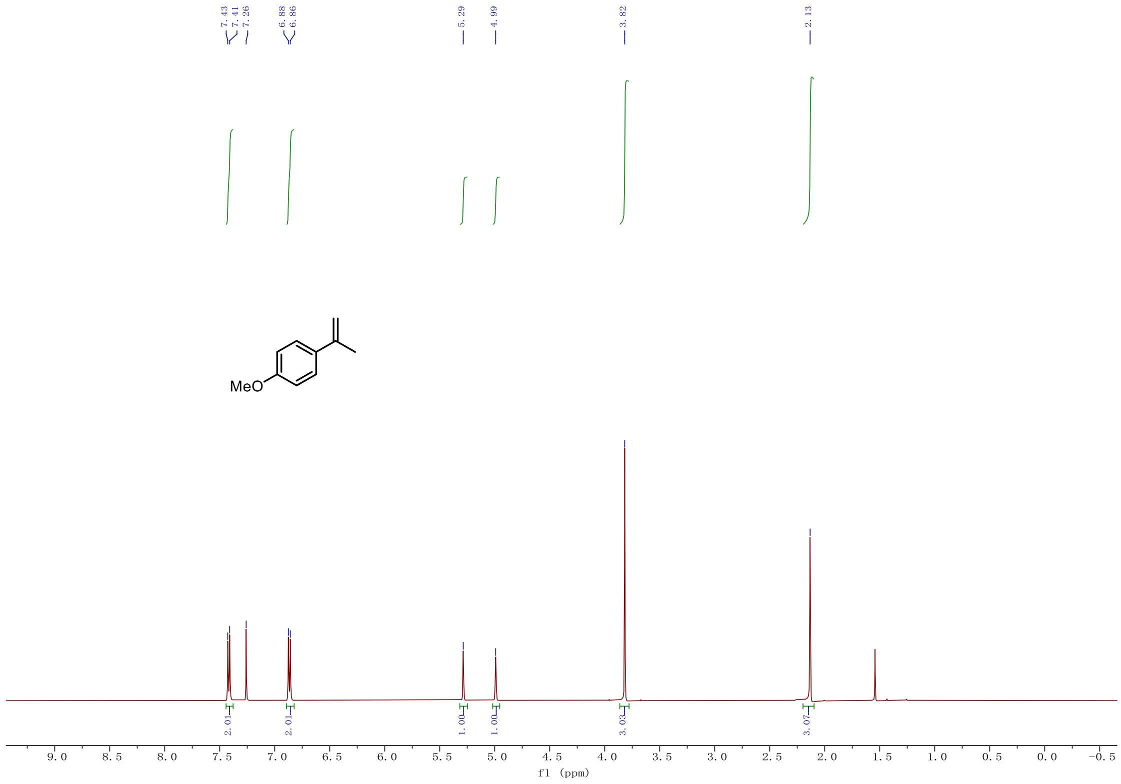
f1 (ppm)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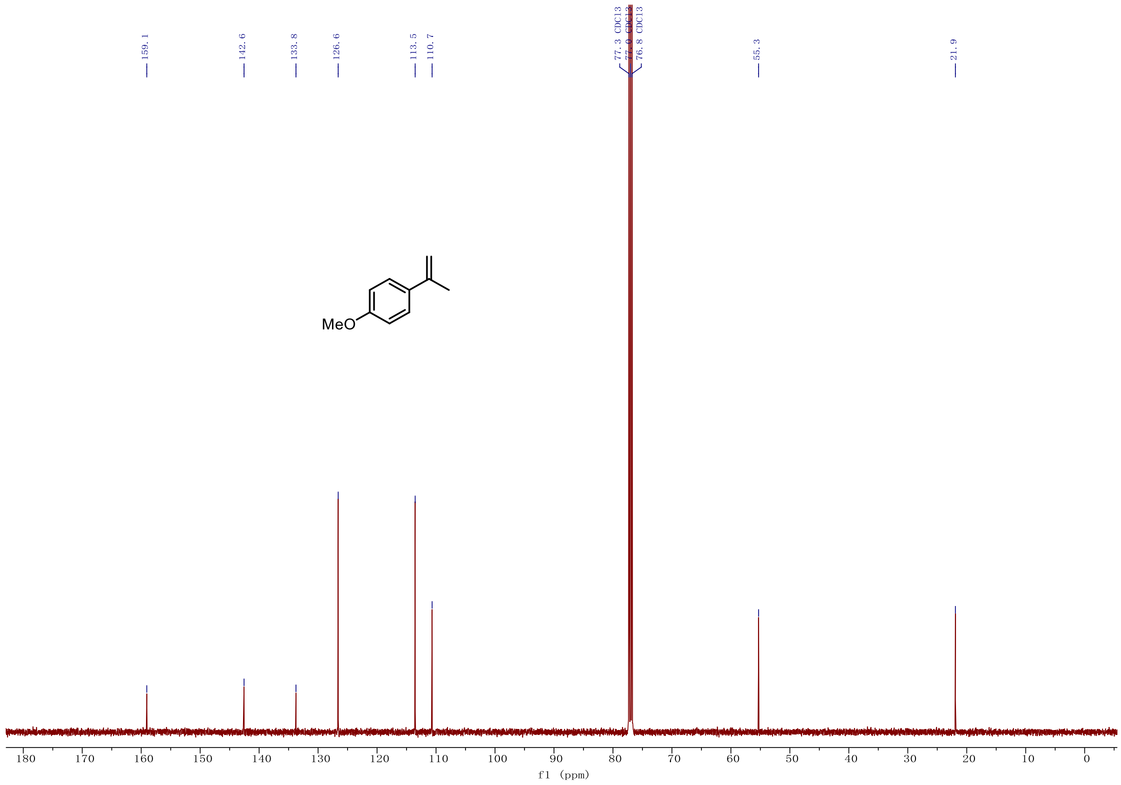
MeO
2.01
2.01
1.00
1.00
3.03
3.07
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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76.8 CDCl3
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MeO
180
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110
100
90
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70
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50
40
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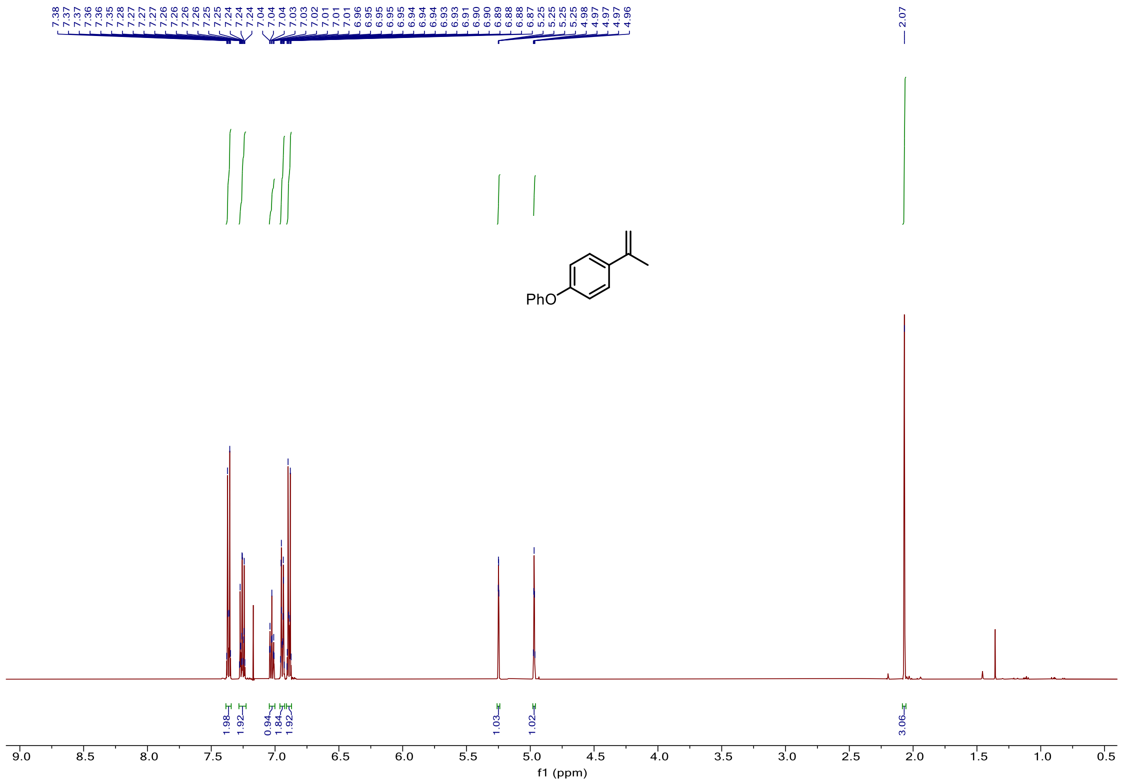
f1 (ppm)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7.04
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7.03
7.02
7.01
7.01
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5.25
5.25
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4.97
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PhO
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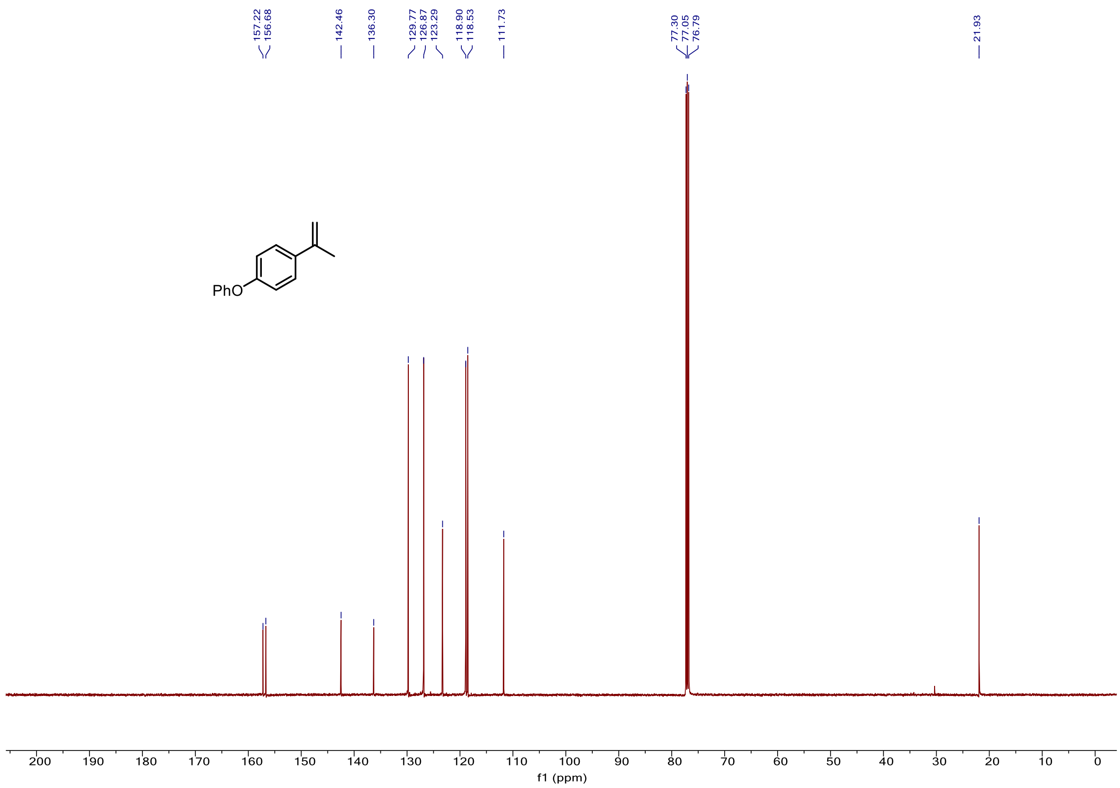
0.5
f1 (ppm)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21.93
PhO
200
190
180
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110
100
90
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50
40
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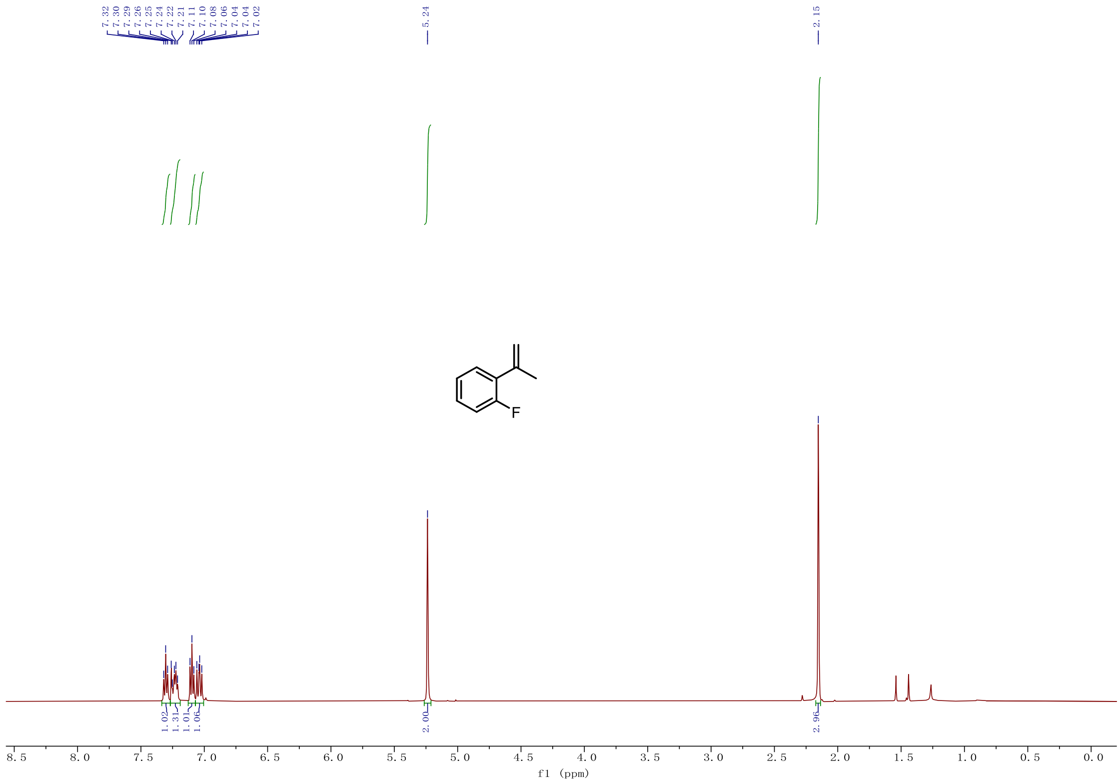
20
10
0
f1 (ppm)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7.04
7.04
7.02
5.24
2.15
F
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1.01
1.06
2.00
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2.0
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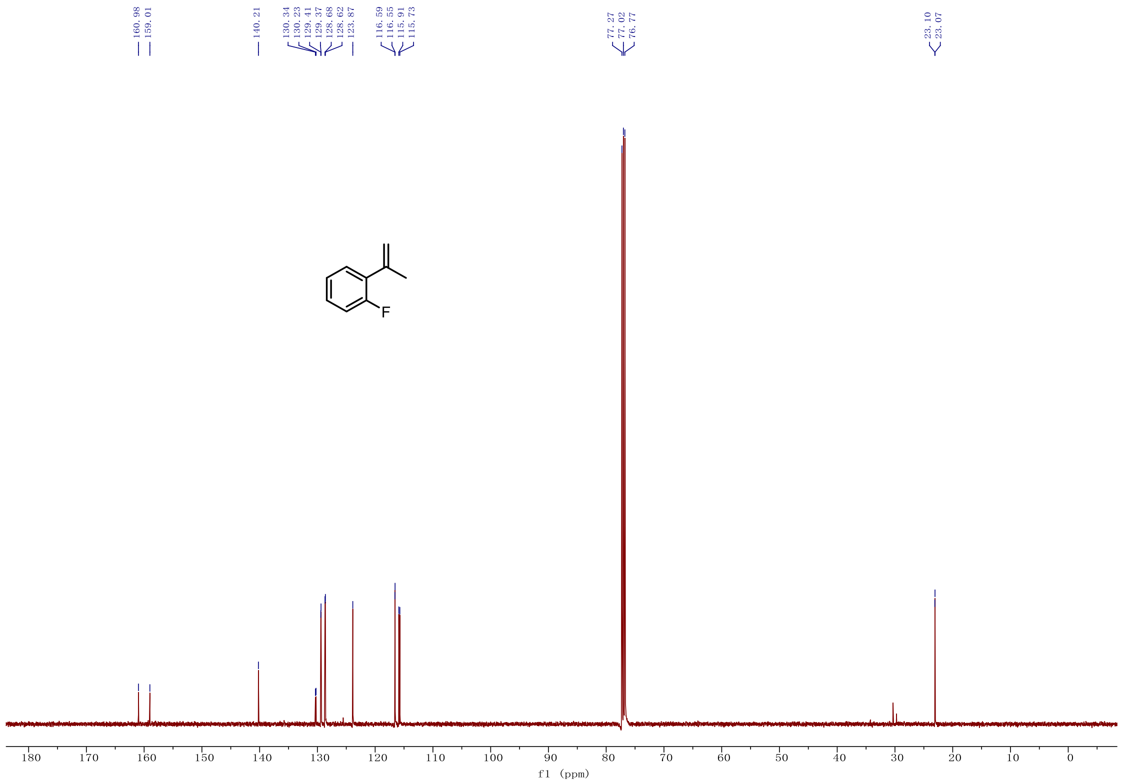
0.0
f1 (ppm)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123.87
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115.91
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76.77
23.10
23.07
F
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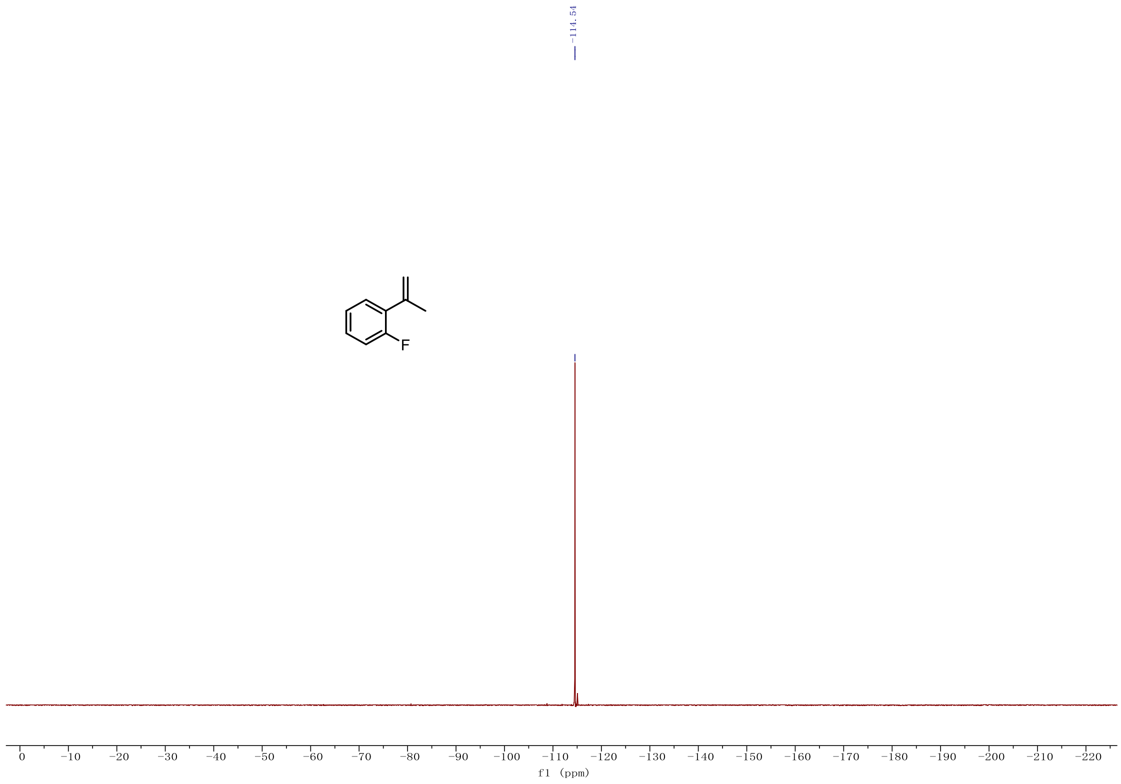
f1 (ppm)


-114.54
F
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
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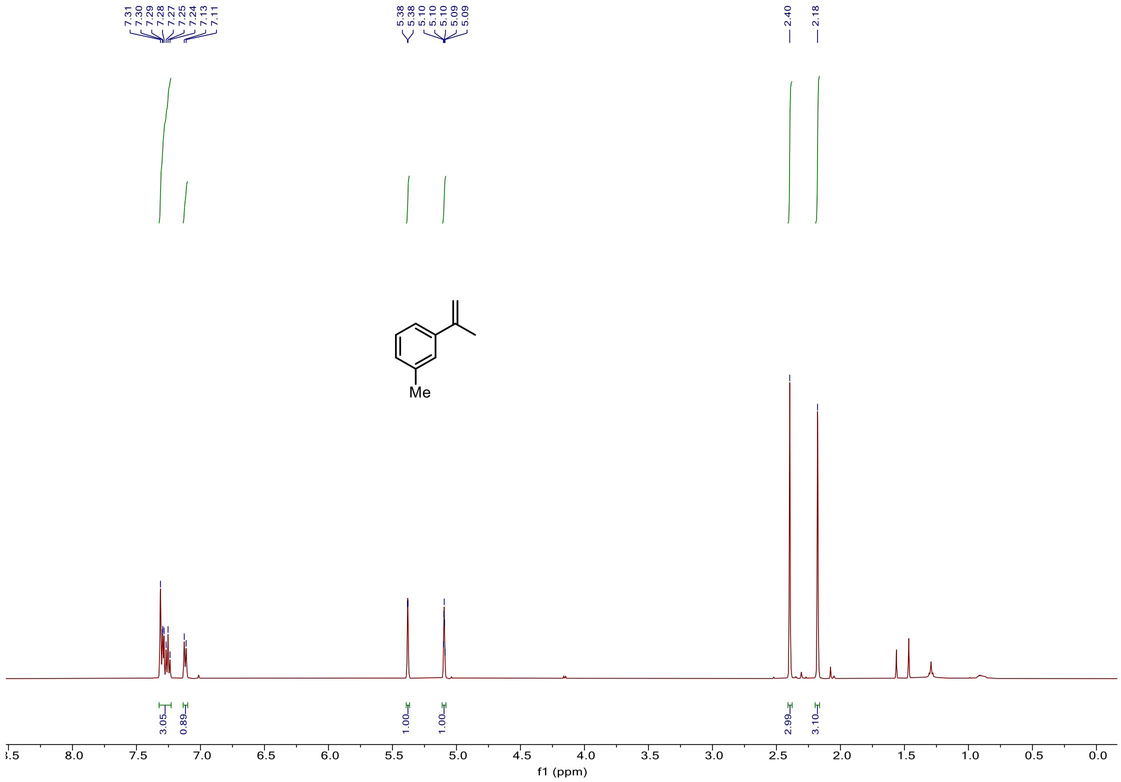
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5.10
5.09
5.09
2.40
2.18
Me
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0.89
1.00
1.00
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6.0
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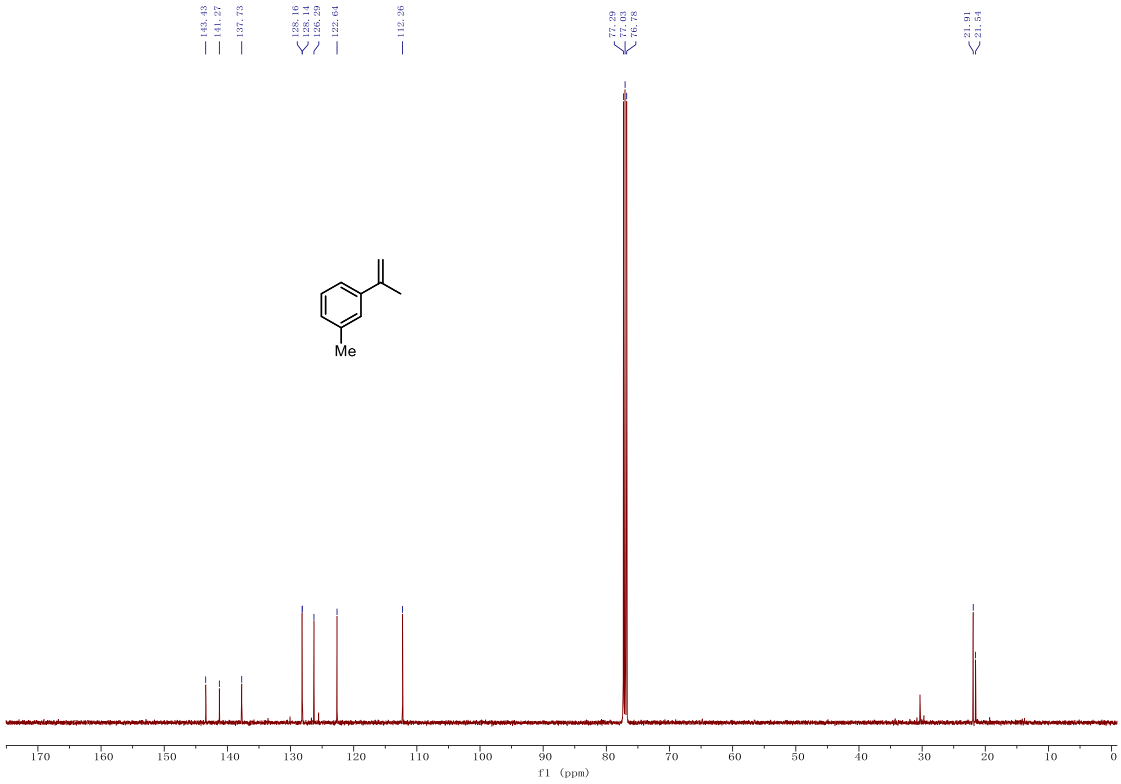
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77.03
76.78
21.91
21.54
Me
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
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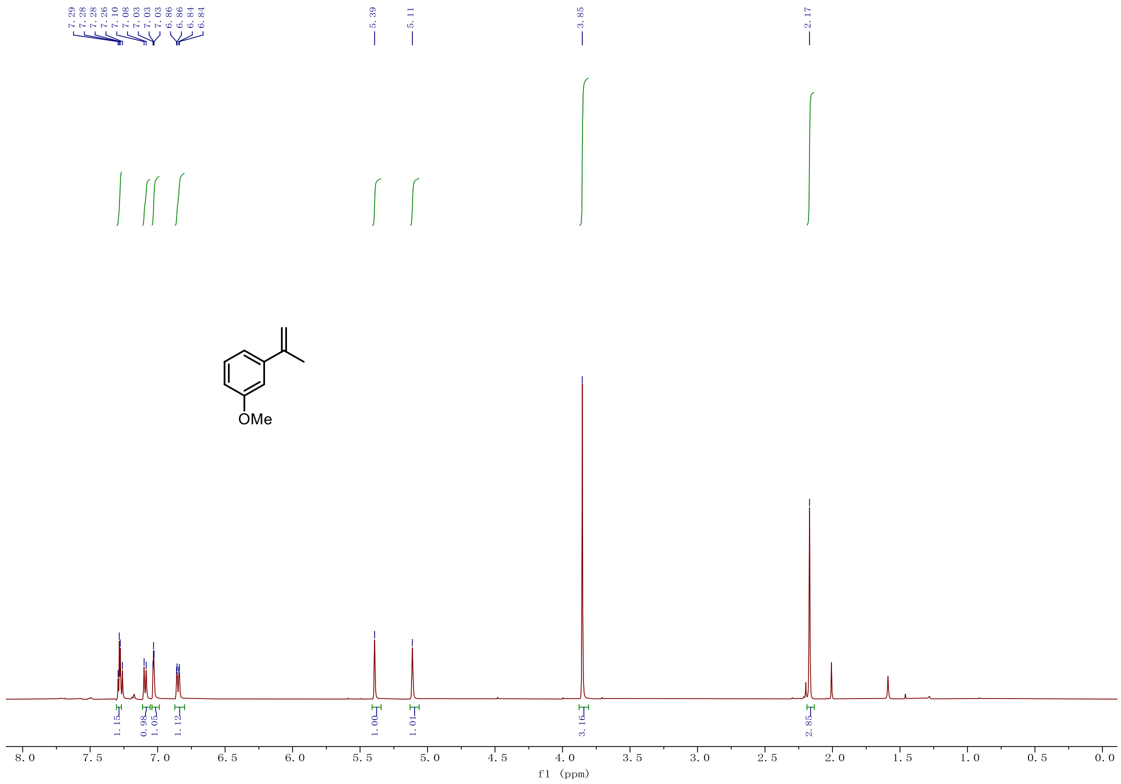
f1 (ppm)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6.84
5.39
5.11
3.85
2.17
OMe
1.15
0.98
1.05
1.12
1.00
1.01
3.16
2.85
8.0
7.5
7.0
6.5
6.0
5.5
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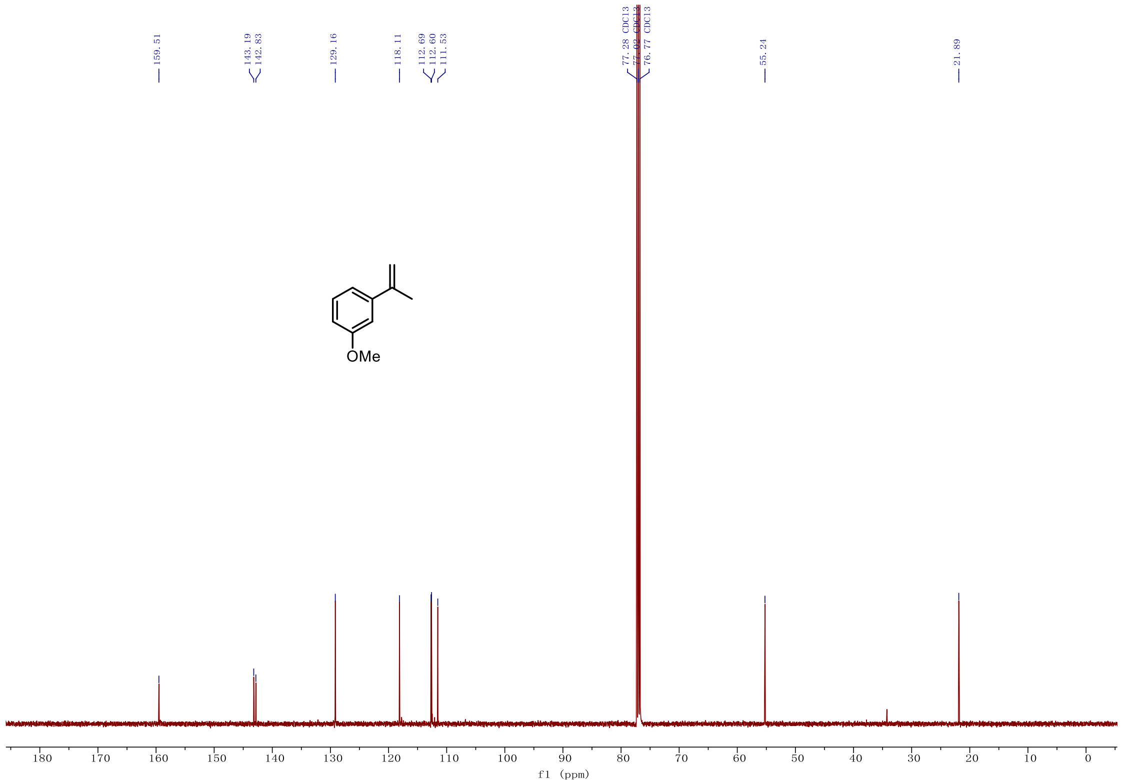
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55.24
21.89
OMe
180
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50
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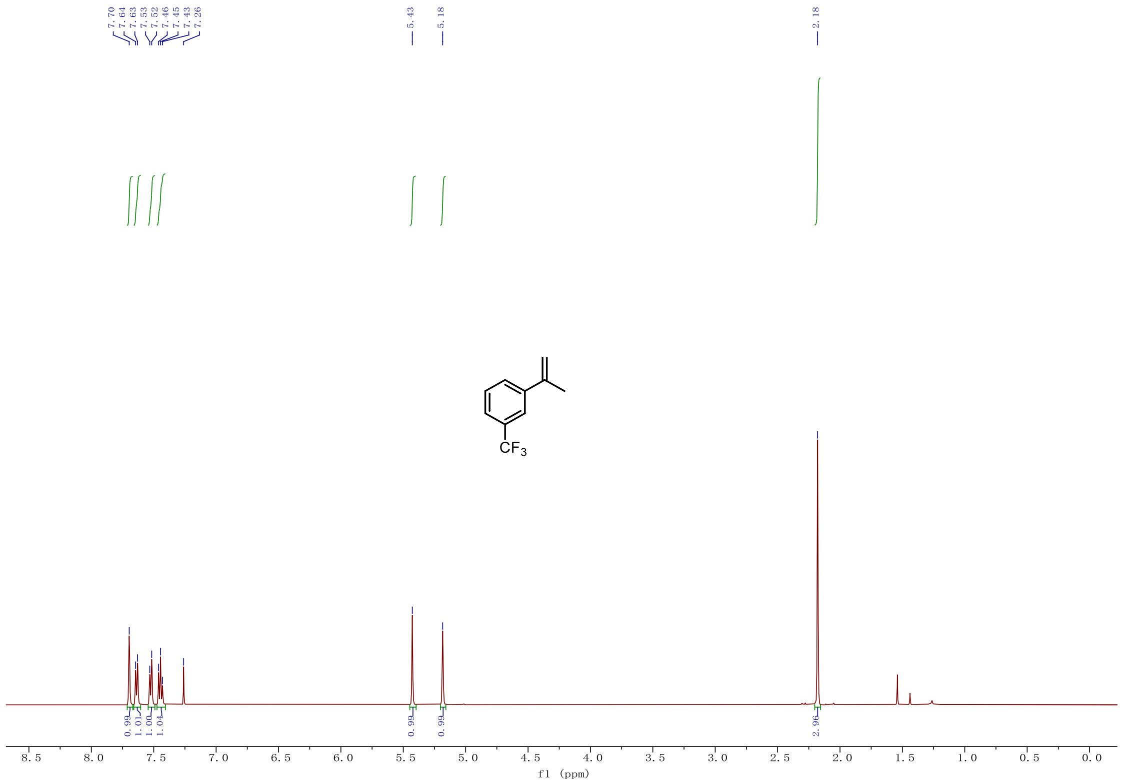
10
0
f1 (ppm)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CF3
0.99
1.01
1.00
1.04
0.99
0.99
2.96
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6.5
6.0
5.5
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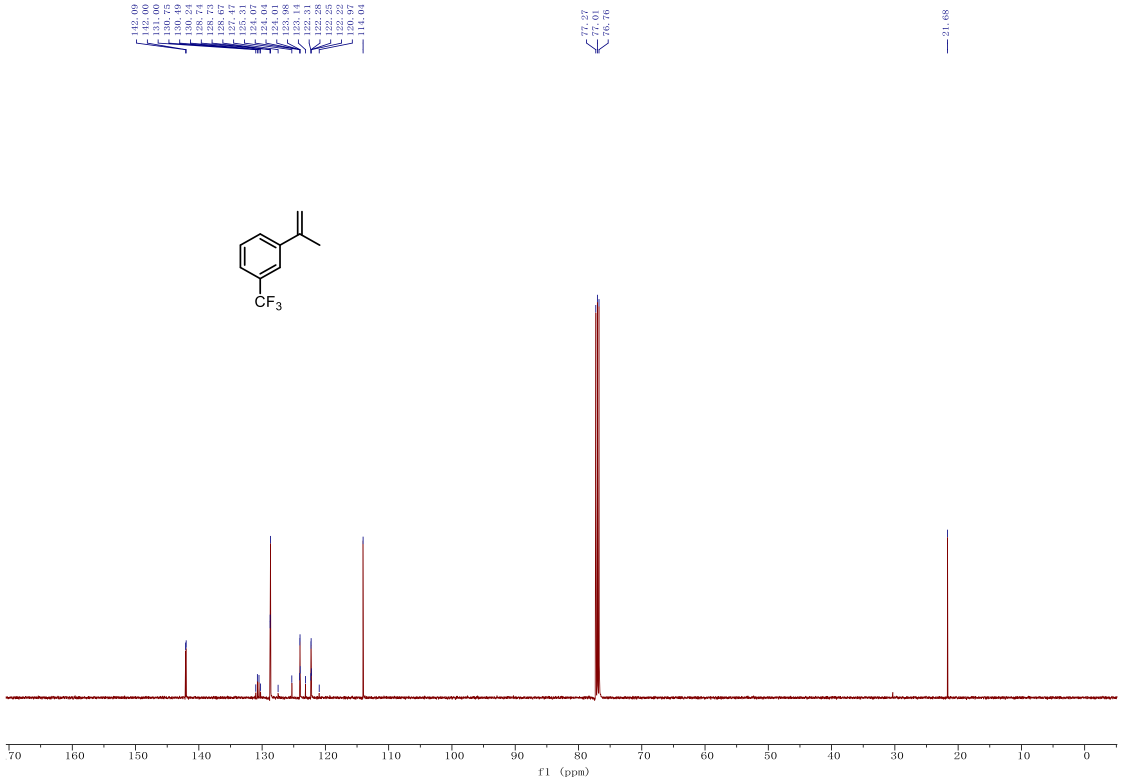
f1 (ppm)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124.04
124.01
123.98
123.14
122.31
122.28
122.25
122.22
120.97
114.04
77.27
77.01
76.76
21.68
CF3
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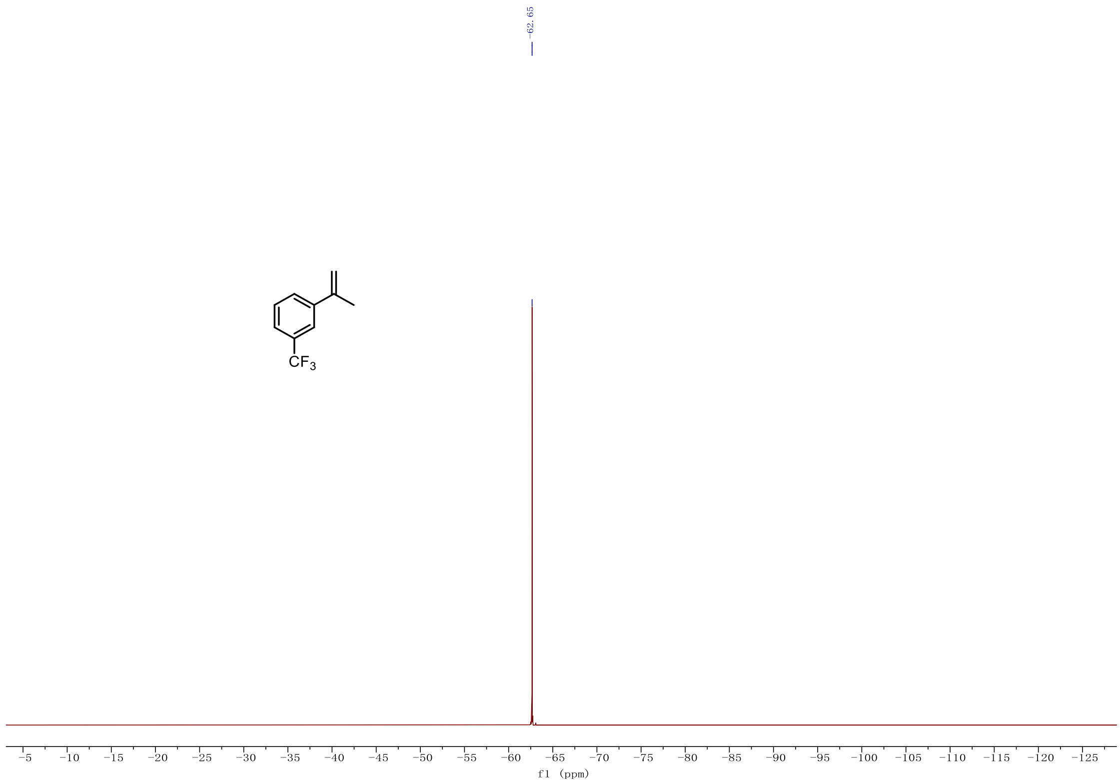
0
f1 (ppm)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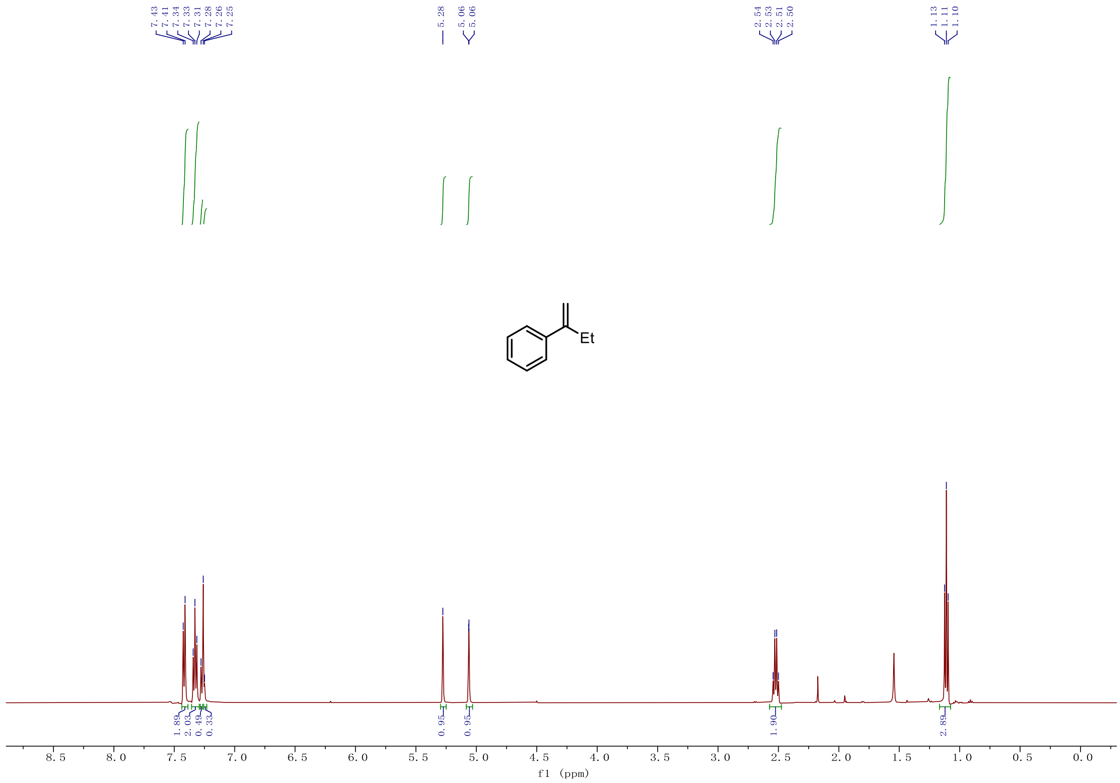
f1 (ppm)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2.51
2.50
1.13
1.11
1.10
Et
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2.03
0.49
0.33
0.95
0.95
1.90
2.89
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7.5
7.0
6.5
6.0
5.5
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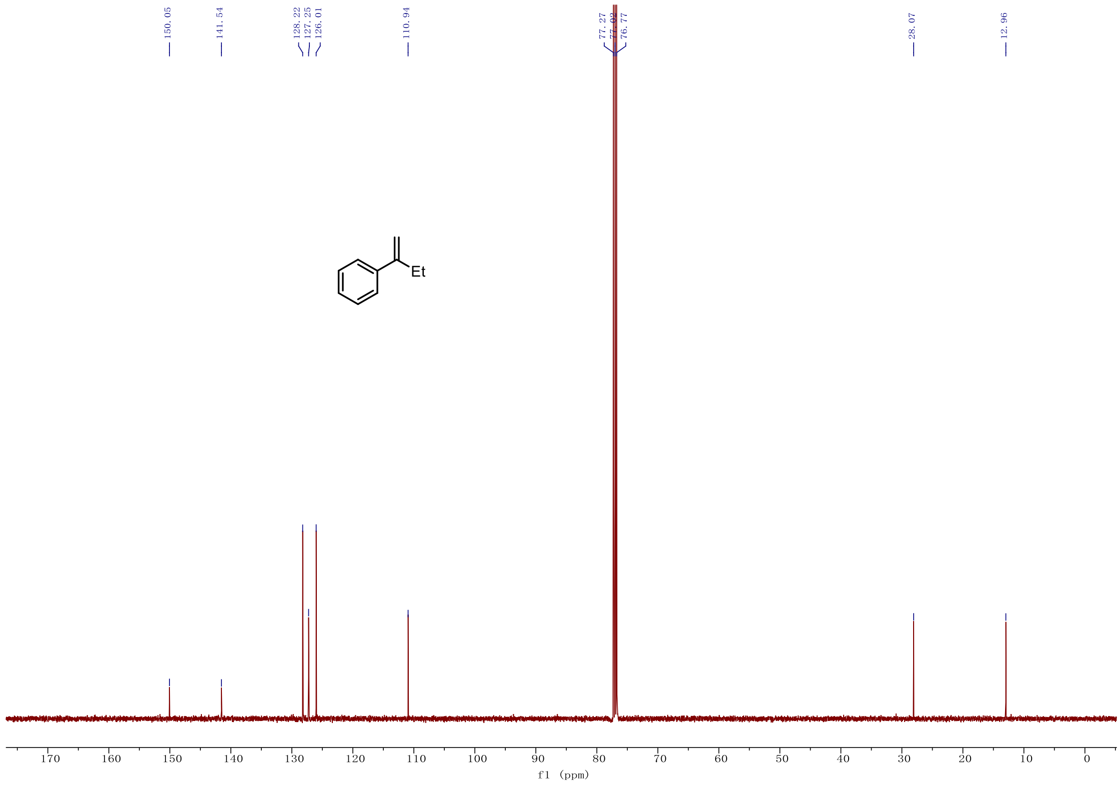
f1 (ppm)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12.96
Et
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150
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20
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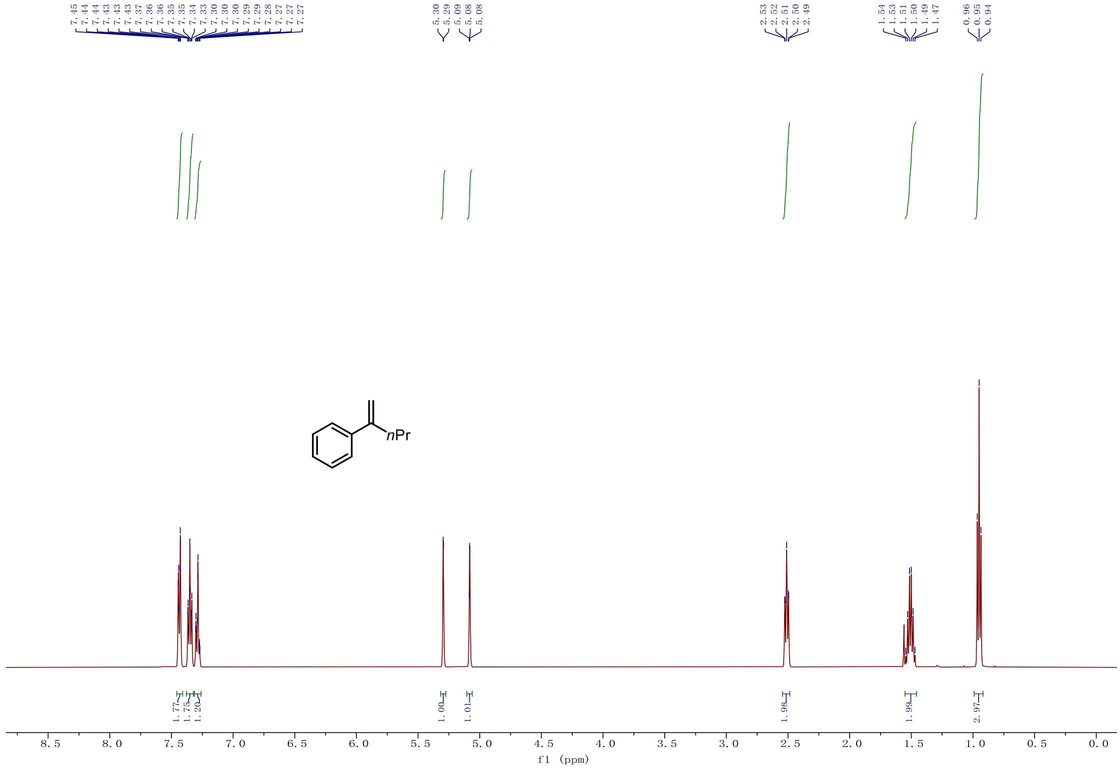
f1 (ppm)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7.28
7.27
7.27
7.27
5.30
5.29
5.09
5.08
2.53
2.52
2.51
2.50
2.49
1.54
1.53
1.51
1.50
1.49
1.47
0.96
0.95
0.94
nPr
1.77
1.75
1.20
1.00
1.01
1.98
1.99
2.97
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.5
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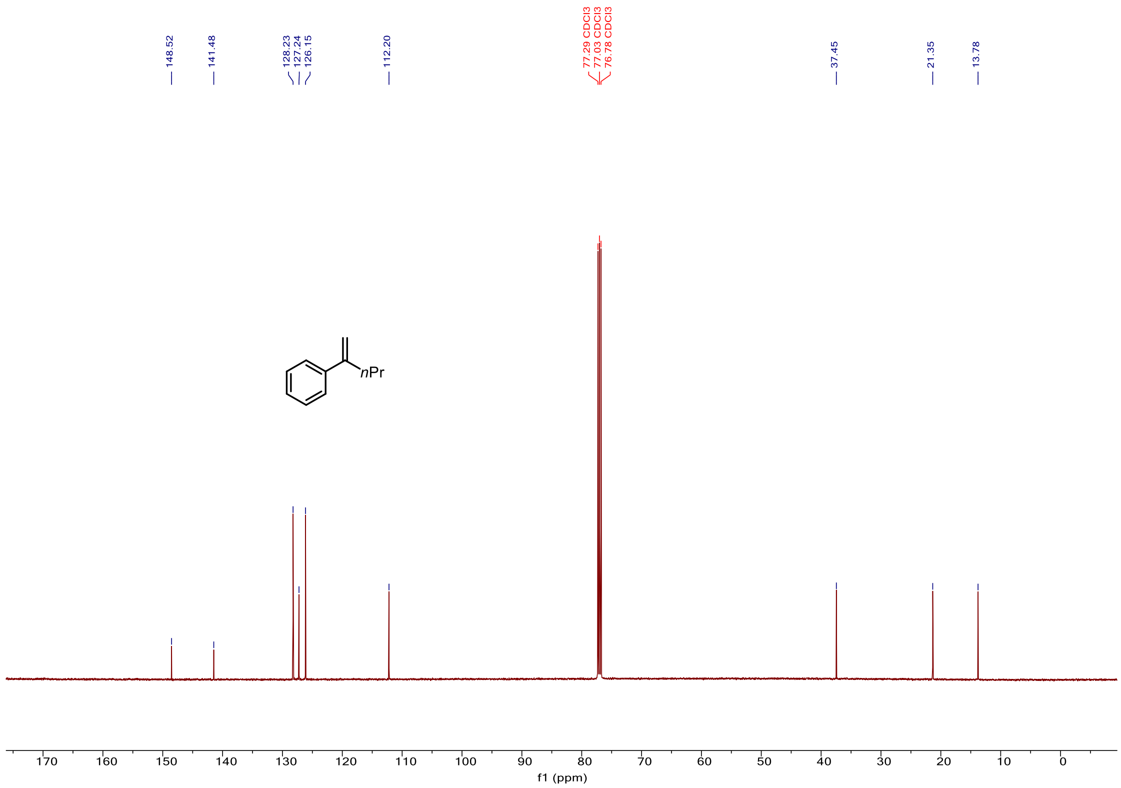
1.0
0.5
0.0
f1 (ppm)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76.78 CDCl3
37.45
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13.78
nPr
170
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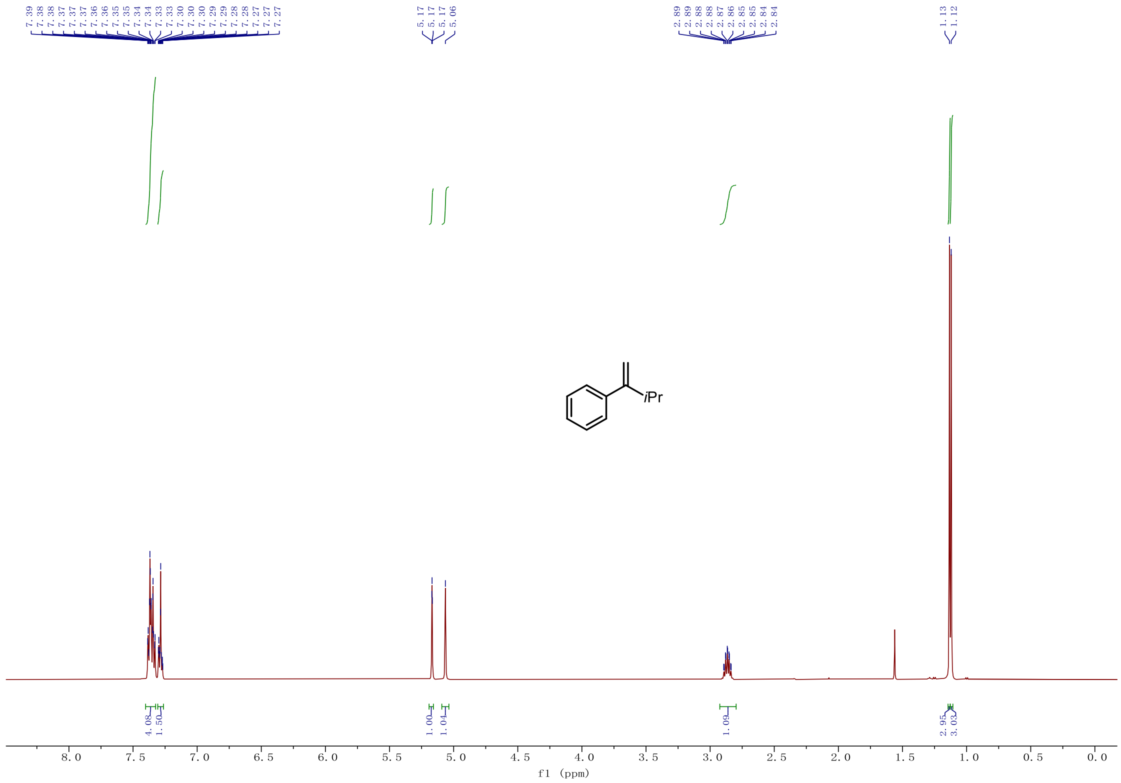
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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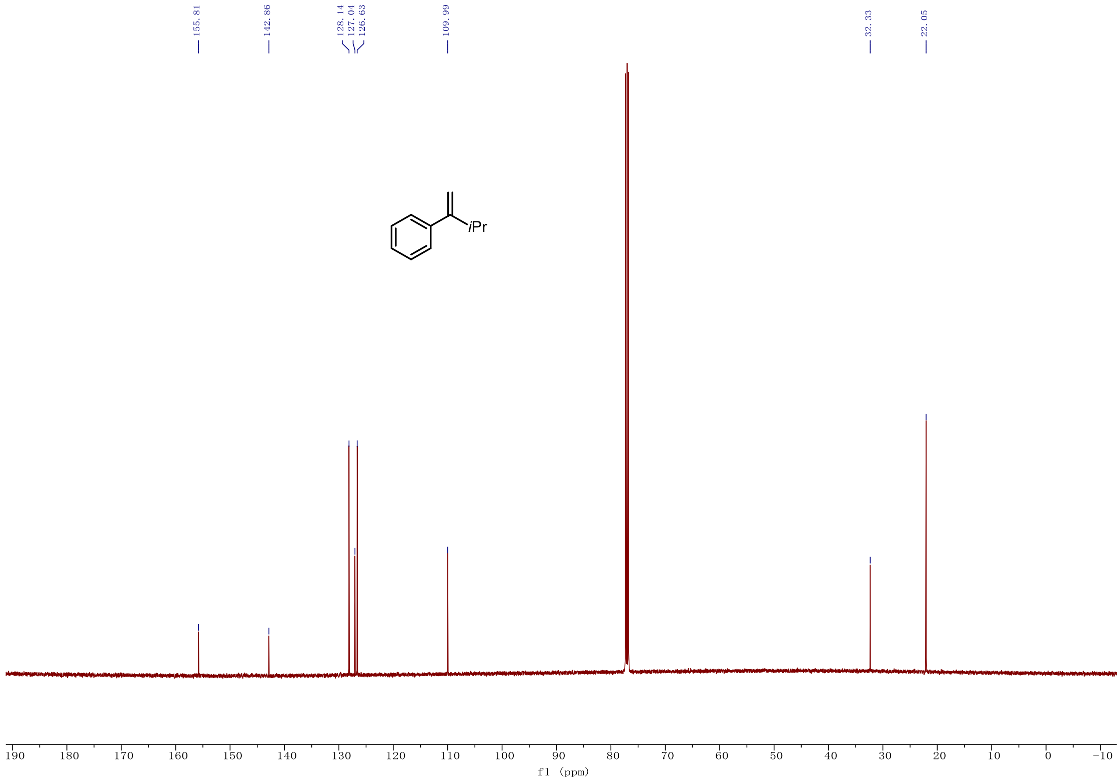
7.33
7.30
7.30
7.30
7.29
7.29
7.28
7.28
7.27
7.27
7.27
5.17
5.17
5.17
5.06
2.89
2.89
2.88
2.88
2.87
2.86
2.85
2.85
2.84
2.84
1.13
1.12
iPr
4.08
1.50
1.00
1.04
1.09
2.95
3.03
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



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128.14
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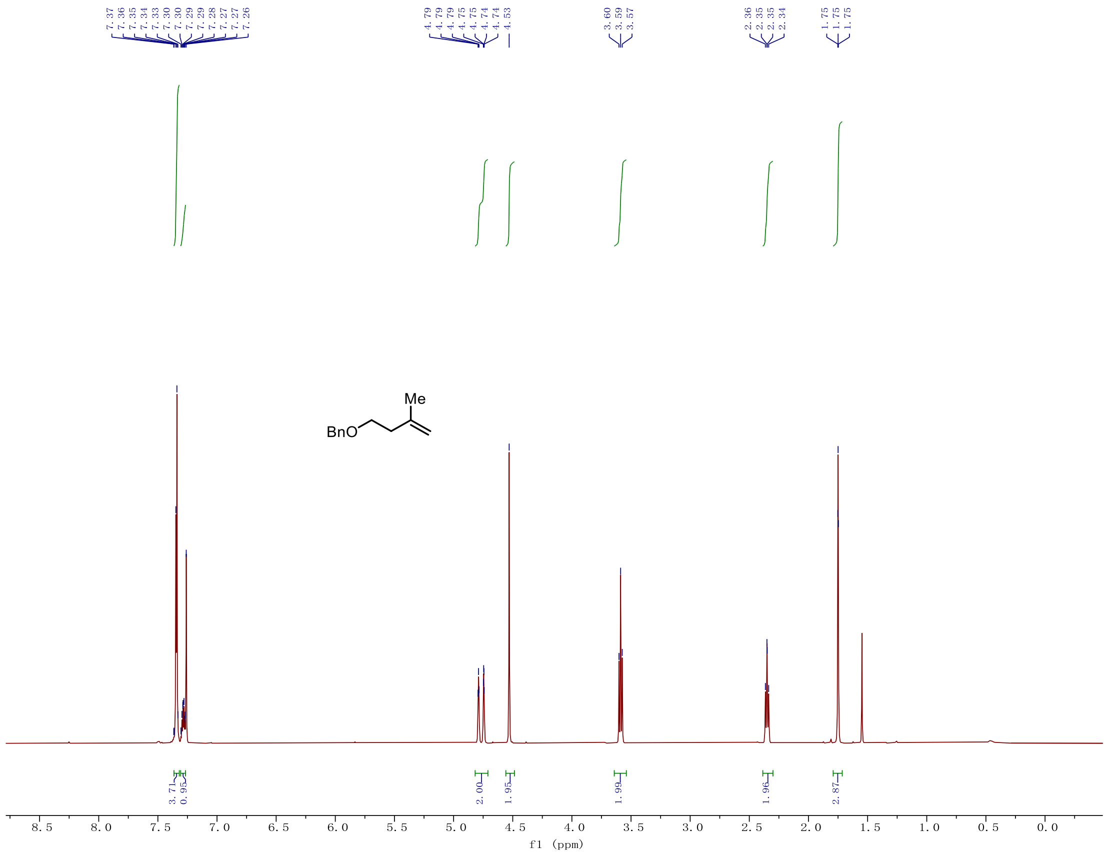
109.99
32.33
22.05
iPr
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



7.37 7.36 7.35 7.34 7.33 7.30 7.30 7.29 7.29 7.28 7.27 7.27 7.26
4.79 4.79 4.75 4.75 4.74 4.74 4.53
3.60 3.59 3.57
2.36 2.35 2.35 2.34
1.75 1.75 1.75
Me
BnO
3.71
0.95
2.00
1.95
1.99
1.96
2.87
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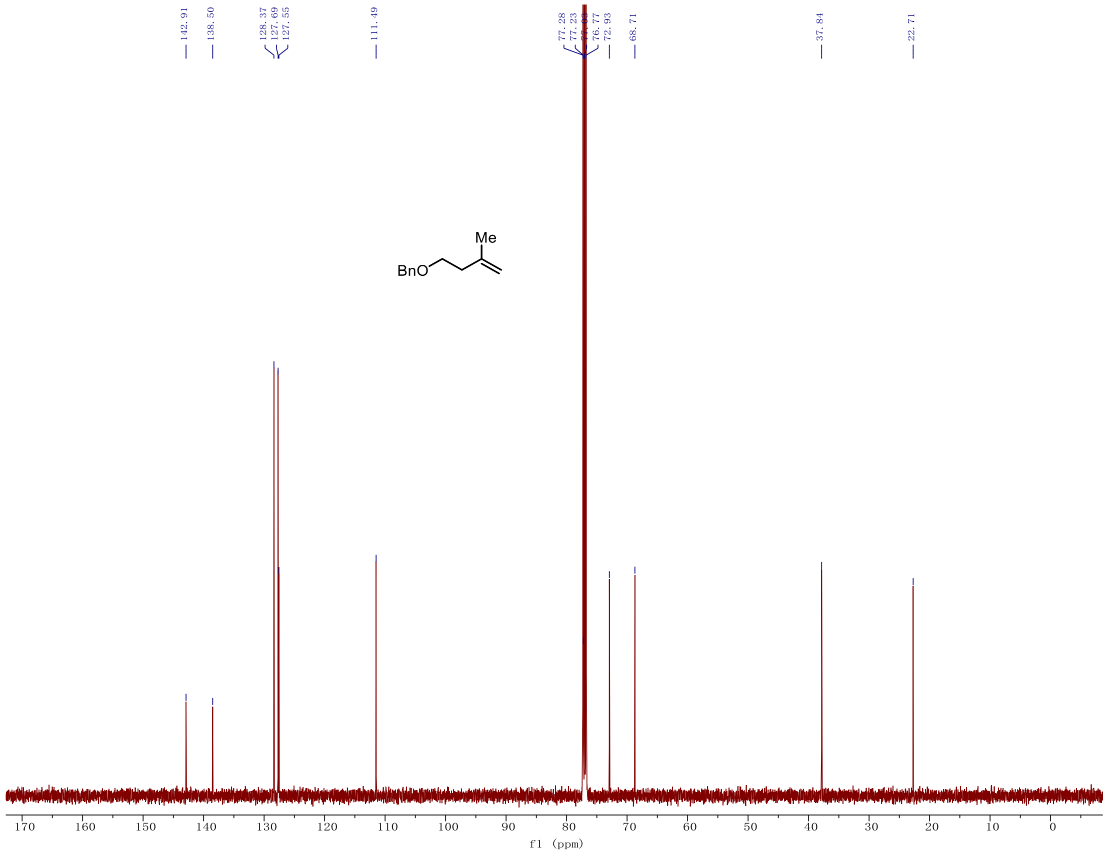
f1 (ppm)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76.77
72.93
68.71
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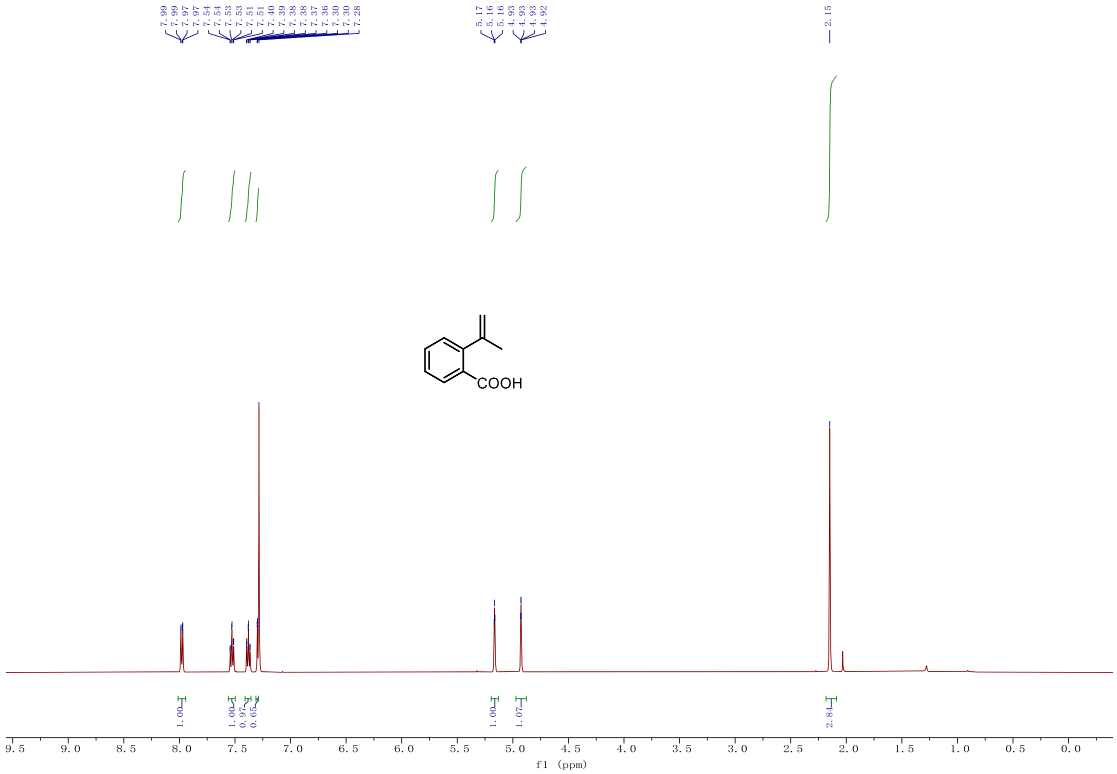
22.71
Me
BnO
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.51
7.40
7.39
7.38
7.38
7.37
7.36
7.30
7.30
7.28
5.17
5.16
5.16
4.93
4.93
4.93
4.92
2.15
COOH
1.00
1.00
0.97
0.65
1.00
1.07
2.84
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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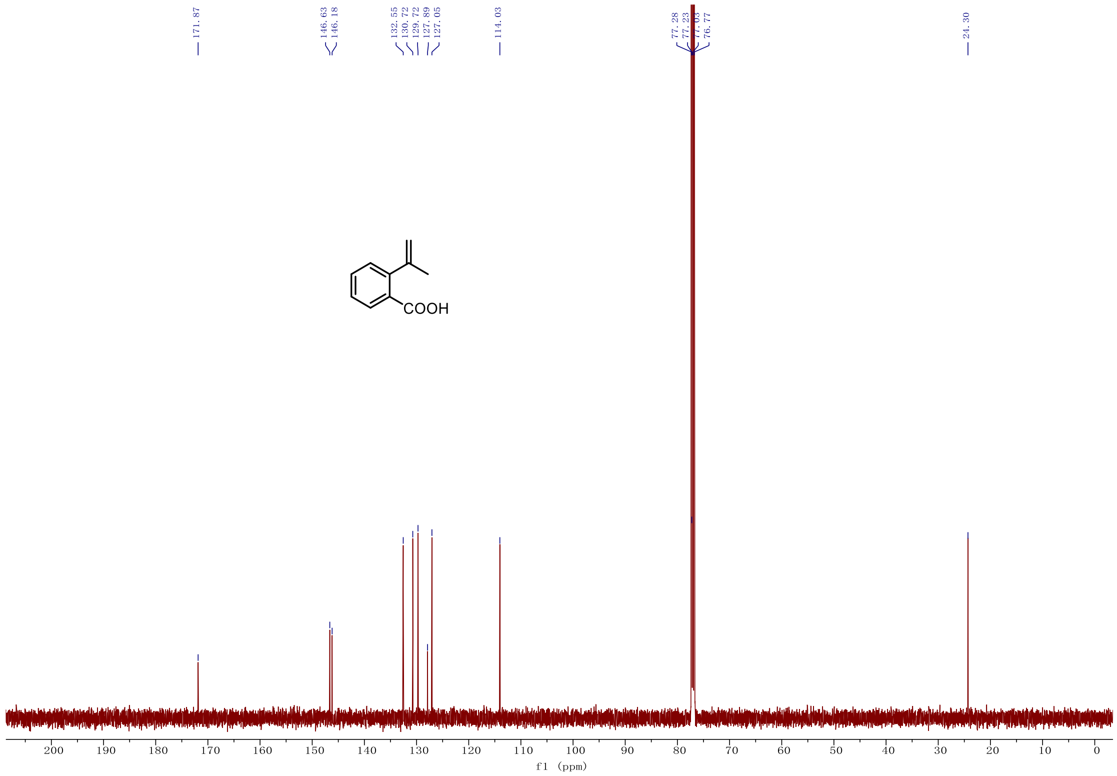
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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127.05
114.03
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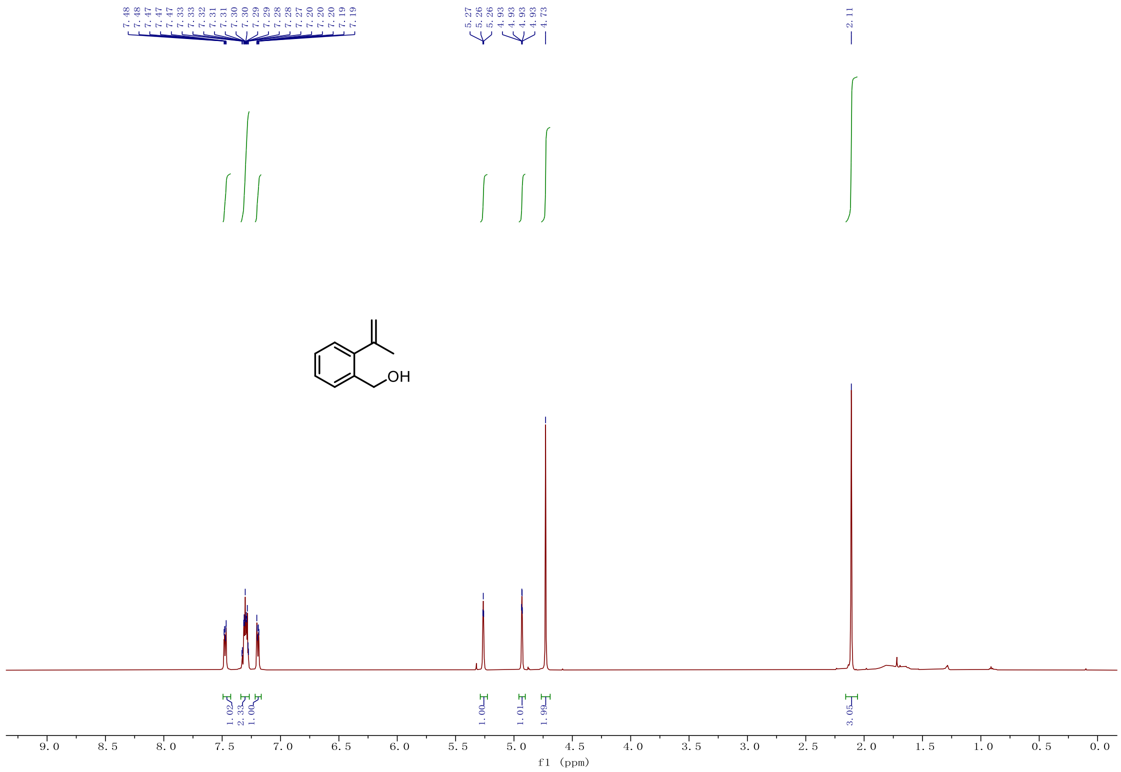
76.77
24.30
COOH
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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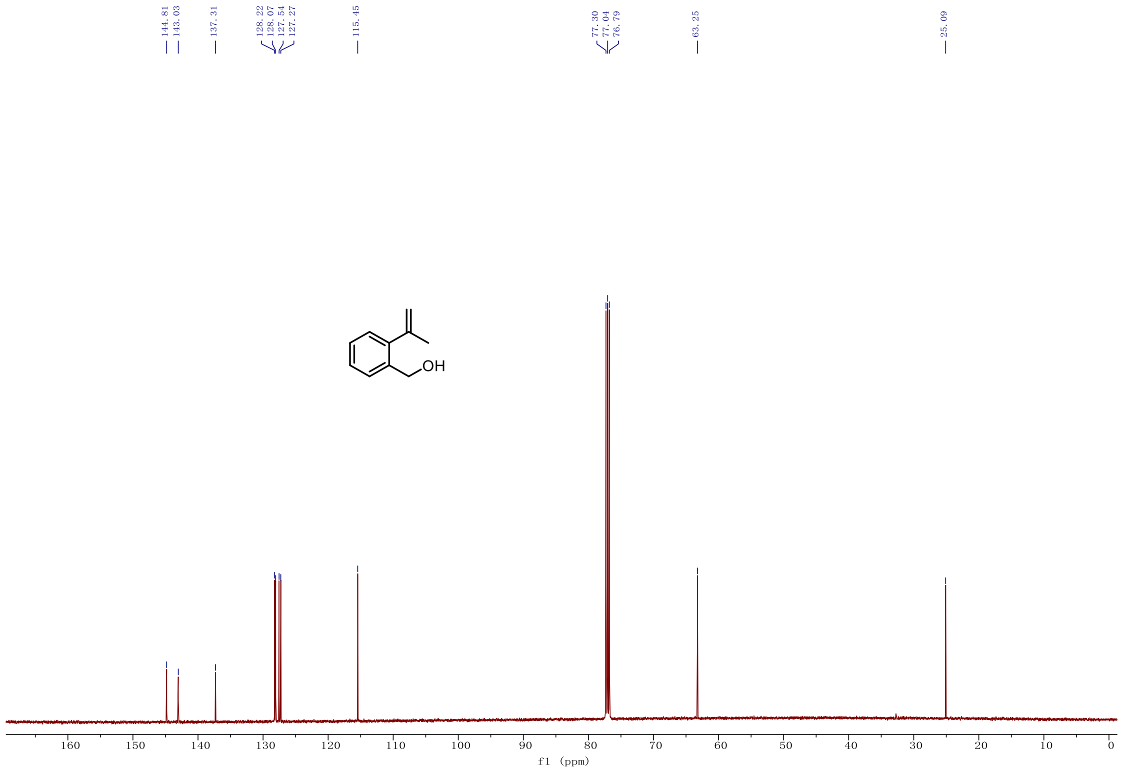
7.30
7.29
7.29
7.28
7.28
7.27
7.20
7.20
7.20
7.19
7.19
5.27
5.26
5.26
4.93
4.93
4.93
4.93
4.73
2.11
OH
1.02
2.33
1.00
1.00
1.01
1.99
3.05
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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128.07
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127.27
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77.30
77.04
76.79
63.25
25.09
OH
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

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