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Supplementary Information

Phase-transfer-catalyzed asymmetric desymmetrizations of cyclopentanones

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General Information

^{1}H NMR spectra were measured on JEOL JNM-FX 400 NMR instrument (400 MHz for ^{1}H NMR). ^{13}C NMR spectra were measured on JEOL JNM-FX 400 NMR instrument (100 MHz for ^{13}C NMR). Tetramethylsilane (TMS) served as the internal standard (0 ppm) for ^{1}H NMR, and $CDCl_3$ served as the internal standard (77.0 ppm) for ^{13}C NMR. The following abbreviations were used to express the multiplicities: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; br = broad. High performance liquid chromatography (HPLC) was performed on Shimadzu 10A instruments using Daicel Chiralpak AD-H or IC (4.6 mm × 250 mm) columns. High-resolution mass spectra (HRMS) were performed on BRUKER microTOF focus–KR. Optical rotations were measured on a JASCO DIP-1000 digital polarimeter. All reactions were monitored by thin-layer chromatography carried out on Merck precoated TLC plates (silica gel 60GF-254, 0.25 mm), visualization by using UV (254 nm), or dyes such as $KMnO_4$. The products were purified by flash column chromatography on silica gel 60N [Kanto Chemical Co., Inc. (spherical, neutral)] or Merck preparative thin layer chromatography on silica gel (PLC 60 F254, 0.5 mm). All simple chemicals were purchased and used as received.

Experimental Section

Synthesis of substrates 1 and 6.

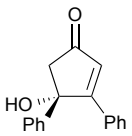
Substrates **1** and **6** were prepared according to the literature.[1]

Synthesis of chiral phase-transfer catalysts.

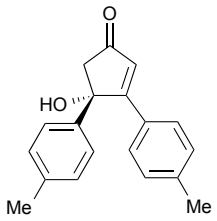
Catalysts (*S*)-**3**,[2] (*S*)-**4**,[3] and (*S*)-**5**[4] were prepared according to the literature.

General procedure for the catalytic asymmetric desymmetrization of epoxy ketones 1 (Table 2).

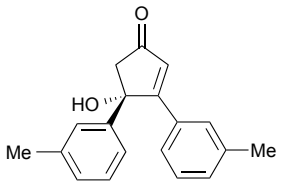
To a solution of epoxy ketone **1** (0.050 mmol) and chiral phase-transfer catalyst (*S*)-**4b** (1 mol %, 0.00050 mmol) in toluene (0.50 mL) was added 5% aqueous K_2CO_3 (0.35 mL) at 0 °C. The reaction mixture was vigorously stirred for 24 h at 0 °C. The resulting mixture was quenched with saturated aqueous NH_4Cl and diluted with ethyl acetate. The organic phase was separated and the aqueous phase was extracted with ethyl acetate. The combined extracts were dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate as eluent) to give product **2**. The enantiomeric excess of the product **2** was determined by chiral HPLC analysis.



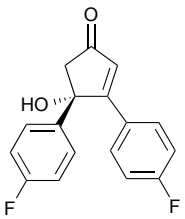
2a:[1a] $[\alpha]^{23}_D = -142.4$ (*c* = 0.40, $CHCl_3$), HPLC analysis (92% ee): Daicel Chiralpak AD-H, haxane/2-propanol = 9:1, flow rate = 1.0 mL/min, 254 nm; retention time: 8.7 min (major) and 9.7 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.56 (m, 4H), 7.26–7.39 (m, 6H), 6.71 (s, 1H), 3.02 (d, *J* = 18.4 Hz, 1H), 2.91 (d, *J* = 18.4 Hz, 1H), 2.59 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.7, 173.9, 144.1, 131.4, 130.8, 129.1, 128.9, 128.8, 127.5, 124.2, 81.7, 56.6; IR (neat) 3392, 1681, 1592, 1569, 1494, 1447, 1249, 1208, 1051, 977, 766, 723, 701, 689 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{17}H_{14}NaO_2^+$: 273.0886 ($[M+Na]^+$), found 273.0880.



2b: $[\alpha]^{25}_{D}$ = –83.3 (*c* = 0.36, $CHCl_3$), HPLC analysis (90% ee): Daicel Chiralpak AD-H, haxane/2-propanol = 9:1, flow rate = 1.0 mL/min, 254 nm; retention time: 9.2 min (major) and 12.2 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.65 (s, 1H), 2.98 (d, *J* = 18.4 Hz, 1H), 2.85 (d, *J* = 18.4 Hz, 1H), 2.66 (br, 1H), 2.32 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.8, 173.9, 141.4, 141.3, 137.1, 129.5, 129.2, 129.1, 128.6, 128.2, 124.1, 81.6, 56.7, 21.4, 21.0; IR (neat) 3390, 1679, 1610, 1590, 1511, 1323, 1301, 1275, 1248, 1220, 1203, 819, 730 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{19}H_{18}NaO_2^+$: 301.1199 ($[M+Na]^+$), found 301.1194.

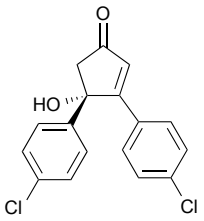


2c: $[\alpha]^{26}_{D}$ = –100.7 (*c* = 0.38, $CHCl_3$), HPLC analysis (91% ee): Daicel Chiralpak AD-H, haxane/2-propanol = 9:1, flow rate = 1.0 mL/min, 254 nm; retention time: 7.3 min (major) and 8.1 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (s, 1H), 7.22–7.27 (m, 4H), 7.14–7.21 (m, 2H), 7.05–7.12 (m, 1H), 6.67 (s, 1H), 2.99 (d, *J* = 18.8 Hz, 1H), 2.88 (d, *J* = 18.8 Hz, 1H), 2.55 (br, 1H), 2.33 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.7, 174.1, 144.2, 138.6, 138.5, 131.7, 131.4, 129.7, 129.1, 128.7, 128.2, 126.2, 124.8, 121.2, 116.7, 81.7, 56.6, 21.6, 21.4; IR (neat) 3392, 1680, 1591, 1576, 1487, 1304, 1283, 1252, 1210, 1178, 1058, 788, 722, 703 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{19}H_{18}NaO_2^+$: 301.1199 ($[M+Na]^+$), found 301.1207.

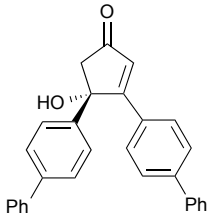


2d: $[\alpha]^{23}_{D}$ = –210.8 (*c* = 0.78, $CHCl_3$), HPLC analysis (93% ee): Daicel Chiralpak AD-H, haxane/2-propanol = 9:1, flow rate = 1.0 mL/min, 254 nm; retention time: 6.9 min (major) and 8.5 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.61 (m, 2H), 7.36–7.44 (m, 2H), 6.96–7.06 (m, 4H), 6.64 (s, 1H), 2.99 (d, *J* = 18.8 Hz, 1H), 2.88 (d, *J* = 18.8 Hz, 1H), 2.72 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.0, 172.4, 164.1 (d, J_{C-F} = 255.1 Hz), 162.1 (d, J_{C-F} = 247.8 Hz), 139.5 (d, J_{C-F} = 3.3 Hz), 131.3 (d, J_{C-F} = 9.0 Hz), 128.8, 127.4 (d, J_{C-F} = 3.3 Hz), 126.1 (d, J_{C-F} = 8.3 Hz), 116.0 (d, J_{C-F} = 22.2 Hz), 115.8 (d, J_{C-F} = 21.4 Hz), 81.3, 56.6; IR (neat) 3381, 1684, 1601, 1579, 1508, 1414, 1279, 1238, 1208, 1163, 1052, 980, 837 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{17}H_{12}F_2NaO_2^+$:

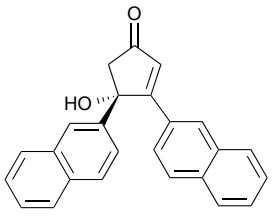
309.0698 ([M+Na]$^+$), found 309.0686.



2e: $[\alpha]^{26}_D$ = –145.9 (*c* = 0.36, $CHCl_3$), HPLC analysis (90% ee): Daicel Chiralpak AD-H, haxane/2-propanol = 9:1, flow rate = 1.0 mL/min, 254 nm; retention time: 6.9 min (major) and 8.8 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.8 Hz, 2H), 7.35 (d, *J* = 8.8 Hz, 2H), 7.30 (d, *J* = 8.8 Hz, 2H), 7.27 (d, *J* = 8.8 Hz, 2H), 6.63 (s, 1H), 2.98 (d, *J* = 18.8 Hz, 1H), 2.96 (br, 1H), 2.87 (d, *J* = 18.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.1, 172.3, 142.2, 137.3, 133.6, 130.4, 129.6, 129.2, 129.13, 129.07, 125.7, 81.2, 56.5; IR (neat) 3390, 1680, 1589, 1490, 1319, 1210, 1093, 1013, 975, 827, 749, 730 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{17}H_{12}Cl_2NaO_2^+$: 341.0107 ([M+Na]$^+$), found 341.0108.



2f: $[\alpha]^{25}_D$ = +8.6 (*c* = 0.78, $CHCl_3$), HPLC analysis (96% ee): Daicel Chiralpak IC, haxane/2-propanol = 9:1, flow rate = 0.75 mL/min, 254 nm; retention time: 28.5 min (minor) and 34.0 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63–7.69 (m, 2H), 7.51–7.62 (m, 10H), 7.39–7.46 (m, 4H), 7.31–7.38 (m, 2H), 6.77 (s, 1H), 3.07 (d, *J* = 18.8 Hz, 1H), 2.96 (d, *J* = 18.8 Hz, 1H), 2.77 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.5, 173.3, 143.6, 143.1, 140.4, 139.7, 130.2, 129.7, 128.9, 128.8, 128.1, 127.5, 127.44, 127.37, 127.0, 124.7, 81.6, 56.7; IR (neat) 3367, 1678, 1588, 1487, 1408, 1298, 1208, 1007, 978, 908, 841, 768, 734, 696 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{29}H_{22}NaO_2^+$: 425.1512 ([M+Na]$^+$), found 425.1501.

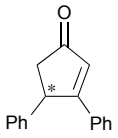


2g: $[\alpha]^{22}_D$ = –126.1 (*c* = 1.57, $CHCl_3$), HPLC analysis (90% ee): Daicel Chiralpak AD-H, haxane/2-propanol = 9:1, flow rate = 1.0 mL/min, 254 nm; retention time: 13.2 min (major) and 15.7 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 1.6 Hz, 1H), 8.07 (d, *J* = 1.6 Hz, 1H), 7.78–7.86 (m, 3H), 7.71–7.75 (m, 2H), 7.61–7.66 (m, 2H), 7.43–7.52 (m, 4H), 7.39 (dd, *J* = 7.6, 7.6 Hz, 1H), 6.88 (s, 1H), 3.12 (d, *J* = 18.8 Hz, 1H), 3.01 (d, *J* = 18.8 Hz, 1H), 2.96 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.6, 173.6, 141.5, 134.1, 133.3, 132.8, 132.6, 130.2, 129.5, 129.1, 129.0, 128.7, 128.5, 128.2, 127.8, 127.6, 127.5, 126.6, 126.5, 126.2, 125.4, 123.1, 122.4, 82.0,

56.7; IR (neat) 3368, 1679, 1600, 1584, 1567, 1299, 1272, 1250, 1197, 907, 857, 817, 749, 731 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{25}H_{18}NaO_2^+$: 373.1199 ($[M+Na]^+$), found 373.1200.

Procedure for the catalytic asymmetric isomerization of ketone 6 (Scheme 2).

To a solution of ketone **6** (0.050 mmol) and chiral phase-transfer catalyst (*S*)-**4b** (3 mol %, 0.0015 mmol) in trifluoromethylbenzene (0.50 mL) was added 50% aqueous Cs_2CO_3 (0.50 mL) at –20 °C. The reaction mixture was vigorously stirred for 48 h at –20 °C. The resulting mixture was quenched with saturated aqueous NH_4Cl and diluted with ethyl acetate. The organic phase was separated and the aqueous phase was extracted with ethyl acetate. The combined extracts were dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate 10:1–3:1 as eluent) to give product **7**. The enantiomeric excess of the product **7** was determined by chiral HPLC analysis.



7: $[\alpha]^{26}_D$ = –315.1 (*c* = 0.75, $CHCl_3$), HPLC analysis (85% ee): Daicel Chiralpak AD-H, haxane/2-propanol = 9:1, flow rate = 1.0 mL/min, 254 nm; retention time: 8.8 min (major) and 11.6 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 1.6, 8.0 Hz, 2H), 7.22–7.36 (m, 5H), 7.11–7.21 (m, 3H), 6.75 (d, *J* = 1.2 Hz, 1H), 4.64 (d, *J* = 7.2 Hz, 1H), 3.12 (dd, *J* = 7.2, 19.2 Hz, 1H), 2.46 (dd, *J* = 2.0, 19.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.9, 175.1, 142.5, 133.3, 130.8, 129.2, 129.1, 128.7, 127.9, 127.1, 127.0, 46.9, 46.7; IR (neat) 1708, 1683, 1594, 1570, 1494, 1447, 1326, 1307, 1268, 1186, 943, 788, 760, 701, 690 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{17}H_{14}NaO^+$: 257.0937 ($[M+Na]^+$), found 257.0938.

Determination of absolute configuration of products 2.

The absolute configuration of product **2a** was determined by comparison of the optical rotation with the literature value.[1a]

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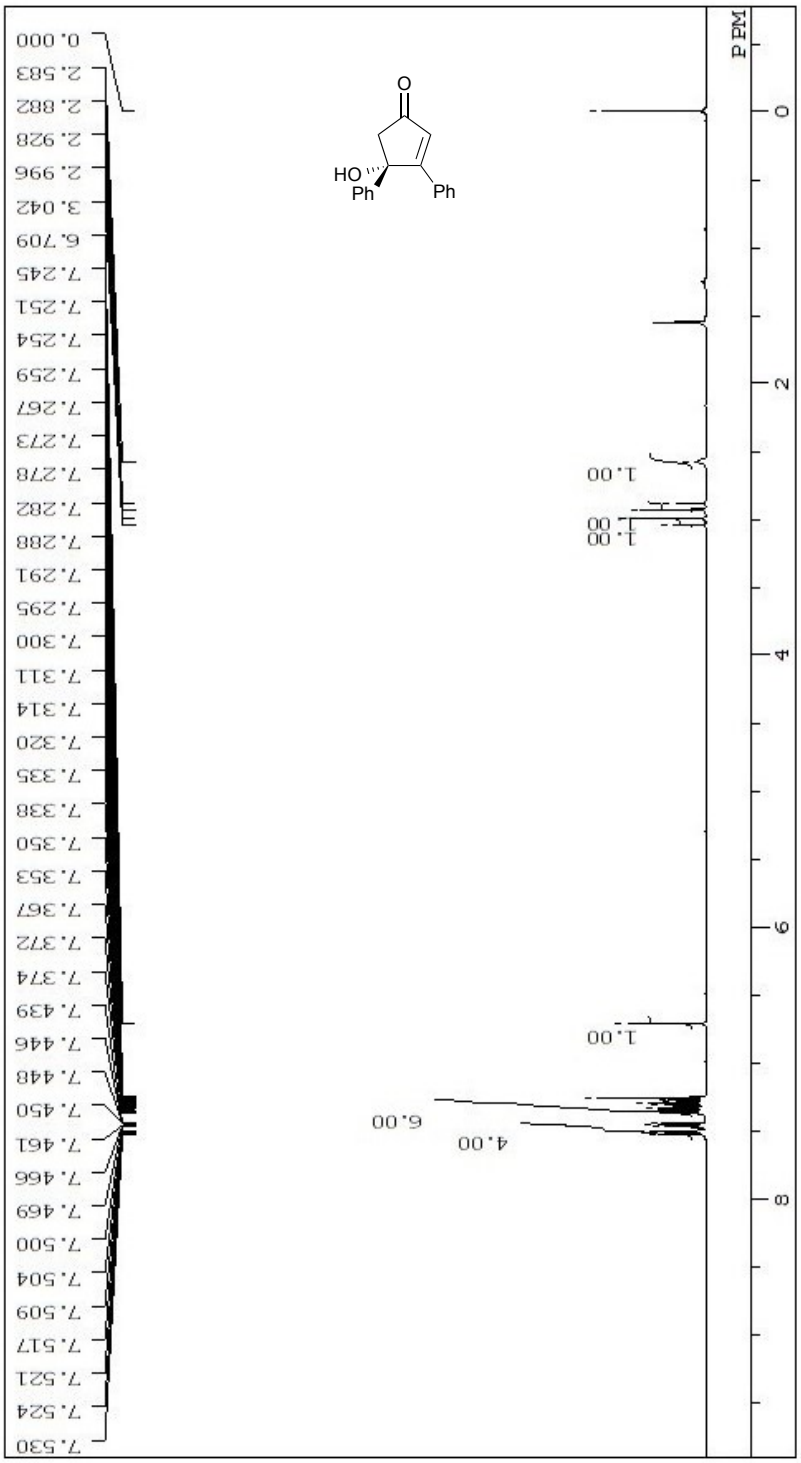
4. (*a*) S. Shirakawa, A. Kasai, T. Tokuda and K. Maruoka, *Chem. Sci.*, 2013, **4**, 2248; (*b*) S. Shirakawa, T. Tokuda, A. Kasai and K. Maruoka, *Org. Lett.*, 2013, **15**, 3350; (*c*) S. Shirakawa, K. Koga, T. Tokuda, K. Yamamoto and K. Maruoka, *Angew. Chem.*, *Int. Ed.*, 2014, **53***,* 6220.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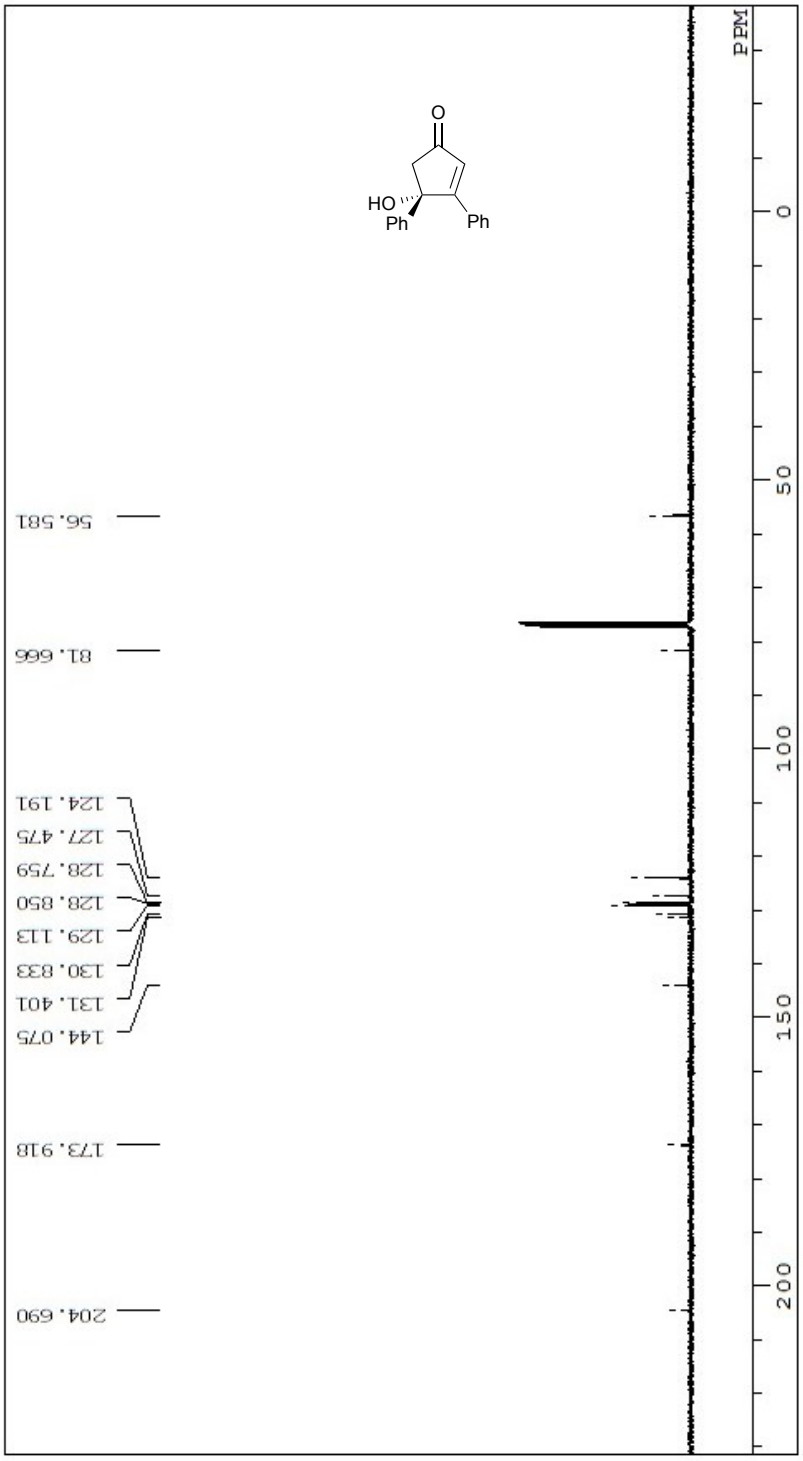
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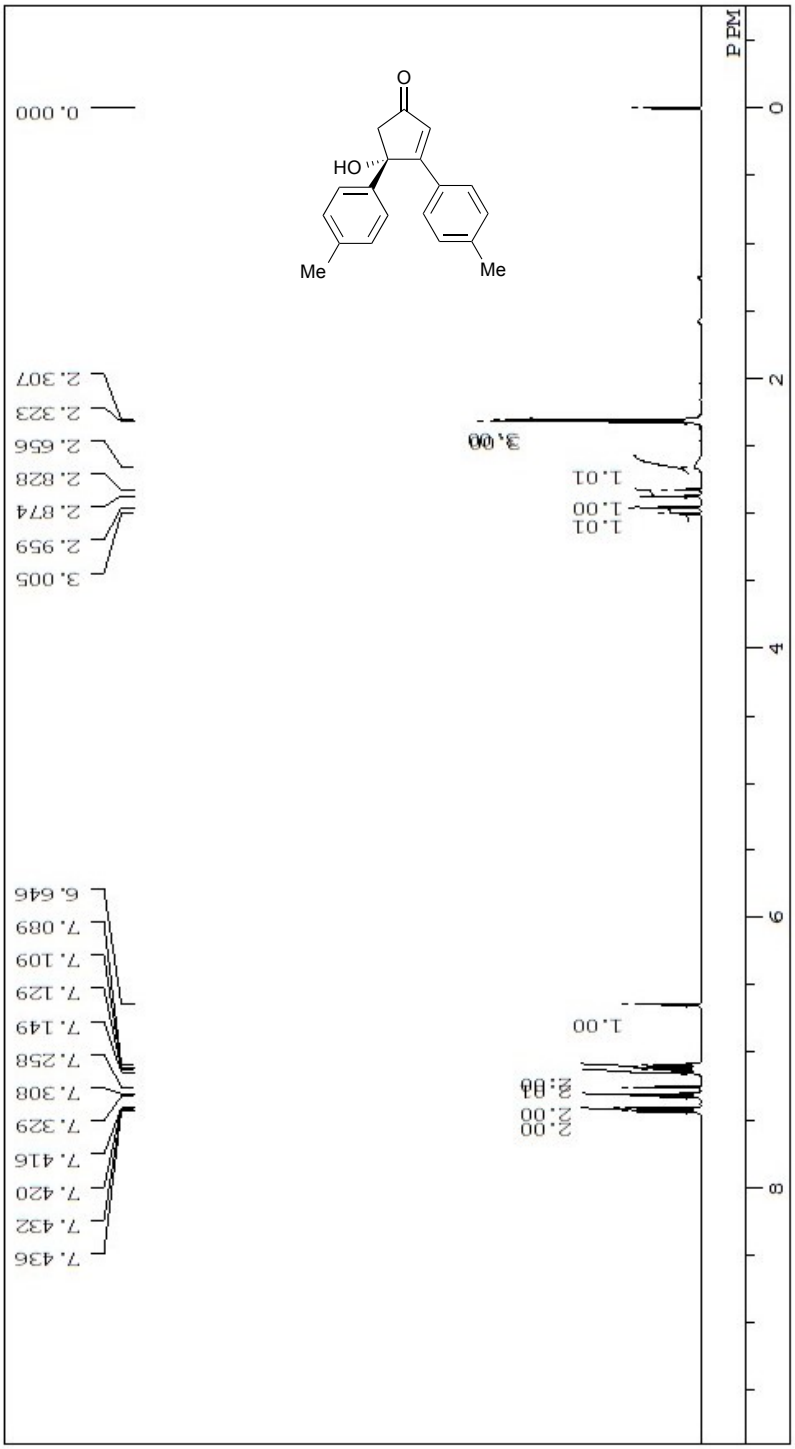
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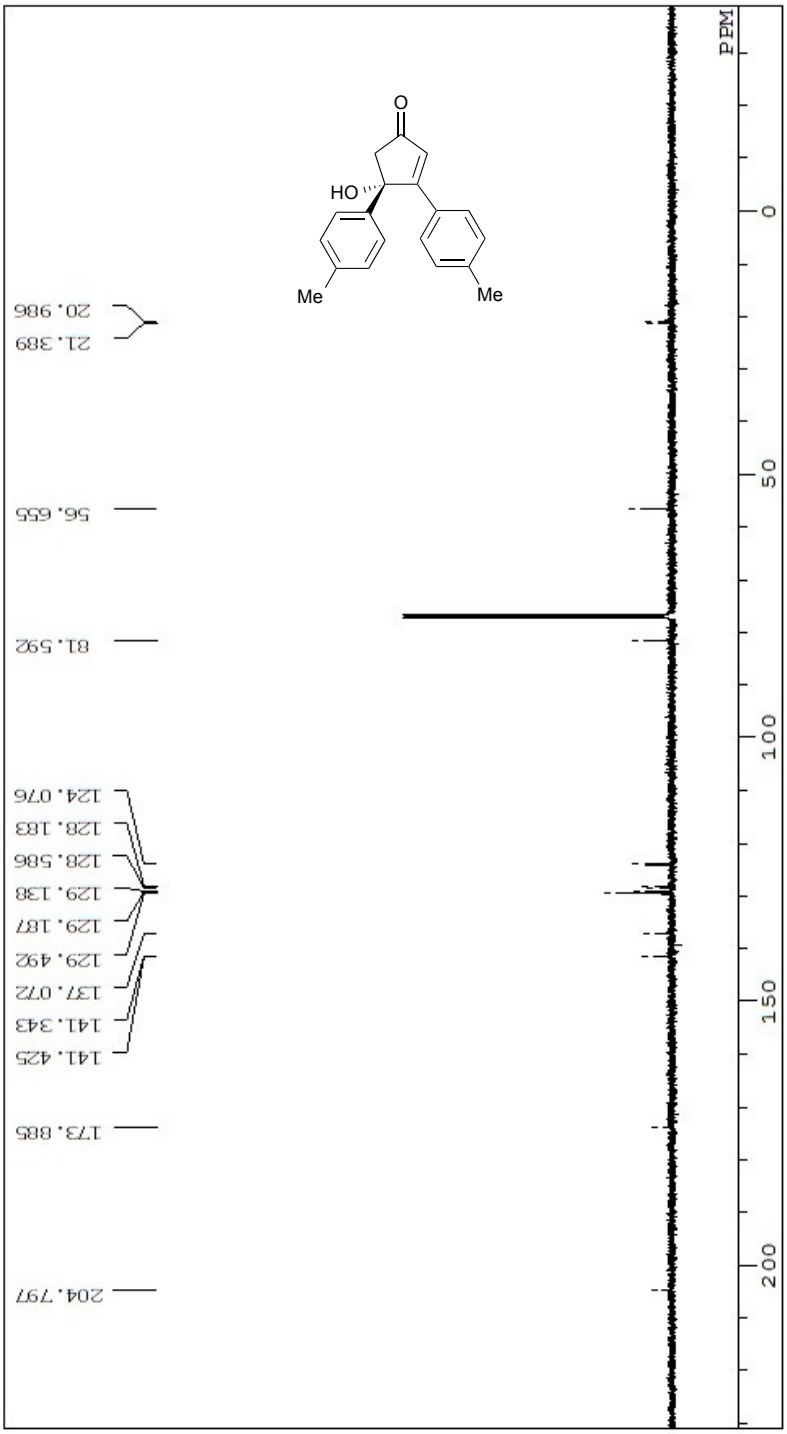
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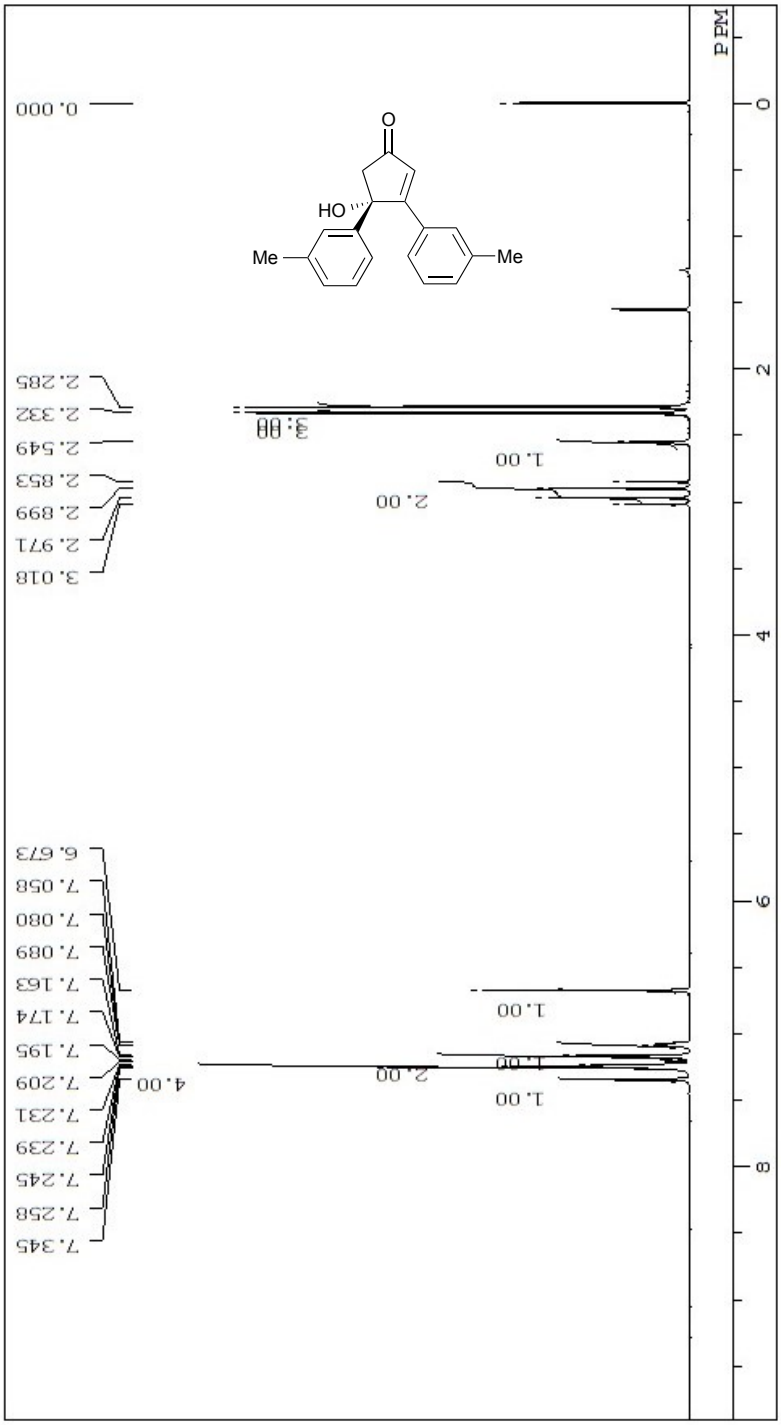
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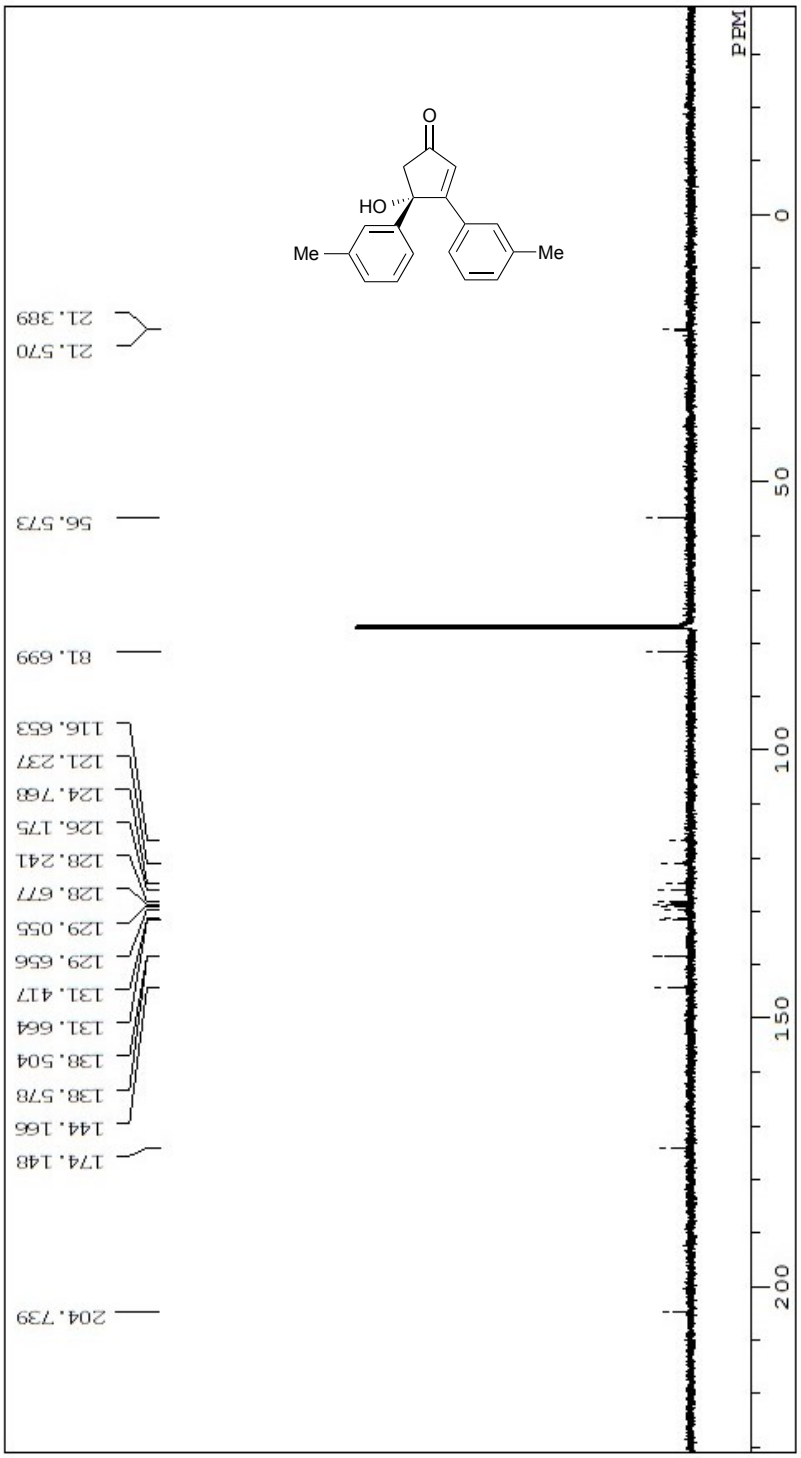
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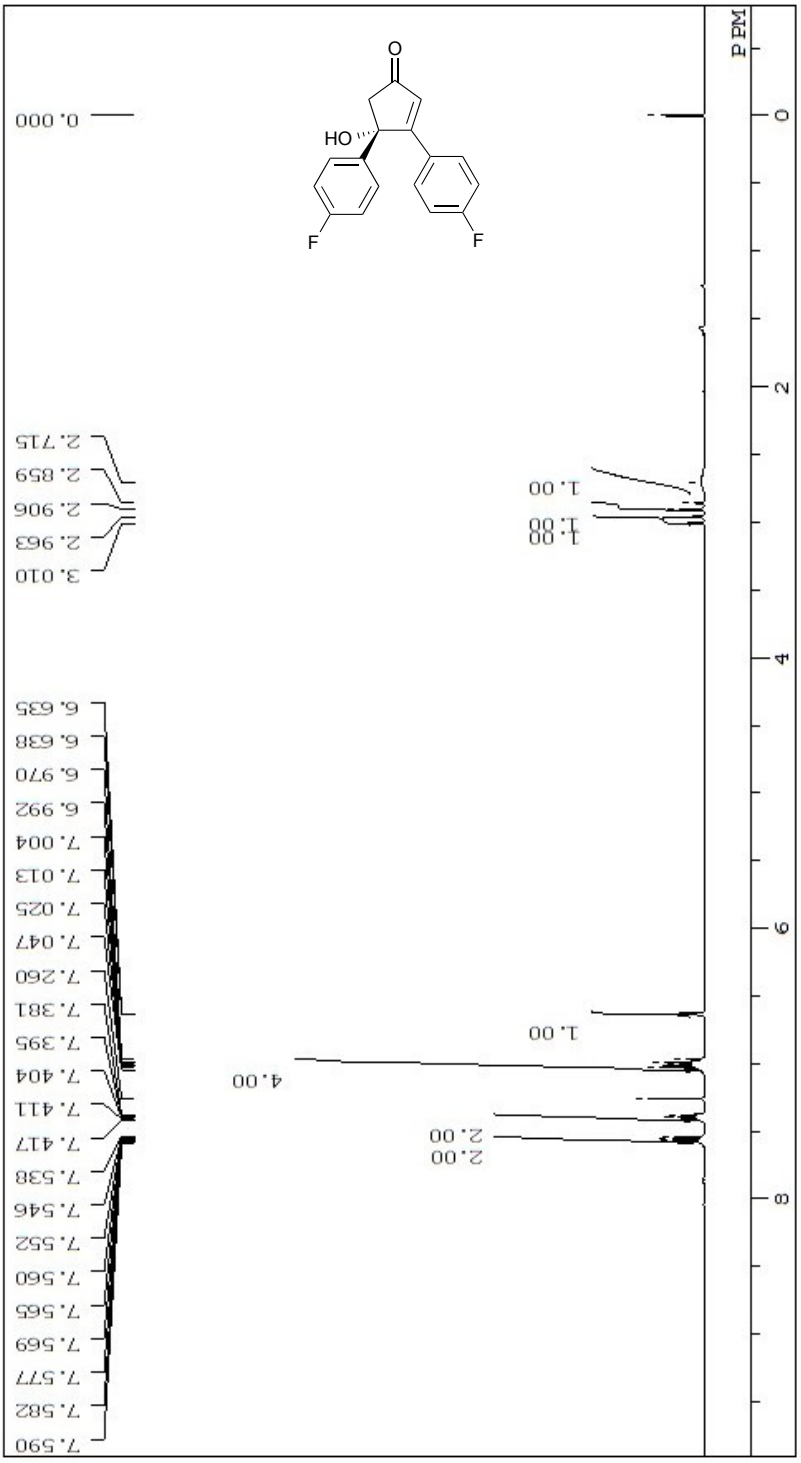
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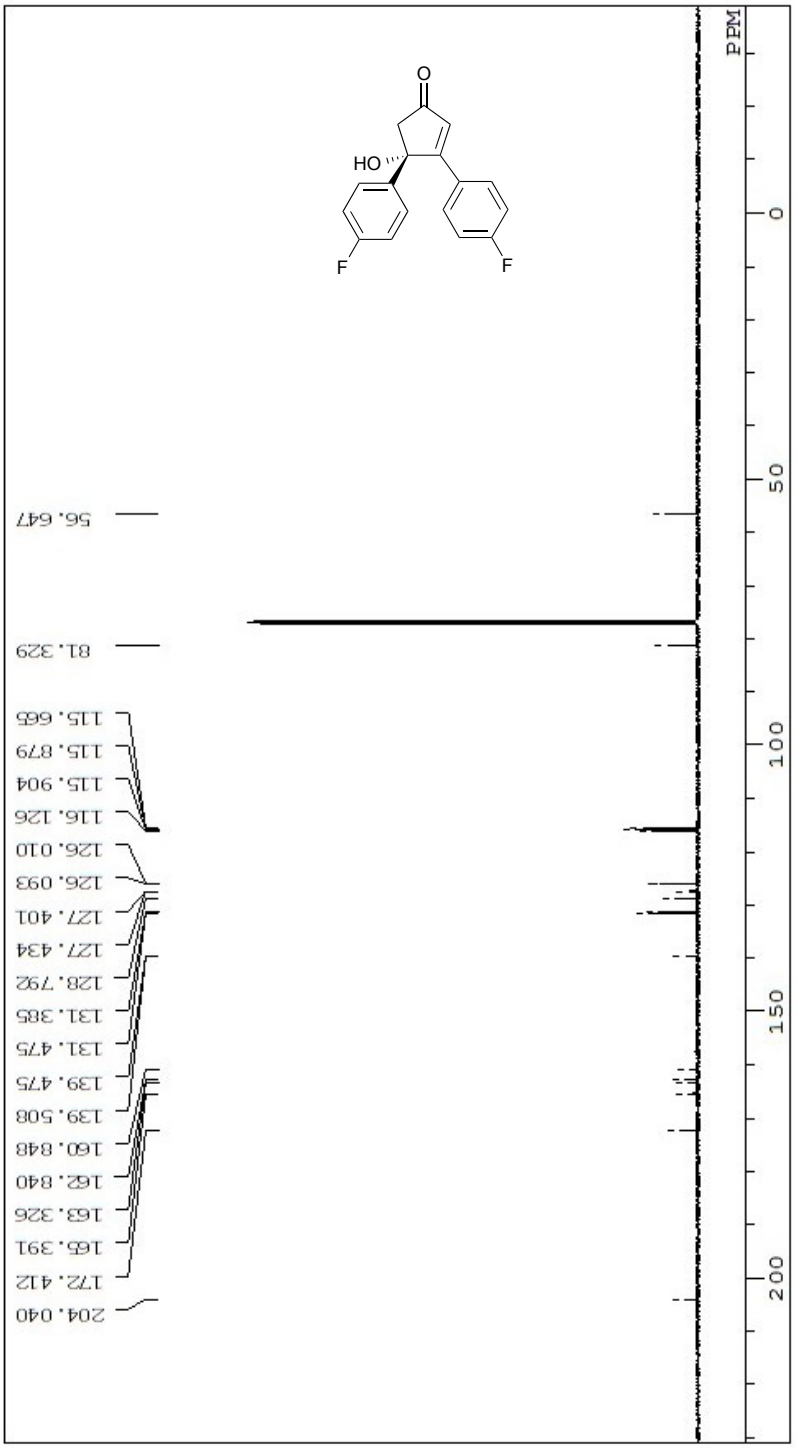
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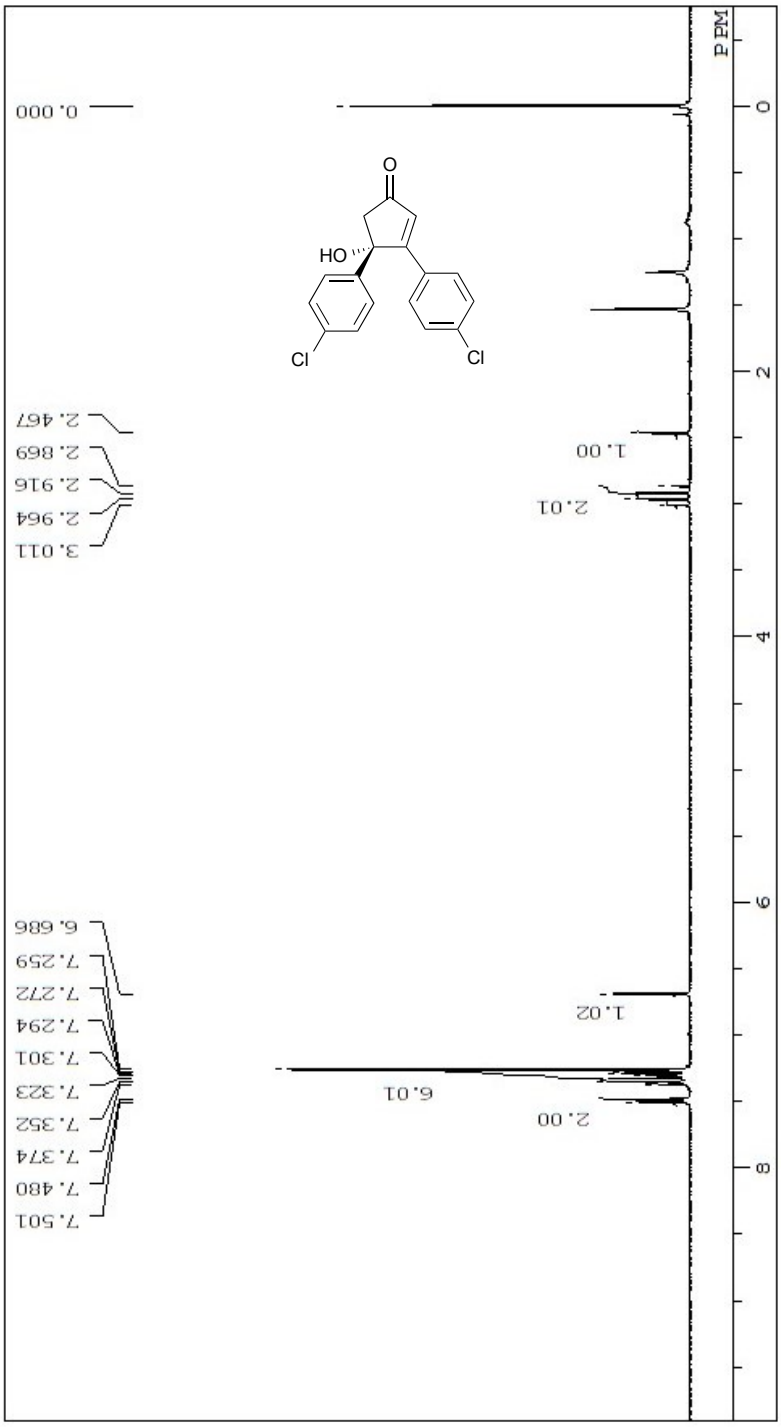
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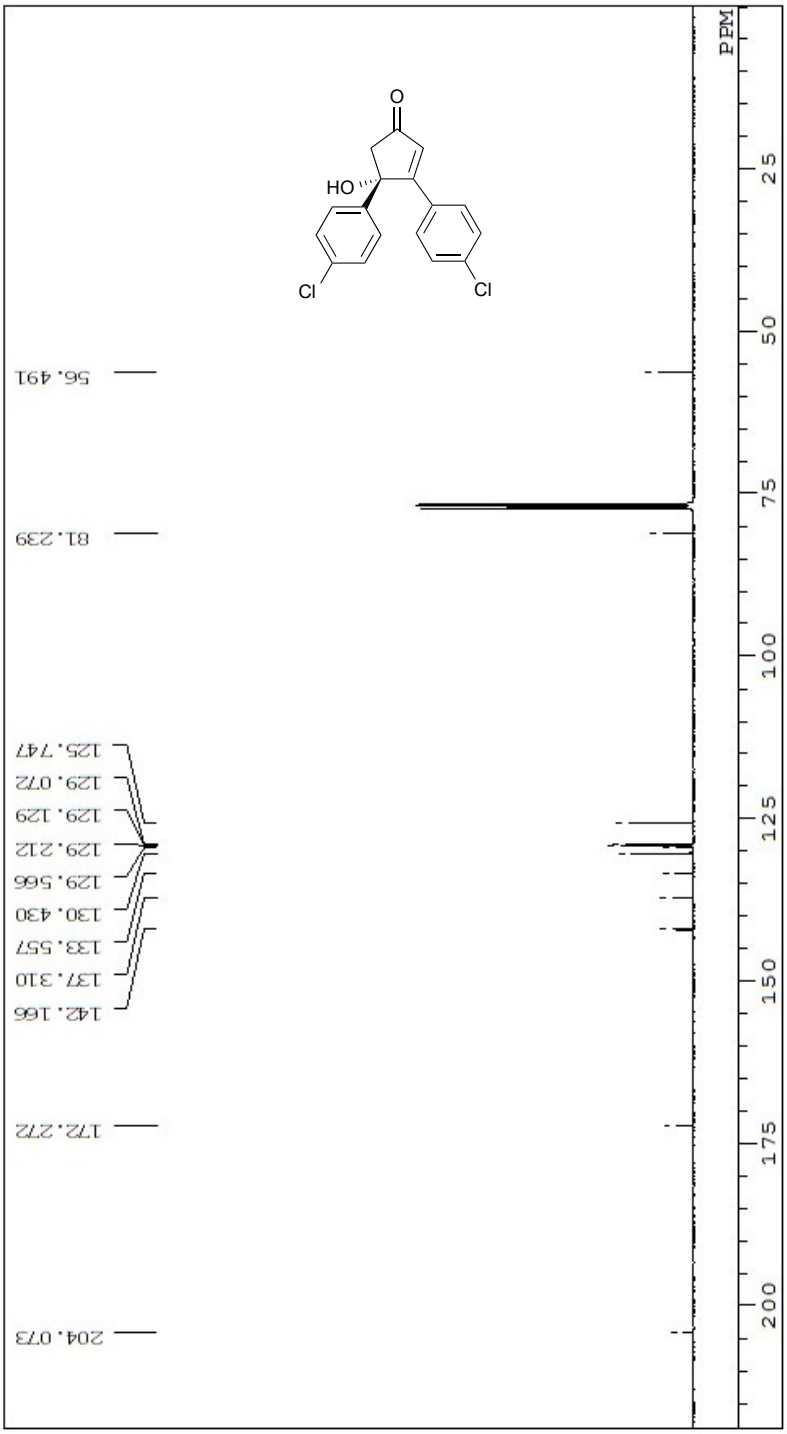
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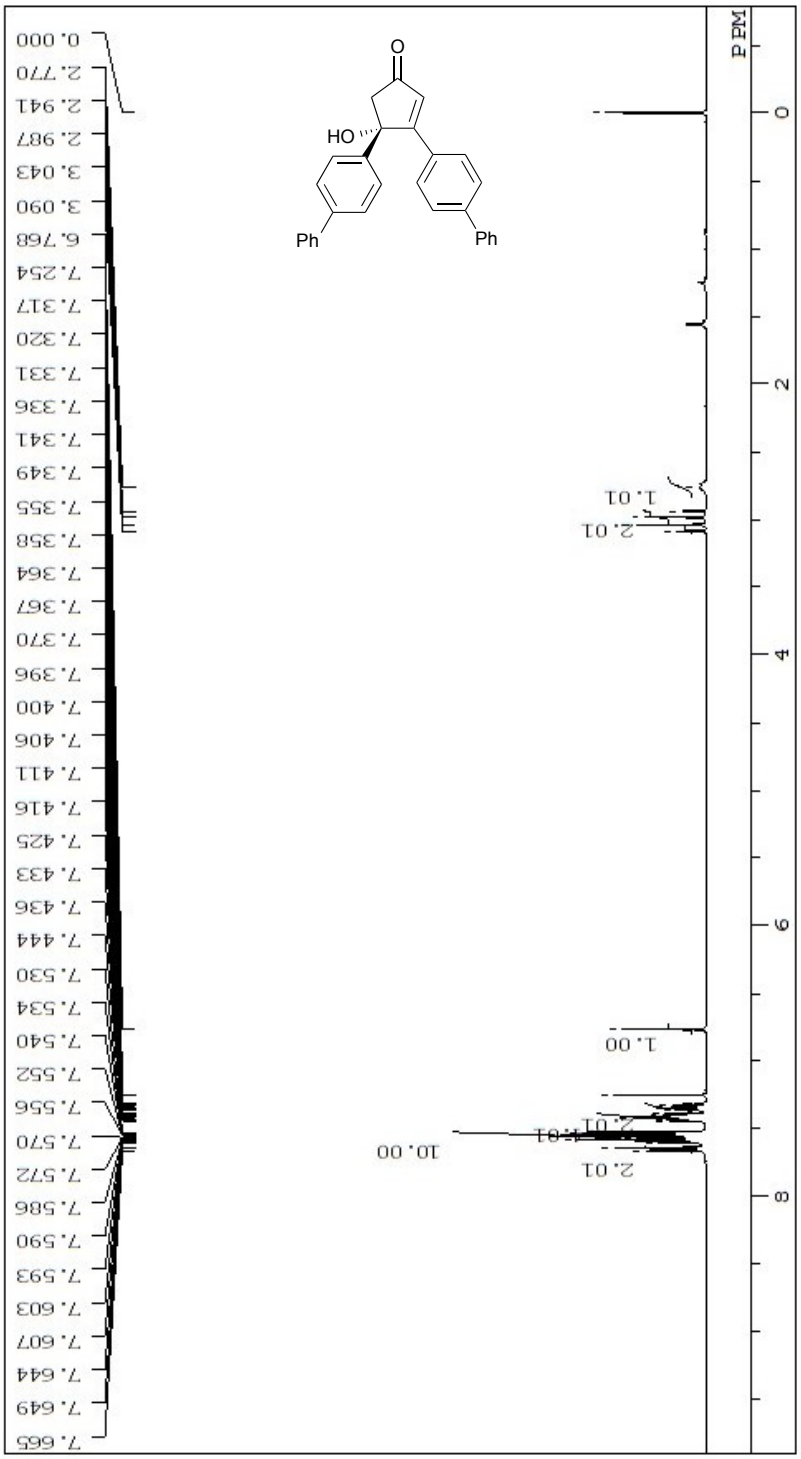
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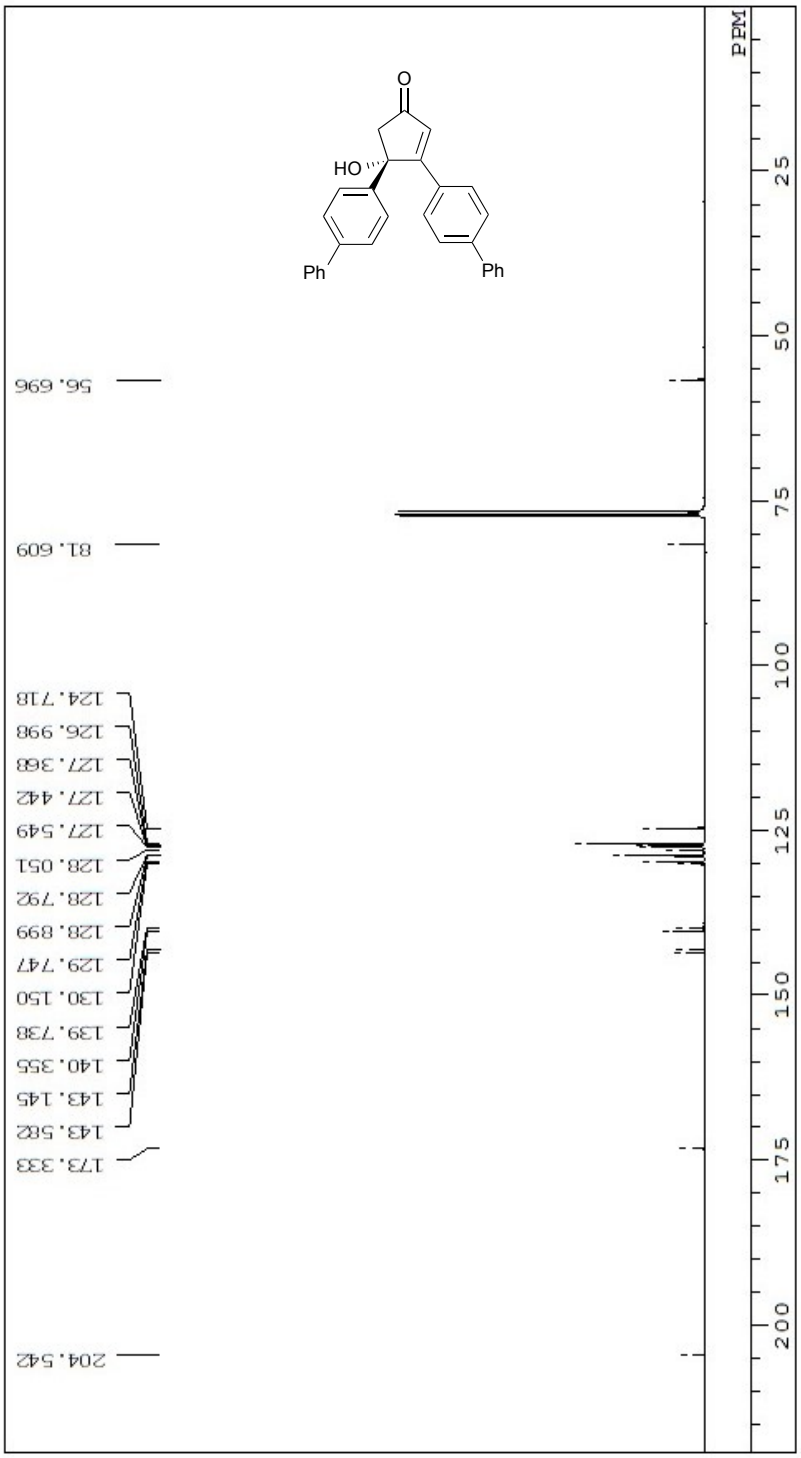
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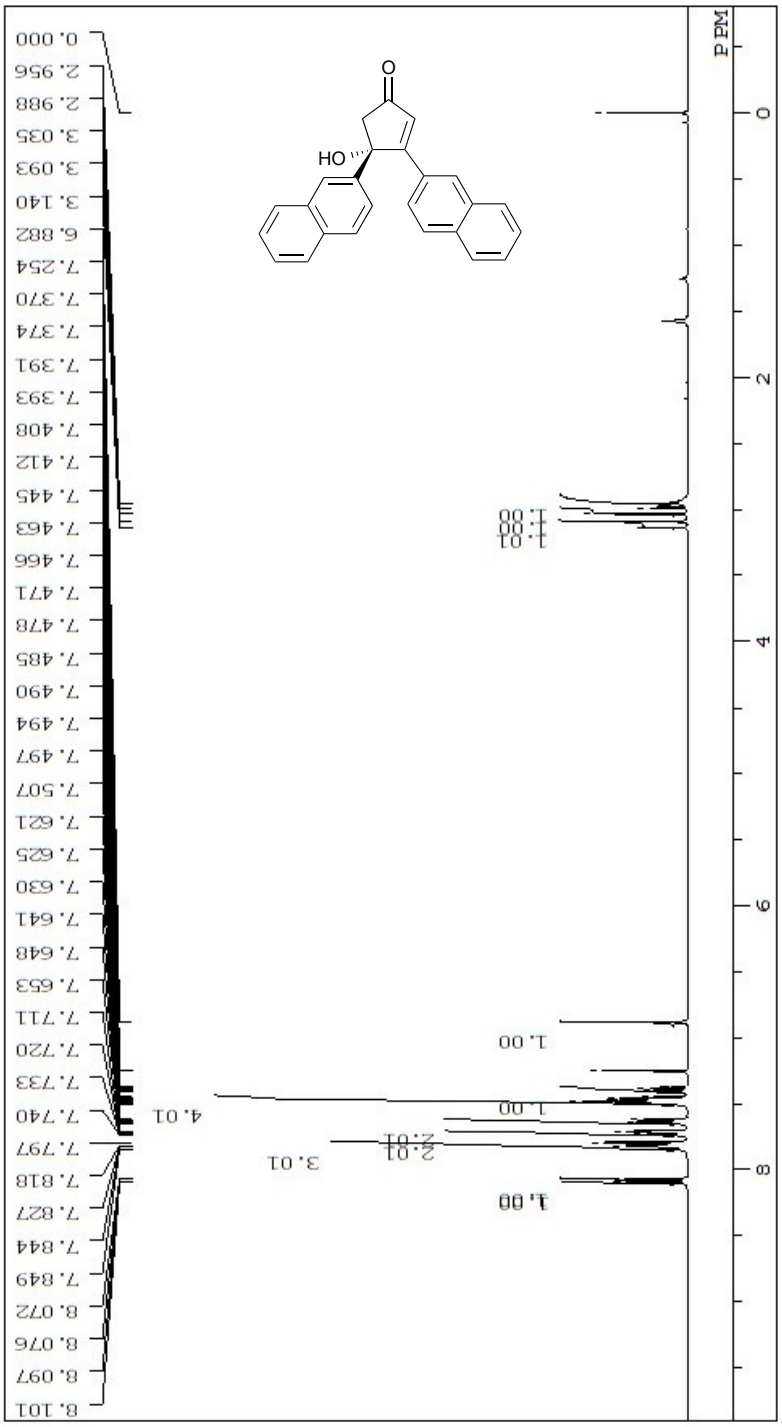
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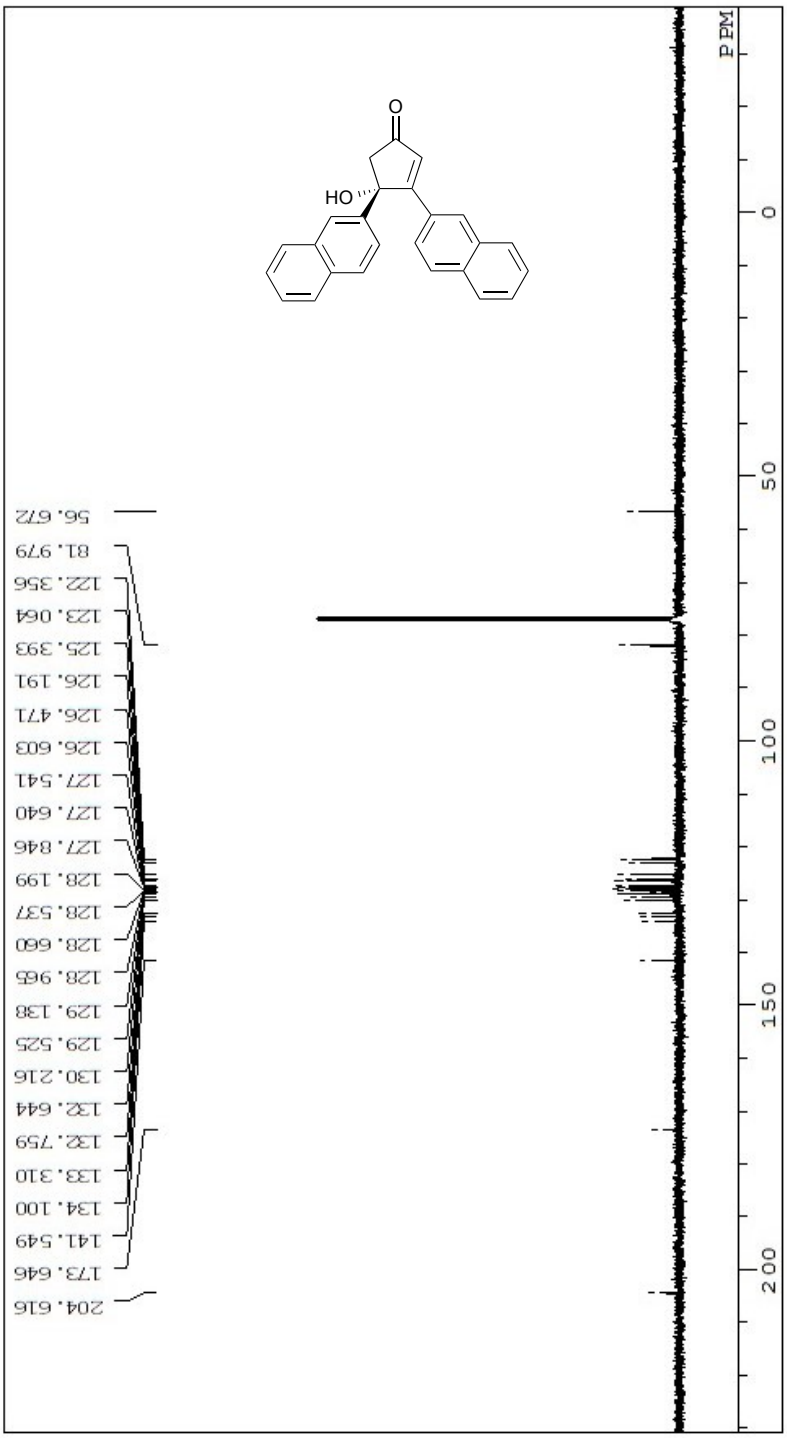
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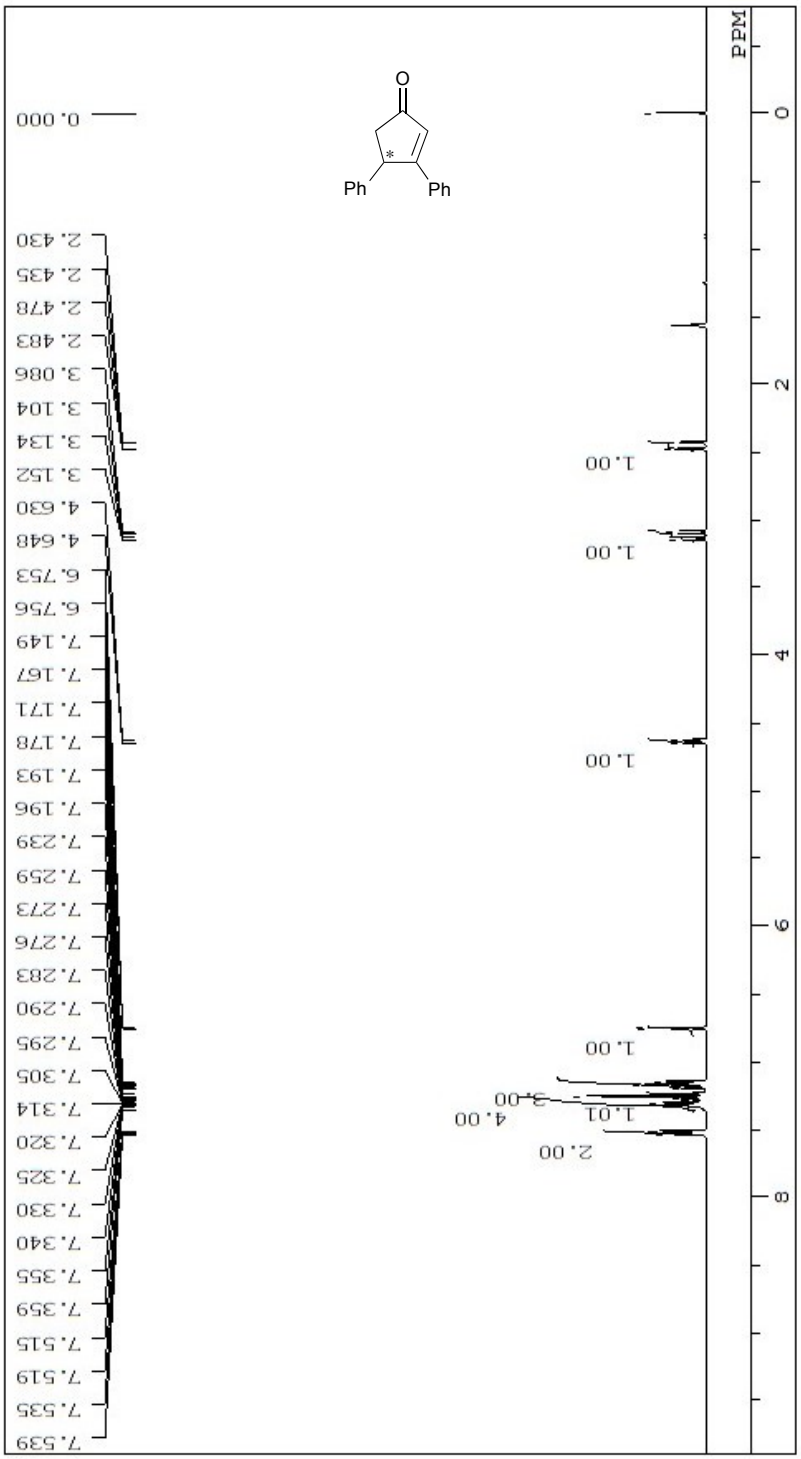
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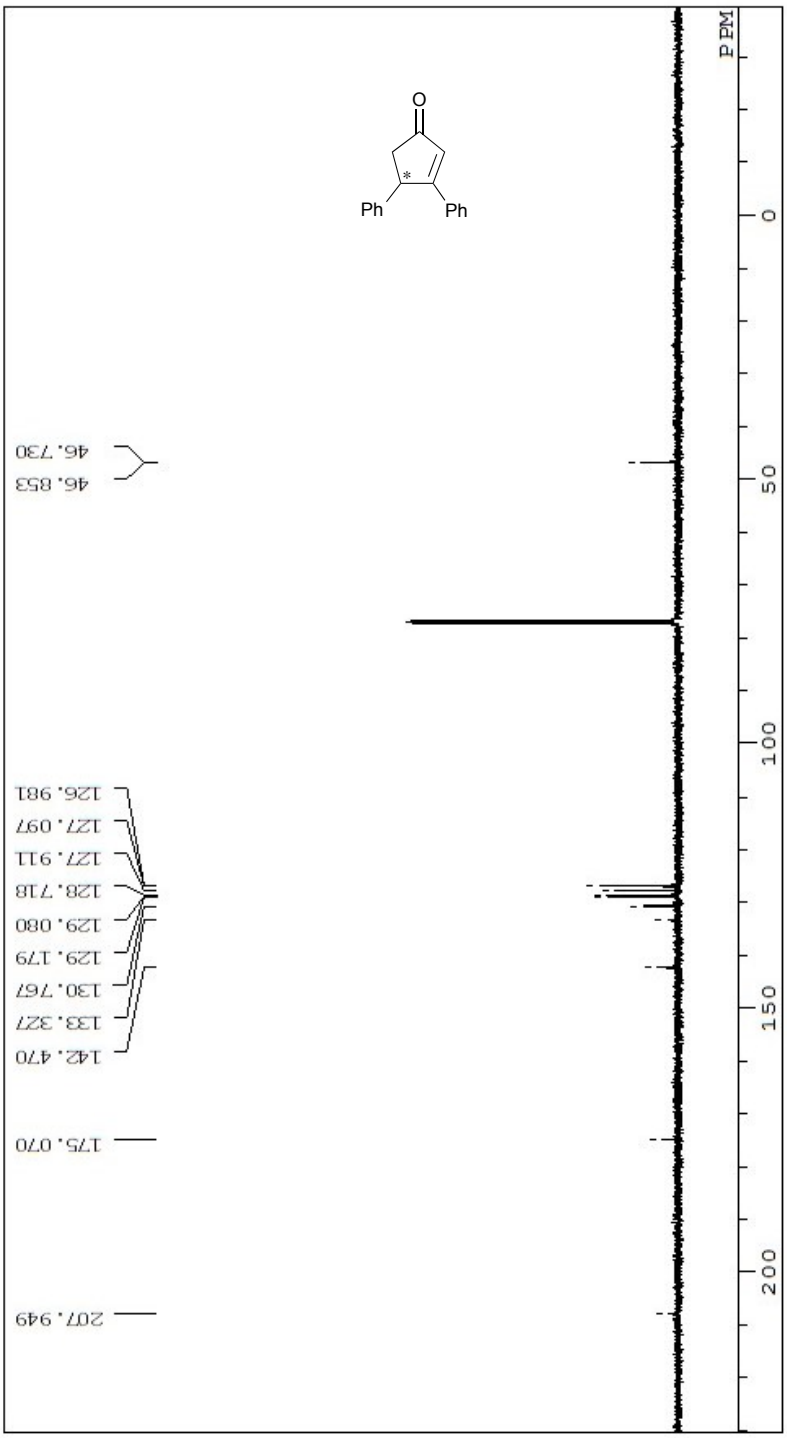
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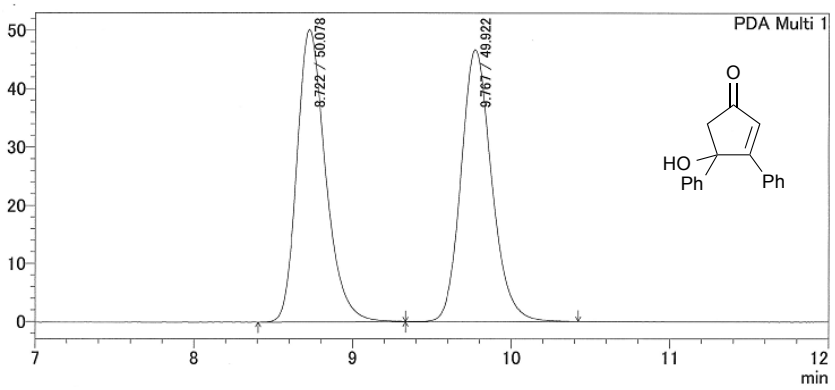
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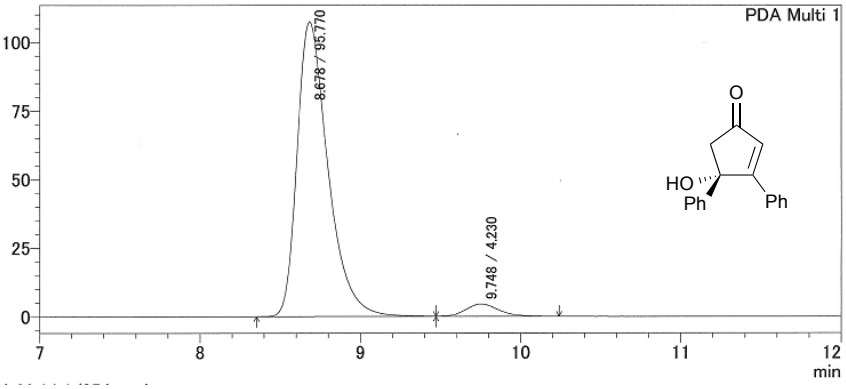
Ph
Ph
min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9.748 / 4.230
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HO
Ph
Ph
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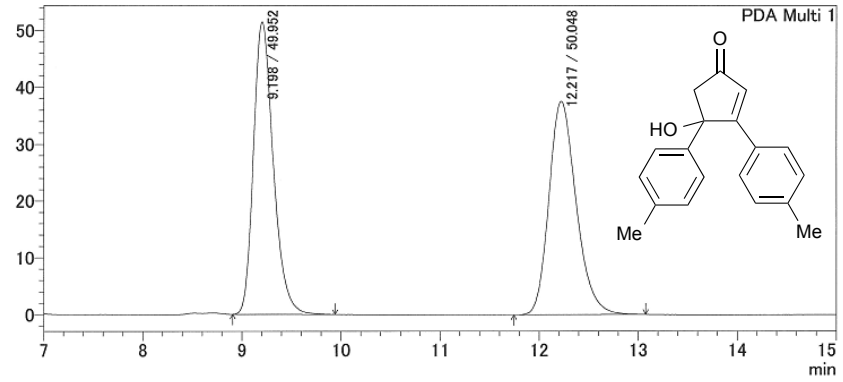
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12.217 / 50.048
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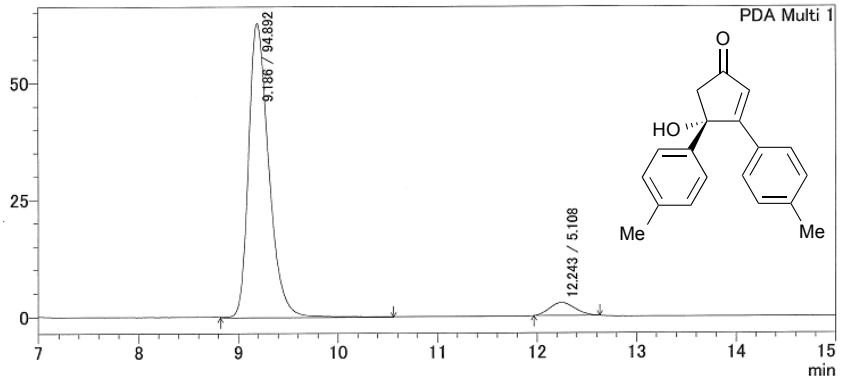
HO
Me
Me
min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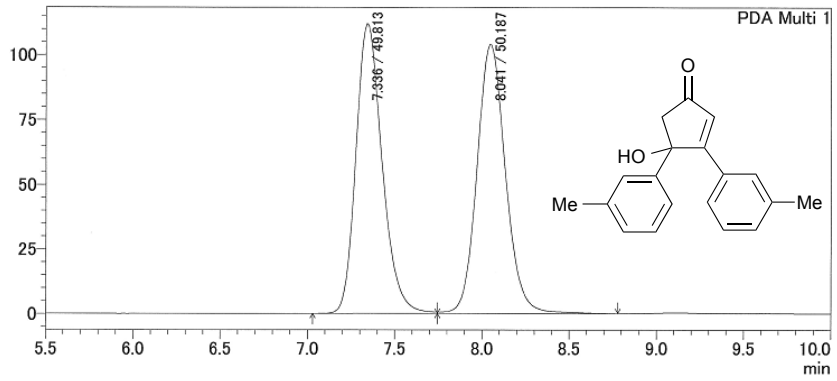
HO
Me
Me
min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8.041 / 50.187
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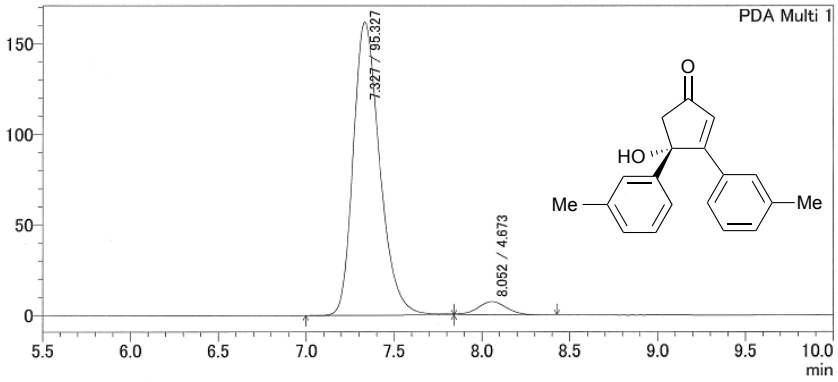
HO
Me
Me
min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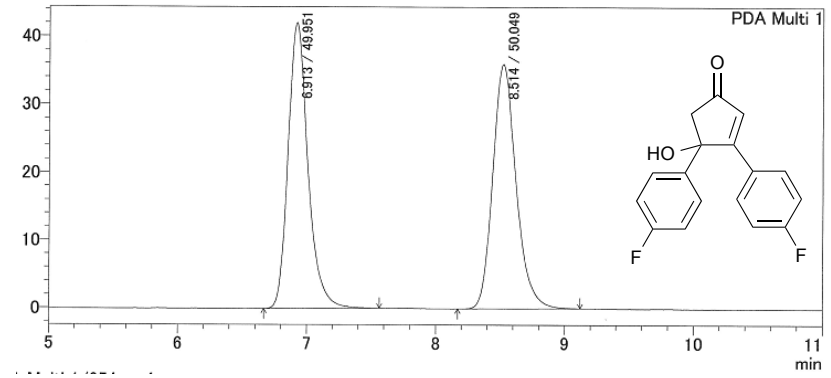
HO
Me
Me
min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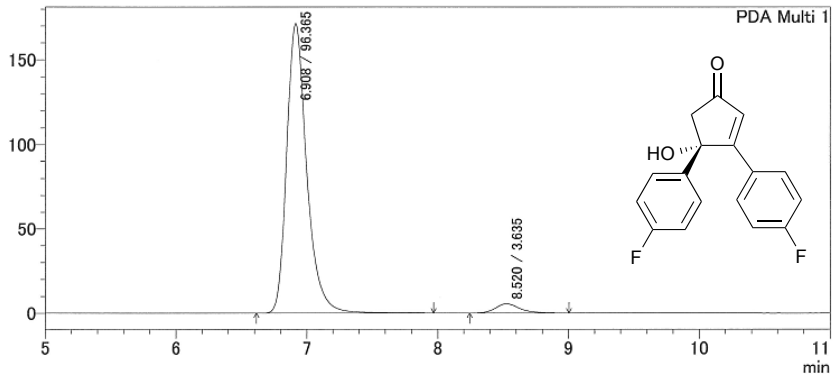
HO
F
F
min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8.520 / 3.635
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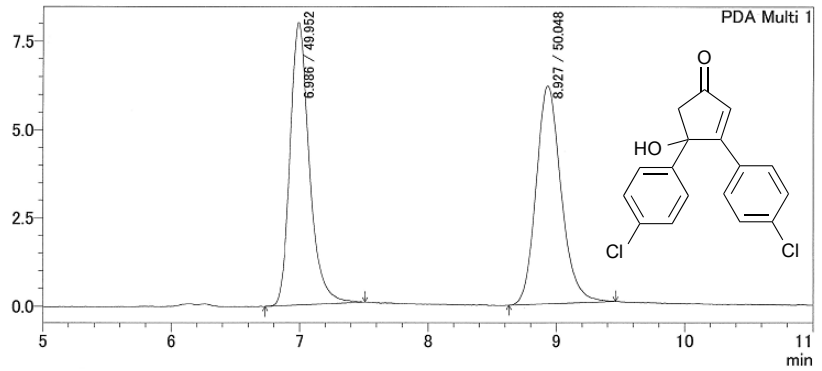
HO
F
F
min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8.927 / 50.048
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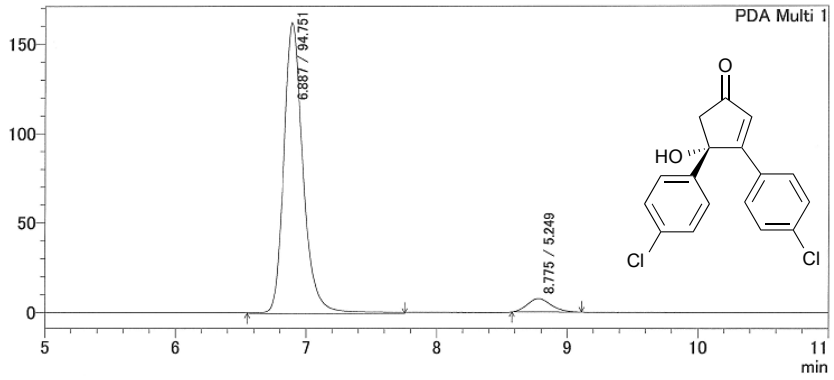
HO
Cl
Cl
min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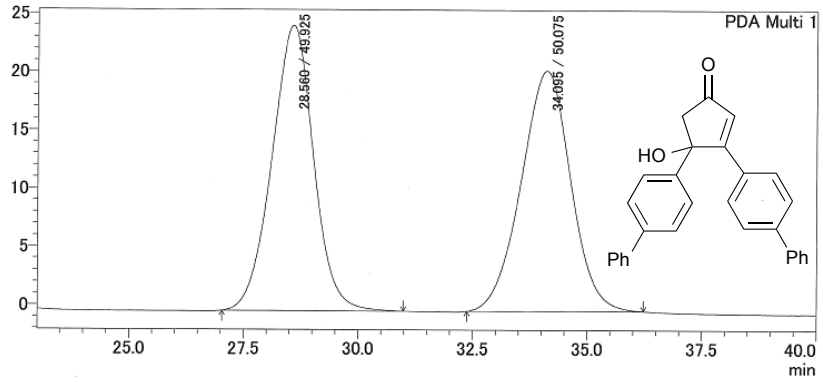
HO
Cl
Cl
min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34.095 / 50.075
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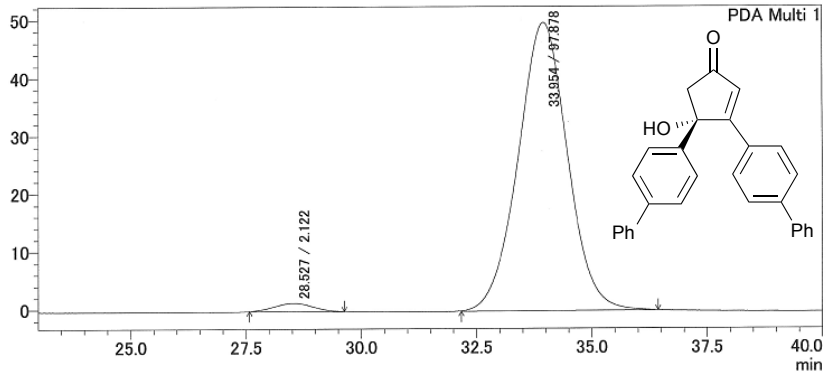
Ph
Ph
min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28.527 / 2.122
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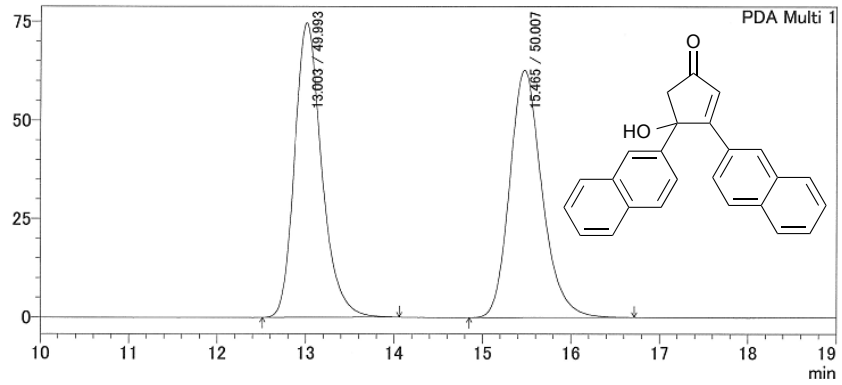
Ph
min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15.465 / 50.007
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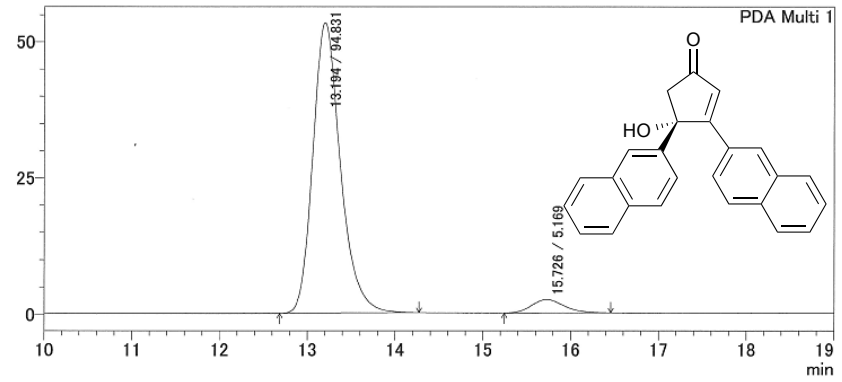
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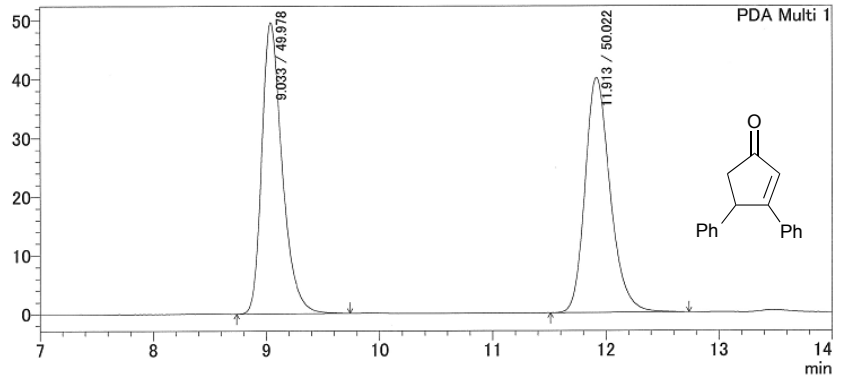
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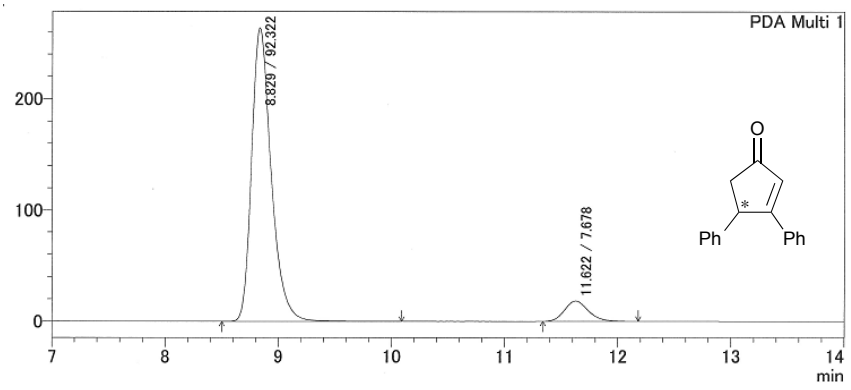
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Ph
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