Cooperative *N*-Heterocyclic Carbene/Lewis Acid Catalysis for Highly Stereoselective Annulation Reactions with Homoenolates

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Supporting Information

General Information

All reactions were carried out under a nitrogen atmosphere in flame-dried glassware with magnetic stirring. CH_2Cl_2 was purified by passage through a bed of activated alumina.[1] Reagents were purified prior to use following the guidelines of Perrin and Armarego unless otherwise stated.[2] Purification of reaction products was carried out by flash chromatography using EM Reagent silica gel 60 (230-400 mesh). Analytical thin layer chromatography was performed on EM Reagent 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light and ceric ammonium nitrate stain or potassium permangenate stain followed by heating. Infrared spectra were recorded on a Perkin Elmer 1600 series FT-IR spectrometer. ^{1}H-NMR spectra were recorded on a Varian Inova 500 (500 MHz) spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 7.26 ppm). Data are reported as (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; coupling constant(s) in Hz; integration). Proton-decoupled ^{13}C-NMR spectra were recorded on a Varian Inova 500 (125 MHz) spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 77.0 ppm). Mass spectra data were obtained on a Hewlett-Packard/Agilent 5972-A GC-MSD system with electron impact (EI) ionization source.

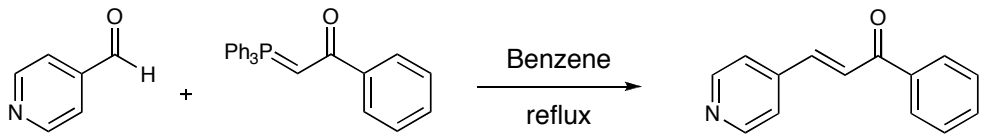
4-bromo cinnamaldehyde was prepared according to a procedure analogous to Moloney and coworkers.[3] 4-chloro cinnamaldehyde, 4-fluoro cinnamaldehyde and 3-(naphtalen-1-yl)acrylaldehyde were prepared according to the general procedure of Cacchi and coworkers.[4] 4-Methoxy cinnamaldehyde was purchased from Acros Chemical Company and the remaining aldehydes were purchased from Sigma-Aldrich Chemical Company and distilled over CaH_2 prior use.

trans-Chalcone was purchased from Sigma-Aldrich Chemical Company and was recrystallized once from hot hexanes prior use. (*E*)-3-(4-bromophenyl)-1-(4-chlorophenyl)prop-2-en-1-one, (*E*)-1,3-bis(4-chlorophenyl)prop-2-en-1-one, (*E*)-3-(2-chlorophenyl)-1-(4-chlorophenyl)prop-2-en-1-one, (*E*)-1-(4-chlorophenyl)-3-(4-fluorophenyl)prop-2-en-1-one, (*E*)-1-(4-chlorophenyl)-3-(3-nitrophenyl)prop-2-en-1-one, (*E*)-1-(4-chlorophenyl)-3-*p*-tolylprop-2-en-1-one and (*E*)-1-(furan-2-yl)-3-phenylprop-2-en-1-one were prepared according to the general procedure of Dannhardt and coworkers.[5] (*E*)-1-(4-chlorophenyl)-3-(4-methoxyphenyl)prop-2-en-1-one, (*E*)-1-(4-chlorophenyl)-3-(furan-2-yl)prop-2-en-1-one and (*E*)-1-(4-chlorophenyl)-3-(thiophen-2-yl)prop-2-en-1-one were prepared according to the procedure of Emerson and coworkers.[6] If precipitation of the compound did not occur, the organic solvents were removed under reduced pressure. Water was added and the mixture was extracted twice with EtOAc. The combined organic layers were then dried over Na_2SO_4, filtered and concentrated. The crude mixture was finally prurified by flash chromatography. In the case of (*E*)-1-(furan-2-yl)-3-phenylprop-2-en-1-

1. Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometal*. **1996**, *15*, 1518-1520.
2. Perrin, D. D. and Armarego, W. L. *Purification of Laboratory Chemicals;* 3rd Ed., Pergamon Press, Oxford. 1988.
3. Baldwin, J. E.; Turner, S. C. M.; Moloney, M. G. *Tetrahedron* **1994**, *50*, 9411-9424.
4. Battistuzzi, G.; Cacchi, S.; Fabrizi, G. *Org. Lett*. **2003**, *5*, 777-780.
5. Dannhardt, G.; Kiefer, W.; Kramer, G.; Maehrlein, S.; Nowe, U.; Fiebich, B. *Eur. J. Med. Chem*. **2000**, 499-510.
6. Emerson, W. S.; Patrick, T. M., Jr. *J. Org. Chem*. **1949**, *14*, 790-797.

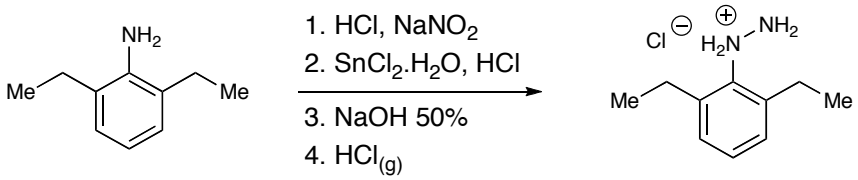
one, flash chromatography was followed by recrystallization from hot hexanes/EtOAc (20:1) to afford the pure compound.

Procedure for the Synthesis of (*E*)-1-phenyl-3-(pyridin-4-yl)prop-2-en-1-one[7]



Into a flame-dried round bottom flask equipped with magnetic stirring bar was dissolved 4-pyridinecarboxaldehyde (1.07g, 10.0 mmol) in 50 mL of dry benzene under positive N_2 atmosphere. The Wittig reagent was then added in one portion and the reaction mixture was refluxed for 6 hours. The mixture was concentrated under vacuum and purified twice by flash chromatography using 30% EtOAc/hexanes to 50% EtOAc/hexanes to afford a yellowish solid (1.71 g, 82%).

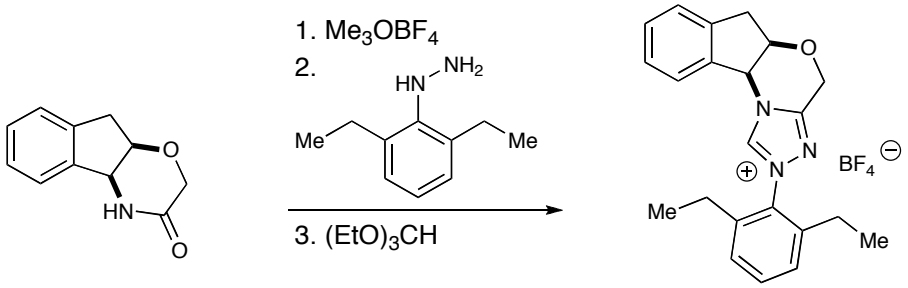
Preparation of the Chiral Triazolium Catalyst D



2,6-diethylphenylhydrazine hydrochloride salt. To a rapidly stirring solution of 10.93 mL 12M HCl in 4.91 mL water was added 5.0 mL (30 mmol) 2,6-diethylaniline dropwise over 1 hour. Slurry was placed under N_2, cooled to 0 °C and a solution of $NaNO_2$ (2.26 g, 1.08 equiv., in 3.40 mL water) was added dropwise over 2.5 hours. (Note: while adding the $NaNO_2$ it is better to add more slowly in the beginning of the addition. The mixture will be a thick slurry and the nitrite solution must be mixed in slowly and thoroughly to avoid expulsion of NO gas.) Upon completed addition of $NaNO_2$, the solution is mostly homogeneous and orange. Continue to stir for 30 minutes at 0 °C then add a solution of 15.24 g (2.24 equiv.) $SnCl_2 \bullet H_2O$ in 20.52 mL of aqueous 6M HCl slowly dropwise. Over the course of this addition, the mixture will becoming a very thick cream to light orange colored slurry. A small amount of water may be added if the slurry solidifies. At this stage, the mixture is allowed to warm to room temperature and stir for 3-5 days. (Note: This long reduction time is necessary to achieve reproducible results.) After stirring is complete, the slurry is filtered and washed with a small amount of water then a small amount of ether. Most of the orange color from the slurry should wash out with the ether. The solid was then added gradually to a cold (-10 °C) 50% (w/w) solution of NaOH (100 mL) and 70 mL ether under nitrogen. (Note: At this point the compound becomes very air sensitive.) Allow the biphasic mixture to stir rapidly at -10 °C until the solid all dissolves, about 2-3 hours. After 2-3 hours, separate the layers, extract the aqueous layer twice with diethyl ether. Combine the organic fractions and stir briefly over $MgSO_4$ under nitrogen. Filter the dried solution and treat

7. Robinson, C. N.; Wiseman, L. J., Jr.; Slater, C. D. *Tetrahedron* **1989**, *45*, 4103-4112.

with HCl gas to precipitate out the hydrazine hydrochloride (3.13 g, 52% yield.) Spectral data matched that found in the literature.[8]



(5aR,10bS)-2-(2,6-diethylphenyl)-4,5a,6,10b-tetrahydroindeno[2,1-b][1,2,4]triazolo[4,3-d][1,4]oxazin-2-ium tetrafluoroborate (D). Prepared according to the general procedure by Rovis and coworkers[9] with modifications from the corresponding morpholin-3-one (643 mg, 3.4 mmol). 2,6-Diethylphenylhydrazine hydrochloride (750 mg, 1.1 equiv) was freebased immediately prior to use with 1 M NaOH and was isolated by subsequent extraction with diethyl ether, drying with $MgSO_4$ and concentration *in vacuo*. The intensely orange oil was added as a solution in a minimal amount of dichloromethane to the preformed imidate. The condensation of the hydrazine and imidate was allowed to proceed at room temperature until judged complete by ^{1}H NMR spectroscopy. The solution was then concentrated *in vacuo* and placed under high vacuum for 1 hour. The red residue was then dissolved in chlorobenzene (0.15 M) and 5 equivalents of triethylorthoformate. The red solution was then heated to 110 °C. The resultant darkened solution was concentrated and purified by flash column chromatography (50-90% EtOAc/hexanes) followed by precipitation from the resultant orange oil with a minute amount of dichloromethane and hexanes followed by a generous portion of diethyl ether to yield 884 mg (60%) **D** as a white solid. Analytical Data for **D**: IR (film): 3088, 2981, 2942, 2881, 1580, 1185, 1085; ^{1}H NMR (500 MHz; D_3COD): δ 11.04 (s, 1H), 7.62 (t, J = 7.7 Hz, 1H), 7.47-7.34 (m, 6H), 6.10 (d, J = 4.1 Hz, 1H), 5.24 (d, J = 16.1 Hz, 1H), 5.11 (d, J = 16.1 Hz, 1H), 5.09 (t, J = 4.5 Hz, 1H), 3.48 (dd, J = 17.1 Hz, 4.9 Hz, 1H), 3.29 (d, J = 18.0 Hz, 2H), 2.54 (bs, 2H), 2.33 (bs, 1H), 1.22 (bs, 3H), 1.14 (bs, 3H); ^{13}C NMR (125 MHz; D_3COD): δ 152.1, 142.1, 137.0, 133.8, 133.6, 130.9, 128.7, 127.0, 124.2, 78.7, 63.3, 61.1, 38.3, 25.1, 24.9, 15.6, 15.4. LRMS (electrospray): Exact mass calcd for $C_{22}H_{24}BF_4N_3O$ [M] = 433 Found [M-BF_4] 346. $[\alpha]_D^{20}$: (*c* 1.00, MeOH): +10.2.

General Procedure for the Enantioselective Synthesis of *cis*-cyclopentenes

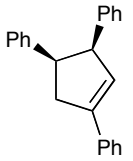
Into an oven-dried screw-capped vial equipped with a magnetic stirbar were weighed the α,β-unsaturated ketone (3 equiv) and azolium salt **B** (0.1 equiv) in a nitrogen-filled drybox. The vial with reagents was capped and removed from the drybox. Into the vial were then successively added degassed (three freeze-pump-thaw cycles) CH_2Cl_2 (1 mL for 0.1 mmol of aldehyde, 0.1M), cinnamaldehyde (1 equiv), Ti(O*i*-Pr)$_4$ (0.2 equiv unless otherwise noted), *i*-PrOH (0.2 equiv) and finally DBU (0.15 equiv). Upon consumption of the aldehyde (all reactions were completed within 24 hours), the reaction mixture was filtered through a short plug of SiO_2 (in a

8. Miller, B.; Matjeka, E. R. *J. Am. Chem. Soc.* **1980**, *102*, 4772-4780.
9. Kerr, M. S., Read de Alaniz, J., Rovis, T. *J. Org. Chem.* **2005,** *70* 5725-5728.

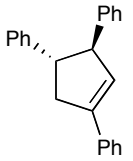
pipette) and washed with EtOAc. The solution was then concentrated under reduced pressure and purified by flash chromatography with EtOAc/hexanes to afford the corresponding *cis*-cyclopentene.

The corresponding racemic compounds were prepared by employing the same protocol but with achiral azolium salt **A** (15 mol%).

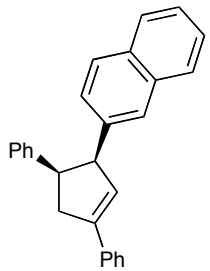
Characterization of Cyclopentenes



***cis*-1,3(*S*)-4(*R*)-Triphenylcyclopent-1-ene (3)**: Prepared according to general procedure using cinnamaldehyde (21.5 μL, 0.17 mmol) and chalcone (106 mg, 0.51 mmol) and purified by flash chromatography using 1% EtOAc/hexanes to afford 37 mg (74% yield) of **1** (>20:1 dr) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.3 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.07-7.00 (m, 6H), 6.89 (dd, *J* = 7.7, 1.8 Hz, 2H), 6.84 (dd, *J* = 7.5, 1.9 Hz, 2H), 6.37 (s, 1H), 4.36 (d, *J* = 8.5 Hz, 1H), 4.06 (ddd, *J* = 8.3, 8.3, 8.3 Hz, 1H), 3.19 (dddd, *J* = 15.6, 8.3, 1.7, 1.7 Hz, 1H), 3.12 (dddd, *J* = 15.5, 8.2, 0.8, 0.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7, 141.5, 140.6, 136.0, 128.7, 128.5, 128.4, 128.0, 127.7, 127.54, 127.50, 126.0, 125.8, 56.8, 50.1, 38.1; IR (film) 3079, 3021, 2925, 2906, 2883, 2846, 1600, 1493, 1452 cm^{-1}; LRMS (EI): Mass calcd for $C_{23}H_{20}$ [M$^+$]: 296, found [M]$^+$: 296; $[\alpha]_D^{20}$: (*c* 1.00, $CHCl_3$): +257.0; Enantiomeric ratio was measured by reverse phase HPLC (Chiralcel AD-RH, 60% MeCN/H_2O, 1 mL/min), Rt (*cis*) = 17.0 and 23.3 min, Rt (*trans*) = 20.4 and 35.9 min; ee *cis* = 99%.



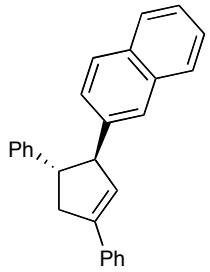
(±)-*trans*-1,3(*S*)-4(*S*)-Triphenylcyclopent-1-ene: Prepared according to the procedure reported by Nair.[10] This compound was reported previously in the same communication.



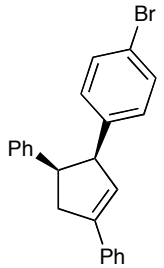
***cis*-1,4(*R*)-Diphenyl-3(*S*)-(2-naphtyl)-cyclopent-1-ene (4)**: Prepared according to general procedure using (*E*)-3-(naphthalen-1-yl)prop-2-enal (26.3 mg, 0.144 mmol) and chalcone (90 mg, 0.433 mmol) and purified by flash chromatography using 1% EtOAc/hexanes to afford 38

10. Nair, V.; Vellalath, S.; Poonoth, M.; Suresh, E. *J. Am. Chem. Soc.* **2006**, *128*, 8736-8737.

mg (76% yield) of **2** (>20:1 dr) as a yellowish oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69-7.64 (m, 4H), 7.48-7.42 (m, 3H), 7.40 (s, 1H), 7.33-7.39 (m, 3H), 6.98-6.91 (m, 5H), 6.86 (dd, *J* = 8.5, 1.7 Hz, 1H), 6.45 (dd, *J* = 4.1, 1.7 Hz, 1H), 4.52 (ddd, *J* = 8.6, 1.8, 1.8 Hz, 1H), 4.14 (ddd, *J* = 8.4, 8.4, 8.4 Hz, 1H), 3.26 (dddd, *J* = 15.7, 8.4, 2.0, 2.0 Hz, 1H), 3.17 (dddd, *J* = 15.7, 8.2, 1.0, 1.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.8, 141.4, 138.4, 136.1, 133.1, 132.1, 128.5, 128.4, 128.0, 127.7, 127.6, 127.5, 127.4, 127.0, 126.9, 125.85, 125.83, 125.5, 125.0, 56.8, 50.1, 38.2; IR (film) 3055, 3024, 2899, 2841, 1600, 1494, 1453, 1446, 853, 818 cm^{-1}; LRMS (EI): Mass calcd for $C_{27}H_{22}$ [M$^+$]: 346, found [M]$^+$: 346; $[\alpha]_D^{20}$: (*c* 1.68, $CHCl_3$): +235.8; Enantiomeric ratio was measured by reverse phase HPLC (Chiralcel AD-RH, 68% MeCN/H_2O, 1 mL/min), Rt (*cis*) = 11.3 and 15.2 min, Rt (*trans*) = 18.1 and 25.5 min; ee *cis* = 99%.

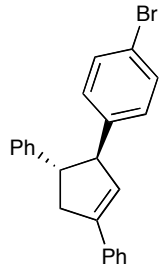


(±)-*trans*-1,4(*S*)-Diphenyl-3(*S*)-(2-naphtyl)-cyclopent-1-ene: Prepared according to the procedure reported by Nair[10] using (*E*)-3-(naphthalen-1-yl)prop-2-enal and chalcone and purified by flash chromatography using 1% EtOAc/hexanes. The compound was obtained in 77% yield (16:1 dr) as a yellowish oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 6.3, 2.7 Hz, 1H), 7.78 (d, *J* = 8.5 Hz, 1H), 7.75 (dd, *J* = 6.7, 2.7 Hz, 1H), 7.61-7.57 (m, 3H), 7.45-7.42 (m, 2H), 7.42-7.38 (m, 2H), 7.33-7.27 (m, 6H), 7.25-7.21 (m, 1H), 6.35 (dd, *J* = 3.1, 1.8 Hz, 1H), 4.30 (ddd, *J* = 7.0, 4.2, 2.0 Hz, 1H), 3.55 (ddd, *J* = 8.2, 7.4, 7.4 Hz, 1H), 3.42 (dddd, *J* = 15.9, 8.9, 2.0, 1.5 Hz, 1H), 3.08 (dddd, *J* = 15.9, 7.4, 2.2, 2.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.4, 142.4, 142.3, 135.9, 133.5, 132.4, 128.50, 128.49, 128.1, 128.0, 127.6, 127.58, 127.57, 127.3, 126.3, 126.2, 125.9, 125.8, 125.5, 125.3, 61.1, 54.4, 42.0; IR (film) 3055, 3024, 2923, 2848, 1632, 1600, 1506, 1494, 1454, 1446, 854, 815 cm^{-1}; LRMS (EI): Mass calcd for $C_{27}H_{22}$ [M$^+$]: 346, found [M]$^+$: 346.

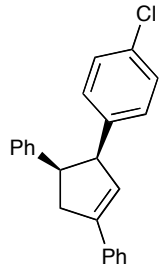


***cis*-3(*S*)-(4-Bromophenyl)-1,4(*R*)-diphenylcyclopent-1-ene (5)**: Prepared according to general procedure using 4-bromocinnamaldehyde (56 mg, 0.266 mmol) and chalcone (166 mg, 0.266 mmol) and purified by flash chromatography using 1% EtOAc/hexanes to afford 67 mg (67% yield) of **3** (>20:1 dr) as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62-7.58 (m, 2H), 7.43-7.39 (m, 2H), 7.33 (tt, *J* = 7.4, 1.5 Hz, 1H), 7.15 (ddd, *J* = 9.1, 2.5, 1.9 Hz, 2H), 7.09-7.01 (m, 3H), 6.90-6.87 (m, 2H), 6.70 (ddd, *J* = 9.1, 4.3, 1.8 Hz, 2H), 6.31 (dd, *J* = 4.2, 1.8 Hz, 1H), 4.30 (ddd, *J* = 8.6, 2.0, 2.0 Hz, 1H), 4.04 (ddd, *J* = 8.3, 8.3, 8.3 Hz, 1H), 3.16 (dddd, *J* = 15.7, 8.3, 2.0,

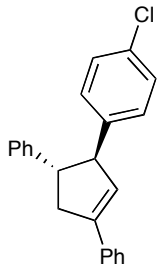
2.0 Hz, 1H), 3.10 (dddd, *J* = 15.7, 8.2, 1.2, 1.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.2, 141.1, 139.7, 135.8, 130.7, 130.4, 128.5, 128.3, 127.7, 127.4, 126.0, 125.8, 119.9, 56.2, 49.9, 37.8; IR (film) 3081, 3059, 3027, 2871, 1600, 1485, 1453, 1447, 1072, 1010, 860, 829, 754, 719, 699, 693 cm^{-1}; LRMS (EI): Mass calcd for $C_{23}H_{19}Br$ [M^+]: 374, found [M]$^+$: 374; $[\alpha]_D^{20}$: (*c* 1.33, $CHCl_3$): +84.4; Enantiomeric ratio was measured by HPLC (Chiralcel AD-H, 0.6% IPA/hexanes, 0.9 mL/min), Rt (*cis*) = 7.5 and 8.5 min, Rt (*trans*) = 10.0 and 11.8 min; ee *cis* = 98%.



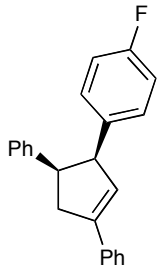
(±)-*trans*-3(*S*)-(4-Bromophenyl)-1,4(*S*)-diphenylcyclopent-1-ene: Prepared according to the procedure reported by Nair.[10] This compound was reported previously in the same communication.



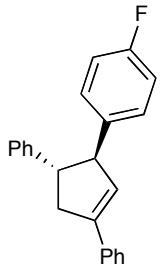
***cis*-3(*S*)-(4-Chlorophenyl)-1,4(*R*)-diphenylcyclopent-1-ene (6)**: Prepared according to general procedure using 4-chlorocinnamaldehyde (50.3 mg, 0.302 mmol) and chalcone (189 mg, 0.90 mmol) and purified by flash chromatography using 1% EtOAc/hexanes to afford 65 mg (65% yield) of **4** (>20:1 dr) as a yellowish solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63-7.59 (m, 2H), 7.44-7.39 (m, 2H), 7.32 (tt, *J* = 1.5, 7.4 Hz, 1H), 7.08-7.02 (m, 3H), 7.00 (ddd, *J* = 9.1, 2.7, 2.0 Hz, 2H), 6.92-6.87 (m, 2H), 6.75 (ddd, *J* = 9.1, 2.6, 1.9 Hz, 2H), 6.32 (dd, *J* = 4.2, 1.8 Hz, 1H), 4.32 (ddd, *J* = 8.6, 1.9, 1.9 Hz, 1H), 4.05 (ddd, *J* = 8.3, 8.3, 8.3 Hz, 1H), 3.17 (dddd, *J* = 15.7, 8.3, 2.0, 2.0 Hz, 1H), 3.11 (dddd, *J* = 15.7, 8.2, 1.1, 1.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.2, 141.2, 139.2, 135.9, 131.8, 130.0, 128.6, 128.4, 127.81, 127.78, 127.5, 126.1, 125.9, 56.2, 50.0, 37.9; IR (film) 3059, 3028, 2910, 2848, 1601, 1490, 1453, 1447, 1409, 1091, 1014, 832, 755, 726, 698 cm^{-1}; LRMS (EI): Mass calcd for $C_{23}H_{19}Cl$ [M^+]: 330, found [M]$^+$: 330; $[\alpha]_D^{20}$: (*c* 1.00, $CHCl_3$): +247.5; Enantiomeric ratio was measured by HPLC (Chiralcel AD-H, 0.3% IPA/hexanes, 1.0 mL/min), Rt (*cis*) = 6.9 and 7.7 min, Rt (*trans*) = 9.8 and 11.4 min; ee *cis* = 99%.



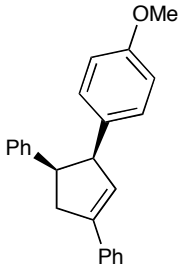
(±)-*trans*-3(*S*)-(4-Chlorophenyl)-1,4(*S*)-diphenylcyclopent-1-ene: Prepared according to the procedure reported by Nair[10] using 4-chlorocinnamaldehyde and chalcone and purified by flash chromatography using 1% EtOAc/hexanes. The compound was obtained in 71% yield (16:1 dr) as a yellowish solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56-7.53 (m, 2H), 7.41-7.36 (m, 2H), 7.34-7.28 (m, 3H), 7.26-7.21 (m, 5H), 7.07 (ddd, *J* = 9.2, 2.9, 1.6 Hz, 2H), 6.24-6.21 (m, 1H), 4.11 (ddd, *J* = 6.7, 4.5, 2.1 Hz, 1H), 3.42-3.30 (m, 2H), 3.03 (dddd, *J* = 14.8, 6.5, 3.2, 2.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.8, 143.3, 142.6, 135.7, 132.1, 128.7, 128.53, 128.52, 128.48, 127.7, 127.4, 127.3, 126.4, 125.8, 60.2, 54.8, 41.9; IR (film) 3081, 3059, 3027, 2923, 2849, 1601, 1491, 1454, 1447, 1409, 1090, 1014, 828, 755, 697 cm^{-1}; LRMS (EI): Mass calcd for $C_{23}H_{19}Cl$ [M^+]: 330, found [M]$^+$: 330.



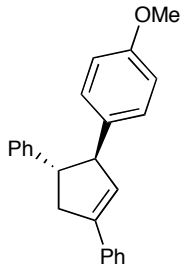
***cis*-1,4(*R*)-Diphenyl-3(*S*)-(4-fluorophenyl)-cyclopent-1-ene (7)**: Prepared according to general procedure using 4-fluorocinnamaldehyde (47.8 mg, 0.318 mmol) and chalcone (199 mg, 0.954 mmol) and purified by flash chromatography using 1% EtOAc/hexanes to afford 74 mg (74% yield) of **5** (>20:1 dr) as a yellowish solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62-7.59 (m, 2H), 7.44-7.39 (m, 2H), 7.33 (tt, *J* = 7.4, 1.3 Hz, 1H), 7.09-7.00 (m, 3H), 6.90-6.86 (m, 2H), 6.80-6.76 (m, 2H), 6.73 (tt, *J* = 8.7, 2.3 Hz, 2H), 6.33 (dd, *J* = 4.1, 1.8 Hz, 1H), 4.33 (dd, *J* = 8.5, 1.7 Hz, 1H), 4.03 (ddd, *J* = 8.4, 8.4, 8.4 Hz, 1H), 3.16 (dddd, *J* = 15.7, 8.3, 2.0, 2.0 Hz, 1H), 3.10 (dddd, *J* = 15.7, 8.2, 1.1, 1.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.5 (d, *J* = 244 Hz, 1C), 143.9, 141.3, 136.2 (d, *J* = 3.5 Hz, 2C), 135.9, 130.02, 129.95, 128.5, 128.4, 127.72, 127.66, 127.64, 125.9, 125.8, 114.4 (d, *J* = 21.3 Hz, 2C), 114.3, 56.0, 50.0, 37.8; IR (film) 3081, 3057, 3030, 2913, 2849, 1602, 1507, 1494, 1453, 1446, 1220, 1157, 836 cm^{-1}; LRMS (EI): Mass calcd for $C_{23}H_{19}F$ [M^+]: 314, found [M]$^+$: 314; $[\alpha]_D^{20}$: (*c* 0.95, $CHCl_3$): +188.9; Enantiomeric ratio was measured by reverse phase HPLC (Chiralcel AD-RH; 0-45 min: isocratic 55% MeCN/H_2O; 45-65 min: gradient 55% MeCN/H_2O to 65% MeCN/H_2O; 65-75 min: isocratic 65% MeCN/H_2O, 1.0 mL/min), Rt (*cis*) = 33.1 and 41.2 min, Rt (*trans*) = 37.5 and 68.2 min; ee *cis* = 99%.



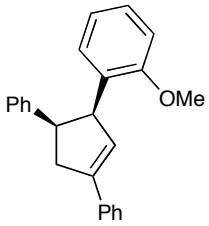
(±)-*trans*-1,4(*S*)-Diphenyl-3(*S*)-(4-fluorophenyl)-cyclopent-1-ene: Prepared according to the procedure reported by Nair[10] using 4-fluorocinnamaldehyde and chalcone and purified by flash chromatography using 1% EtOAc/hexanes. The compound was obtained in 73% yield (15:1 dr) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56-7.52 (m, 2H), 7.40-7.35 (m, 2H), 7.33-7.27 (m, 3H), 7.25-7.21 (m, 3H), 7.11-7.07 (m, 2H), 6.98-6.93 (m, 2H), 6.23 (dd, *J* = 3.5, 2.1 Hz, 1H), 4.11 (ddd, *J* = 6.9, 4.8, 2.4 Hz, 1H), 3.38 (ddd, *J* = 8.7, 7.1, 7.1 Hz, 1H), 3.33 (dddd, *J* = 15.1, 8.8, 2.2, 1.5 Hz, 1H), 3.02 (dddd, *J* = 14.9, 6.7, 3.1, 2.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.6 (d, *J* = 244 Hz, 1C), 145.0, 142.3, 140.5 (d, *J* = 3.3 Hz, 2C), 135.8, 128.8, 128.7, 128.51, 128.48, 127.8, 127.6, 127.3, 126.4, 125.8, 115.2 (d, *J* = 21.0 Hz, 2C), 60.0, 54.9, 41.8; IR (film) 3057, 3027, 2923, 2846, 1601, 508, 1494, 1446, 1221, 1156, 834 cm^{-1}; LRMS (EI): Mass calcd for $C_{23}H_{19}F$ [M$^+$]: 314, found [M]$^+$: 314.



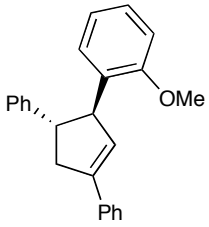
***cis*-1,4(*R*)-Diphenyl-3(*S*)-(4-methoxyphenyl)-cyclopent-1-ene (8)**: Prepared according to general procedure using 4-methoxycinnamaldehyde (49.7 mg, 0.306) and chalcone (191 mg, 0.918) and purified by flash chromatography using 1% EtOAc/hexanes to afford 80 mg (80% yield) of **6** (>20:1 dr) as a yellowish solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63-7.59 (m, 2H), 7.44-7.39 (m, 2H), 7.34-7.30 (m, 1H), 7.09-7.01 (m, 3H), 6.93-6.81 (m, 2H), 6.78-6.73 (m, 2H), 6.63-6.58 (m, 2H), 6.37-6.34 (m, 1H), 4.30 (d, *J* = 8.4 Hz, 1H), 4.01 (ddd, *J* = 8.4, 8.4, 8.4 Hz, 1H), 3.70 (s, 3H), 3.16 (dddd, *J* = 15.6, 8.5, 3.4, 1.7 Hz, 1H), 3.09 (dddd, *J* = 15.6, 8.1, 1.8, 1.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.9, 143.3, 141.6, 136.1, 132.6, 129.6, 128.49, 128.46, 128.37, 127.54, 127.48, 125.7, 113.1, 55.9, 55.1, 50.1, 37.9; IR (film) 3059, 3029, 2929, 2906, 2835, 1608, 1510, 1494, 1453, 1446, 1301, 1249, 1175, 1036, 832, 758, 747, 698 cm^{-1}; LRMS (EI): Mass calcd for $C_{24}H_{22}O$ [M$^+$]: 326, found [M]$^+$: 326; $[\alpha]_D^{20}$: (*c* 1.00, $CHCl_3$): +259.4; Enantiomeric ratio was measured by HPLC (Chiralcel AD-H, 0.4% IPA/hexanes, 1.0 mL/min), Rt (*cis*) = 10.1 and 11.5 min, Rt (*trans*) = 15.8 and 15.8 min; ee *cis* = 99%.



(±)-*trans*-1,4(*S*)-Diphenyl-3(*S*)-(4-Methoxyphenyl)-cyclopent-1-ene Prepared according to the procedure reported by Nair.[10] This compound was reported previously in the same communication.

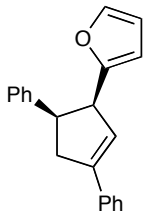


***cis*-3(*S*)-(2-Methoxyphenyl)-1,4(*R*)-diphenylcyclopent-1-ene (9)**: Prepared according to general procedure using 2-methoxycinnamaldehyde (49.7 mg, 0.306 mmol) and chalcone (191 mg, 0.918 mmol). Complete consumption of the aldehyde was achieved after 48h of reaction time. The crude mixture was purified by flash chromatography using 0.75% EtOAc/hexanes to afford 54 mg (54% yield) of **7** (>20:1 dr) as a colorless gum. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (ddd, *J* = 8.2, 0.9, 0.9 Hz, 2H), 7.44-7.39 (m, 2H), 7.32 (tdd, *J* = 7.4, 2.0, 0.9 Hz, 1H), 7.03 (tt, *J* = 7.8, 1.5 Hz, 1H), 7.01-6.95 (m, 4H), 6.90-6.86 (m, 2H), 6.72 (tt, *J* = 7.4, 1.1 Hz, 1H), 6.54 (ddd, *J* = 8.2, 0.7, 0.7 Hz, 1H), 6.34-6.31 (m, 1H), 4.86-4.81 (m, 1H), 4.12-4.06 (m, 1H), 3.49 (d, *J* = 1.0 Hz, 3H), 3.19 (dddd, *J* = 15.8, 8.3, 2.7, 1.4 Hz, 1H), 3.09 (dddd, *J* = 15.8, 7.0, 3.6, 1.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.8, 143.5, 142.7, 136.2, 129.5, 128.52, 128.45, 128.3, 127.6, 127.4, 127.2, 126.9, 125.7, 125.5, 119.7, 109.6, 54.8, 49.4, 48.6, 39.6; IR (film) 3059, 3029, 2932, 2833, 1599, 1586, 1491, 1462, 1454, 1446, 1437, 1244, 1108, 1050, 1032, 752, 698, 692 cm^{-1}; LRMS (EI): Mass calcd for $C_{24}H_{22}O$ [M$^+$]: 326, found [M]$^+$: 326; $[\alpha]_D^{20}$: (*c* 1.04, $CHCl_3$): +158.4; Enantiomeric ratio was measured by HPLC (Chiralcel OJ; 0-15 min: isocratic 2% IPA/hexanes; 15-20 min: gradient 2% IPA/hexanes to 5% IPA/hexanes; 20-30 min: isocratic 5% IPA/hexanes, 1.0 mL/min), Rt (*cis*) = 18.5 and 24.5 min, Rt (*trans*) = 13.0 and 15.5 min; ee *cis* = 99%.

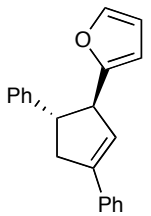


(±)-*trans*-1,4(*S*)-Diphenyl-3(*S*)-(2-methoxyphenyl)-cyclopent-1-ene: Prepared according to the procedure reported by Nair[10] using 2-methoxycinnamaldehyde and chalcone and purified by flash chromatography using 0.75% EtOAc/hexanes. The compound was obtained in 89% yield (8:1 dr) as a colorless gum. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59-7.55 (m, 2H), 7.41-7.37 (m,

2H), 7.35-7.27 (m, 5H), 7.26 (dt, *J* = 7.5, 1.3 Hz, 1H), 7.24-7.19 (m, 2H), 6.96-6.91 (m, 1H), 6.87-6.84 (m, 1H), 6.28-6.25 (s, 1H), 4.60-4.55 (m, 1H), 3.63 (d, *J* = 1.5 Hz, 3H), 3.49-3.44 (m, 1H), 3.34 (m, 1H), 2.97 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.2, 146.8, 142.3, 136.2, 133.3, 128.5, 128.2, 128.1, 127.6, 127.4, 127.2, 126.0, 125.8, 120.6, 110.6, 55.2, 53.3, 52.7, 41.5; IR (film) 3078, 3056, 3024, 2930, 2833, 1598, 1585, 1492, 1461, 1454, 1446, 1438, 1243, 1108, 1051, 1030, 752, 699, 693 cm^{-1}; LRMS (EI): Mass calcd for $C_{24}H_{22}O$ [M$^+$]: 326, found [M]$^+$: 326.

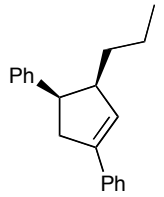


***cis*-1,4(*R*)-Diphenyl-3(*S*)-(furan-2-yl)-cyclopent-1-ene (10)**: Prepared according to general procedure using (*E*)-3-(furan-2-yl)prop-2-enal (42.6 mg, 0.349 mmol) and chalcone (218 mg, 1.047 mmol) and purified by flash chromatography using 0.75% EtOAc/hexanes to afford 73 mg (73% yield) of **8** (>20:1 dr) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60-7.56 (m, 2H), 7.43-7.38 (m, 2H), 7.34-7.30 (m, 1H), 7.18-7.11 (m, 3H), 7.10-7.05 (m, 3H), 6.28-6.25 (m, 1H), 6.12-6.10 (m, 1H), 5.87-5.85 (m, 1H), 4.42 (d, *J* = 8.4 Hz, 1H), 3.97 (ddd, *J* = 8.4, 8.4, 8.4 Hz, 1H), 3.26 (dddd, *J* = 15.6, 8.5, 3.5, 1.8 Hz, 1H), 3.14 (dddd, *J* = 15.6, 8.2, 2.1, 1.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.5, 144.1, 141.6, 141.2, 135.9, 128.5, 128.0, 127.71, 127.65, 126.1, 125.8, 124.8, 109.8, 106.8, 50.4, 49.0, 38.5; IR (film) 3060, 3026, 2921, 2849, 1603, 1494, 1454, 1447, 1171, 1075, 1032, 1013, 884, 850, 808, 758, 732, 694 cm^{-1}; LRMS (EI): Mass calcd for $C_{21}H_{18}O$ [M$^+$]: 286, found [M]$^+$: 286; $[\alpha]_D^{20}$: (*c* 0.98, $CHCl_3$): +232.4; Enantiomeric ratio was measured by reverse phase HPLC (Chiralcel AD-RH; 0-25 min: isocratic 50% MeCN/H_2O; 25-35 min: gradient 50% MeCN/H_2O to 70% MeCN/H_2O ; 35-45 min: isocratic 70% MeCN/H_2O, 1 mL/min), Rt (*cis*) = 33.0 and 37.7 min, Rt (*trans*) = 34.1 and 41.2 min; ee *cis* = 99%.

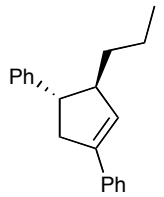


(±)-*trans*-1,4(*S*)-Diphenyl-3(*S*)-(furan-2-yl)-cyclopent-1-ene: Prepared according to the procedure reported by Nair[10] using (*E*)-3-(furan-2-yl)prop-2-enal and chalcone and purified by flash chromatography using 0.75% EtOAc/hexanes. The compound was obtained in 85% yield (11:1 dr) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54-7.50 (m, 2H), 7.39-7.34 (m, 3H), 7.33-7.27 (m, 5H), 7.26-7.22 (m, 1H), 6.30 (dd, *J* = 2.9, 2.1 Hz, 1H), 6.24 (dd, *J* = 3.6, 1.7 Hz, 1H), 6.05-6.03 (m, 1H), 4.23 (ddd, *J* = 6.9, 4.2, 2.3 Hz, 1H), 3.70 (ddd, *J* = 8.7, 7.3, 7.3 Hz, 1H), 3.36 (dddd, *J* = 15.9, 8.9, 1.8, 1.8 Hz, 1H), 2.99 (dddd, *J* = 15.9, 7.3, 2.0, 2.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.3, 145.1, 142.4, 141.4, 135.7, 128.5, 128.4, 127.6, 127.2, 126.4, 125.8, 125.2, 110.1, 104.7, 53.5, 50.3, 41.4; IR (film) 3059, 3031, 2921, 2848, 1601, 1503, 1494, 1454,

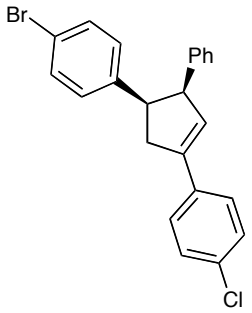
1447, 1171, 1074, 1011, 755, 732, 699 cm^{-1}; LRMS (EI): Mass calcd for $C_{21}H_{18}O$ [M^+]: 286, found [M]$^+$: 286.



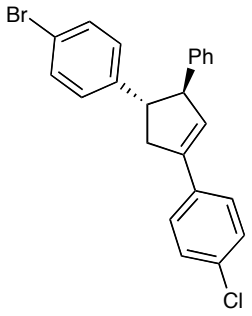
(±)-*cis*-1,4(*R*)-Diphenyl-3(*S*)-(propyl)-cyclopent-1-ene (11): Prepared according to general procedure by reacting hexenal (37.4 mg, 0.381 mmol) and chalcone (238 mg, 1.14 mmol) with 15 mol% of the achiral triazolium catalyst (see Table 1 of the manuscript). The compound was purified by flash chromatography using 1% EtOAc/hexanes to afford 62 mg (62% yield) of **9** (>20:1 dr) as a yellowish oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50-7.45 (m, 2H), 7.35-7.29 (m, 1H), 7.29-7.19 (m, 6H), 7.20-7.14 (m, 1H), 6.28 (s, 1H), 3.70 (ddd, *J* = 7.3, 7.3, 7.3 Hz, 1H), 3.08-2.96 (m, 3H), 1.34-1.23 (m, 1H), 1.20-4.09 (m, 1H), 0.95 (q, *J* = 7.7 Hz, 2H), 0.74 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.9, 141.4, 136.5, 129.9, 128.4, 128.0, 127.1, 126.0, 125.5, 49.7, 47.7, 38.0, 33.2, 21.3, 14.3; IR (film) 3082, 3059, 3028, 2957, 2928, 2871, 1601, 1494, 1464, 1453, 1448, 754, 699 cm^{-1}; LRMS (EI): Mass calcd for $C_{20}H_{22}$ [M^+]: 262, found [M]$^+$: 262.



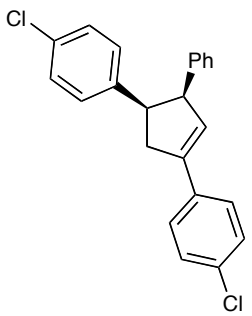
(±)-*trans*-1,4(*S*)-Diphenyl-3(*S*)-(furan-2-yl)-cyclopent-1-ene: Prepared according to the procedure reported by Nair[10] using hexenal and chalcone and purified by flash chromatography using 1% EtOAc/hexanes. The compound was obtained in 62% yield (7:1 dr) as a yellowish oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45-7.41 (m, 2H), 7.33-7.26 (m, 5H), 7.24-7.14 (m, 3H), 6.18 (dd, *J* = 3.6, 2.0 Hz, 1H), 3.18 (dddd, *J* = 15.6, 9.0, 1.7, 1.7 Hz, 1H), 3.08 (ddd, *J* = 8.8, 6.7, 6.7 Hz, 1H), 2.92-2.85 (m, 1H), 2.80 (dddd, *J* = 15.6, 6.9, 2.0, 2.0 Hz, 1H), 1.52-1.30 (m, 4H), 0.85 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.8, 140.3, 136.3, 129.0, 128.4, 128.3, 127.3, 127.1, 126.0, 125.5, 54.9, 50.8, 42.2, 37.7, 21.0, 14.4; IR (film) 3059, 3026, 2956, 2925, 2870, 1601, 1494, 1447754, 700, 692 cm^{-1}; LRMS (EI): Mass calcd for $C_{20}H_{22}O$ [M^+]: 262, found [M]$^+$: 262.



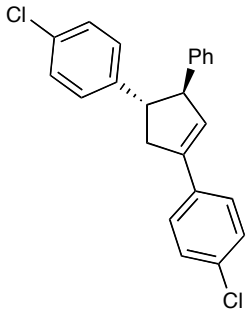
***cis*-4(*R*)-(4-Bromophenyl)-1-(4-chlorophenyl)-3(*S*)-phenyl-cyclopent-1-ene (12)**: Prepared according to general procedure using cinnamaldehyde (15.3 μL, 0.122 mmol) and (*E*)-3-(4-bromophenyl)-1-(4-chlorophenyl)prop-2-en-1-one (118 mg, 0.366 mmol) and purified by flash chromatography using 1% EtOAc/hexanes to afford 35 mg (70% yield) of **10** (>20:1 dr) as a yellowish gum. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (ddd, *J* = 9.2, 2.5, 1.8 Hz, 2H), 7.60 (ddd, *J* = 9.2, 2.5, 1.8 Hz, 2H), 7.14 (ddd, *J* = 9.2, 2.5, 1.7 Hz, 2H), 7.10-7.03 (m, 3H), 6.83-6.79 (m, 2H), 6.73 (ddd, *J* = 9.2, 2.4, 1.5 Hz, 2H), 6.34 (dd, *J* = 4.0, 1.6 Hz, 1H), 4.33 (ddd, *J* = 8.5, 3.1, 1.6 Hz, 1H), 3.99 (ddd, *J* = 8.3, 8.3, 8.3 Hz, 1H), 3.08-3.05 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.5, 140.4, 139.9, 134.3, 133.3, 130.6, 130.1, 128.7, 128.6, 128.5, 127.9, 127.0, 126.4, 119.7, 56.6, 49.5, 38.2; IR (film) 3059, 3030, 2924, 2846, 1600, 1491, 1452, 1404, 1092, 1074, 1010, 818, 715, 701 cm^{-1}; LRMS (EI): Mass calcd for $C_{23}H_{18}BrCl$ [M^+]: 408, found [M]$^+$: 408; $[\alpha]_D^{20}$: (*c* 1.16, $CHCl_3$): +139.2; Enantiomeric ratio was measured by HPLC (Chiralcel AD-H, 1% IPA/hexanes, 1.0 mL/min), Rt (*cis*) = 6.8 and 7.6 min, Rt (*trans*) = 9.9 and 14.2 min; ee *cis* = 99%.



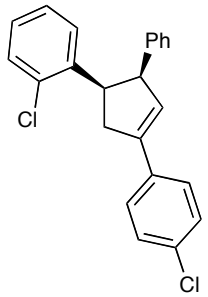
(±)-*trans*-4(*S*)-(4-Bromophenyl)-1-(4-chlorophenyl)-3(*S*)-phenyl-cyclopent-1-ene: Prepared according to the procedure reported by Nair[10] using cinnamaldehyde and (*E*)-3-(4-bromophenyl)-1-(4-chlorophenyl)prop-2-en-1-one and purified by flash chromatography using 1% EtOAc/hexanes. The compound was obtained in 86% yield (14:1 dr) as a colorless gum. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.45 (ddd, *J* = 9.1, 2.3, 1.7 Hz, 2H), 7.41 (ddd, *J* = 9.1, 2.4, 1.6 Hz, 2H), 7.34 (ddd, *J* = 9.1, 2.3, 1.9 Hz, 2H), 7.31-7.27 (m, 2H), 7.23 (tt, *J* = 1.6, 7.3 Hz, 1H), 7.15-7.06 (m, 4H), 6.24 (dd, *J* = 3.7, 1.9 Hz, 1H), 4.06 (ddd, *J* = 7.3, 4.8, 2.5 Hz, 1H), 3.41 (ddd, *J* = 8.0, 8.0, 8.0 Hz, 1H), 3.29 (dddd, *J* = 15.8, 8.8, 1.4, 1.4 Hz, 1H), 2.94 (dddd, *J* = 15.8, 7.6, 2.3, 2.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.2, 143.9, 141.0, 134.2, 133.2, 131.5, 129.1, 128.6, 128.5, 127.3, 127.0, 126.7, 120.0, 60.8, 54.0, 41.8; IR (film) 3059, 3026, 2926, 2848, 1601, 1491, 1452, 1404, 1093, 1073, 1010, 819, 757, 700 cm^{-1}; LRMS (EI): Mass calcd for $C_{23}H_{18}BrCl$ [M^+]: 408.0, found [M]$^+$: 408.



***cis*-1,4(*R*)-bis-(4-Chlorophenyl)-3(*S*)-phenyl-cyclopent-1-ene (13)**: Prepared according to general procedure using cinnamaldehyde (17.2 μL, 0.137 mmol) and (*E*)-1,3-bis(4-chlorophenyl)prop-2-en-1-one (114 mg, 0.411 mmol) and purified by flash chromatography using 1% EtOAc/hexanes to afford 33.5 mg (67% yield) of **11** (>20:1 dr) as a colorless gum. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (ddd, *J* = 9.1, 2.5, 1.9 Hz, 2H), 7.37 (ddd, *J* = 9.1, 2.5, 1.9 Hz, 2H), 7.09-7.04 (m, 3H), 6.99 (ddd, *J* = 9.1, 2.6, 1.9 Hz, 2H), 6.83-6.80 (m, 2H), 6.79 (ddd, *J* = 9.2, 2.4, 1.6 Hz, 2H), 6.34 (dd, *J* = 4.1, 1.7 Hz, 1H), 4.33 (ddd, *J* = 8.5, 3.5, 1.7 Hz, 1H), 4.00 (ddd, *J* = 8.3, 8.3, 8.3 Hz, 1H), 3.08 (dd, *J* = 1.5, 1.5 Hz, 1H), 3.06 (dd, *J* = 1.5, 1.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.5, 139.94, 139.89, 134.3, 133.3, 131.5, 129.7, 128.7, 128.6, 128.5, 127.9, 127.6, 127.0, 126.4, 56.7, 49.4, 38.3; IR (film) 3059, 3028, 2926, 2848, 1600, 1492, 1452, 1404, 1092, 1013, 819, 732, 718, 700 cm^{-1}; LRMS (EI): Mass calcd for $C_{23}H_{18}Cl_2$ [M$^+$]: 364, found [M]$^+$: 364; $[\alpha]_D^{20}$: (*c* 0.83, $CHCl_3$): +208.8; Enantiomeric ratio was measured by HPLC (Chiralcel OD-H, 0.2% IPA/hexanes, 1.0 mL/min), Rt (*cis*) = 18.1 and 20.8 min, Rt (*trans*) = 12.3 and 16.4 min; ee *cis* = 99%.

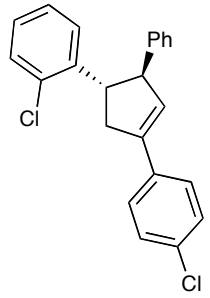


(±)-*trans*-1,4(*S*)-bis-(4-Chlorophenyl)-3(*S*)-phenyl-cyclopent-1-ene: Prepared according to the procedure reported by Nair[10] using cinnamaldehyde and (*E*)-1,3-bis(4-chlorophenyl)prop-2-en-1-one and purified by flash chromatography using 1% EtOAc/hexanes. The compound was obtained in 80% yield (14:1 dr) as a colorless gum. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (ddd, *J* = 9.1, 2.5, 1.9 Hz, 2H), 7.33 (ddd, *J* = 9.1, 2.5, 1.9 Hz, 2H), 7.31-7.21 (m, 5H), 7.16 (ddd, *J* = 9.1, 2.5, 1.9 Hz, 2H), 7.13-7.10 (m, 2H), 6.24 (dd, *J* = 3.6, 2.0 Hz, 1H), 4.06 (ddd, *J* = 7.3, 4.5, 2.2 Hz, 1H), 3.42 (ddd, *J* = 8.4, 7.7, 7.7 Hz, 1H), 3.29 (dddd, *J* = 15.8, 8.8, 1.8, 1.8 Hz, 1H), 2.94 (dddd, *J* = 15.8, 7.7, 2.3, 2.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.2, 143.4, 141.0, 134.2, 133.2, 132.0, 128.7, 128.63, 128.61, 128.60, 128.5, 127.3, 127.0, 126.6, 60.8, 54.0, 41.8; IR (film) 3058, 3027, 2925, 2848, 1600, 1484, 1452, 1403, 1093, 1013, 819, 757, 720, 700 cm^{-1}; LRMS (EI): Mass calcd for $C_{23}H_{18}Cl_2$ [M$^+$]: 364, found [M]$^+$: 364.

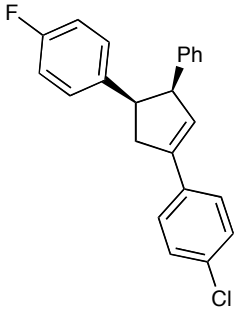


***cis*-4(*R*)-(2-Chlorophenyl)-1-(4-chlorophenyl)-3(*S*)-phenyl-cyclopent-1-ene (14)**: Prepared according to general procedure using cinnamaldehyde (17.2 μL, 0.137 mmol) and (*E*)-3-(2-

chlorophenyl)-1-(4-chlorophenyl)prop-2-en-1-one (114 mg, 0.410 mmol) and purified by flash chromatography using 1% EtOAc/hexanes to afford 41 mg (82% yield) of **12** (>20:1 dr) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (ddd, *J* = 9.1, 2.5, 1.9 Hz, 2H), 7.37 (ddd, *J* = 9.2, 2.6, 1.9 Hz, 2H), 7.22 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.04-6.98 (m, 3H), 6.95 (td, *J* = 7.5, 1.9 Hz, 1H), 6.88-6.81 (m, 4H), 6.35 (dd, *J* = 3.6, 2.4 Hz, 1H), 4.57-4.51 (m, 2H), 3.22-3.15 (m, 1H), 3.03-2.95 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.3, 140.0, 138.6, 134.4, 134.3, 133.2, 128.9, 128.6, 128.5, 128.4, 128.3, 127.7, 127.1, 127.0, 126.3, 126.0, 54.2, 46.0, 36.6; IR (film) 3060, 3026, 2929, 2853, 1600, 1492, 1475, 1453, 1444, 1093, 1035, 1012, 821, 732, 701 cm^{-1}; LRMS (EI): Mass calcd for $C_{23}H_{18}Cl_2$ [M$^+$]: 364, found [M]$^+$: 364; $[\alpha]_D^{20}$: (*c* 1.00, $CHCl_3$): +344.3; Enantiomeric ratio was measured by HPLC (Chiralcel AD-H, 1% IPA/hexanes, 1.0 mL/min), Rt (*cis*) = 6.2 and 6.6 min, Rt (*trans*) = 9.2 and 11.1 min; ee *cis* = 99%.

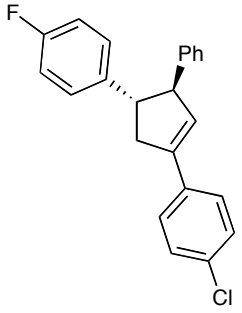


(±)-*trans*-4(*S*)-(2-Chlorophenyl)-1-(4-chlorophenyl)-3(*S*)-phenyl-cyclopent-1-ene: Prepared according to the procedure reported by Nair[10] using cinnamaldehyde and (*E*)-3-(2-chlorophenyl)-1-(4-chlorophenyl)prop-2-en-1-one and purified by flash chromatography using 1% EtOAc/hexanes. The compound was obtained in 72% yield (8:1 dr) as a colorless gum. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48-7.44 (m, 2H), 7.43-7.39 (m, 1H), 7.37-7.31 (m, 3H), 7.31-6.26 (m, 2H), 7.25-7.21 (m, 2H), 7.21-7.18 (m, 2H), 7.17-7.13 (m, 1H), 6.29-6.27 (m, 1H), 4.26-4.21 (m, 1H), 3.99 (dd, *J* = 8.4, 6.7, 6.7 Hz, 1H), 3.42-3.34 (m, 1H), 2.92-2.85 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.1, 142.5, 141.0, 134.2, 133.9, 133.2, 129.7, 128.7, 128.6, 128.5, 128.1, 127.5, 127.4, 127.1, 126.6, 59.2, 49.8, 40.8; IR (film) 3063, 3028, 2928, 2855, 1601, 1492, 1475, 1453, 1436, 1403, 1093, 1035, 1012, 821, 755, 700 cm^{-1}; LRMS (EI): Mass calcd for $C_{23}H_{18}Cl_2$ [M$^+$]: 364, found [M]$^+$: 364.

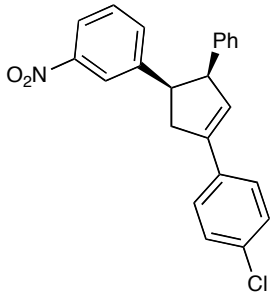


***cis*-1-(4-Chlorophenyl)-4(*R*)-(4-fluorophenyl)-3(*S*)-phenyl-cyclopent-1-ene (15)**: Prepared according to general procedure using cinnamaldehyde (18 μL, 0.143 mmol) and (*E*)-1-(4-chlorophenyl)-3-(4-fluorophenyl)prop-2-en-1-one (112 mg, 0.429 mmol) and purified by flash chromatography using 1% EtOAc/hexanes to afford 35 mg (70% yield) of **13** (>20:1 dr) as a colorless gum. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (ddd, *J* = 9.1, 2.5, 1.9 Hz, 2H), 7.37 (ddd, *J* =

9.1, 2.5, 1.9 Hz, 2H), 7.09-7.03 (m, 3H), 6.83-6.78 (m, 4H), 6.71 (tt, *J* = 8.7, 2.4 Hz, 2H), 6.34 (dd, *J* = 4.2, 1.7 Hz, 2H), 4.32 (ddd, *J* = 8.6, 3.6, 1.9 Hz, 1H), 4.02 (ddd, *J* = 8.3, 8.3, 8.3 Hz, 1H), 3.10-3.06 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.2 (d, *J* = 244 Hz, 1C), 142.5, 140.1, 137.0 (d, *J* = 3.0 Hz, 2C), 134.4, 133.3, 129.7, 129.6, 128.65, 128.64, 128.53, 127.8, 127.0, 126.3, 114.3 (d, *J* = 20.9 Hz, 2C), 56.8, 49.3, 38.4; IR (film) 3058, 3028, 2927, 2910, 2848, 1602, 1510, 1492, 1452, 1223, 1160, 1093, 1012, 821, 700 cm^{-1}; LRMS (EI): Mass calcd for $C_{23}H_{18}FCl$ [M$^+$]: 348, found [M]$^+$: 348; $[\alpha]_D^{20}$: (*c* 1.03, $CHCl_3$): +143.5; Enantiomeric ratio was measured by reverse phase HPLC (Chiralcel AD-RH, 62.5% MeCN/H_2O, 1.0 mL/min), Rt (*cis*) = 44.3 and 48.1 min, Rt (*trans*) = 39.8 and 53.1 min; ee *cis* = 99%.

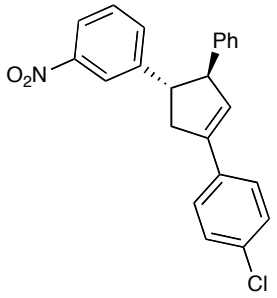


(±)-*trans*-1-(4-Chlorophenyl)-4(*S*)-(2-chlorophenyl)-3(*S*)-phenyl-cyclopent-1-ene: Prepared according to the procedure reported by Nair[10] using cinnamaldehyde and (*E*)-1-(4-chlorophenyl)-3-(4-fluorophenyl)prop-2-en-1-one and purified by flash chromatography using 1% EtOAc/hexanes. The compound was obtained in 84% yield (13:1 dr) as a colorless gum. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (ddd, *J* = 9.1, 2.5, 1.9 Hz, 2H), 7.34 (ddd, *J* = 4.4, 2.5, 1.9 Hz, 2H), 7.29 (tt, *J* = 7.3, 1.5 Hz, 2H), 7.23 (tt, *J* = 7.3, 1.8 Hz, 1H), 7.18 (dddd, *J* = 5.2, 3.1, 3.1, 3.1 Hz, 2H), 7.13-7.10 (m, 2H), 6.98 (tt, *J* = 8.7, 2.4 Hz, 2H), 6.24 (dd, *J* = 3.6, 2.0 Hz, 1H), 4.06 (ddd, *J* = 7.3, 4.7, 2.3 Hz, 1H), 3.43 (ddd, *J* = 7.7, 7.7, 7.7 Hz, 1H), 3.29 (dddd, *J* = 15.8, 8.8, 1.8, 1.8 Hz, 1H), 2.94 (dddd, *J* = 15.8, 7.7, 2.3, 2.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.5 (*J* = 244 Hz, 1C), 144.3, 141.0, 140.6 (d, *J* = 3.0 Hz, 2C), 134.3, 133.2, 128.70, 128.69, 128.63, 128.60, 128.5, 127.3, 127.0, 126.6, 115.2 (d, *J* = 20.9 Hz, 2C), 60.9, 41.9; IR (film) 3058, 3028, 2925, 2849, 1602, 1510, 1492, 1452, 1403, 1224, 1158, 1094, 1012, 821, 700 cm^{-1}; LRMS (EI): Mass calcd for $C_{23}H_{18}FCl$ [M$^+$]: 348, found [M]$^+$: 348.

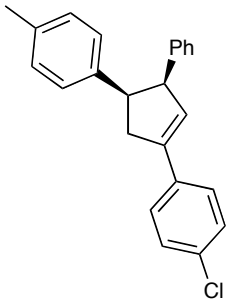


***cis*-1-(4-Chlorophenyl)-4(*R*)-(3-nitrophenyl)-3(*S*)-phenyl-cyclopent-1-ene (16)**: Prepared according to general procedure using cinnamaldehyde (16.7 μL, 0.133 mmol) and (*E*)-1-(4-chlorophenyl)-3-(3-nitrophenyl)prop-2-en-1-one (115 mg, 0.399 mmol) and purified by flash chromatography using 1.5% EtOAc/hexanes to 3% EtOAc/hexanes to afford 32.5 mg (65% yield) of **14** (>20:1 dr) as a yellowish gum. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (ddd, *J* = 7.0,

2.3, 2.1 Hz, 1H), 7.74-7.71 (m, 1H), 7.52 (ddd, *J* = 9.1, 2.3, 1.7 Hz, 2H), 7.38 (ddd, *J* = 9.1, 2.3, 1.8 Hz, 2H), 7.22 -7.16 (m, 2H), 7.08-7.00 (m, 3H), 6.83-6.80 (m, 2H), 6.36 (dd, *J* = 3.9, 1.6 Hz, 1H), 4.42 (ddd, *J* = 8.6, 3.0, 1.8 Hz, 1H), 4.15 (ddd, *J* = 8.3, 8.3, 8.3 Hz, 1H), 3.18-3.15 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.6, 143.7, 142.4, 139.4, 134.5, 134.0, 133.5, 128.7, 128.5, 128.4, 128.1, 128.1, 127.0, 126.7, 123.3, 121.1, 56.7, 49.4, 38.2; IR (film) 3063, 3030, 2924, 2851, 1600, 1527, 1492, 1452, 1346, 1093, 1012, 823, 703, 690 cm^{-1}; LRMS (EI): Mass calcd for $C_{23}H_{18}ClNO_2$ [M$^+$]: 375, found [M]$^+$: 375; $[\alpha]_D^{20}$: (*c* 0.81, $CHCl_3$): +149.0; Enantiomeric ratio was measured by HPLC (Chiralcel OD-H, 1.2% IPA/Hexanes, 1.0 mL/min), Rt (*cis*) = 26.6 and 30.2 min, Rt (*trans*) = 17.9 and 22.3 min; ee *cis* = 99%.

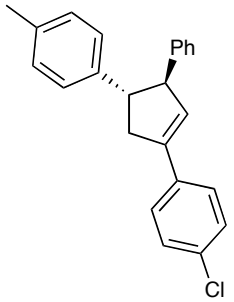


(±)-*trans*-1-(4-Chlorophenyl)-4(*S*)-(3-nitrophenyl)-3(*S*)-phenyl-cyclopent-1-ene: Prepared according to the procedure reported by Nair[10] using cinnamaldehyde and (*E*)-1-(4-chlorophenyl)-3-(3-nitrophenyl)prop-2-en-1-one and purified by flash chromatography using 1% EtOAc/hexanes. The compound was obtained in 88% yield (13:1 dr) as a yellowish gum. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (t, *J* = 1.9 Hz, 1H), 8.11-8.08 (m, 1H), 7.54-7.51 (m, 1H), 7.48-7.44 (m, 3H), 7.35 (ddd, *J* = 9.1, 1.7, 2.4 Hz, 2H), 7.30 (tt, *J* = 7.3, 1.4 Hz, 2H), 7.25 (tt, *J* = 7.3, 1.8 Hz, 1H), 7.14 -7.11 (m, 2H), 6.26 (dd, *J* = 3.5, 1.9 Hz, 1H), 4.13 (ddd, *J* = 7.3, 4.4, 2.2 Hz, 1H), 3.58 (dd, *J* = 7.8, 7.8, 7.8 Hz, 1H), 3.37 (dddd, *J* = 15.9, 8.8, 1.6, 1.6 Hz, 1H), 3.00 (dddd, *J* = 15.9, 7.7, 2.3, 2.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.4, 147.0, 143.6, 140.8, 133.9, 133.8, 133.5, 129.5, 128.71, 128.68, 128.5, 127.3, 127.0, 126.9, 122.1, 121.6, 60.8, 54.1, 41.7; IR (film) 3063, 3030, 2928, 2855, 1600, 1529, 1492, 1452, 1348, 1093, 1012, 821, 736, 700, 687 cm^{-1}; LRMS (EI): Mass calcd for $C_{23}H_{18}ClNO_2$ [M$^+$]: 375, found [M]$^+$: 375.

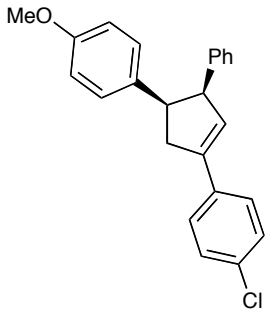


***cis*-1-(4-Chlorophenyl)-4(*R*)-(*p*-tolyl)-3(*S*)-phenyl-cyclopent-1-ene (17)**: Prepared according to general procedure using cinnamaldehyde (18.3 μL, 0.145 mmol) and (*E*)-1-(4-chlorophenyl)-3-*p*-tolylprop-2-en-1-one (112 mg, 0.435 mmol) and purified by flash chromatography using 0.75% EtOAc/hexanes to afford 30 mg (60% yield) of **15** (>20:1 dr) as a colorless gum. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (ddd, *J* = 9.1, 2.3, 1.6 Hz, 2H), 7.36 (ddd, *J* = 9.1, 2.2, 1.6 Hz, 2H), 7.08-7.02 (m, 3H), 6.86-6.81 (m, 4H), 6.77-6.74 (m, 2H), 6.35 (dd, *J* = 3.6, 1.9 Hz, 1H), 4.31 (ddd, *J* = 8.5, 1.9, 1.9 Hz, 1H), 4.00 (ddd, *J* = 8.4, 8.4, 8.4 Hz, 1H), 3.11 (dddd, *J* = 15.6,

8.6, 1.9, 1.9 Hz, 1H), 3.04 (dd, *J* = 15.6, 8.2 Hz, 1H), 2.19 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.6. 140.4, 138.1, 135.3, 134.6, 133.1, 128.81, 128.75, 128.6, 128.2, 127.7, 127.0, 126.1, 56.7, 49.8, 38.2, 20.9; IR (film) 3055, 3026, 2921, 2850, 1601, 1515, 1492, 1452, 1093, 1012, 815, 700 cm^{-1}; LRMS (EI): Mass calcd for $C_{24}H_{21}Cl$ [M^+]: 344, found [M]$^+$: 344; $[\alpha]_D^{20}$: (*c* 0.93, $CHCl_3$): +161.5; Enantiomeric ratio was measured by reverse phase HPLC (Chiralcel AD-RH, 65% MeCN/H_2O, 1.0 mL/min), Rt (*cis*) = 21.5 and 25.7 min, Rt (*trans*) = 31.6 and 50.4 min; ee *cis* = 99%.

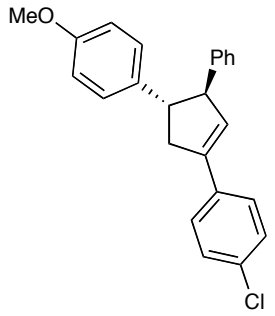


(±)-*trans*-1-(4-Chlorophenyl)-4(*S*)-(*p*-tolyl)-3(*S*)-phenyl-cyclopent-1-ene: Prepared according to the procedure reported by Nair[10] using cinnamaldehyde and (*E*)-1-(4-chlorophenyl)-3-*p*-tolylprop-2-en-1-one and purified by flash chromatography using 1% EtOAc/hexanes. The compound was obtained in 80% yield (17:1 dr) as a colorless gum. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (ddd, *J* = 9.2, 2.4, 1.8 Hz, 2H), 7.33 (ddd, *J* = 9.2, 2.4, 1.7 Hz, 2H), 7.30-7.26 (m, 2H), 7.21 (tt *J* = 7.3, 1.6 Hz, 1H), 7.15-7.09 (m, 6H), 6.24 (dd, *J* = 3.6, 1.9 Hz, 1H), 4.11 (ddd, *J* = 7.2, 4.6, 2.2 Hz, 1H), 3.42 (ddd, *J* = 8.4, 7.6, 7.6 Hz, 1H), 3.28 (dddd, *J* = 15.8, 8.9, 1.7, 1.7 Hz, 1H), 2.96 (dddd, *J* = 15.8, 7.6, 2.3, 2.3 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.7, 142.0, 141.0, 135.8, 134.4, 133.1, 129.2, 128.8, 128.6, 128.4, 127.4, 127.2, 127.0, 126.4, 60.7, 54.1, 42.0, 21.0; IR (film) 3055, 3025, 2920, 2849, 1600, 1514, 1492, 1452, 1402, 1091, 1012, 815, 700 cm^{-1}; LRMS (EI): Mass calcd for $C_{24}H_{21}Cl$ [M^+]: 344, found [M]$^+$: 344.

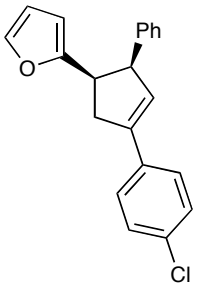


***cis*-1-(4-Chlorophenyl)-4(*R*)-(4-methoxyphenyl)-3(*S*)-phenyl-cyclopent-1-ene (18)**: Prepared according to general procedure using cinnamaldehyde (17.4 μL, 0.138 mmol) and (*E*)-1-(4-chlorophenyl)-3-(4-methoxyphenyl)prop-2-en-1-one (113 mg, 0.415 mmol) and purified by flash chromatography using 1% EtOAc/hexanes to afford 31 mg (62% yield) of **16** (>20:1 dr) as a yellowish gum. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (ddd, *J* = 9.1, 2.4, 1.9 Hz, 2H), 7.36 (ddd, *J* = 9.2, 2.5, 1.8 Hz, 2H), 7.09-7.02 (m, 3H), 6.84-6.80 (m, 2H), 6.77 (ddd, *J* = 9.1, 2.5, 2.0 Hz, 2H), 6.57 (ddd *J* = 9.7, 3.0, 1.9 Hz, 2H), 6.35 (dd, *J* = 3.8, 1.6 Hz, 1H), 4.29 (d, *J* = 8.6 Hz, 1H), 3.99 (ddd, *J* = 8.4, 8.4, 8.4 Hz, 1H), 3.69 (s, 3H), 3.10-3.00 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.6, 142.6, 140.4, 134.5, 133.4, 133.1, 129.3, 128.74, 128.75, 128.6, 127.8, 127.0,

126.1, 112.9, 56.7, 55.1, 49.4, 38.4; IR (film) 3028, 2930, 2835, 1601, 1513, 1492, 1452, 1248, 1179, 1092, 1035, 1012, 820, 749, 700 cm^{-1}; LRMS (EI): Mass calcd for $C_{24}H_{21}ClO$ $[M^+]$: 360, found $[M]^+$: 360; $[\alpha]_D^{20}$: (*c* 0.70, $CHCl_3$): +175.1; Enantiomeric ratio was measured by HPLC (Chiralcel AD-H, 1% IPA/Hexanes, 1.0 mL/min), Rt (*cis*) = 9.9 and 11.0 min, Rt (*trans*) = 17.9 and 21.6 min; ee *cis* = 99%.

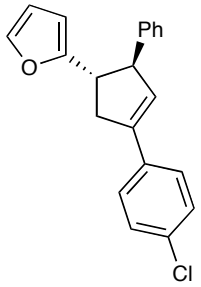


(±)-*trans*-1-(4-Chlorophenyl)-4(*S*)-(4-methoxyphenyl)-3(*S*)-phenyl-cyclopent-1-ene: Prepared according to the procedure reported by Nair[10] using cinnamaldehyde and (*E*)-1-(4-chlorophenyl)-3-(4-methoxyphenyl)prop-2-en-1-one and purified by flash chromatography using 1% EtOAc/hexanes. The compound was obtained in 60% yield (15:1 dr) as a colorless gum. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (ddd, *J* = 9.1, 2.5, 2.0 Hz, 2H), 7.33 (ddd, *J* = 9.2, 2.5, 2.0 Hz, 2H), 7.30-7.26 (m, 2H), 7.22 (tt, *J* = 7.3, 1.5 Hz, 1H), 7.15 (ddd, *J* = 9.7, 3.1, 2.1 Hz, 2H), 7.14-7.11 (m, 2H), 6.84 (ddd *J* = 9.6, 3.0, 2.1 Hz, 2H), 6.24 (dd, *J* = 3.6, 2.1 Hz, 1H), 4.08 (ddd, *J* = 7.4, 4.6, 2.3 Hz, 1H), 3.80 (s, 3H), 3.40 (ddd, *J* = 8.5, 7.7, 7.7 Hz, 1H), 3.27 (dddd, *J* = 15.8, 8.8, 2.1, 1.5 Hz, 1H), 2.95 (dddd, *J* = 15.7, 7.8, 2.4, 2.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.0, 144.6, 141.0, 137.0, 134.5, 133.1, 128.8, 128.6, 128.4, 128.2, 127.4, 127.0, 126.4, 113.8, 60.8, 55.2, 53.9, 42.0; IR (film) 3027, 2929, 2835, 1610, 1512, 1492, 1453, 1249, 1178, 1092, 1035, 1012, 821, 752, 700 cm^{-1}; LRMS (EI): Mass calcd for $C_{24}H_{21}ClO$ $[M^+]$: 360, found $[M]^+$: 360.

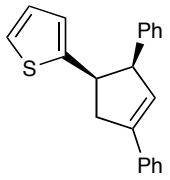


***cis*-1-(4-Chlorophenyl)-4(*R*)-(furan-2-yl)-3(*S*)-phenyl-cyclopent-1-ene (19)**: Prepared according to general procedure using cinnamaldehyde (19.5 μL, 0.155 mmol) and (*E*)-1-(4-chlorophenyl)-3-(furan-2-yl)prop-2-en-1-one (109 mg, 0.465 mmol) and purified by flash chromatography using 1% EtOAc/hexanes to afford 33.5 mg (67% yield) of **17** (>20:1 dr) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (ddd, *J* = 9.1, 2.5, 1.9 Hz, 2H), 7.35 (ddd, *J* = 9.2, 2.5, 1.9 Hz, 2H), 7.14-7.09 (m, 3H), 7.08-7.06 (m, 1H), 6.98-6.95 (m, 2H), 6.31-6.29 (m, 1H), 6.04 (dd, *J* = 3.1, 1.9 Hz, 1H), 5.74 (ddd, *J* = 3.2, 0.6, 0.6 Hz, 1H), 4.37 (ddd, *J* = 8.7, 2.2, 2.2 Hz, 1H), 4.10 (ddd, *J* = 8.7, 8.7, 8.7 Hz, 1H), 3.11 (dddd, *J* = 15.6, 8.9, 2.2, 2.2 Hz, 1H), 3.04 (dddd, *J* = 15.5, 8.6, 0.8, 0.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.4, 141.9, 140.7, 140.3, 134.3, 133.2, 128.7, 128.6, 128.3, 127.7, 127.0, 126.3, 109.7, 105.9, 55.5, 43.3, 36.6; IR (film)

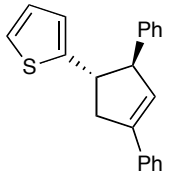
3059, 3028, 2929, 2850, 1596, 1492, 1453, 1404, 1092, 1012, 822, 732, 701 cm^{-1}; LRMS (EI): Mass calcd for $C_{21}H_{17}ClO$ [M^+]: 320, found [$M]^+$: 320; $[\alpha]_D^{20}$: (*c* 1.02, $CHCl_3$): +205.0; Enantiomeric ratio was measured by HPLC (Chiralcel AD-H, 2% IPA/Hexanes, 0.5 mL/min), Rt (*cis*) = 10.9 and 11.5 min, Rt (*trans*) = 14.6 and 18.0 min; ee *cis* = 98%.



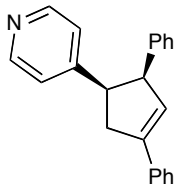
(±)-*trans*-1-(4-Chlorophenyl)-4(*S*)-(furan-2-yl)-3(*S*)-phenyl-cyclopent-1-ene: Prepared according to the procedure reported by Nair[10] using cinnamaldehyde and (*E*)-1-(4-chlorophenyl)-3-(furan-2-yl)prop-2-en-1-one and purified by flash chromatography using 1% EtOAc/hexanes. The compound was obtained in 74% yield (16:1 dr) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46-7.42 (m, 2H), 7.38-7.36 (m, 1H), 7.35-7.29 (m, 4H), 7.26-7.19 (m, 3H), 6.32-6.29 (m, 1H), 6.23-6.20 (m, 1H), 6.06-6.04 (m, 1H), 4.26-4.21 (m, 1H), 3.53 (ddd, *J* = 8.3, 8.3, 8.3 Hz, 1H), 3.25-3.18 (m, 1H), 3.09-3.02 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.1, 144.2, 141.3, 140.9, 134.3, 133.1, 128.6, 128.55, 128.49, 127.5, 127.0, 126.6, 110.1, 104.9, 57.4, 47.5, 39.0; IR (film) 3059, 3028, 2927, 2852, 1600, 1506, 1492, 1453, 1404, 1147, 1093, 1076, 1012, 817, 732, 700 cm^{-1}; LRMS (EI): Mass calcd for $C_{21}H_{17}ClO$ [M^+]: 320, found [$M]^+$: 320.



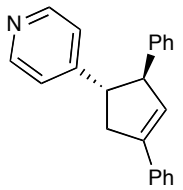
***cis*-1,3(*S*)-Diphenyl-4(*R*)-(thiophen-2-yl)-cyclopent-1-ene (20)**: Prepared according to general procedure using cinnamaldehyde (20.8 μL, 0.165 mmol) and (*E*)-1-(4-chlorophenyl)-3-(thiophen-2-yl)prop-2-en-1-one (106 mg, 0.495 mmol) and purified by flash chromatography using 1% EtOAc/hexanes to afford 25 mg (50% yield) of **18** (>20:1 dr) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60-7.57 (m, 2H), 7.42-7.38 (m, 2H), 7.31 (tt, *J* = 7.4, 1.3, 1.3 Hz, 1H), 7.15-7.08 (m, 3H), 6.98-6.95 (m, 2H), 6.92 (dd, *J* = 5.1, 0.9 Hz, 1H), 6.71 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.55 (m, 1H), 6.38-6.36 (m, 1H), 4.33-4.26 (m, 2H), 3.24-3.17 (m, 1H), 3.17-3.10 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.2, 143.4, 140.1, 135.8, 128.9, 128.5, 128.1, 127.8, 127.6, 126.4, 126.0, 125.8, 124.7, 123.1, 56.9, 45.5, 40.1; IR (film) 3063, 3026, 2928, 2842, 1600, 1494, 1452, 1076, 1030, 757, 692 cm^{-1}; LRMS (EI): Mass calcd for $C_{21}H_{18}S$ [M^+]: 302, found [$M]^+$: 302; $[\alpha]_D^{20}$: (*c* 1.01, $CHCl_3$): +215.8; Enantiomeric ratio was measured by reverse phase HPLC (Chiralcel AD-RH, 60% MeCN/H_2O, 1.0 mL/min), Rt (*cis*) = 17.6 and 22.5 min, Rt (*trans*) = 20.3 and 41.2 min; ee *cis* = 98%.



(±)-*trans*-1,3(*S*)-Diphenyl-4(*S*)-(thiophen-2-yl)-cyclopent-1-ene): Prepared according to the procedure reported by Nair[10] using cinnamaldehyde and (*E*)-1-(4-chlorophenyl)-3-(thiophen-2-yl)prop-2-en-1-one and purified by flash chromatography using 1% EtOAc/hexanes. The compound was obtained in 72% yield (>20:1 dr) as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54-7.52 (m, 2H), 7.39-7.35 (m, 2H), 7.33-7.29 (m, 3H), 7.25-7.21 (m, 3H), 7.15 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.92 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.79 (ddd, *J* = 3.4, 1.1, 0.8 Hz, 1H), 6.24 (ddd, *J* = 2.2, 2.2, 1.3 Hz, 1H), 4.14 (ddd, *J* = 7.8, 4.4, 2.1 Hz, 1H), 3.74 (ddd, *J* = 8.2, 8.2, 8.2 Hz, 1H), 3.39 (dddd, *J* = 15.6, 8.6, 1.9, 1.4 Hz 1H), 3.06 (dddd, *J* = 15.6, 8.3, 2.5, 2.5 Hz 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.3, 144.0, 141.9, 135.7, 128.5, 128.1, 127.63, 127.58, 126.68, 126.65, 125.7, 123.7, 123.0, 61.1, 50.0, 42.6; IR (film) 3058, 3026, 2926, 2845, 1599, 1493, 1447, 1075, 1030, 753, 692 cm^{-1}; LRMS (EI): Mass calcd for $C_{21}H_{18}S$ [M^+]: 302, found [M]$^+$: 302

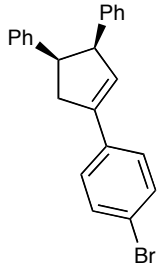


***cis*-1,3(*S*)-Diphenyl-4(*R*)-(pyridin-4-yl)-cyclopent-1-ene (21)**: Prepared according to general procedure using cinnamaldehyde (21.1 μL, 0.168 mmol) and (*E*)-1-(4-chlorophenyl)-3-phenylprop-2-en-1-one (105 mg, 0.504 mmol) and purified by flash chromatography using 30% EtOAc/hexanes to afford 39 mg (78% yield) of **19** (>20:1 dr) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25-8.22 (m, 2H), 7.61-7.58 (m, 2H), 7.44-7.40 (m, 2H), 7.33 (tt, *J* = 7.4, 1.5 Hz, 1H), 7.09-7.02 (m, 3H), 6.88-6.83 (m, 2H), 6.82-6.79 (m, 2H), 6.36 (dd, *J* = 4.2, 1.7 Hz, 1H), 4.42 (ddd, *J* = 8.6, 2.8, 1.5 Hz, 1H), 4.00 (ddd, *J* = 8.2, 8.2, 8.2 Hz, 1H), 3.18 (dddd, *J* = 15.7, 7.8, 1.9, 1.9 Hz, 1H), 3.14 (dddd, *J* = 15.7, 8.1, 1.4, 1.4 Hz 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.8, 149.0, 143.4, 139.6, 135.6, 128.6, 128.5, 128.0, 127.8, 127.7, 126.6, 125.8, 123.7, 56.5, 49.3, 37.6; IR (film) 3057, 3026, 2927, 2848, 1598, 1493, 1451, 1415, 819, 757, 700 cm^{-1}; LRMS (EI): Mass calcd for $C_{22}H_{19}N$ [M^+]: 297, found [M]$^+$: 297; $[\alpha]_D^{20}$: (*c* 1.01, $CHCl_3$): +222.2; Enantiomeric ratio was measured by HPLC (Chiralcel OD-H, 20% IPA/Hexanes, 1.0 mL/min), Rt (*cis*) = 9.9 and 27.4 min, Rt (*trans*) = 15.0 and 36.0 min; ee *cis* = 99%.

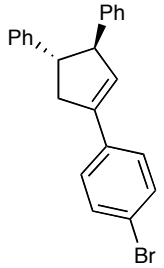


(±)-*trans*-1,3(*S*)-Diphenyl-4(*S*)-(pyridin-4-yl)-cyclopent-1-ene: Prepared according to the procedure reported by Nair[10] using cinnamaldehyde and (*E*)-1-(4-chlorophenyl)-3-phenylprop-2-en-1-one and purified by flash chromatography using 30% EtOAc/hexanes. The compound was obtained in 60% yield (>20:1 dr) as a colorless gum. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53-8.50 (m, 2H), 7.55-7.52 (m, 2H), 7.41-7.36 (m, 2H), 7.33-7.28 (m, 3H), 7.26-7.22 (m, 1H), 7.18-7.15

(m, 2H), 7.15-7.13 (m, 2H), 6.26 (dd, *J* = 3.8, 1.9 Hz, 1H), 4.10 (ddd, *J* = 6.8, 4.6, 2.3 Hz, 1H), 3.43 (ddd, *J* = 8.6, 6.9, 6.9 Hz, 1H), 3.37 (dddd, *J* = 15.6, 8.8, 2.2, 1.5 Hz, 1H), 3.00 (dddd, *J* = 15.5, 7.0, 2.3, 2.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.1, 150.0, 144.0, 142.0, 135.5, 128.6, 128.5, 127.8, 127.4, 127.0, 125.8, 122.6, 60.3, 53.6, 41.1; IR (film) 3058, 3026, 2926, 2849, 1597, 1494, 1448, 1414, 816, 755, 700 cm^{-1}; LRMS (EI): Mass calcd for $C_{22}H_{19}N$ [M$^+$]: 297.2, found [M]$^+$: 297.1

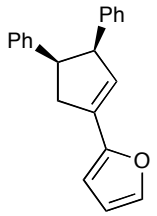


***cis*-1-(4-Bromophenyl)-3(*S*),4(*R*)-diphenylcyclopent-1-ene (22)**: Prepared according to general procedure using cinnamaldehyde (16.7 μL, 0.133 mmol) and (*E*)-1-(4-bromophenyl)-3-phenylprop-2-en-1-one (115 mg, 0.400 mmol) and purified by flash chromatography using 0.75% EtOAc/hexanes to 1% EtOAc/hexanes to afford 40.5 mg (81% yield) of **20** (>20:1 dr) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (ddd, *J* = 8.9, 2.4, 2.0 Hz, 2H), 7.46 (ddd, *J* = 8.9, 2.3, 2.0 Hz, 2H), 7.07-6.98 (m, 6H), 6.89-6.86 (m, 2H), 6.83-6.80 (m, 2H), 6.37 (dd, *J* = 4.2, 1.7 Hz, 1H), 4.34 (ddd, *J* = 8.6, 1.7, 1.7 Hz, 1H), 4.05 (ddd, *J* = 8.4, 8.4, 8.4 Hz, 1H), 3.15 (dddd, *J* = 15.6, 8.3, 2.0, 2.0 Hz, 1H), 3.07 (dddd, *J* = 15.7, 8.2, 1.1, 1.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.7, 141.3, 140.3, 134.9, 131.6, 128.8, 128.7, 128.4, 127.7, 127.5, 127.3, 126.1, 125.9, 121.3, 56.8, 50.0, 38.0; IR (film) 3061, 3023, 2930, 2848, 1602, 1489, 1452, 1398, 1074, 1007, 816, 762, 698 cm^{-1}; LRMS (EI): Mass calcd for $C_{23}H_{19}Br$ [M$^+$]: 374, found [M]$^+$: 374; $[\alpha]_D^{20}$: (*c* 1.01, $CHCl_3$): +209.4; Enantiomeric ratio was measured by reverse phase HPLC (Chiralcel OD-RH, 66% MeCN/H_2O, 1.0 mL/min), Rt (*cis*) = 51.5 and 71.3 min, Rt (*trans*) = 41.6 and 55.7 min; ee *cis* = 99%.

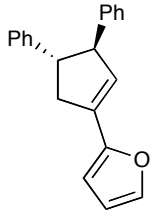


(±)-*trans*-1-(4-Bromophenyl)-3(*S*),4(*S*)-diphenylcyclopent-1-ene: Prepared according to the procedure reported by Nair[10] using cinnamaldehyde and (*E*)-1-(4-bromophenyl)-3-phenylprop-2-en-1-one and purified by flash chromatography using 0.75% EtOAc/hexanes. The compound was obtained in 85% yield (16:1 dr) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (ddd, *J* = 9.1, 2.4, 2.0 Hz, 2H), 7.39 (ddd, *J* = 9.1, 2.4, 1.9 Hz, 2H), 7.32-7.28 (m, 4H), 7.25-7.20 (m, 4H), 7.15-7.12 (m, 2H), 6.27 (dd, *J* = 3.7, 2.1 Hz, 1H), 4.12 (ddd, *J* = 7.2, 4.6, 2.3 Hz, 1H), 3.46 (ddd, *J* = 8.6, 7.5, 7.5 Hz, 1H), 3.31 (dddd, *J* = 15.9, 8.8, 2.1, 1.6 Hz, 1H), 2.98 (dddd, *J* = 15.8, 7.6, 2.3, 2.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.1, 144.5, 141.1, 134.8, 131.5, 128.50, 128.47, 127.4, 127.33, 127.28, 126.5, 126.3, 121.3, 60.8, 54.4, 41.9; IR (film) 3059, 3026, 2923,

2847, 1601, 1489, 1453, 1398, 1074, 1008, 816, 761, 698 cm^{-1}; LRMS (EI): Mass calcd for $C_{23}H_{19}Br$ $[M^+]$: 374, found $[M]^+$: 374.



***cis*-1-(Furan-2-yl)-3(*S*),4(*R*)-diphenylcyclopent-1-ene (23)**: Prepared according to general procedure using cinnamaldehyde (21.9 μL, 0.174 mmol) and (*E*)-1-(furan-2-yl)-3-phenylprop-2-en-1-one (103 mg, 0.522 mmol) and purified by flash chromatography using 4% EtOAc/hexanes to afford 37.5 mg (75% yield) of **21** (>20:1 dr) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 1.3 Hz, 1H), 7.07-6.98 (m, 6H), 6.87 (dd, *J* = 7.9, 1.6 Hz, 2H), 6.84 (dd, *J* = 7.9, 1.7 Hz, 2H), 6.47 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.37 (d, *J* = 3.2 Hz, 1H), 6.28-6.25 (m, 1H), 4.35 (ddd, *J* = 8.5, 1.9, 1.9 Hz, 1H), 4.02 (ddd, *J* = 8.3, 8.3, 8.3 Hz, 1H), 3.08 (dddd, *J* = 15.5, 8.2, 1.7, 1.7 Hz, 1H), 3.02 (dddd, *J* = 15.6, 8.2, 0.9, 0.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.7, 142.2, 141.3, 140.4, 134.0, 128.7, 128.4, 127.6, 127.5, 126.5, 126.0, 125.8, 111.2, 107.1, 56.6, 50.0, 37.3; IR (film) 3060, 3027, 2921, 2851, 1602, 1490, 1453, 995, 800, 760, 738, 698 cm^{-1}; LRMS (EI): Mass calcd for $C_{21}H_{18}O$ $[M^+]$: 286, found $[M]^+$: 286; $[\alpha]_D^{20}$: (c 0.95, $CHCl_3$): +233.1; Enantiomeric ratio was measured by reverse phase HPLC (Chiralcel OD-H, 2% IPA/hexanes, 1.0 mL/min), Rt (*cis*) = 6.8 and 15.5 min, Rt (*trans*) = 5.2 and 8.6 min; ee *cis* = 99%.



(±)-*trans*-1-(Furan-2-yl)-3(*S*),4(*R*)-diphenylcyclopent-1-ene Prepared according to the procedure reported by Nair[10] using cinnamaldehyde and (*E*)-1-(furan-2-yl)-3-phenylprop-2-en-1-one and purified by flash chromatography using 4% EtOAc/hexanes. The compound was obtained in 70% yield (8:1 dr) as a colorless gum. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 1.6 Hz, 1H), 7.32-7.26 (m, 4H), 7.25-7.19 (m, 4H), 7.15-7.12 (m, 2H), 6.43 (dd, *J* = 3.3, 1.9 Hz, 1H), 6.30 (d, *J* = 3.3 Hz, 1H), 6.16 (dd, *J* = 3.7, 1.8 Hz, 1H), 4.13 (ddd, *J* = 6.9, 4.5, 2.2 Hz, 1H), 3.41 (ddd, *J* = 8.6, 7.4, 7.4 Hz, 1H), 3.25 (dddd, *J* = 15.8, 8.9, 1.9, 1.9 Hz, 1H), 2.92 (dddd, *J* = 15.8, 7.6, 2.3, 2.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.0, 144.6, 142.1, 132.5, 128.5, 128.4, 127.4, 127.3, 126.7, 126.4, 126.3, 111.1, 107.0, 60.7, 54.5, 41.1; IR (film) 3060, 3027, 2912, 2851, 1601, 1492, 1453, 1154, 801, 761, 738, 699 cm^{-1}; LRMS (EI): Mass calcd for $C_{21}H_{18}O$ $[M^+]$: 286.1, found $[M]^+$: 286.1.

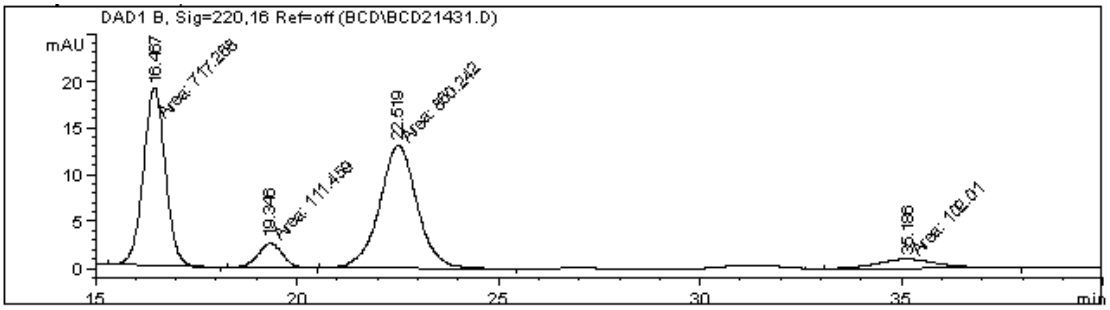
General Procedure for the Lewis Acid Catalyzed Enantioselective Synthesis of *cis*-γ-butyrolactone 24

Into a flame-dried 5 mL round bottom flask equipped with a magnetic stirbar was weighed (*R*,*R*)-TADDOL (18.7 mg, 0.04 mmol). The flask was purged with N_2 and toluene (1 mL), followed successively by $Ti(O\textit{i}Pr)_4$ (11.8 μL, 0.04 mmol), were added. The solution was heated to 103 ºC for 4 hours and then cooled to 23 ºC. Toluene was removed under vacuum. The residue was azeotroped twice with toluene, and the flask was dried under high vacuum for 1 hour. Into an oven-dried vial was weighed the azolium salt (10.2 mg, 0.04 mmol) in a nitrogen-filled drybox. The vial was capped, removed from the drybox and put under positive N_2 pressure. The azolium salt was dissolved in 375 μL CH_2Cl_2 and transferred to the flask via canula. The vial was rinsed with an additionnal 375 μL CH_2Cl_2 and the solution was transferred to the flask via canula. Finally, the reaction mixture was adjusted to the appropriate temperature before the successive addition of cinnamaldehyde (25 μL, 0.2 mmol), *i*PrOH (3 μL, 0.03 mmol) and DBU (4.5 μL, 0.03 mmol). Upon consumption of the aldehyde (or after satisfactory conversion), the reaction mixture was filtered through a short plug of SiO_2 (in a pipette) and washed with EtOAc. The solution was then concentrated under reduced pressure and purified by flash chromatography with EtOAc/hexanes to afford the *cis*-γ-butyrolactones.[11] Enantiomeric ratio was measured by HPLC (Chiralcel AD-H, 5% IPA/hexanes, 1.0 mL/min), Rt (*cis*) = 13.9 and 16.2 min; ee *cis* = 60%.

11. Sohn, S. S.; Rosen, E. L.; Bode, J. W. *J. Am. Chem. Soc.* **2004**, *126*, 14370-14371 (Supporting Information).

HPLC Traces of Racemic and Enantioenriched Cyclopentenes

Racemic 3

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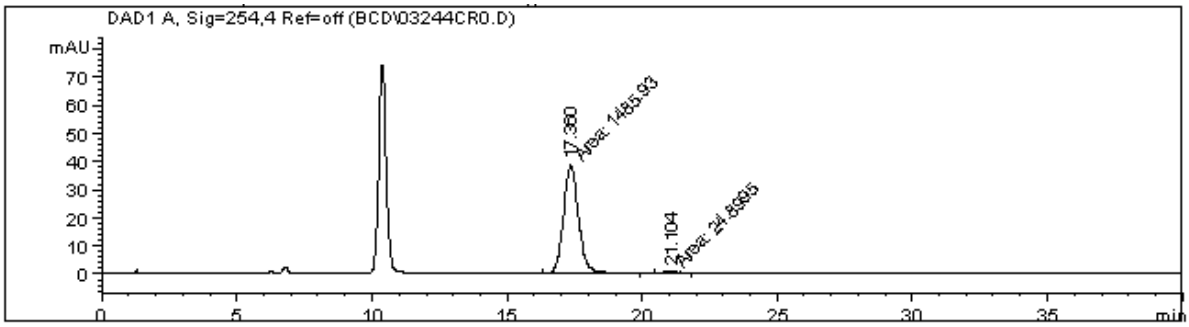
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  16.467 MM    0.6327  717.26825   18.89365  40.0490
   2  19.346 MM    0.7166  111.45865    2.59238   6.2233
   3  22.519 MM    1.0948  860.24158   13.09566  48.0319
   4  35.186 MM    1.8224  102.01012 9.32915e-1   5.6958
```

Enantioenriched 3 crude

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                     Area Percent Report
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Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|-------|
   1  17.360 MM    0.6425 1485.92578   38.54806  98.3519
   2  21.104 MM    0.6652   24.89951 6.23875e-1   1.6481
```
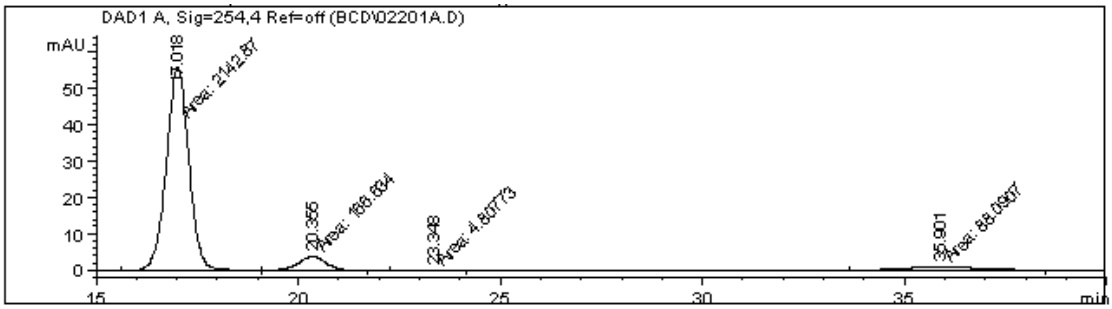

Enantioenriched 3 pure

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                        Area Percent Report
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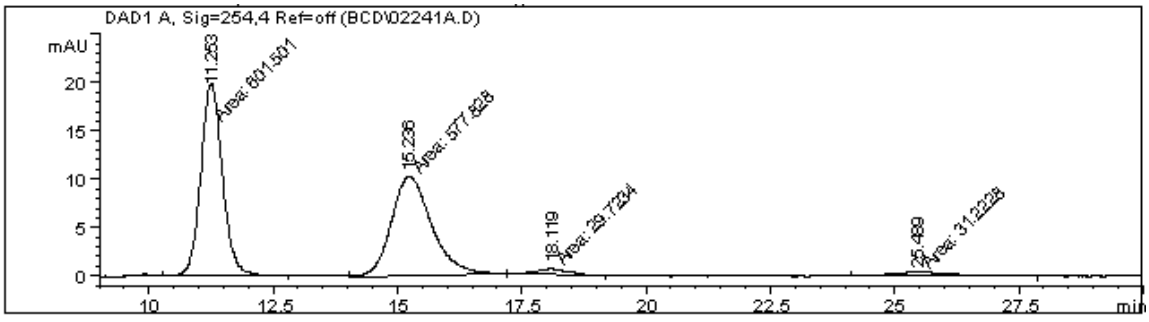
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  17.018 MM    0.6416 2142.87158   55.66506  89.1970
   2  20.355 MM    0.7451  166.63391    3.72748   6.9361
   3  23.348 MM    0.8957    4.80773 8.94600e-2   0.2001
   4  35.901 MM    1.7946   88.09068 8.18131e-1   3.6668
```

Racemic 4

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                        Area Percent Report
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Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.253 MM    0.5048  601.50092   19.85799  48.4974
   2  15.236 MM    0.9399  577.82825   10.24583  46.5887
   3  18.119 MM    0.8030   29.72342 6.16935e-1   2.3965
   4  25.489 MM    1.5232   31.22280 3.41640e-1   2.5174
```
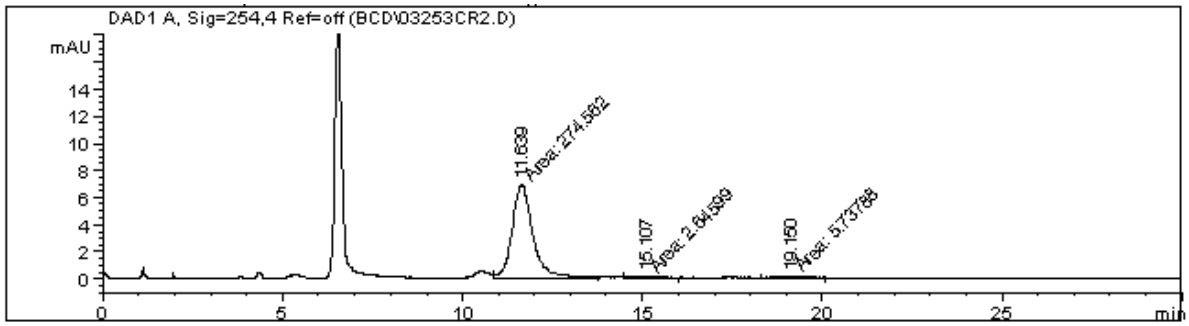

Enantioenriched 4 crude

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                      Area Percent Report
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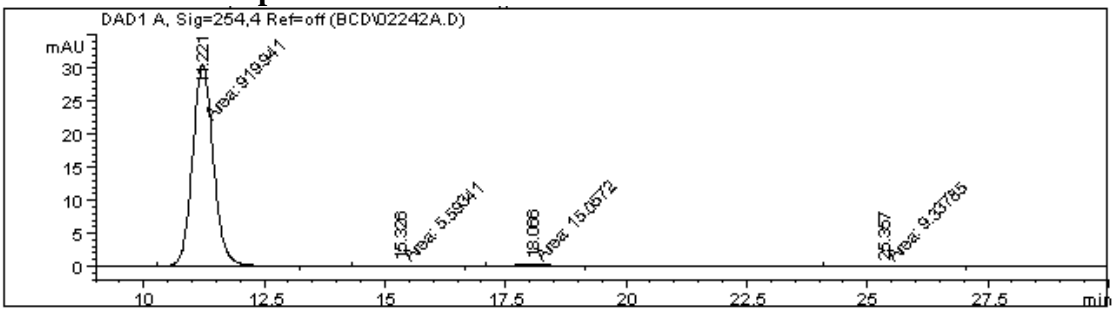
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.639 MM    0.6642  274.56232    6.88929  97.0369
   2  15.107 MM    0.6436    2.64599 6.85242e-2   0.9352
   3  19.150 MM    0.7536    5.73788 1.26897e-1   2.0279
```

Enantioenriched 4 pure

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Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.221 MM    0.5027  919.94141   30.50292  96.8431
   2  15.326 MM    0.9861    5.59341 9.45380e-2   0.5888
   3  18.066 MM    0.8237   15.05724 3.04674e-1   1.5851
   4  25.357 MM    1.4382    9.33785 1.08215e-1   0.9830
```
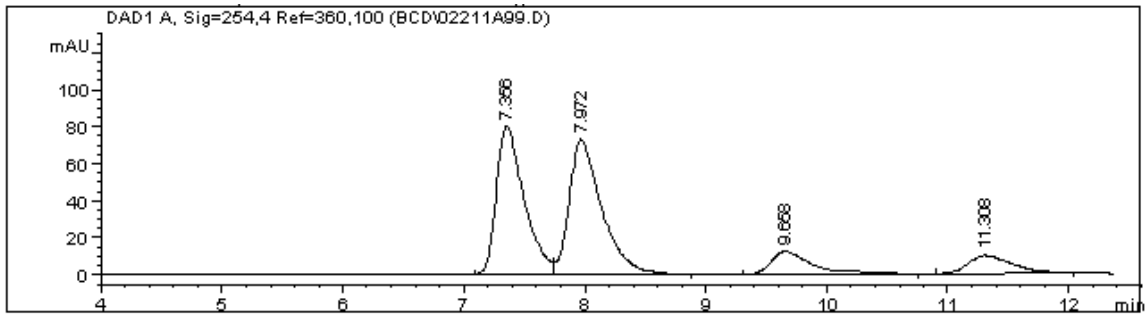

Racemic 5

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=====================================================================
                        Area Percent Report
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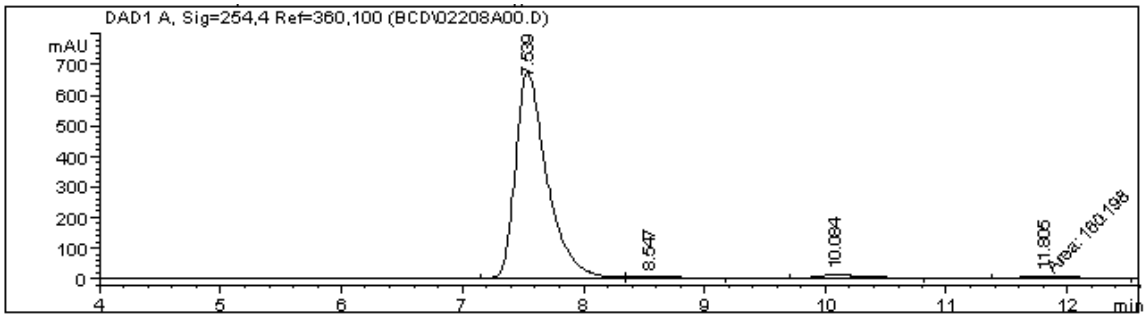
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.356 BV    0.2376 1277.97278   80.32507  40.3492
   2   7.972 VB    0.2751 1355.85718   72.85351  42.8082
   3   9.658 PP    0.3442  287.41550   12.22820   9.0745
   4  11.308 BB    0.3880  246.03831    9.63251   7.7681
```

Enantioenriched 5

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

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


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.539 BV    0.2675 1.22581e4   676.15051  95.0936
   2   8.547 VB    0.3283  154.65965    7.03867   1.1998
   3  10.084 PB    0.3458  317.60248   13.33681   2.4638
   4  11.805 MM    0.4719  160.19814    5.65779   1.2428
```
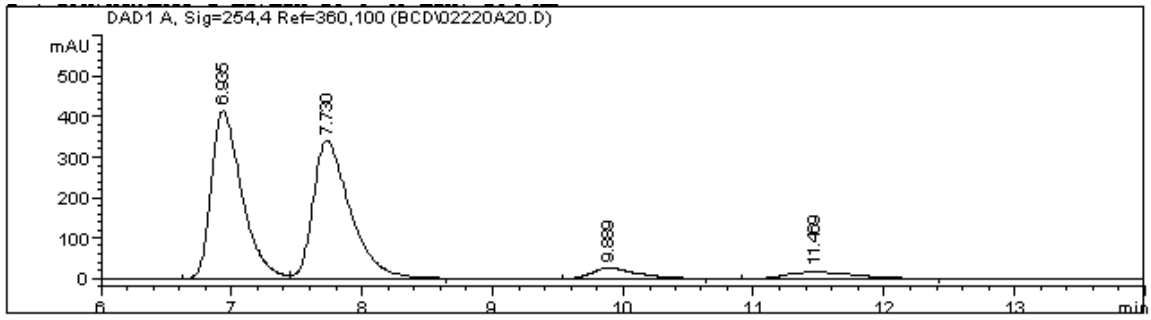

Racemic 6

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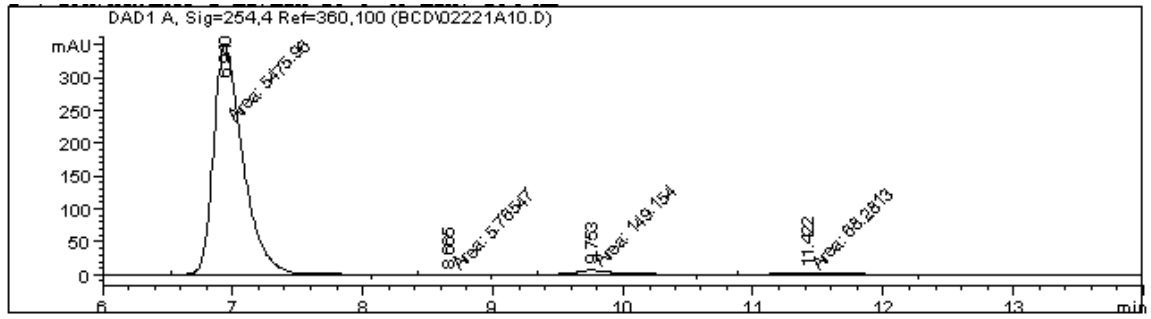
================================================================================
                            Area Percent Report
================================================================================

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


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.935 PV    0.2453 6716.29004  413.81976  46.1280
   2   7.730 VB    0.2970 6679.77246  340.33453  45.8772
   3   9.889 BB    0.3530  602.83875   25.38891   4.1403
   4  11.469 PB    0.5096  561.20276   16.22188   3.8544
```

Enantioenriched 6



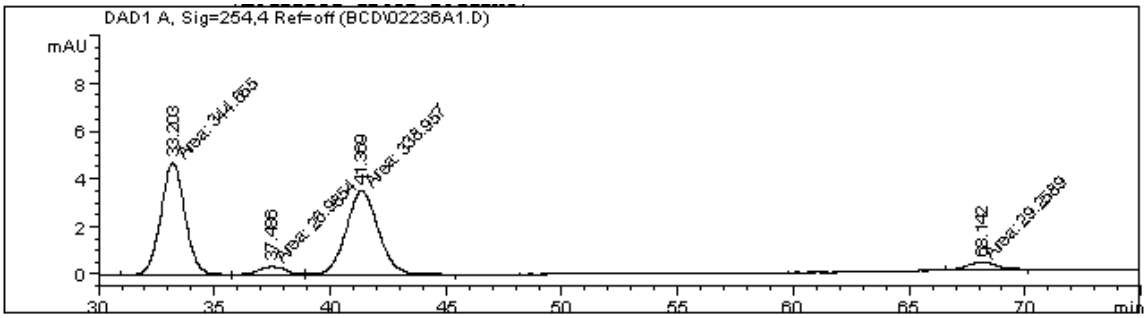

```
================================================================================
                            Area Percent Report
================================================================================

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


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.940 MM    0.2632 5475.95850  346.77090  96.0836
   2   8.665 MM    0.3497    5.76547 2.74801e-1   0.1012
   3   9.753 MM    0.3710  149.15411    6.70124   2.6171
   4  11.422 MM    0.5959   68.28135    1.90984   1.1981
```

Racemic 7

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=====================================================================
                        Area Percent Report
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Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  33.203 MM    1.2213  344.65527    4.70356  46.5841
   2  37.486 MM    1.2862   26.98541 3.49667e-1   3.6474
   3  41.369 MM    1.6144  338.95657    3.49920  45.8138
   4  68.142 MM    1.4907   29.25893 3.27124e-1   3.9547
```
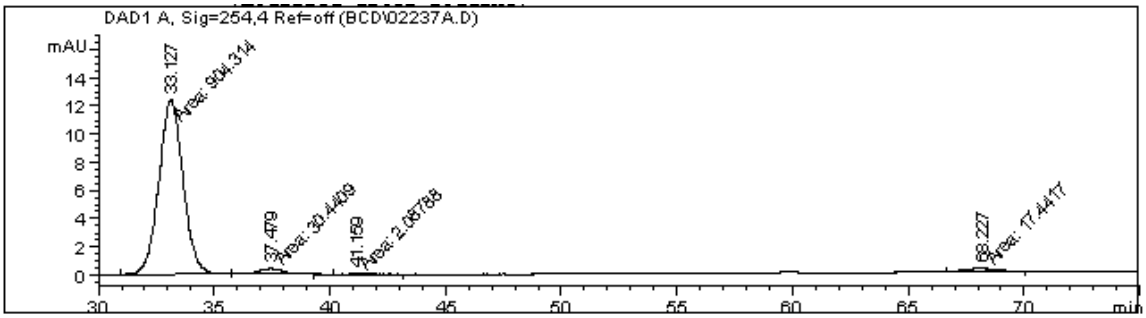
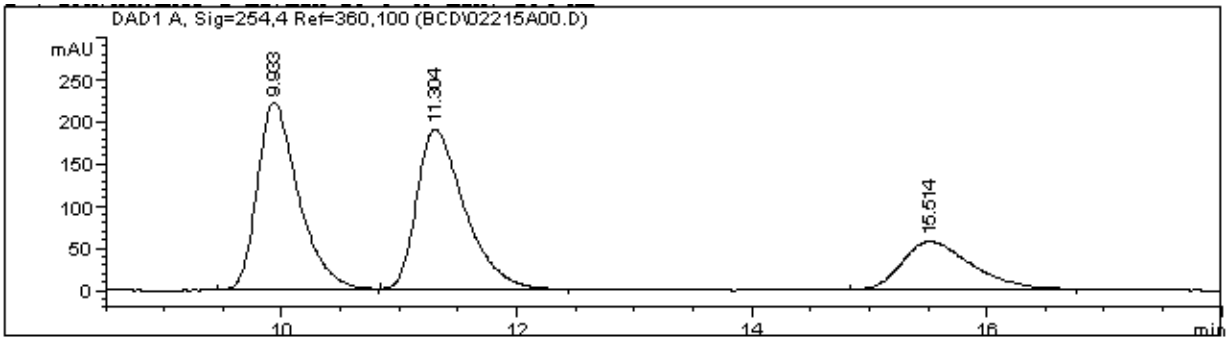

Enantioenriched 7



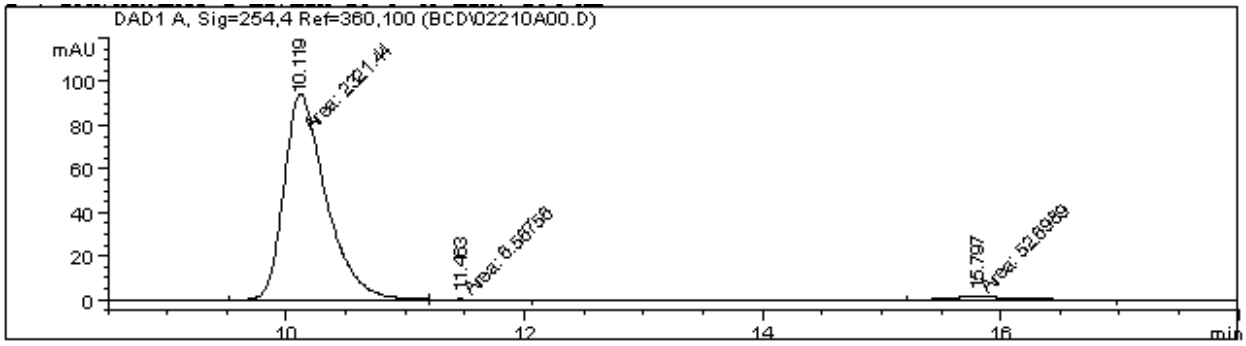

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   0.062 BB    0.0670    5.68025    1.20433   0.5917
   2  33.127 MM    1.2194  904.31415   12.35962  94.2028
   3  37.479 MM    1.3160   30.44087 3.85527e-1   3.1710
   4  41.159 MM    1.3407    2.08788 2.59550e-2   0.2175
   5  68.227 MM    1.5216   17.44173 1.91049e-1   1.8169
```

Racemic 8



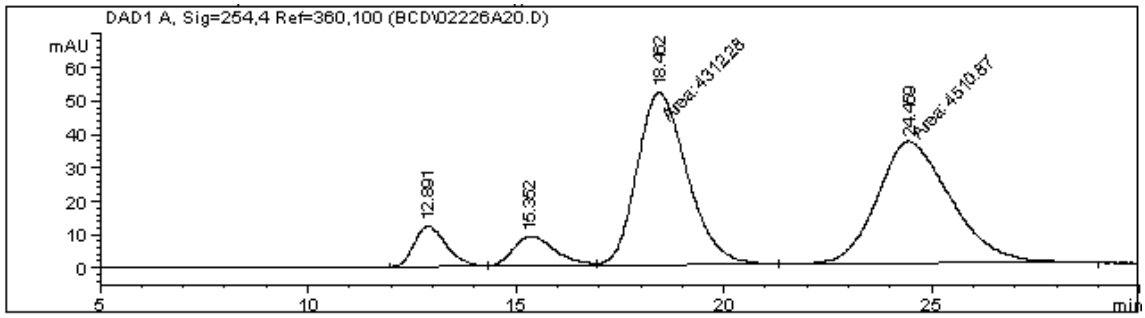

```
=====================================================================
                        Area Percent Report
=====================================================================

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


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.933 BB    0.3705 5480.23486  223.13065  41.0755
   2  11.304 BB    0.4317 5462.43652  190.99648  40.9421
   3  15.514 BB    0.6179 2399.17187   57.60524  17.9823
```

Enantioenriched 8



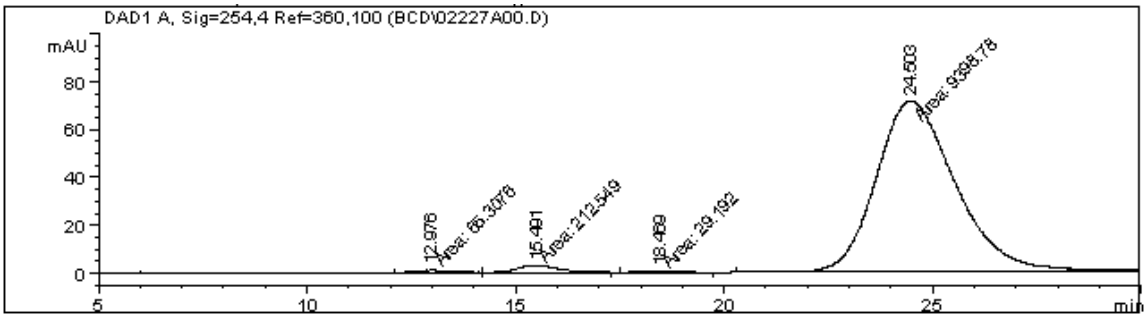

```
=====================================================================
                        Area Percent Report
=====================================================================

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


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.119 MM    0.4105 2321.44165   94.25790  97.5106
   2  11.463 MM    0.4601    6.56756 2.37881e-1   0.2759
   3  15.797 MM    0.6886   52.69886    1.27552   2.2136
```

Racemic 9



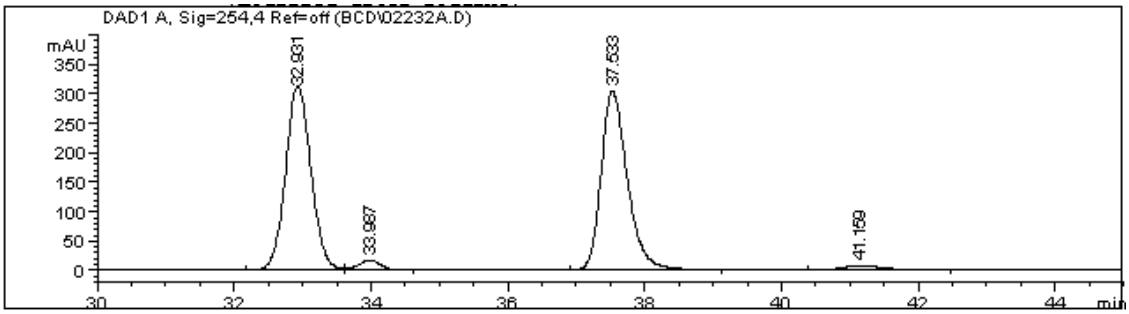

```
=====================================================================
                        Area Percent Report
=====================================================================

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


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  12.891 BB    0.7255  658.35364   12.12434   6.5213
   2  15.352 BV    0.8307  613.93646    8.79221   6.0813
   3  18.462 MM    1.3972 4312.28369   51.44059  42.7151
   4  24.459 MM    2.0621 4510.87402   36.45927  44.6823
```

Enantioenriched 9



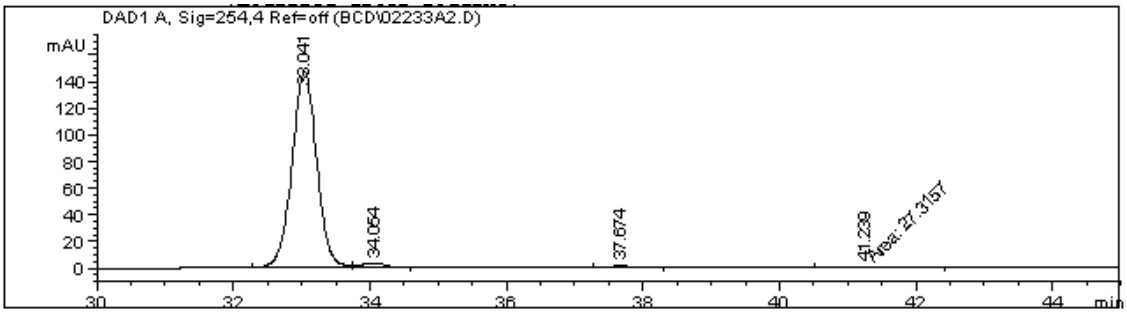

```
=====================================================================
                        Area Percent Report
=====================================================================

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


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  12.976 MM    0.9196   65.30757    1.18357   0.6729
   2  15.491 MM    1.2187  212.54945    2.90687   2.1899
   3  18.469 MM    1.0353   29.19200 4.69929e-1   0.3008
   4  24.503 MM    2.1930 9398.77539   71.42878  96.8364
```

Racemic 10



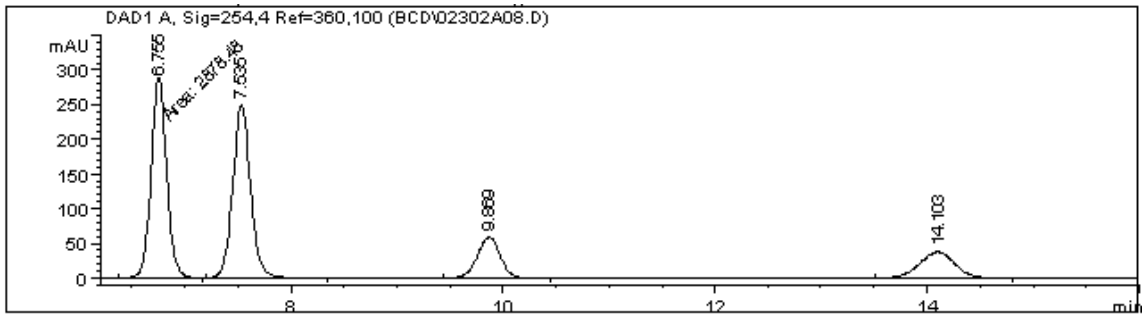

```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  32.931 PV    0.3959 8058.45801  313.51309  47.7027
   2  33.987 VB    0.3475  386.33835   16.97658   2.2870
   3  37.533 PB    0.4075 8117.03516  304.01776  48.0495
   4  41.159 PB    0.6697  331.25137    7.10825   1.9609

Totals :                  1.68931e4   641.61569
```

Enantioenriched 10



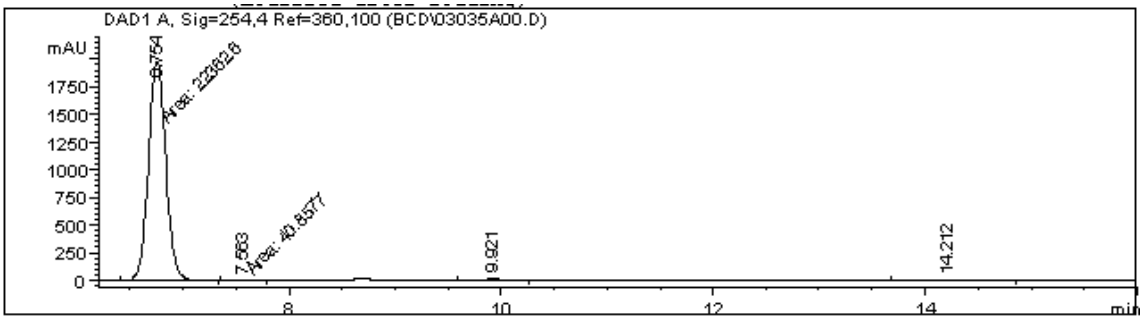

```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  33.041 BV    0.3856 3697.53979  146.90964  96.6747
   2  34.054 VB    0.3467   77.99287    3.41224   2.0392
   3  37.674 BB    0.3944   21.87334 7.96395e-1   0.5719
   4  41.239 MM    0.7950   27.31570 5.72662e-1   0.7142
```

Racemic 12



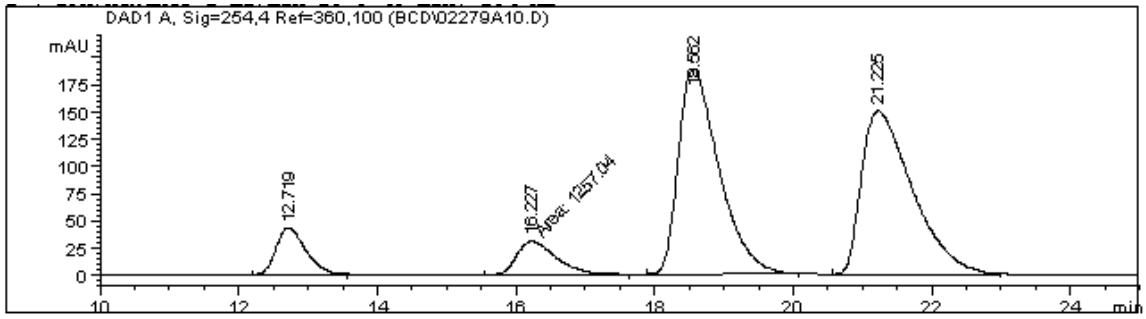

```
==================================================================
                      Area Percent Report
==================================================================

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


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.755 MM    0.1669 2878.48169  287.39407  38.3667
   2   7.535 VB    0.1779 2894.31812  248.51944  38.5778
   3   9.869 BB    0.2290  869.94189   58.65942  11.5953
   4  14.103 BB    0.3640  859.81378   37.15264  11.4603
```

Enantioenriched 12



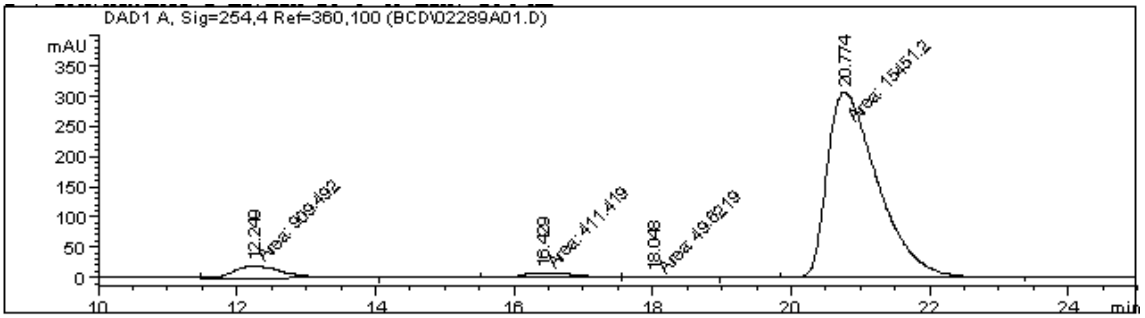

```
==================================================================
                      Area Percent Report
==================================================================

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


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.754 MM    0.1895 2.23626e4  1966.67505  97.8706
   2   7.562 MM    0.1835   40.85771    3.71179   0.1788
   3   9.921 BV    0.2330  247.83131   16.33710   1.0846
   4  14.212 BB    0.3441  197.86414    8.61168   0.8660
```

Racemic 13



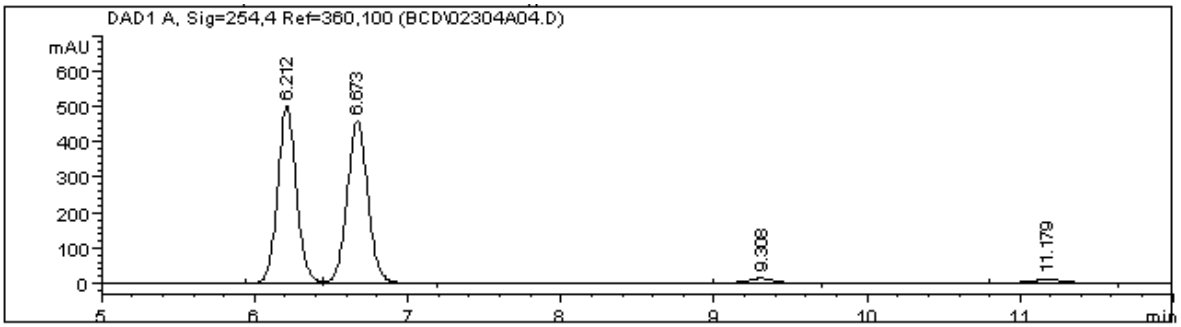

```
=====================================================================
                        Area Percent Report
=====================================================================

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


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  12.719 BB    0.4585 1286.46448   43.32076   7.1870
   2  16.227 MM    0.6775 1257.03699   30.92189   7.0226
   3  18.562 BB    0.6178 7682.71875  188.39708  42.9205
   4  21.225 PB    0.7611 7673.66406  149.93076  42.8699
```

Enantioenriched 13



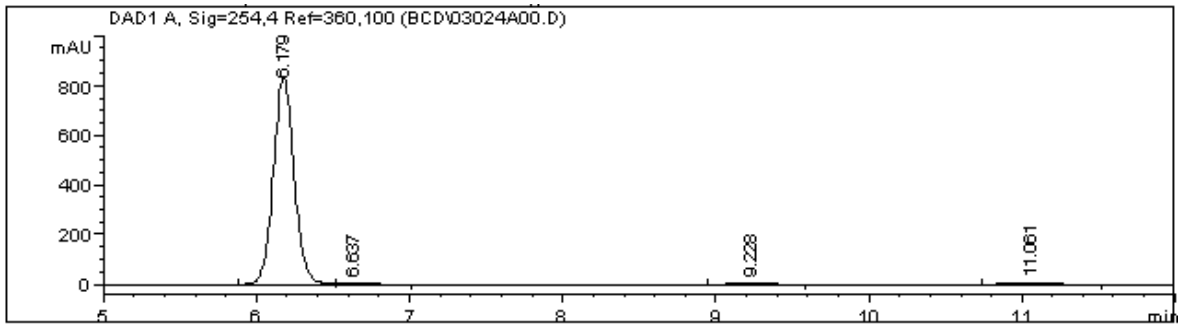

```
=====================================================================
                        Area Percent Report
=====================================================================

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


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  12.249 MM    0.7723  909.49176   19.62820   5.4067
   2  16.429 MM    0.7869  411.41891    8.71359   2.4458
   3  18.048 MM    0.7183   49.62189    1.15130   0.2950
   4  20.774 MM    0.8402 1.54512e4   306.48352  91.8526
```

Racemic 14



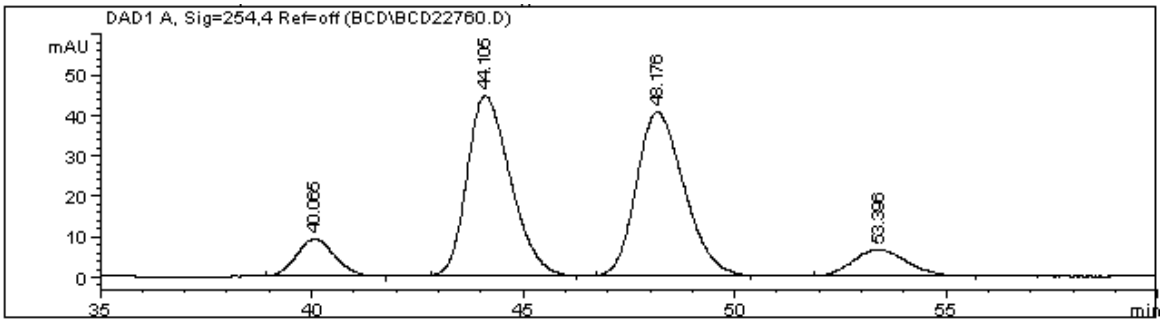

```
=====================================================================
                      Area Percent Report
=====================================================================

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


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.212 BV    0.1314 4275.11963  501.65204  47.7011
   2   6.673 VB    0.1453 4303.37109  459.39783  48.0163
   3   9.308 BP    0.2010  191.21338   14.58192   2.1335
   4  11.179 VB    0.2447  192.61298   12.16867   2.1491
```

Enantioenriched 14



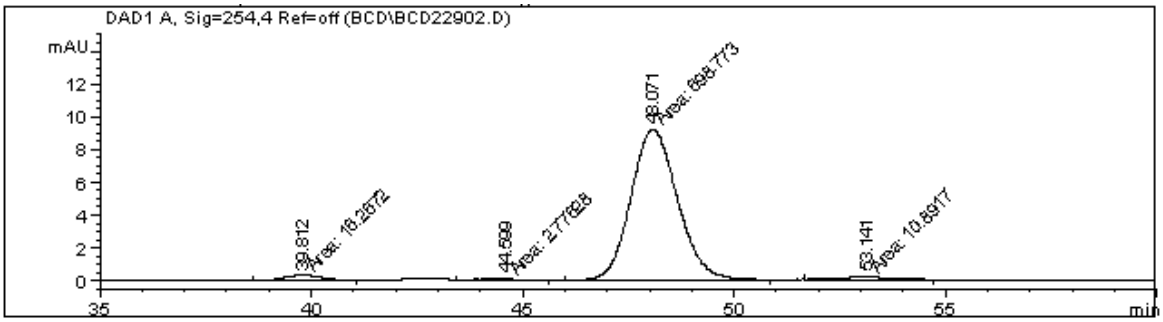

```
=====================================================================
                      Area Percent Report
=====================================================================

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


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.179 BV    0.1441 7777.88281  839.16412  97.5618
   2   6.637 VB    0.1600   57.06207    5.28388   0.7158
   3   9.228 BB    0.2055   53.79602    4.08839   0.6748
   4  11.061 VP    0.2529   83.52129    5.27057   1.0476
```

Racemic 15



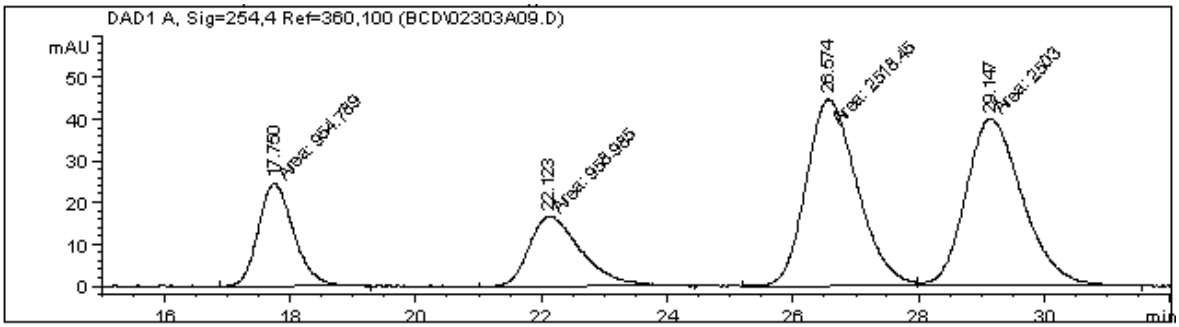

```
================================================================================
                            Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  40.065 BB    0.9416  595.40900    9.29191   7.8787
   2  44.105 BB    1.1073 3182.90112   44.56434  42.1173
   3  48.176 BB    1.2056 3184.50073   40.57549  42.1385
   4  53.396 BB    1.2253  594.41382    6.65961   7.8655
```

Enantioenriched 15



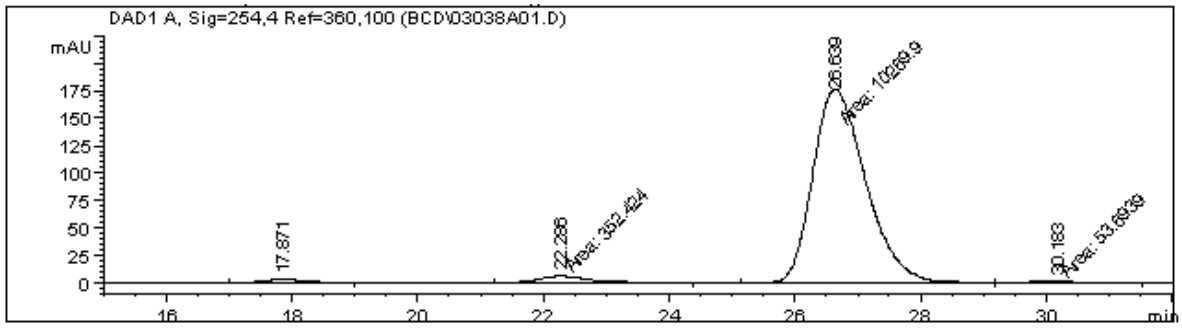

```
================================================================================
                            Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  39.812 MM    0.9926   16.26719 2.73140e-1   2.2323
   2  44.599 MM    0.9958    2.77628 4.64650e-2   0.3810
   3  48.071 MM    1.2708  698.77283    9.16423  95.8920
   4  53.141 MM    1.4442   10.89167 1.25692e-1   1.4947
```

Racemic 16



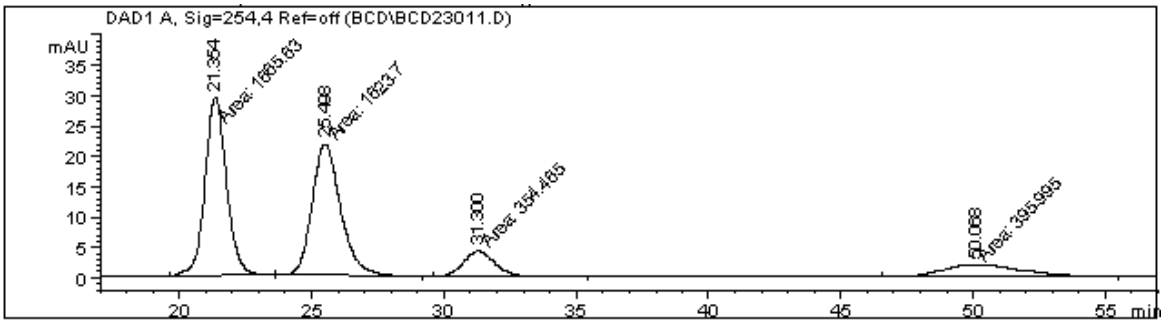

```
=====================================================================
                      Area Percent Report
=====================================================================

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


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  17.750 MM    0.6498  954.78943   24.48929  13.7672
   2  22.123 MM    0.9627  958.98456   16.60286  13.8277
   3  26.574 MM    0.9385 2518.45142   44.72545  36.3139
   4  29.147 MM    1.0430 2502.99756   39.99740  36.0911
```

Enantioenriched 16



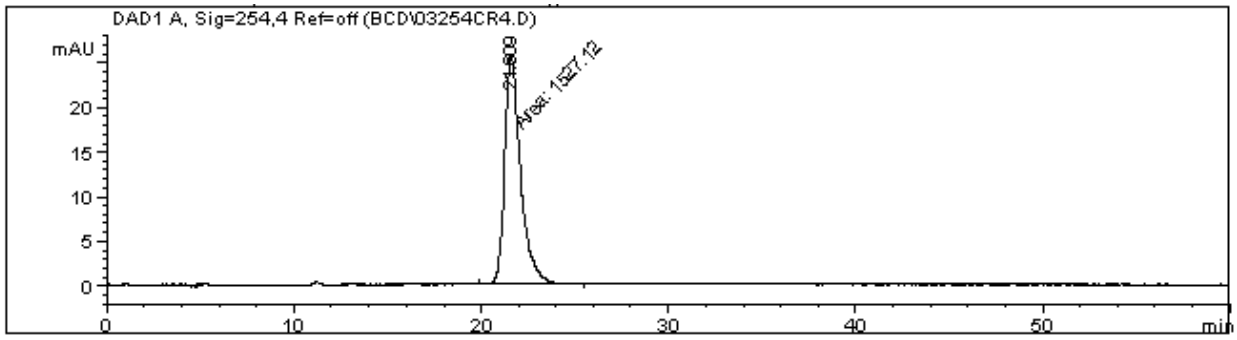

```
=====================================================================
                      Area Percent Report
=====================================================================

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


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  17.871 BB    0.5196  140.74530    3.54175   1.3012
   2  22.286 MM    0.9875  352.42435    5.94780   3.2581
   3  26.639 MM    0.9708 1.02699e4   176.30751  94.9443
   4  30.183 MM    1.0632   53.69390 8.41677e-1   0.4964
```

Racemic 17



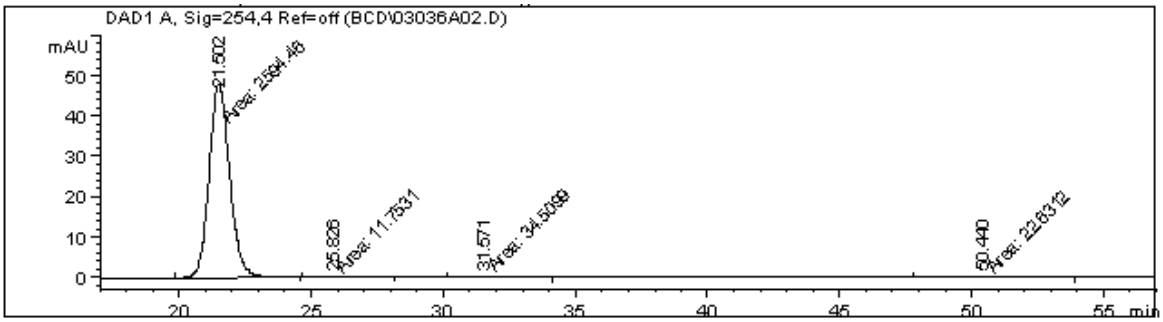

```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  21.354 MM    0.9470 1665.63306   29.31409  41.2306
   2  25.498 MM    1.2491 1623.70178   21.66413  40.1927
   3  31.300 MM    1.4120  354.46512    4.18406   8.7743
   4  50.068 MM    3.4012  395.99542    1.94045   9.8024
```

Enantioenriched 17 crude



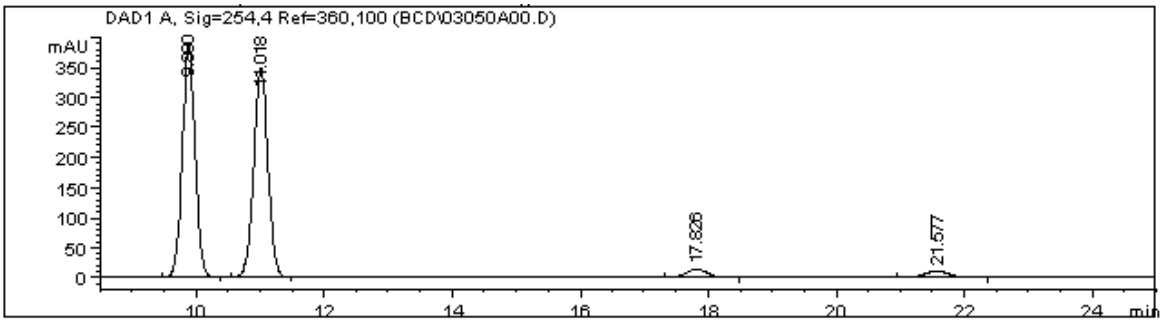

```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  21.609 MM    0.9933 1527.11536   25.62416 100.0000
```

Enantioenriched 17 pure



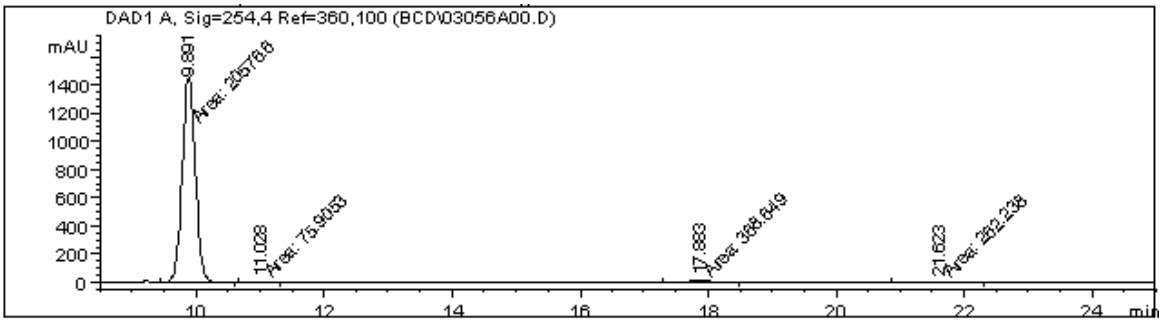

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  21.502 MM    0.8997 2594.46362   48.06348  97.4133
   2  25.826 MM    1.2543   11.75313 1.56174e-1   0.4413
   3  31.571 MM    1.3163   34.50987 4.36968e-1   1.2957
   4  50.440 MM    2.4514   22.63119 1.53863e-1   0.8497
```

Racemic 18



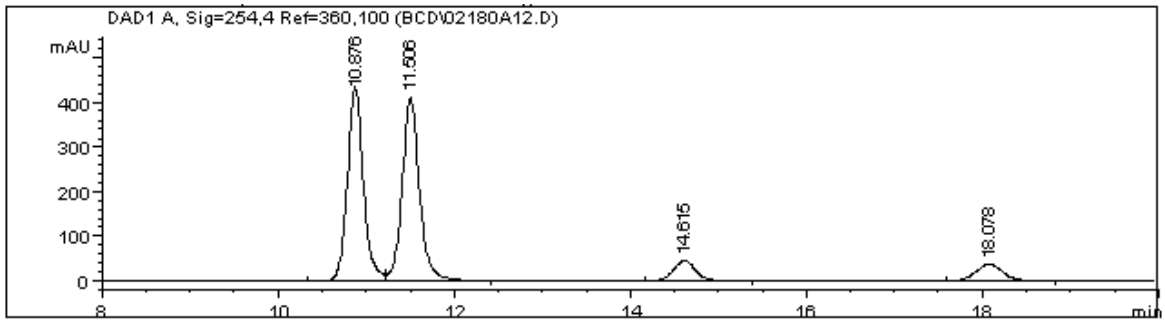

```
=====================================================================
                      Area Percent Report
=====================================================================

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


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.890 BB    0.2156 5391.89014  384.44666  47.1675
   2  11.018 BB    0.2402 5387.81689  348.84540  47.1318
   3  17.826 BB    0.3742  324.46991   12.95661   2.8384
   4  21.577 BP    0.3753  327.19901   10.62311   2.8623
```

Enantioenriched 18



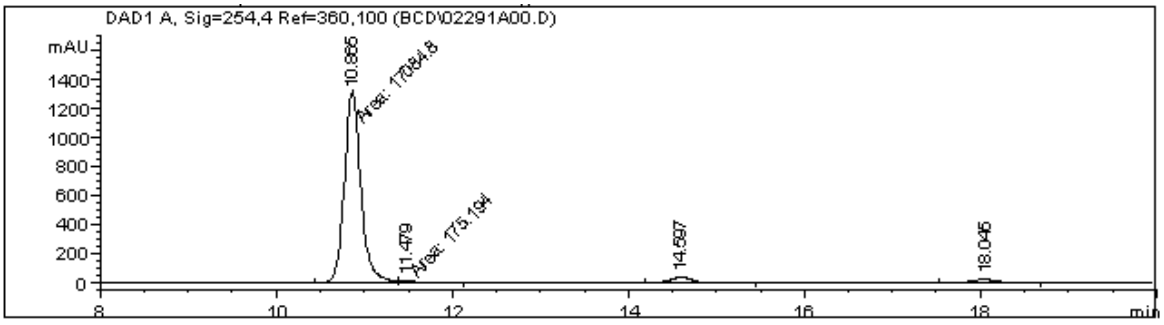

```
=====================================================================
                      Area Percent Report
=====================================================================

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


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.891 MM    0.2365 2.05766e4 1450.02209  96.6791
   2  11.028 MM    0.2471   75.90530    5.11897   0.3566
   3  17.883 MM    0.4295  368.64908   14.30435   1.7321
   4  21.623 MM    0.5330  262.23761    8.20065   1.2321
```

Racemic 19



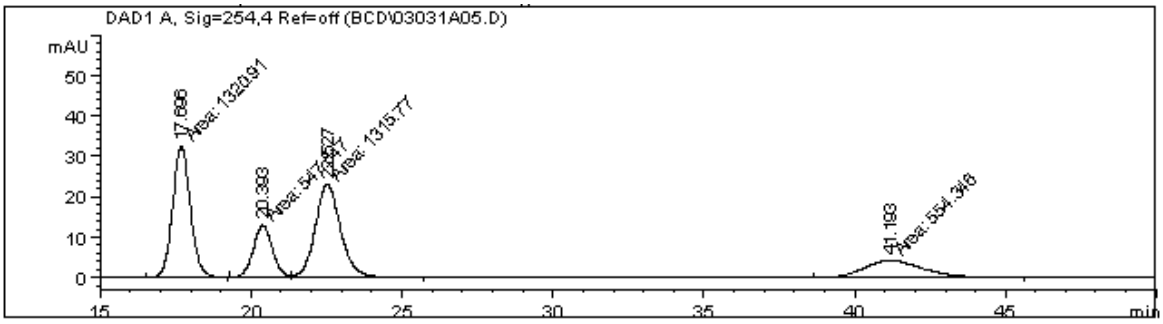

```
=====================================================================
                      Area Percent Report
=====================================================================

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


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.876 PV    0.1912 5468.41260  433.31494  43.2197
   2  11.506 VB    0.2080 5617.56396  409.65561  44.3986
   3  14.615 BP    0.2669  784.41248   45.09694   6.1996
   4  18.078 BB    0.3302  782.19501   36.47874   6.1821
```

Enantioenriched 19



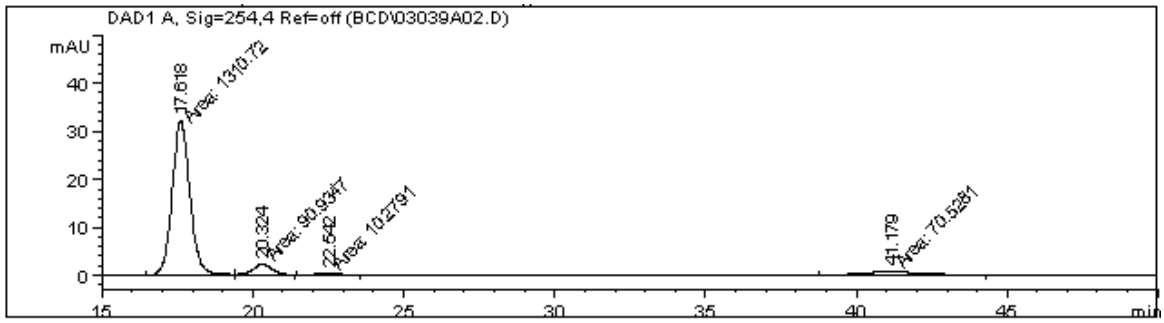

```
=====================================================================
                      Area Percent Report
=====================================================================

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


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.865 MM    0.2159 1.70848e4  1318.71960  93.3419
   2  11.479 MM    0.2324  175.19363   12.56404   0.9572
   3  14.597 BB    0.2669  598.36121   34.40852   3.2691
   4  18.045 BB    0.3242  445.11942   20.91951   2.4319
```

Racemic 20



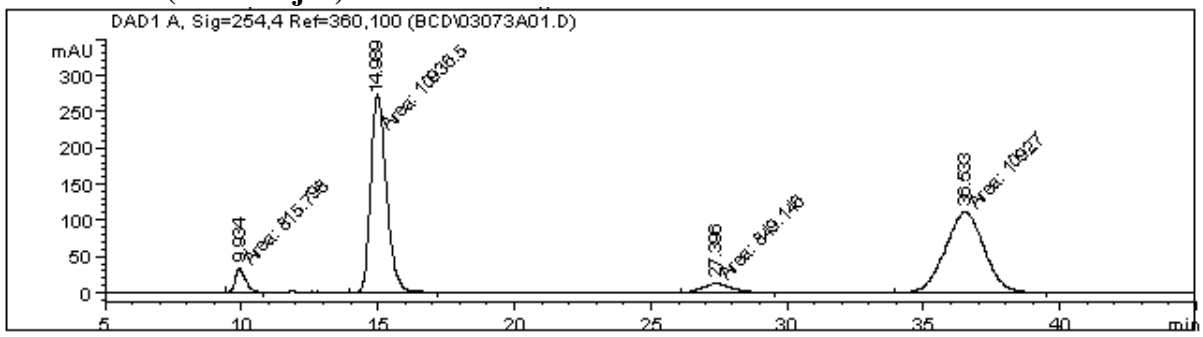

```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  17.696 MM    0.6788 1320.90674   32.43325  35.3290
   2  20.393 MM    0.7237  547.84705   12.61658  14.6527
   3  22.527 MM    0.9605 1315.77478   22.83084  35.1917
   4  41.193 MM    2.2163  554.34589    4.16870  14.8265
```

Enantioenriched 20



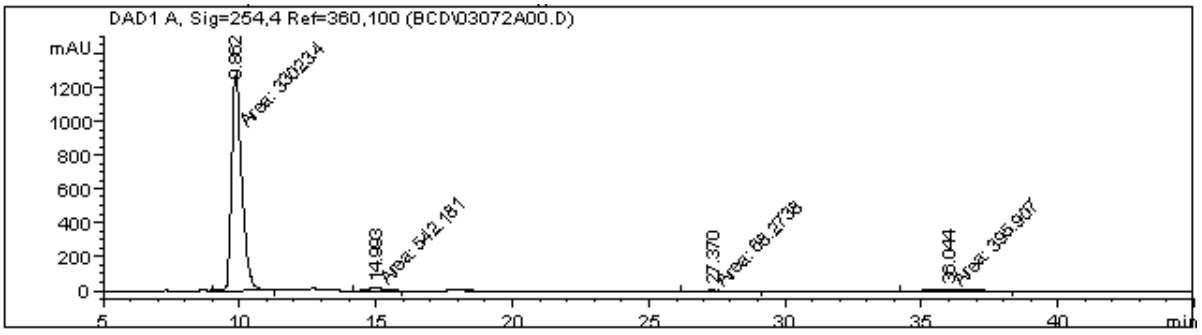

```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  17.618 MM    0.6838 1310.72046   31.94481  88.4151
   2  20.324 MM    0.7299   90.93474    2.07635   6.1340
   3  22.542 MM    0.8392   10.27911 2.04141e-1   0.6934
   4  41.179 MM    2.1621   70.52805 5.43677e-1   4.7575
```

Racemic 21 (*trans* major)



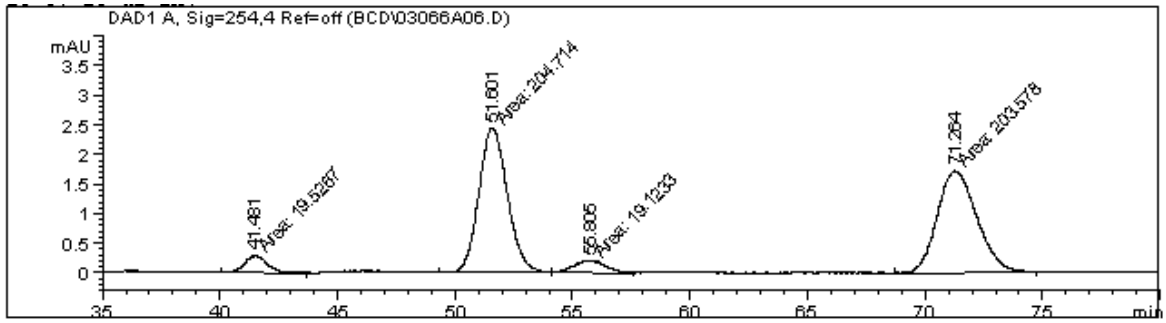

```
=====================================================================
                      Area Percent Report
=====================================================================

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


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.934 MM    0.4252  815.79834   31.97888   3.4673
   2  14.989 MM    0.6657 1.09365e4   273.79510  46.4820
   3  27.396 MM    1.2276  849.14551   11.52875   3.6090
   4  36.533 MM    1.6448 1.09270e4   110.71983  46.4417
```

Enantioenriched 21



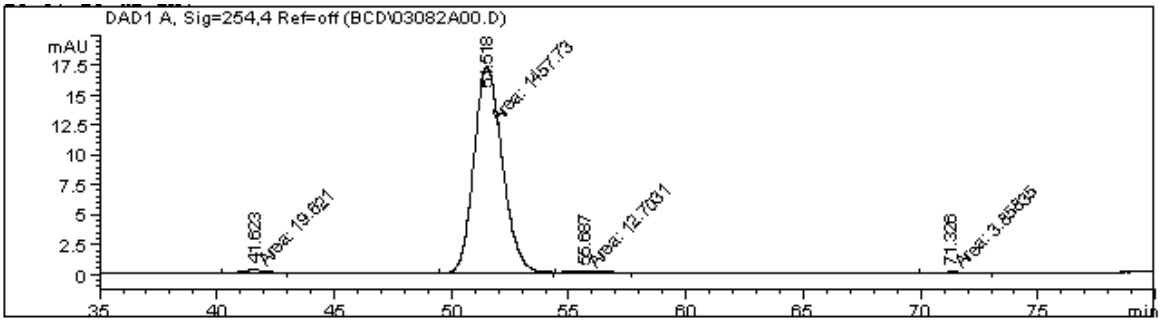

```
=====================================================================
                      Area Percent Report
=====================================================================

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


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.862 MM    0.4358 3.30234e4  1262.89734  97.0427
   2  14.993 MM    0.6395  542.18066   14.13126   1.5933
   3  27.370 MM    1.2340   68.27380 9.22149e-1   0.2006
   4  36.044 MM    1.5938  395.90704    4.14001   1.1634
```

Racemic 22



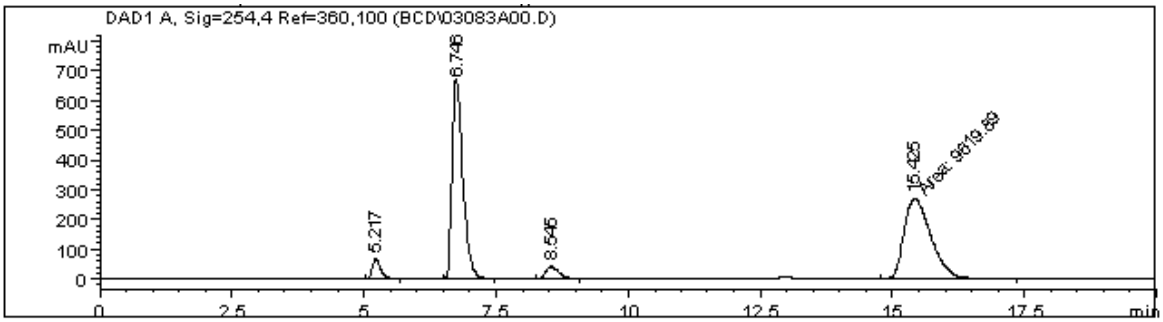

```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  41.481 MM    1.1425   19.52666 2.84864e-1   4.3689
   2  51.601 MM    1.4019  204.71352    2.43373  45.8032
   3  55.805 MM    1.5821   19.12330 2.01449e-1   4.2787
   4  71.264 MM    1.9630  203.57835    1.72848  45.5492
```

Enantioenriched 22



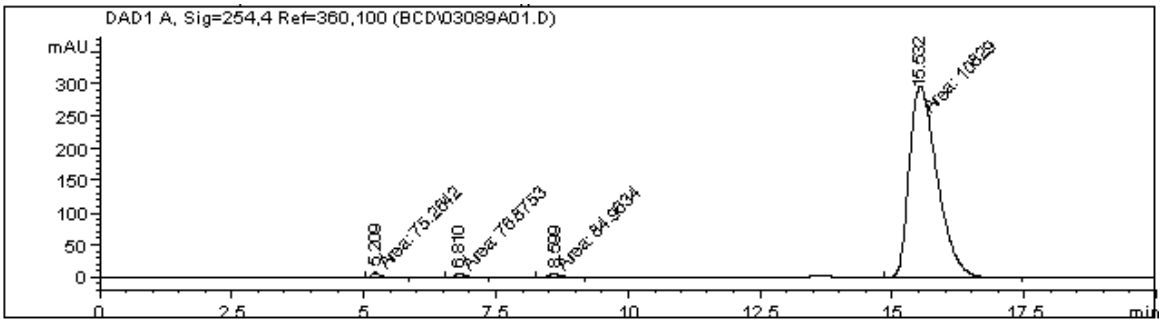

```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  41.623 MM    1.1009   19.62102 2.97037e-1   1.3134
   2  51.518 MM    1.4042 1457.72729   17.30186  97.5780
   3  55.687 MM    1.3777   12.70307 1.53670e-1   0.8503
   4  71.326 MM    1.3887    3.85835 4.63062e-2   0.2583
```

Racemic 23



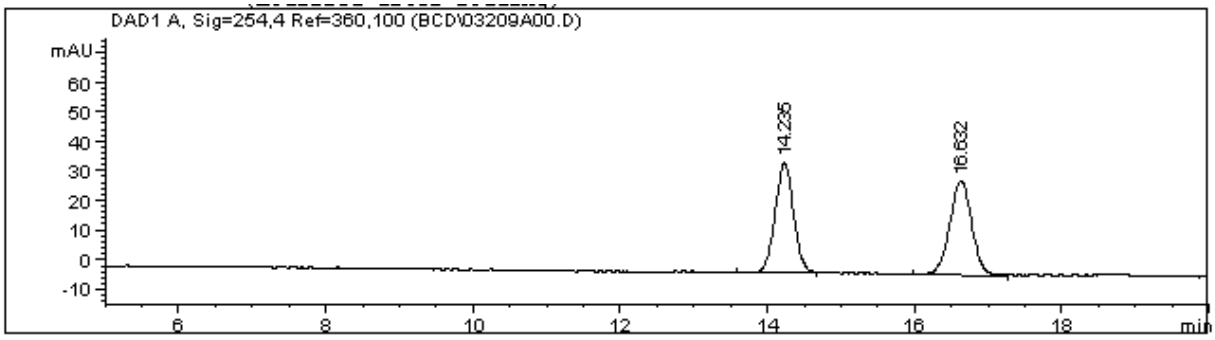

```
==================================================================
                      Area Percent Report
==================================================================

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


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.217 PB    0.1553  733.53015   70.52425   3.5743
   2   6.746 BB    0.2135 9440.03418  673.72266  45.9992
   3   8.545 BB    0.2672  728.70337   41.43128   3.5508
   4  15.425 MM    0.5935 9619.88672  270.13370  46.8756
```

Enantioenriched 23



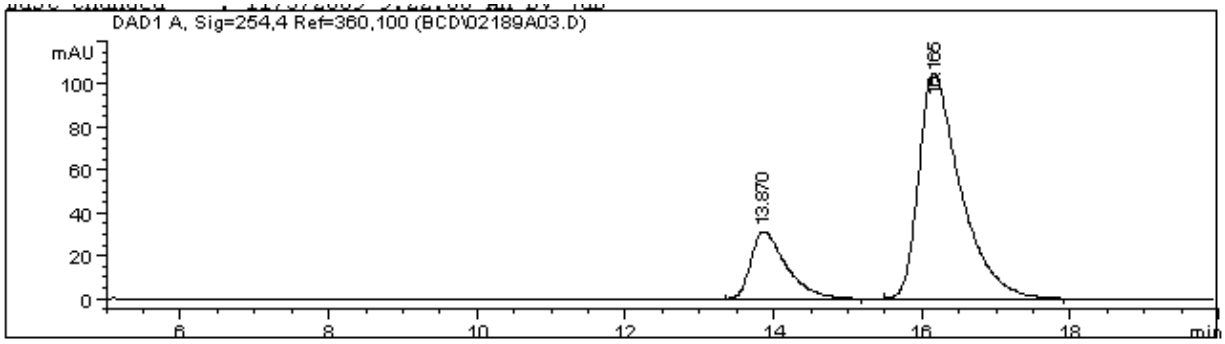

```
==================================================================
                      Area Percent Report
==================================================================

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


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.209 MM    0.1868   75.26424   6.71515   0.6801
   2   6.810 MM    0.2425   76.87533   5.28328   0.6947
   3   8.599 MM    0.3028   84.96345   4.67696   0.7678
   4  15.532 MM    0.6125 1.08290e4  294.68802  97.8574
```

Racemic 24



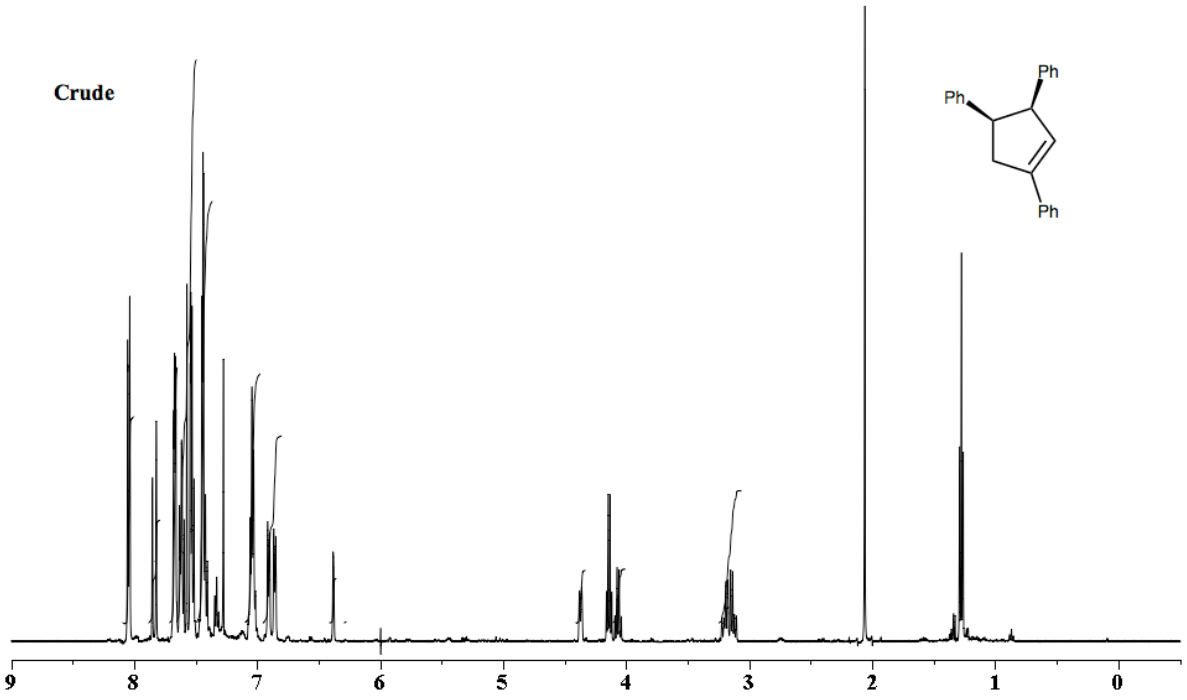

```
=====================================================================
                        Area Percent Report
=====================================================================

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


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  14.235 PV    0.2713  656.69836   37.31744  49.8073
   2  16.632 VB    0.3228  661.77905   31.79712  50.1927
```

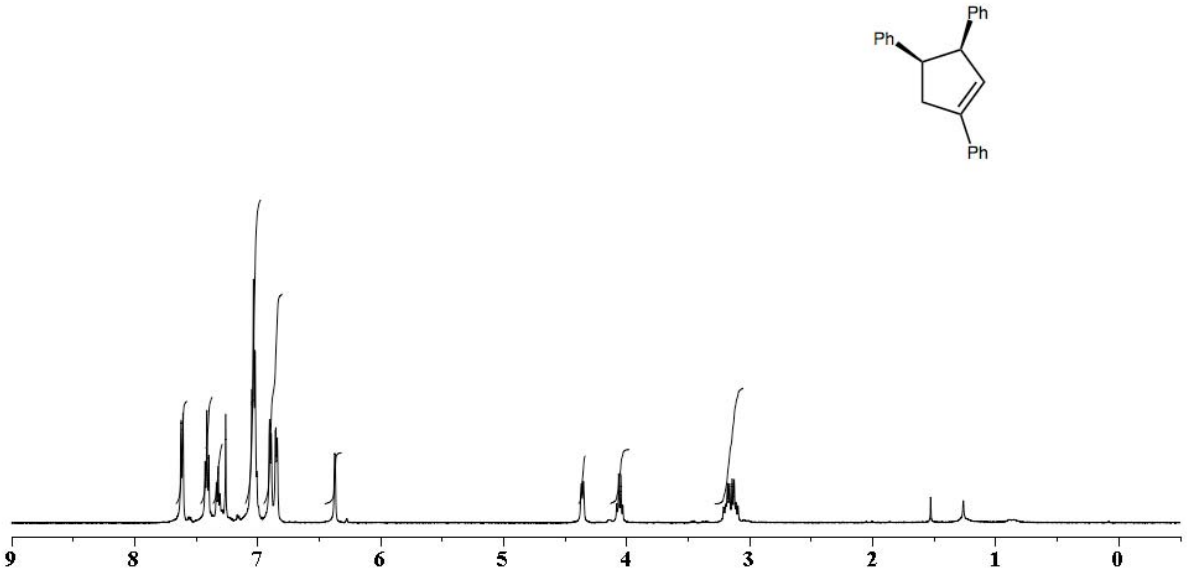
Enantioenriched 24

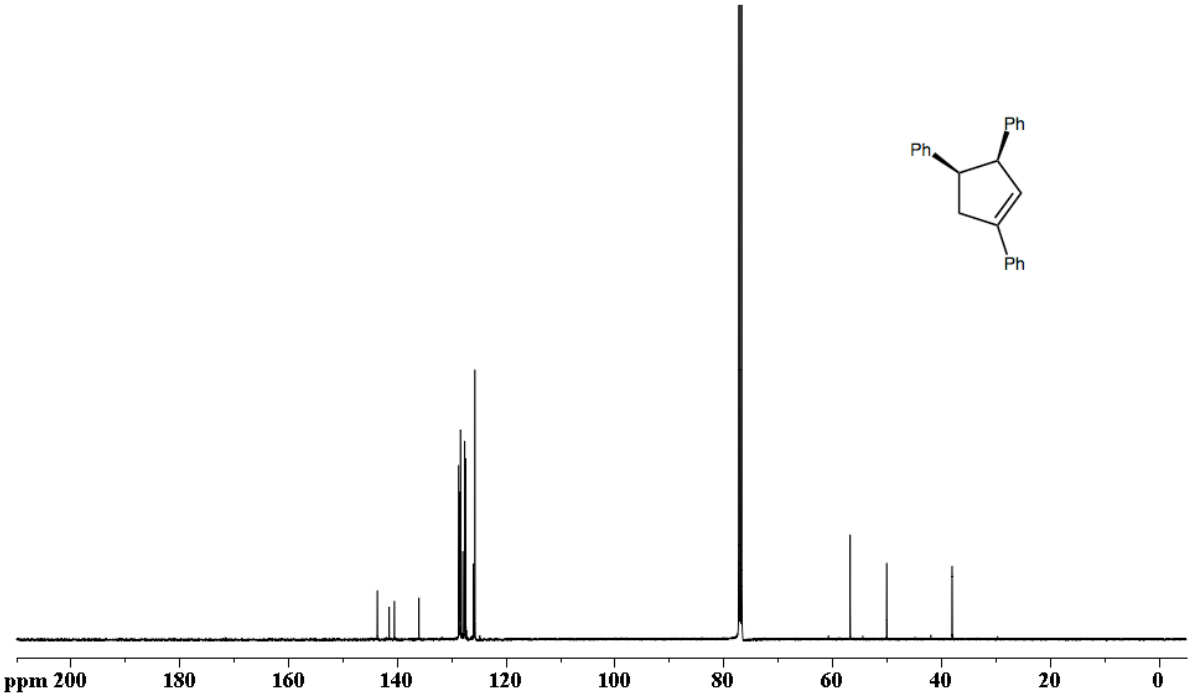


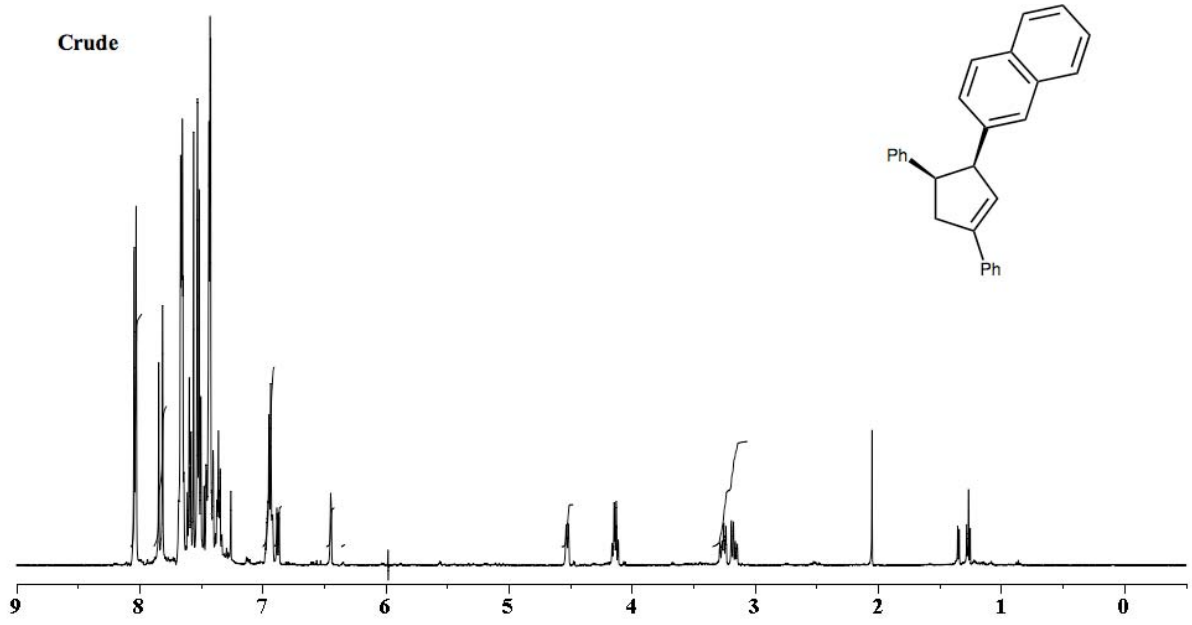

```
=====================================================================
                        Area Percent Report
=====================================================================

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


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  13.870 BB    0.4951 1047.98071   31.41843  20.2919
   2  16.165 BB    0.5785 4116.55566  105.19623  79.7081
```

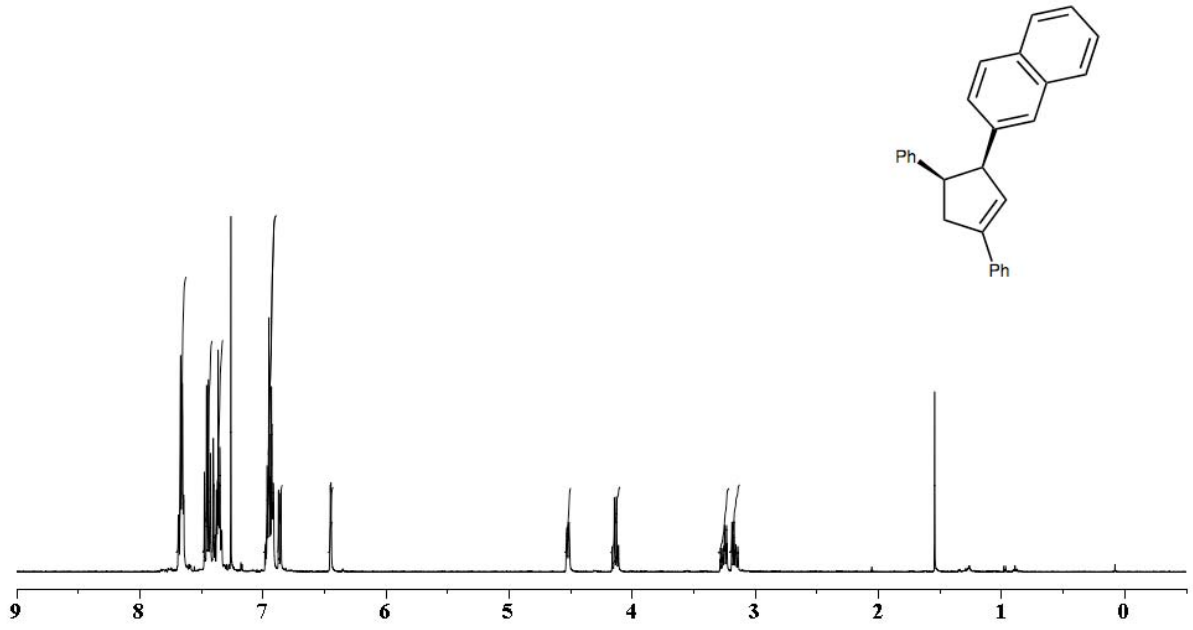
Selected NMR Spectra

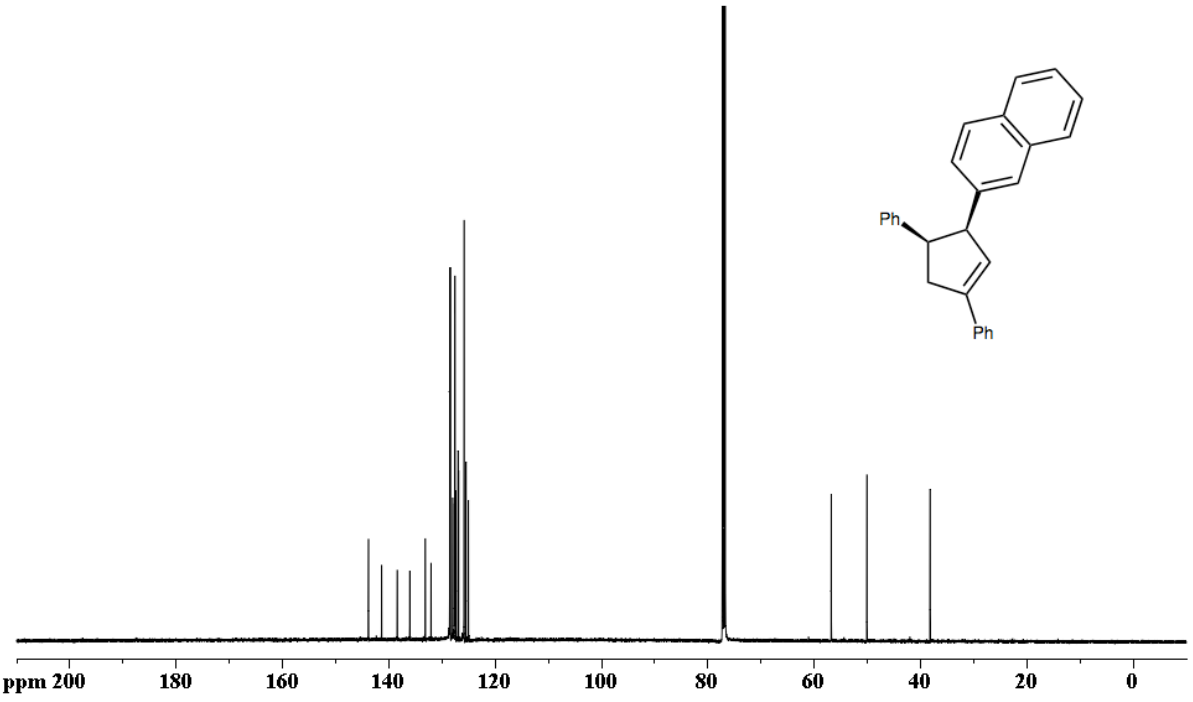


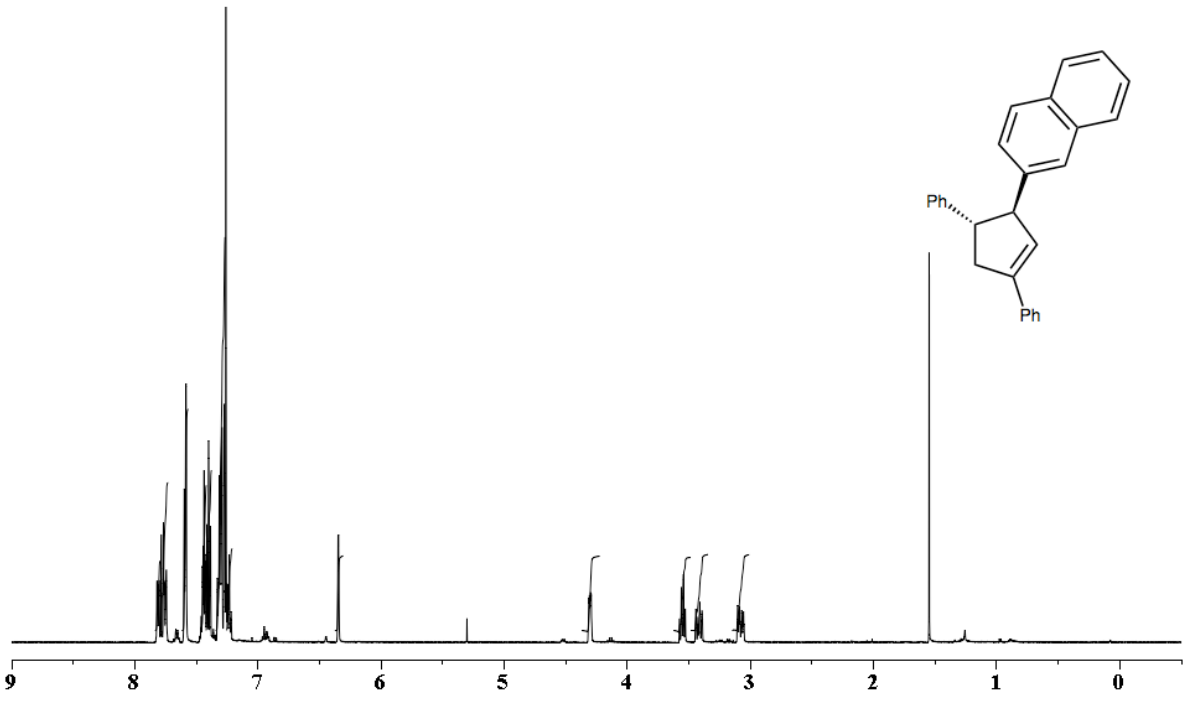


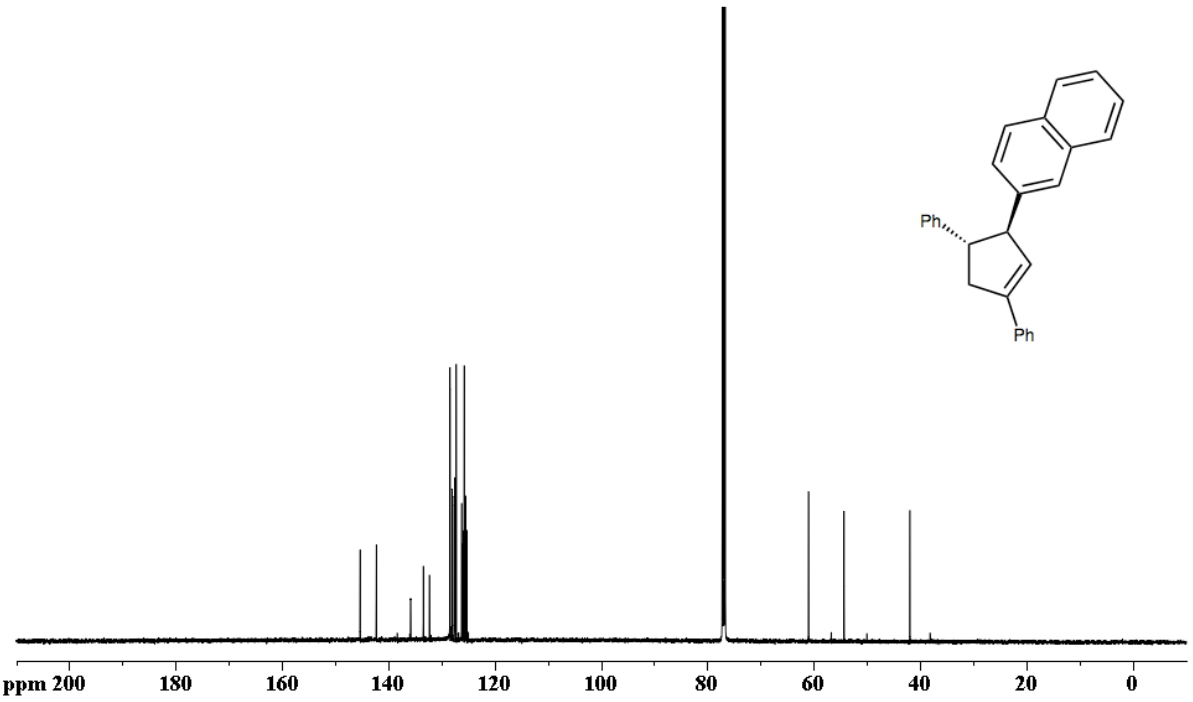

Ph
Ph
Ph
ppm 200
180
160
140
120
100
80
60
40
20
0

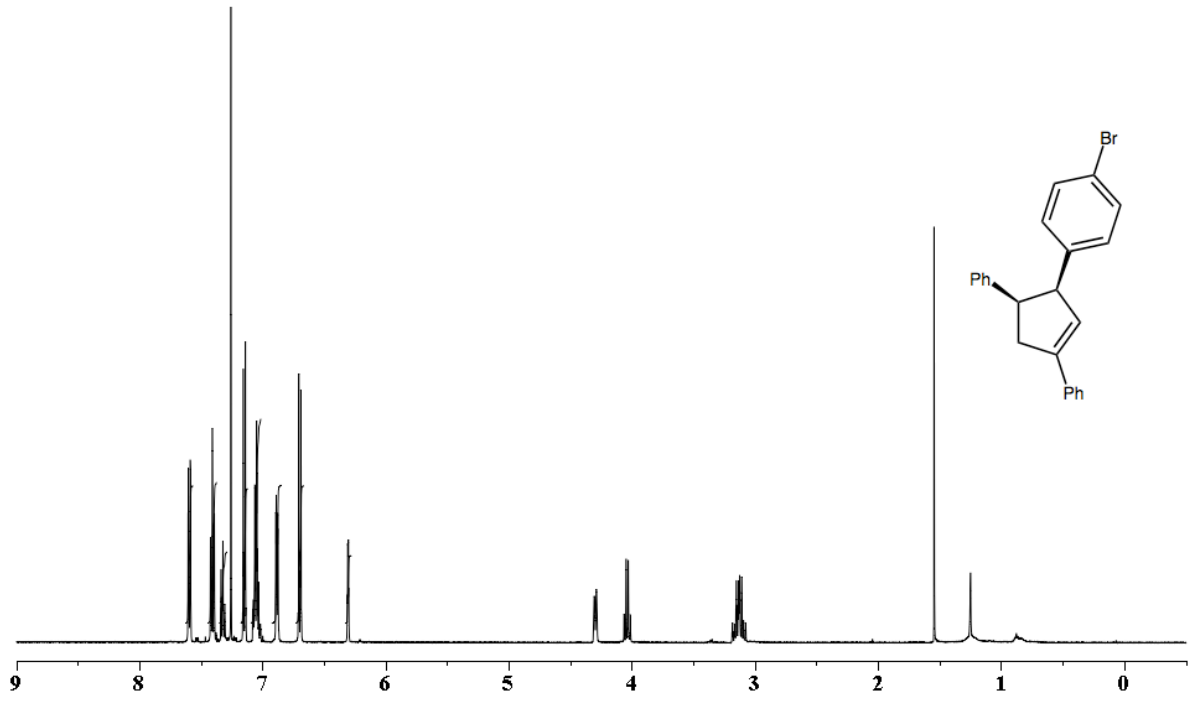

Crude
Ph
Ph
9
8
7
6
5
4
3
2
1
0

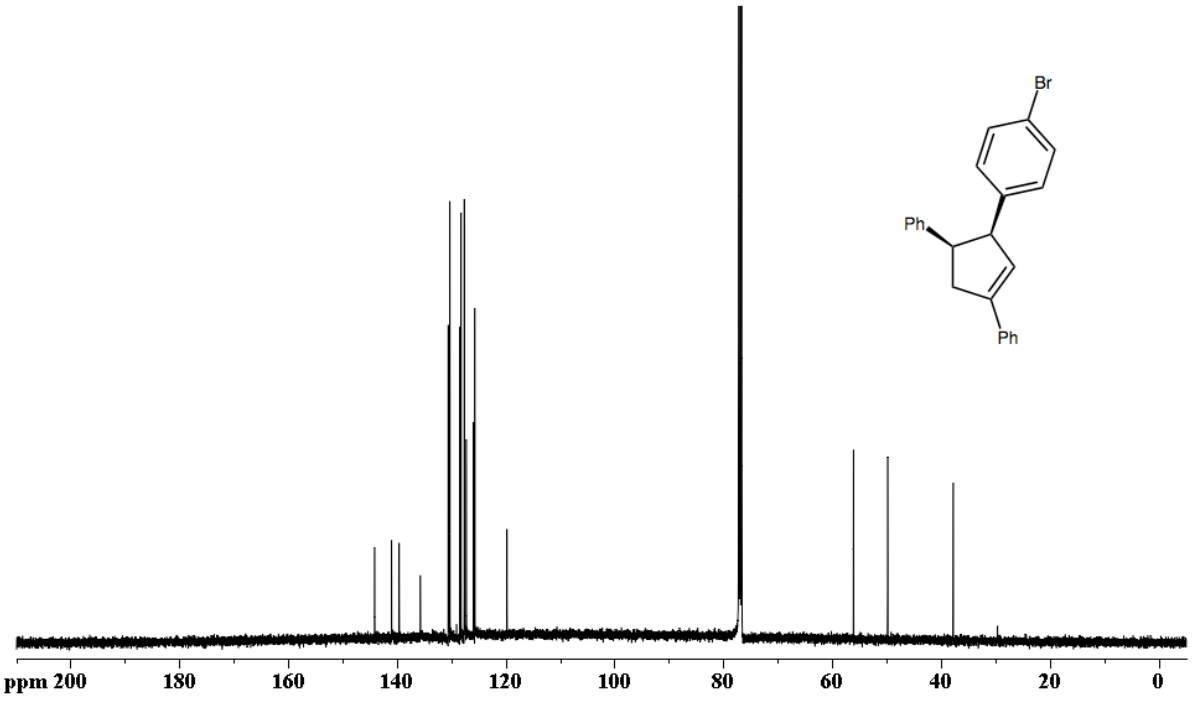

Ph
Ph
9
8
7
6
5
4
3
2
1
0

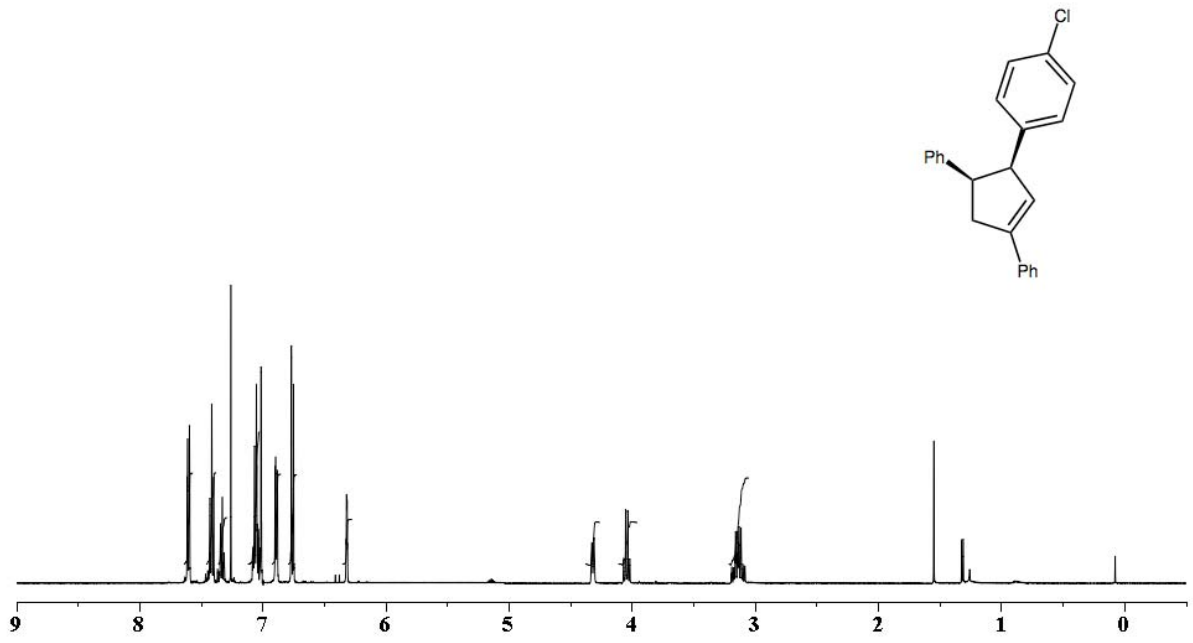

Ph
Ph
ppm 200
180
160
140
120
100
80
60
40
20
0

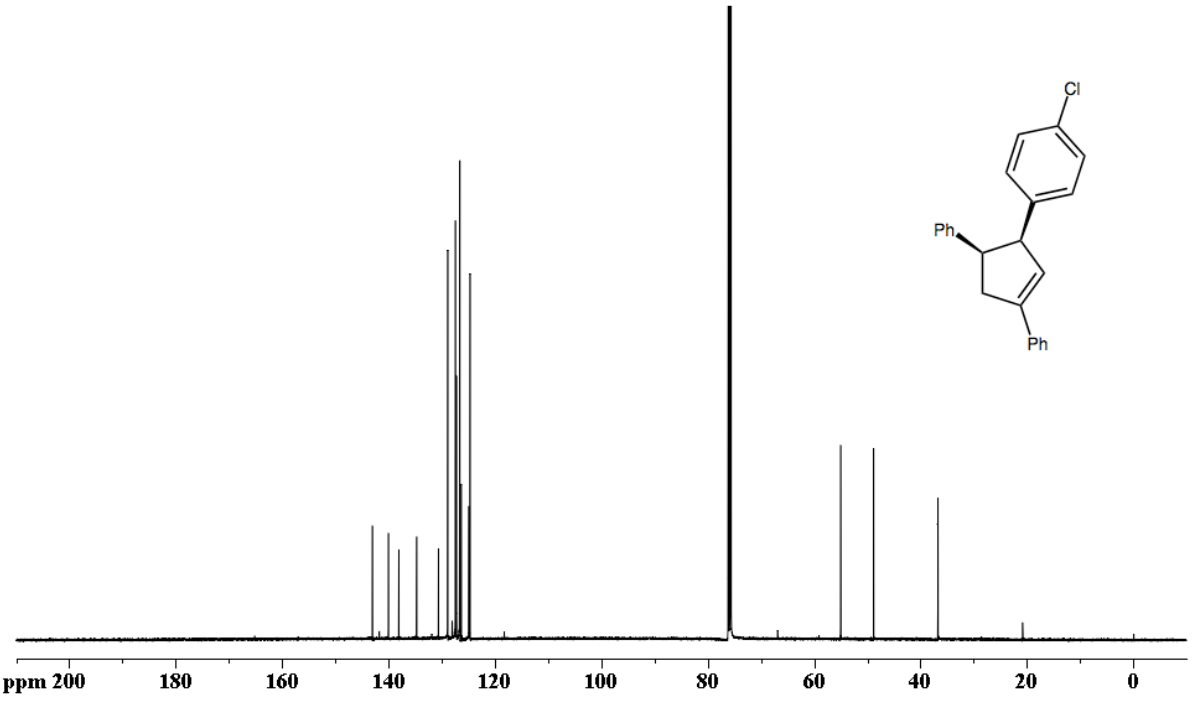

Ph
Ph
9
8
7
6
5
4
3
2
1
0

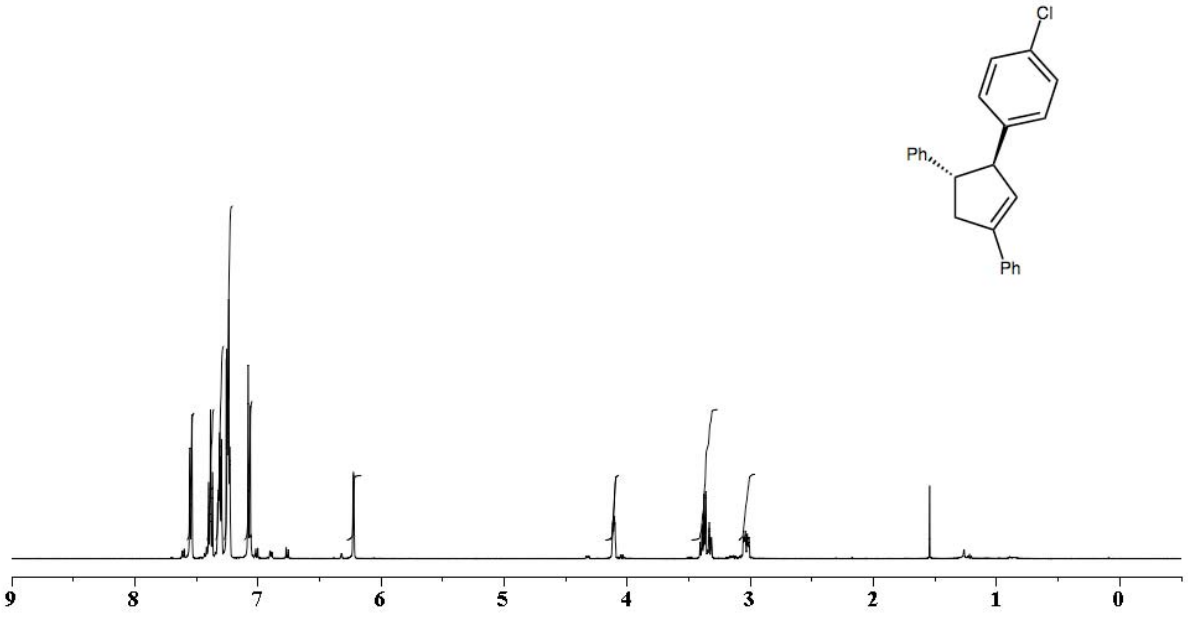

Ph
Ph
ppm 200
180
160
140
120
100
80
60
40
20
0

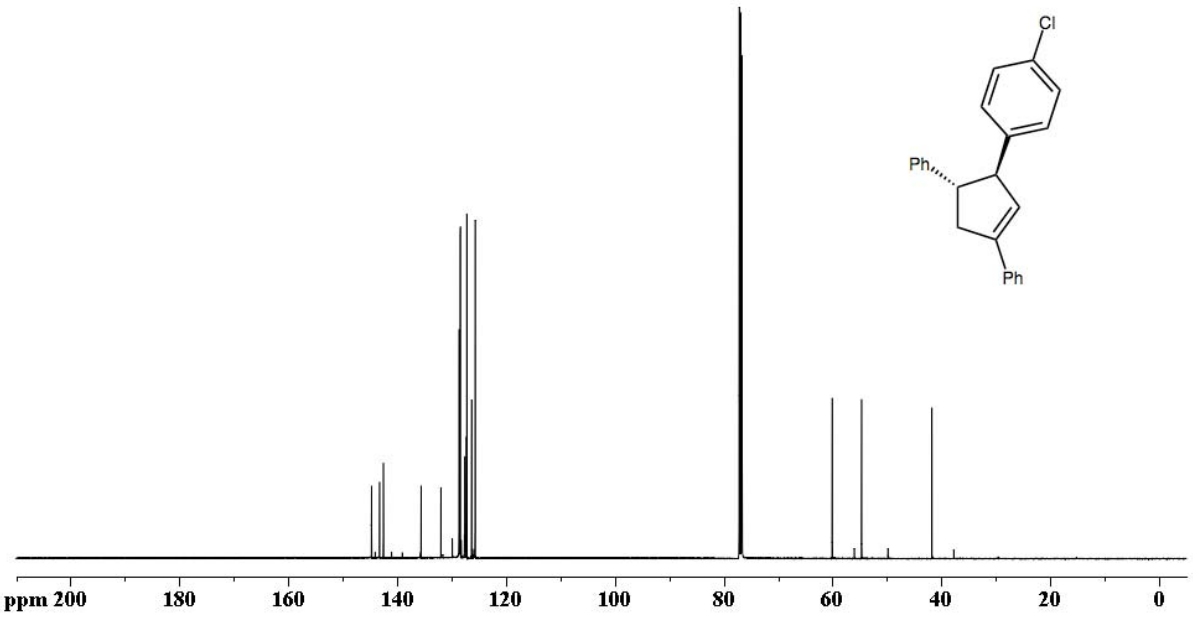

Br
Ph
Ph
9
8
7
6
5
4
3
2
1
0

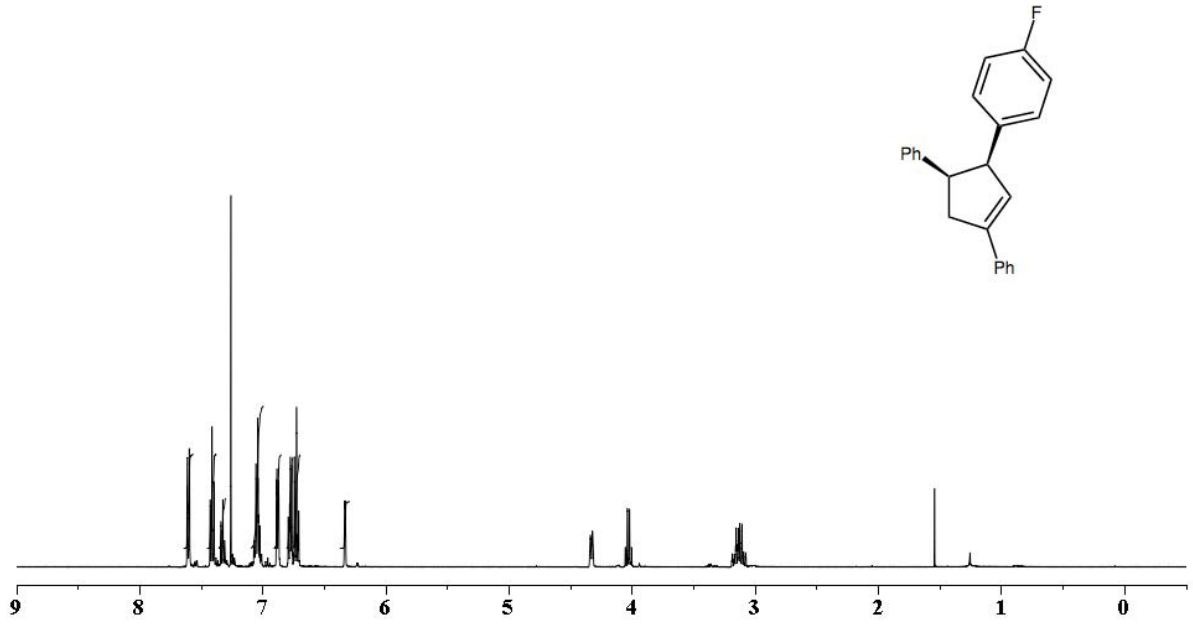

Br
Ph
Ph
ppm 200
180
160
140
120
100
80
60
40
20
0


Cl
Ph
Ph
9
8
7
6
5
4
3
2
1
0


Cl
Ph
Ph
ppm 200
180
160
140
120
100
80
60
40
20
0


Cl
Ph
Ph
9
8
7
6
5
4
3
2
1
0


Cl
Ph
Ph
ppm 200
180
160
140
120
100
80
60
40
20
0


F
Ph
Ph
9
8
7
6
5
4
3
2
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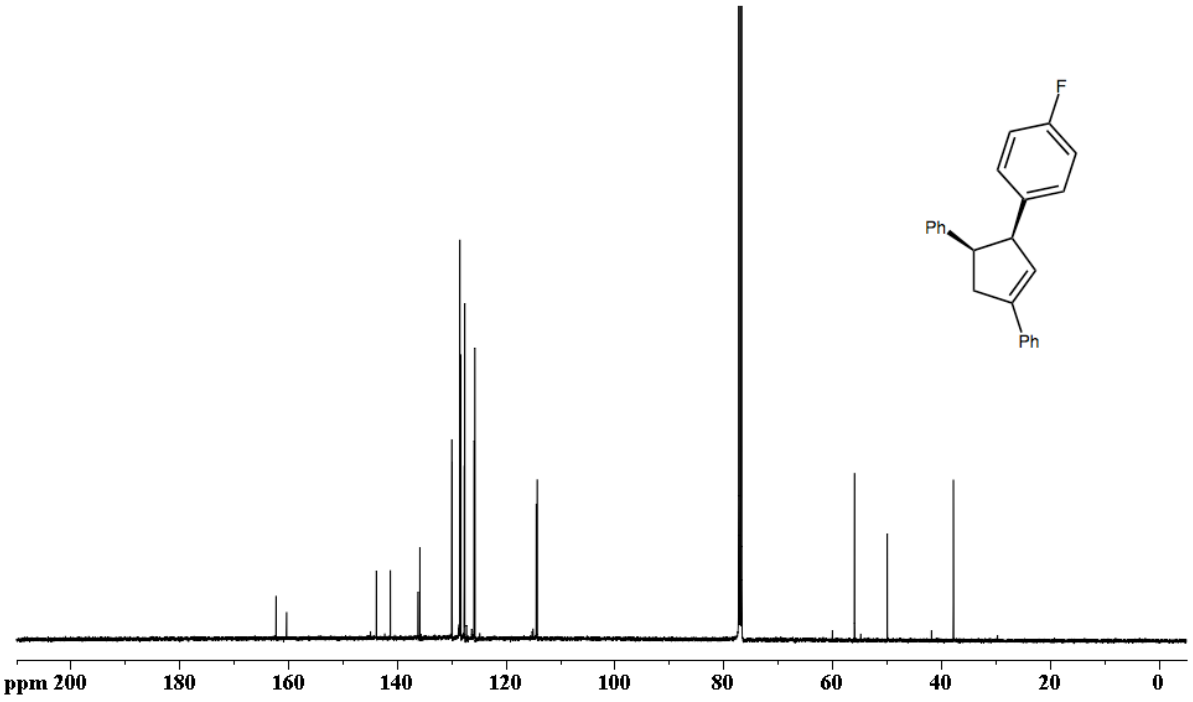
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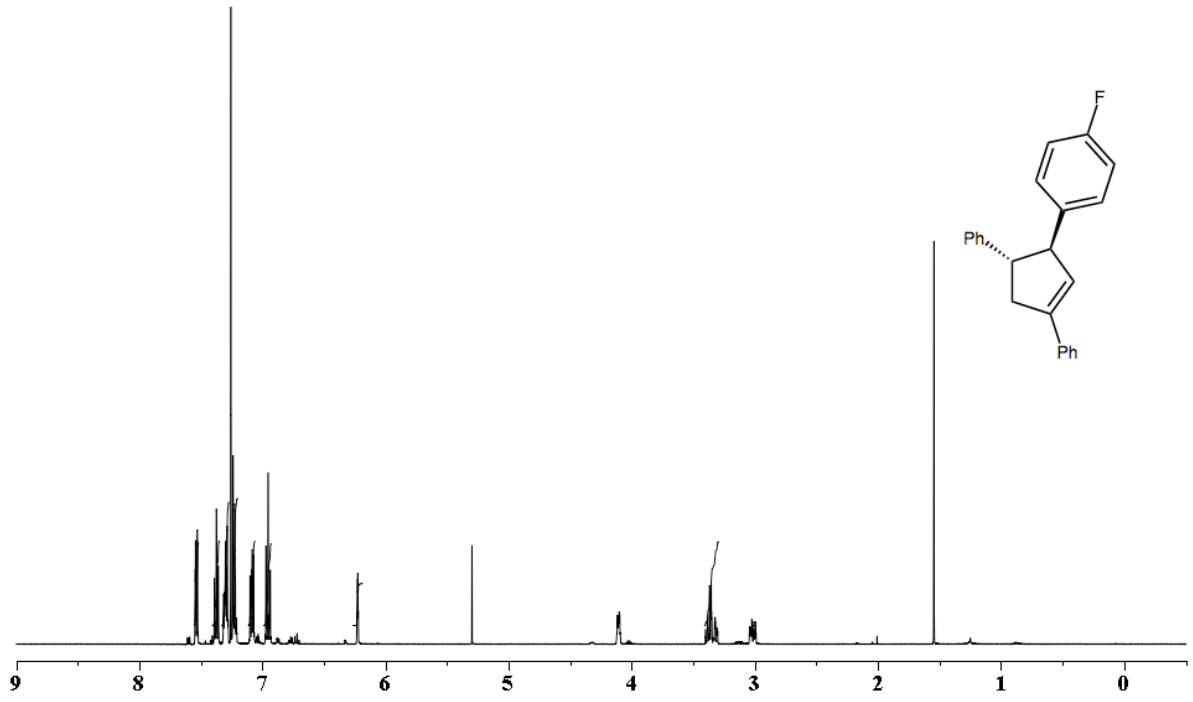
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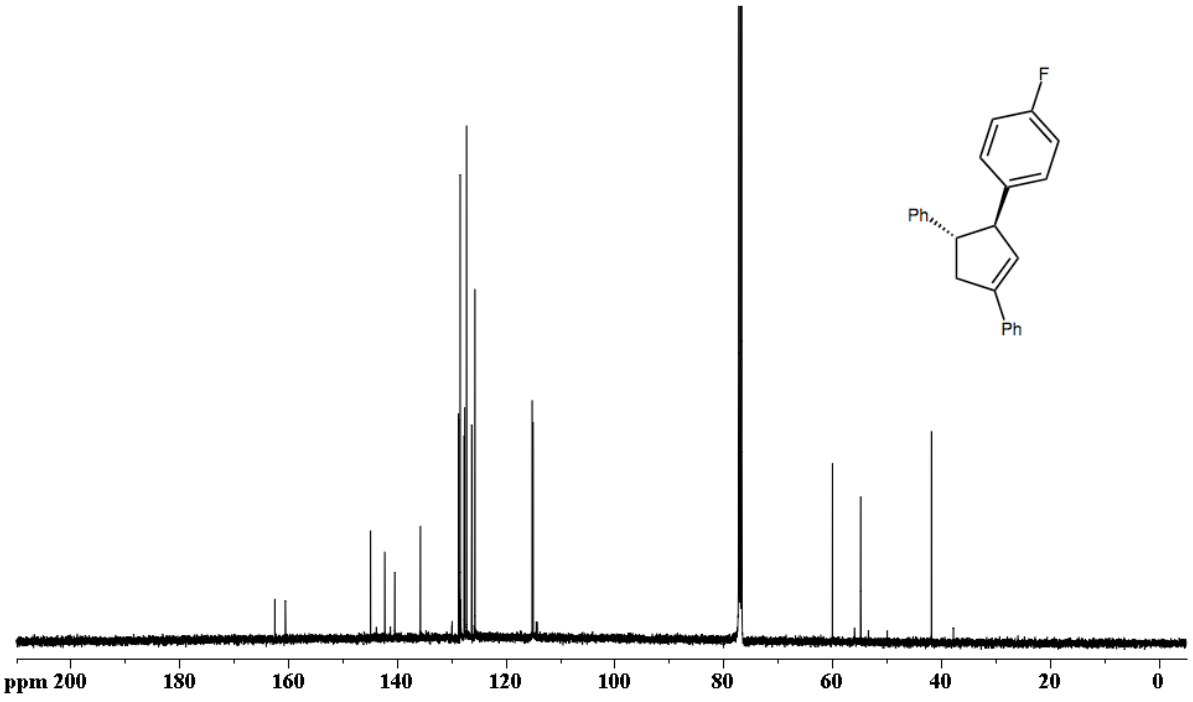
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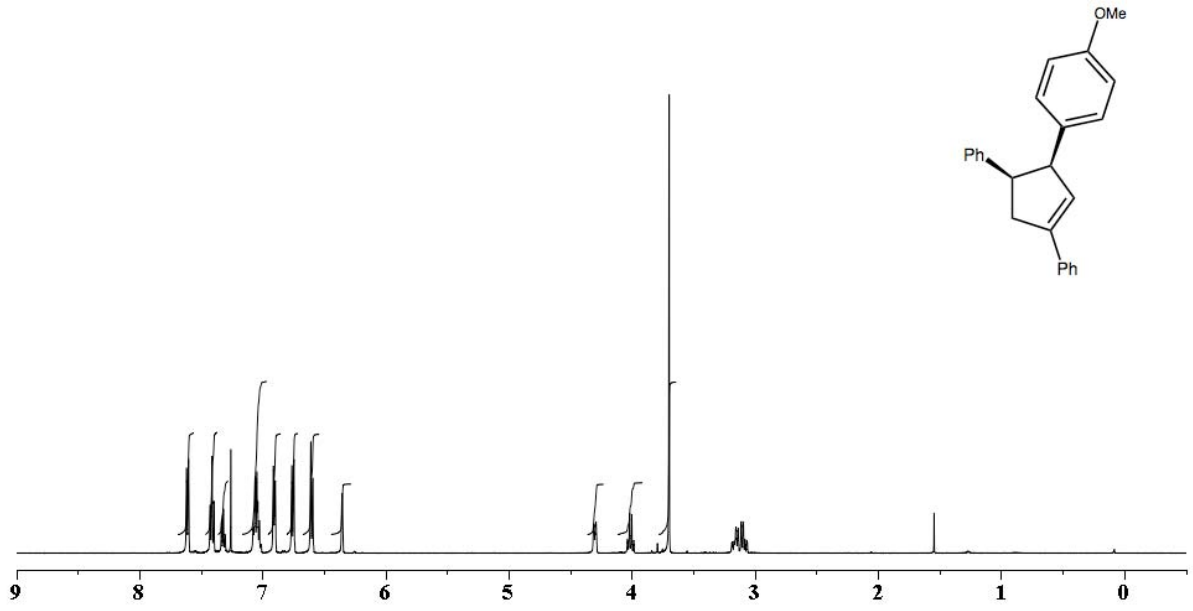
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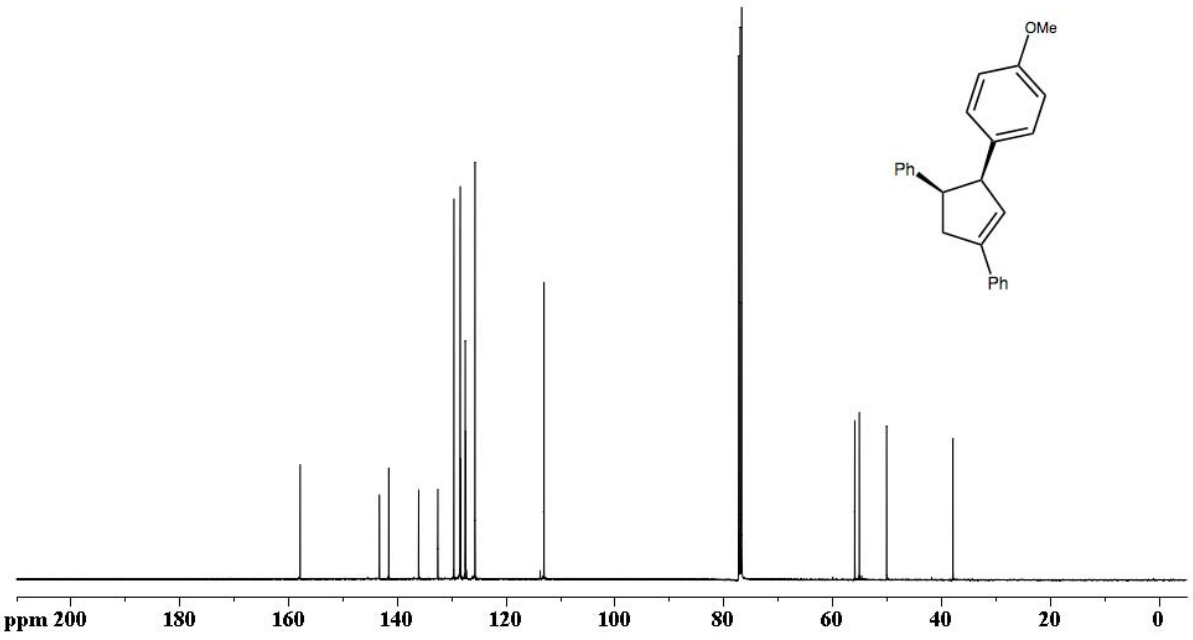
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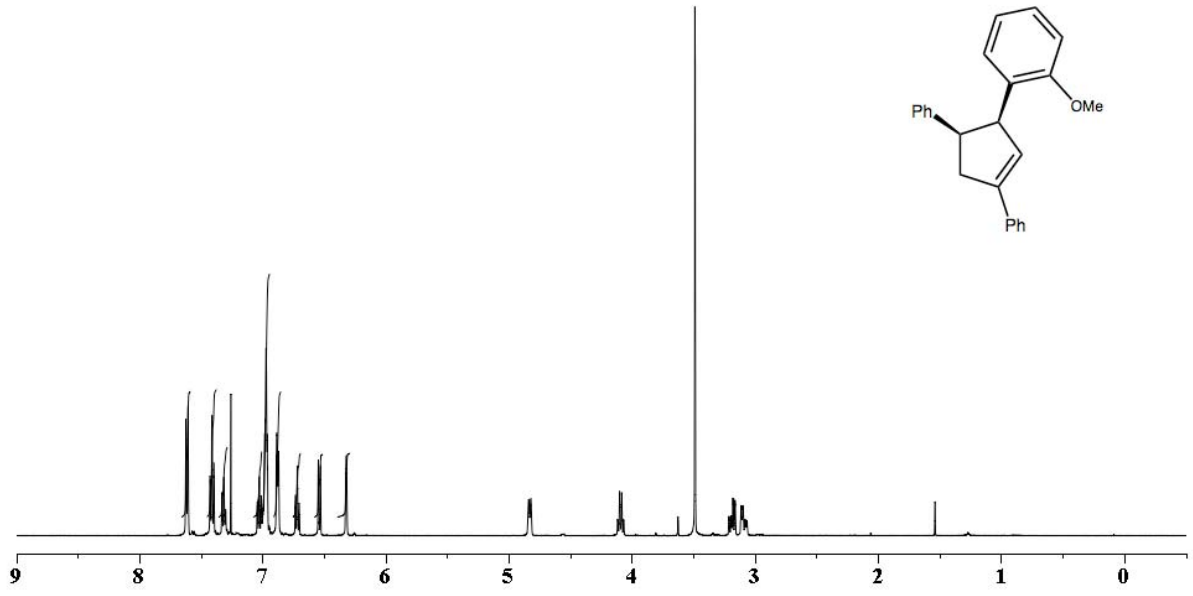
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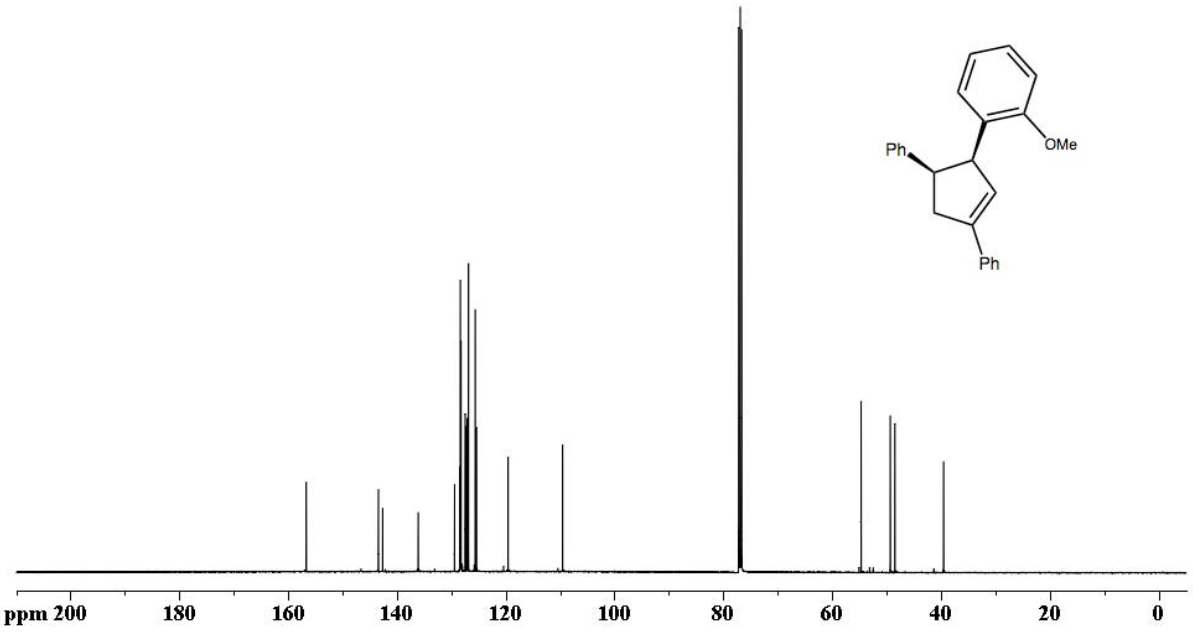
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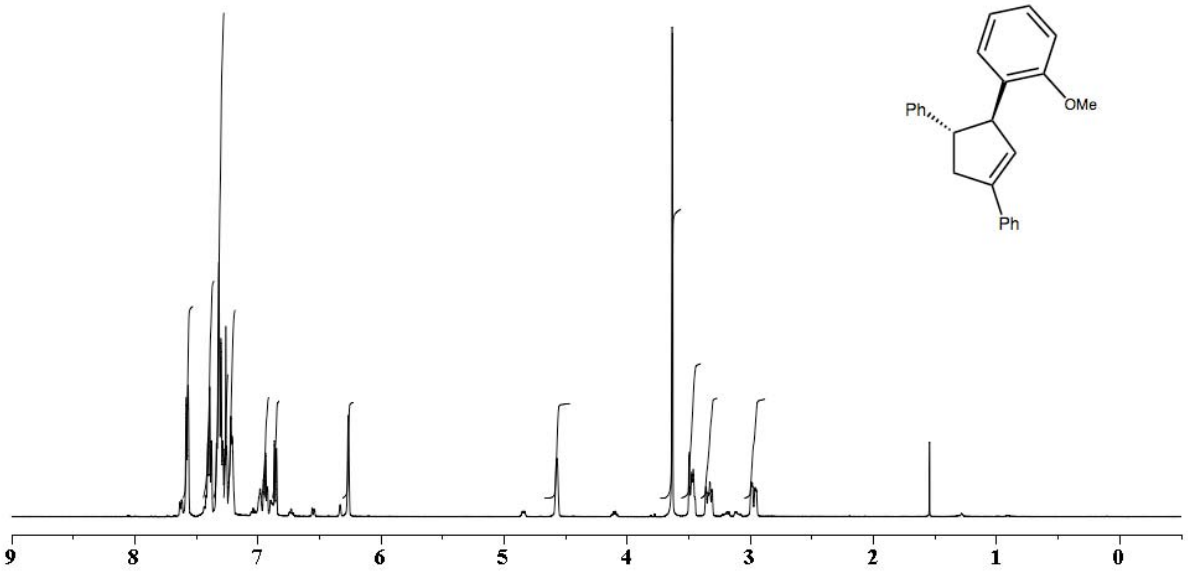
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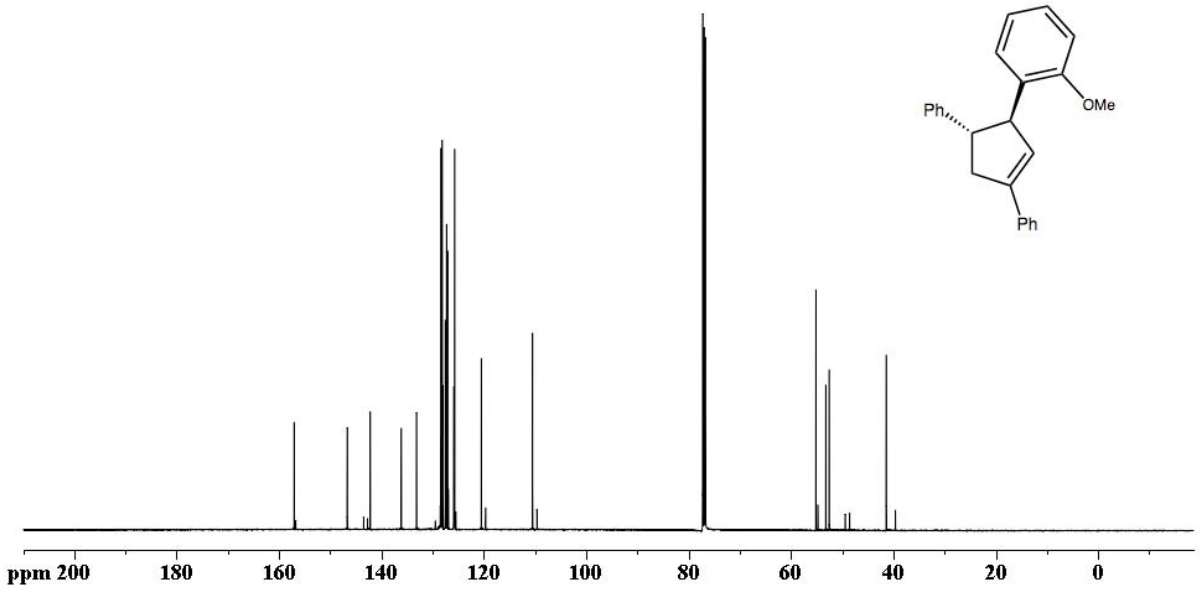
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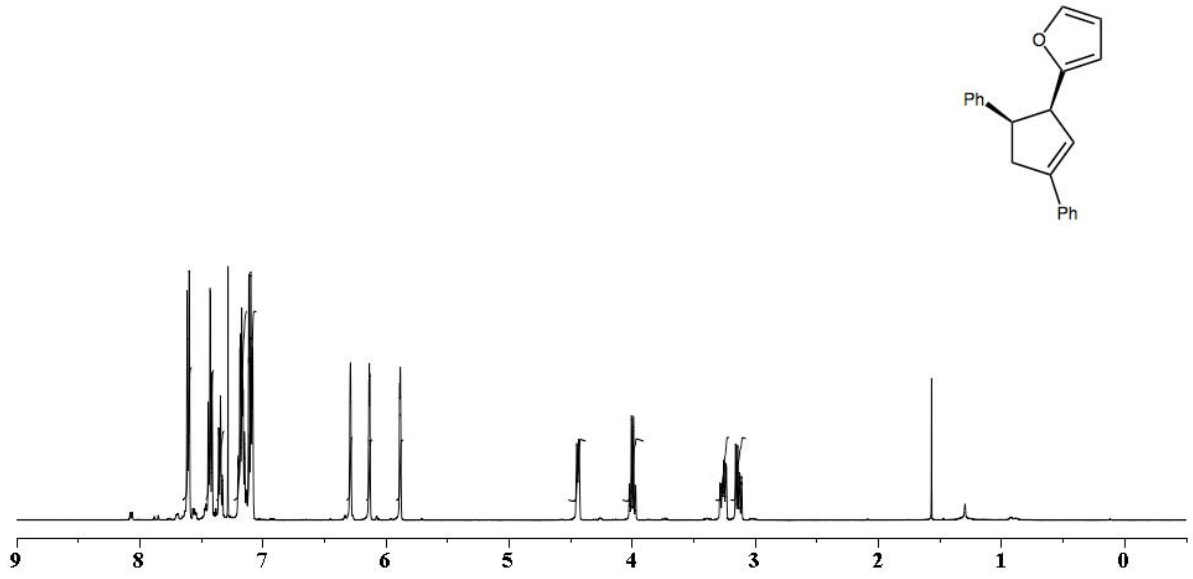
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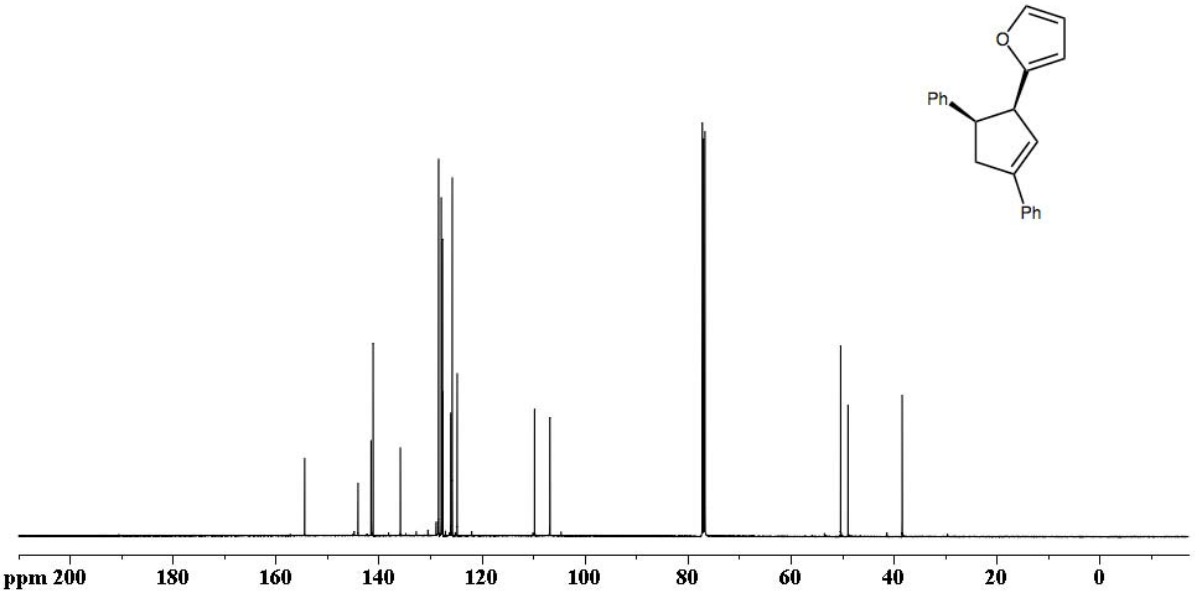
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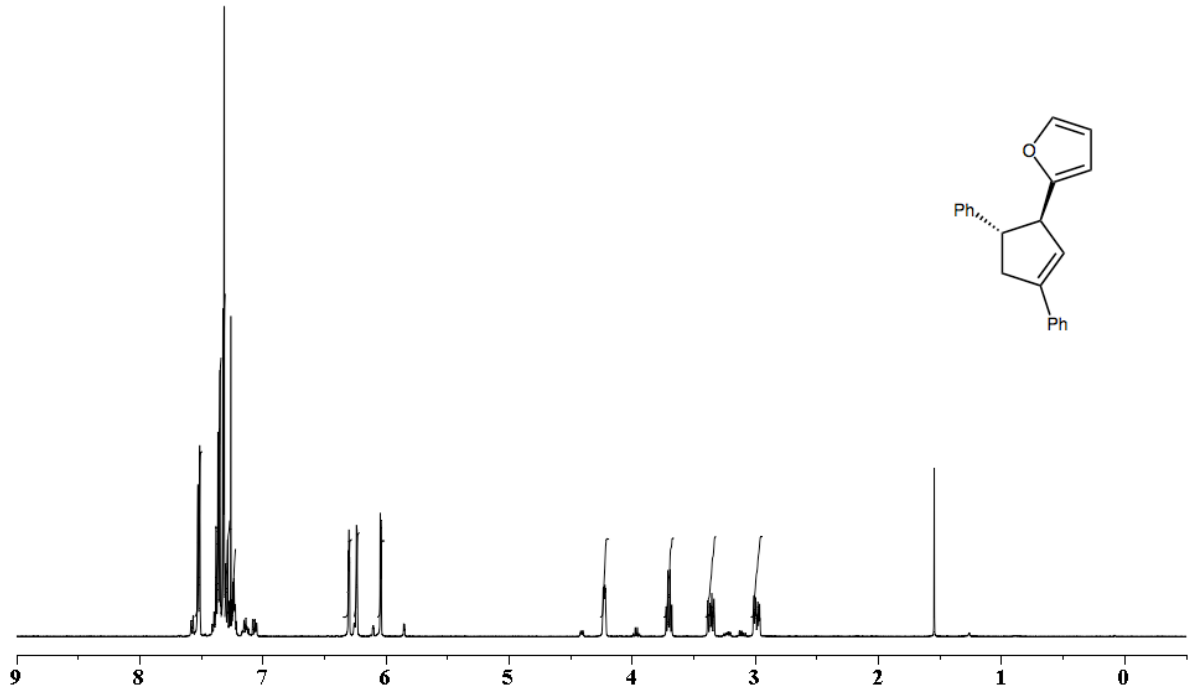
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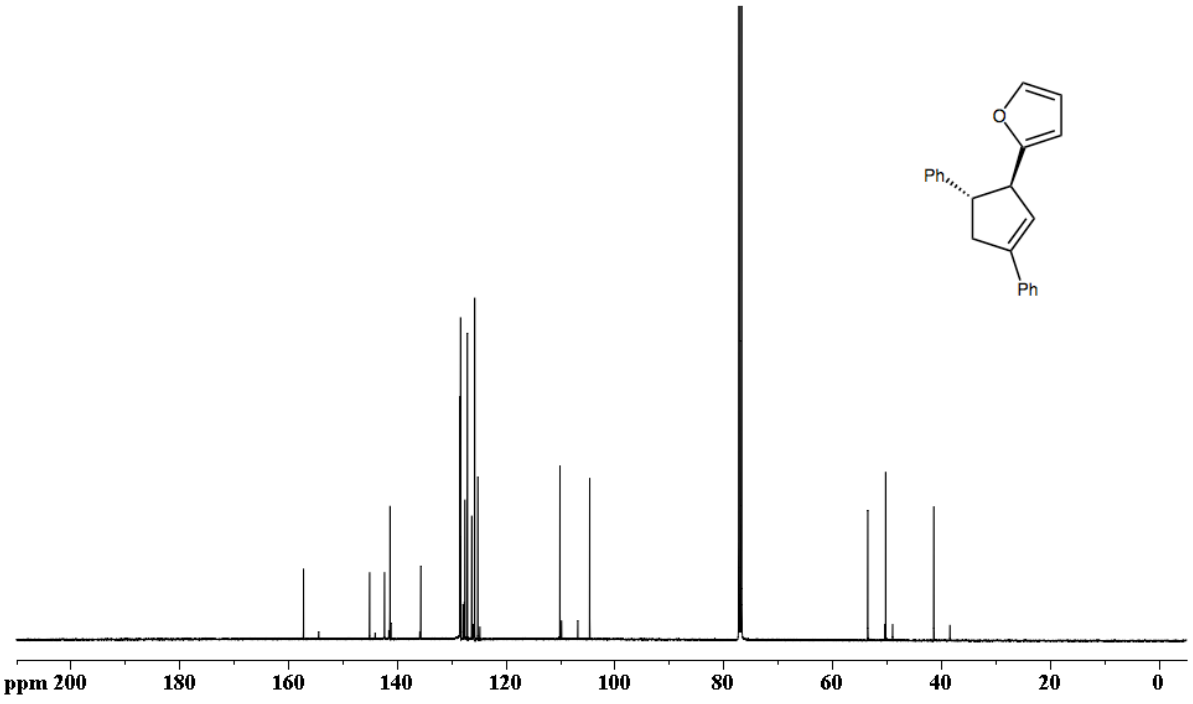
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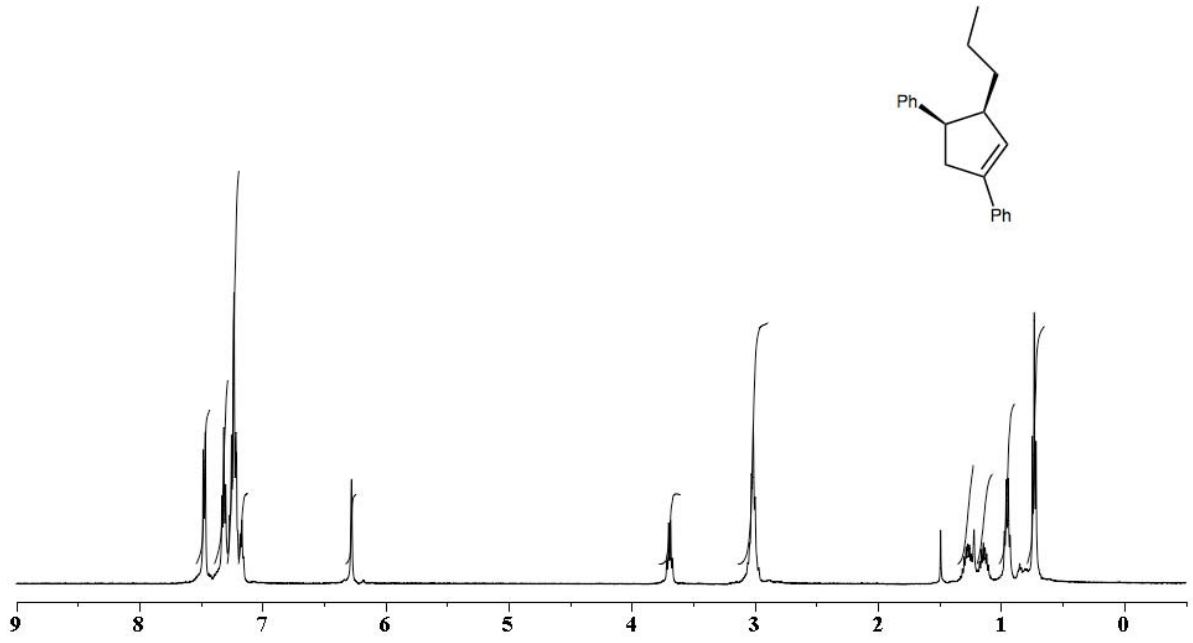
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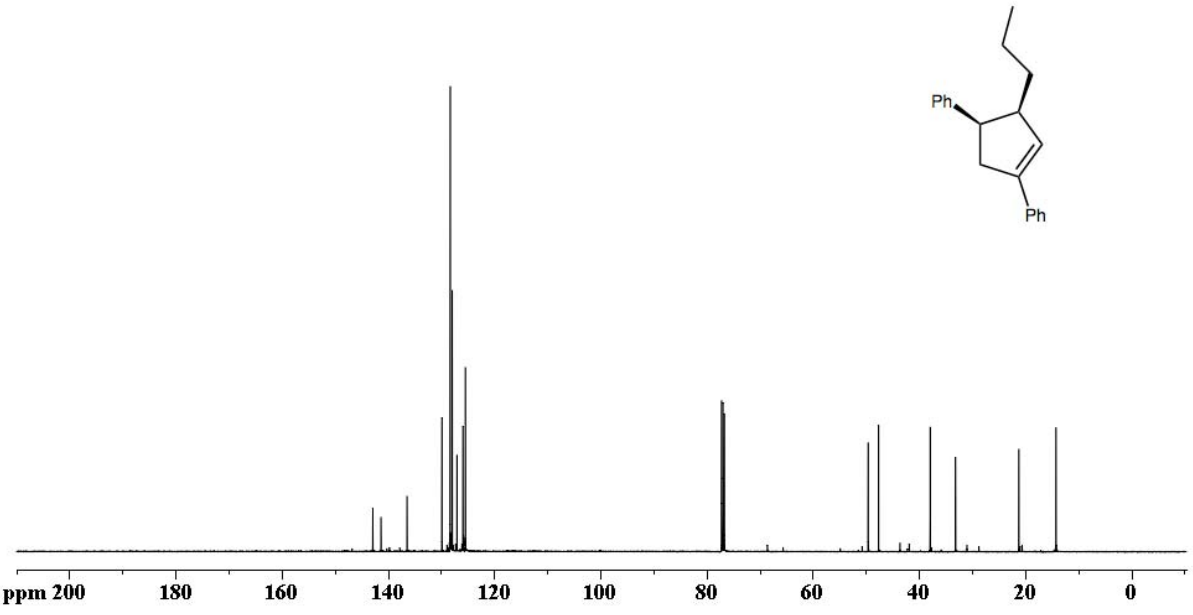
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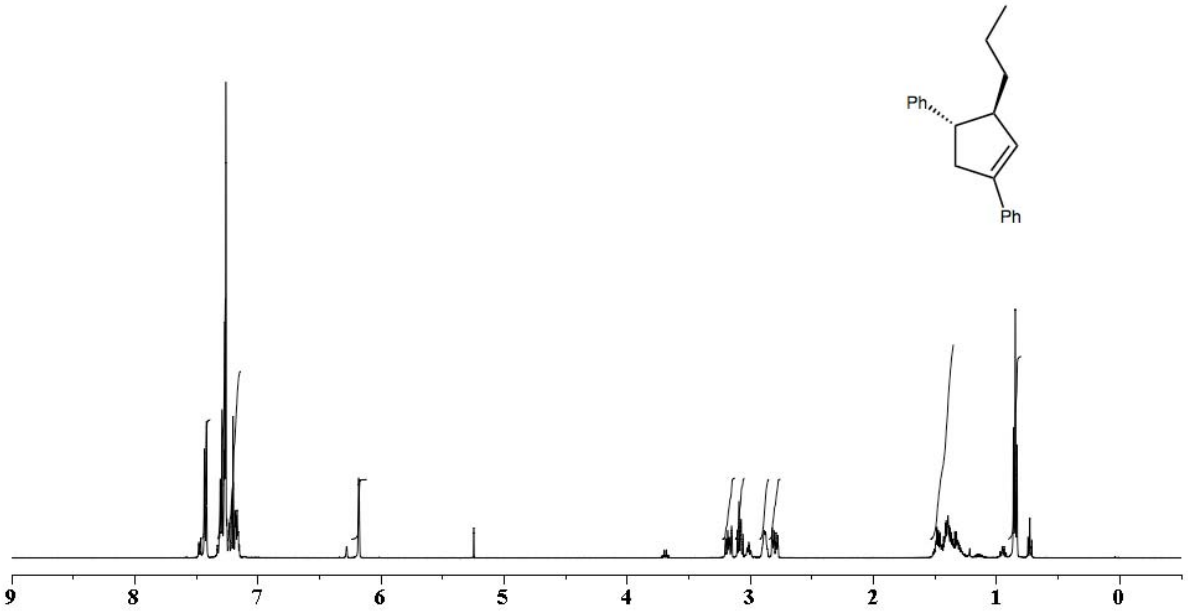
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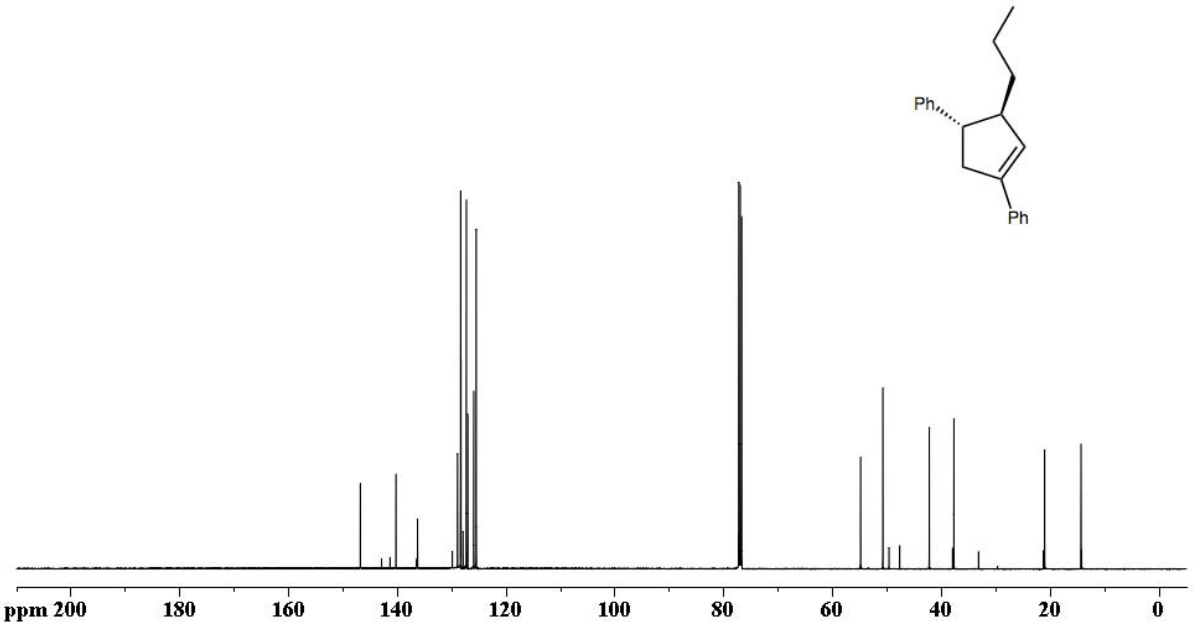
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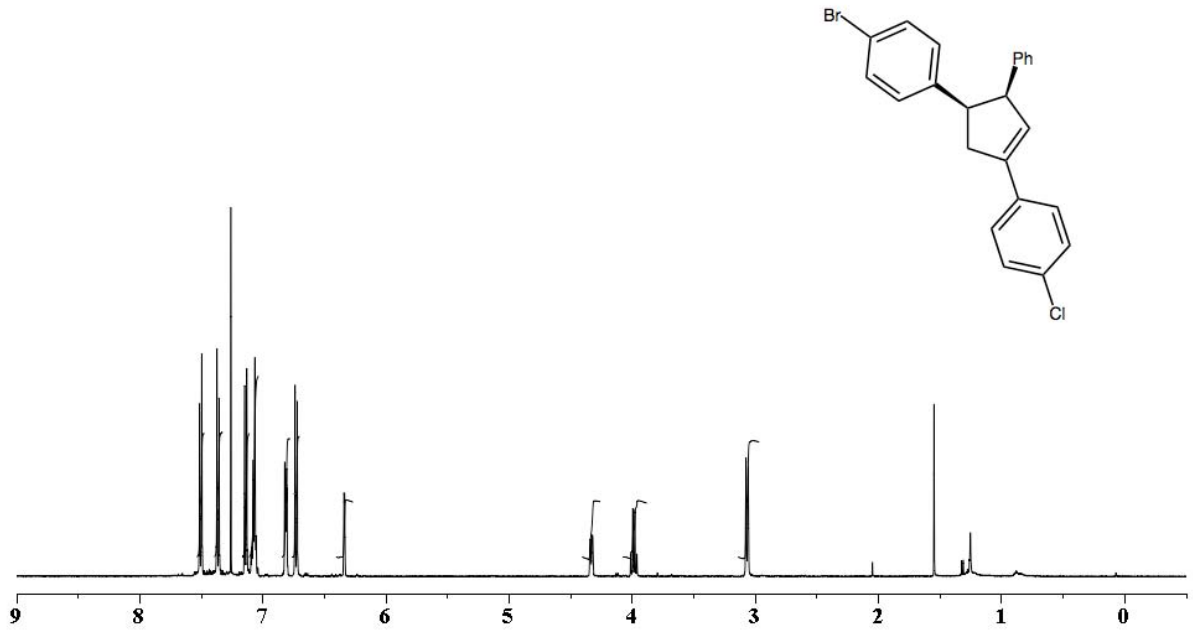
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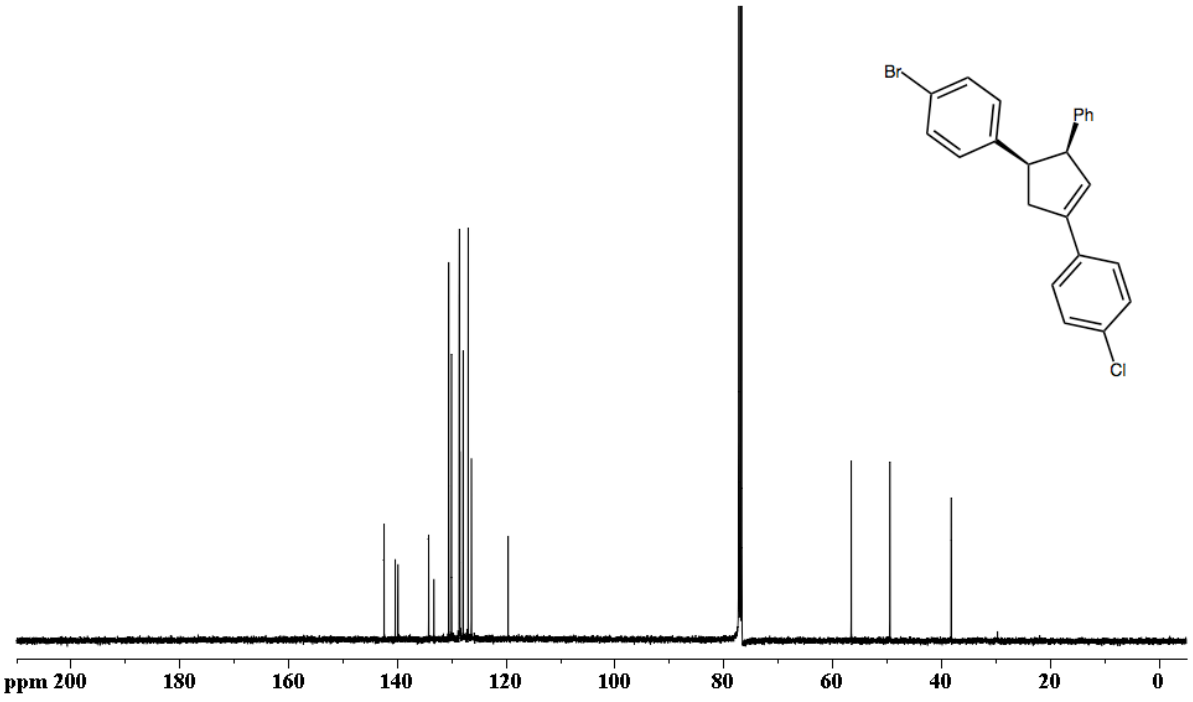
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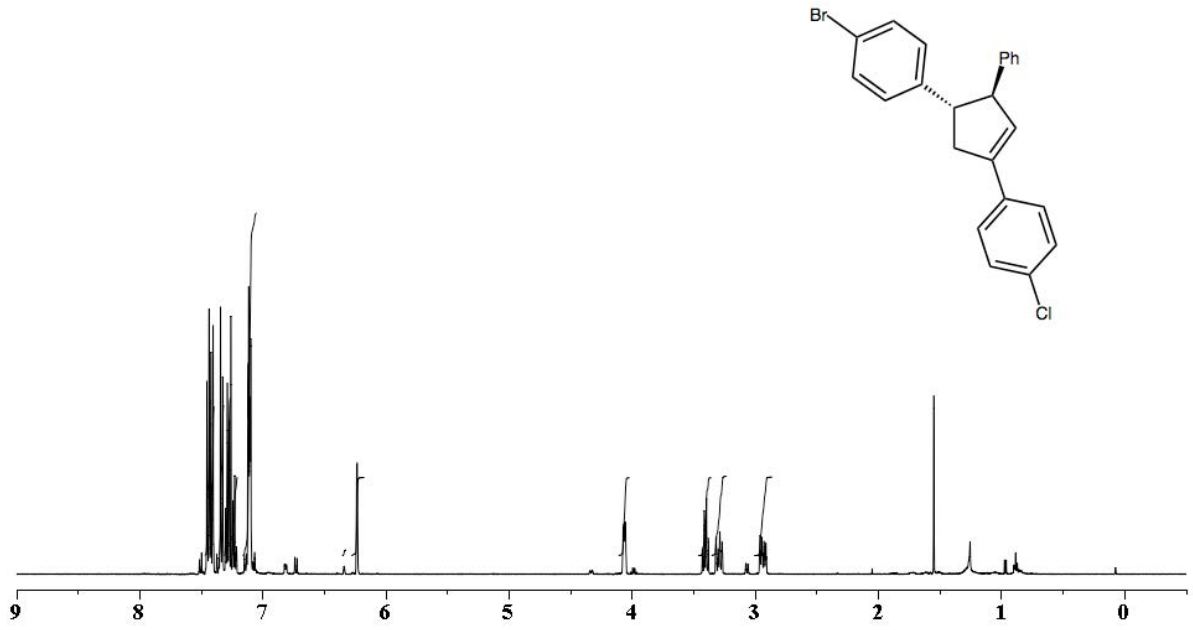
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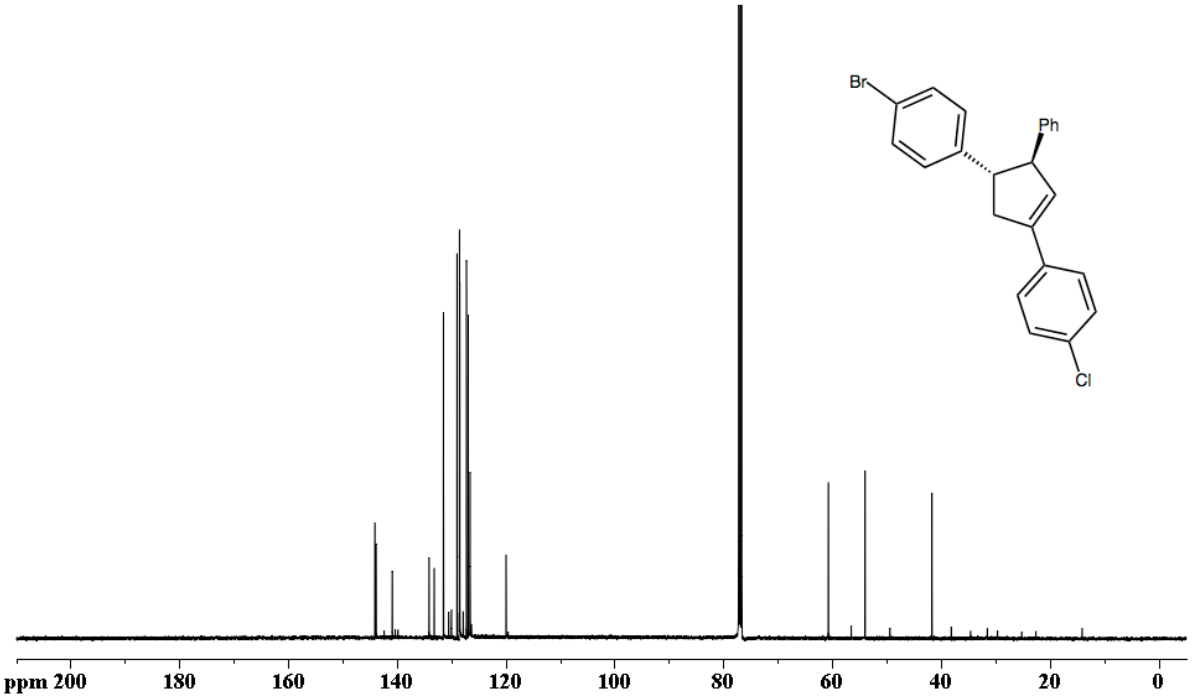
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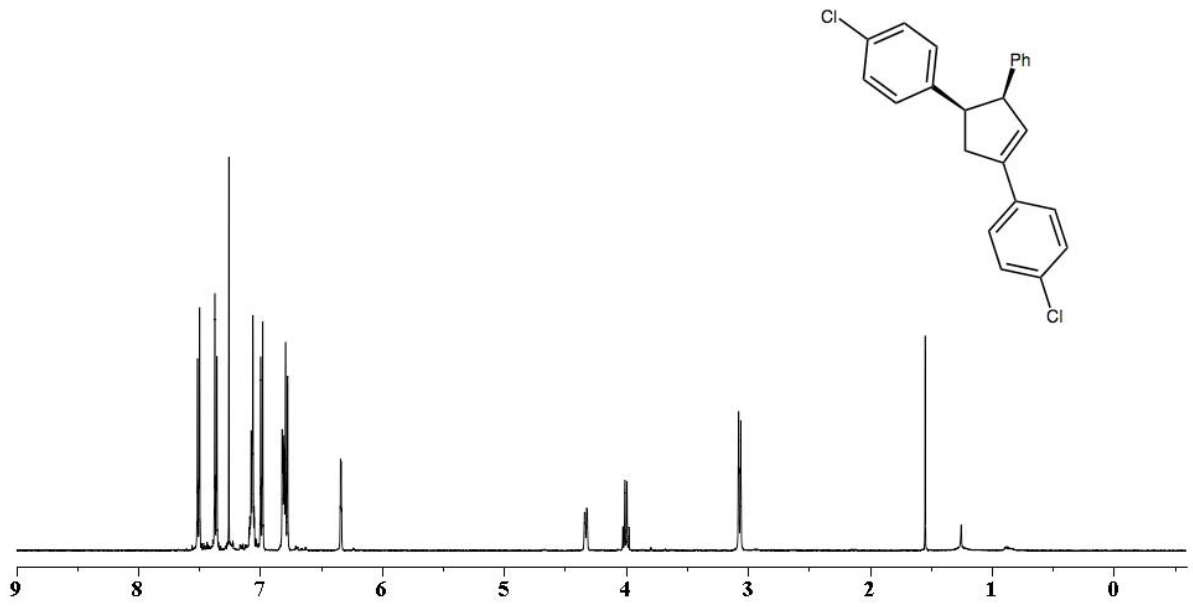
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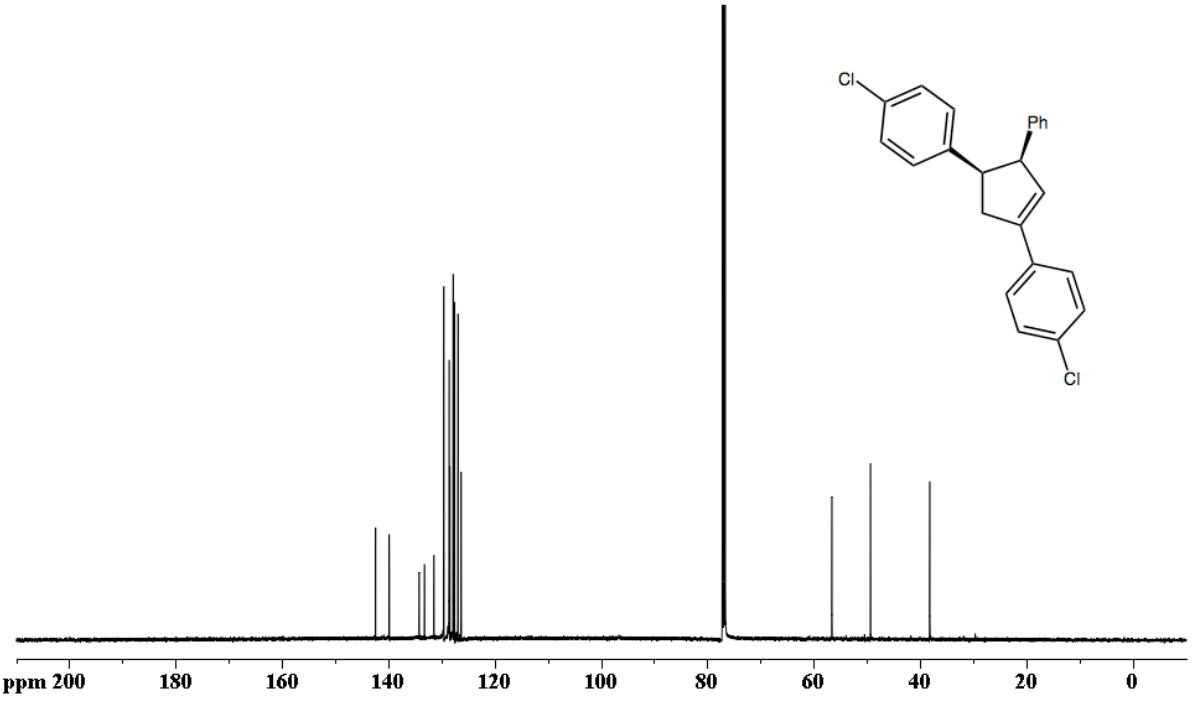
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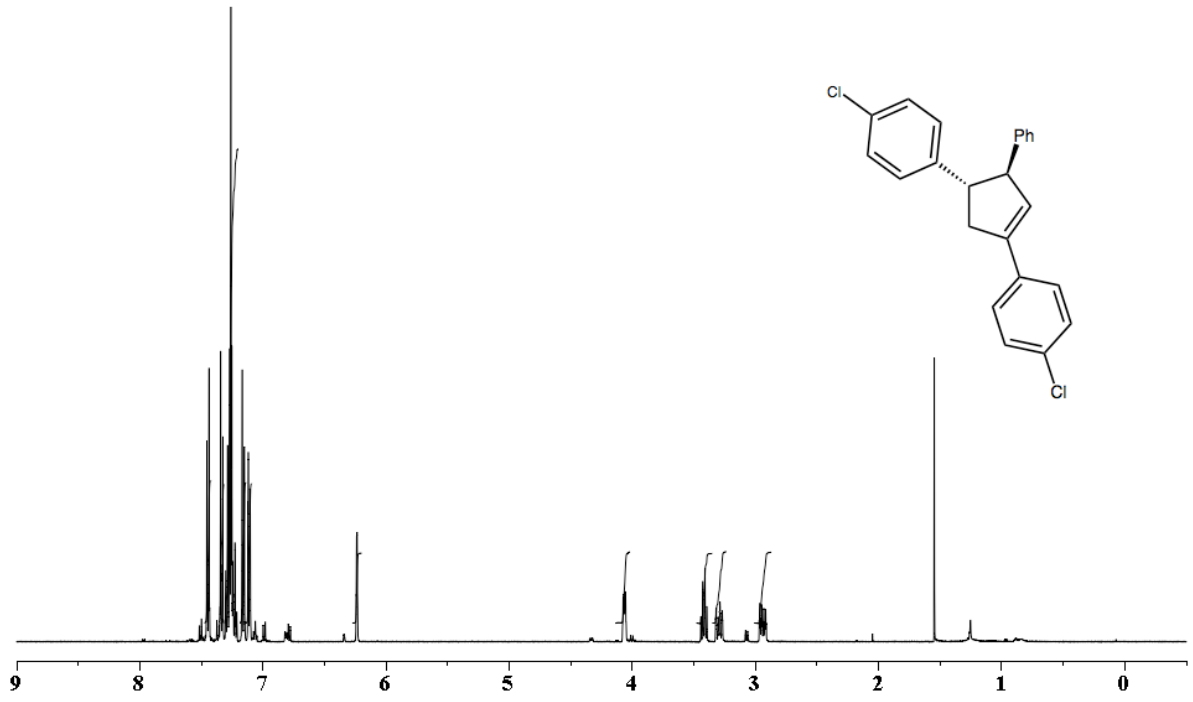
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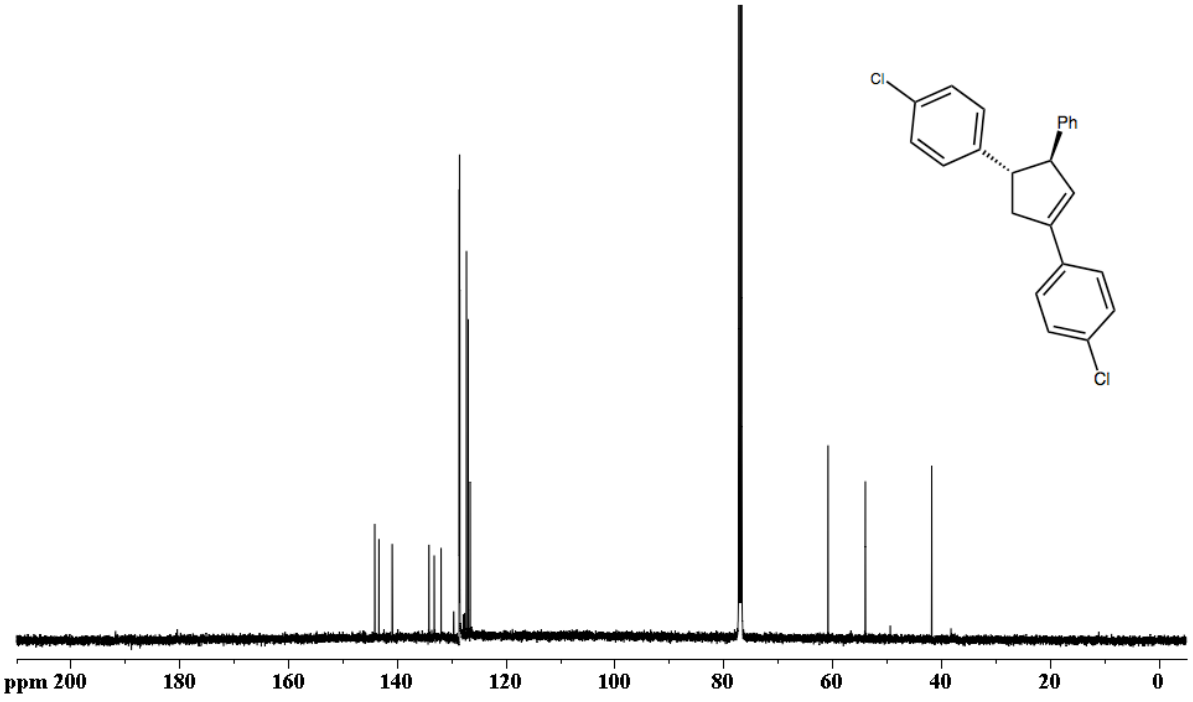
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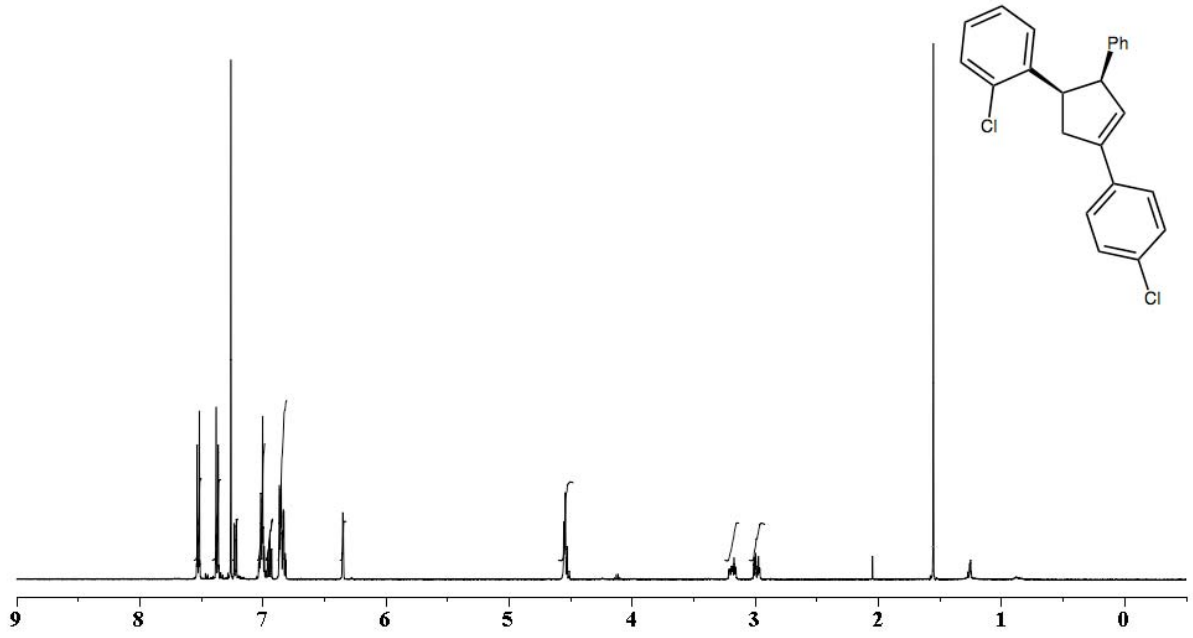
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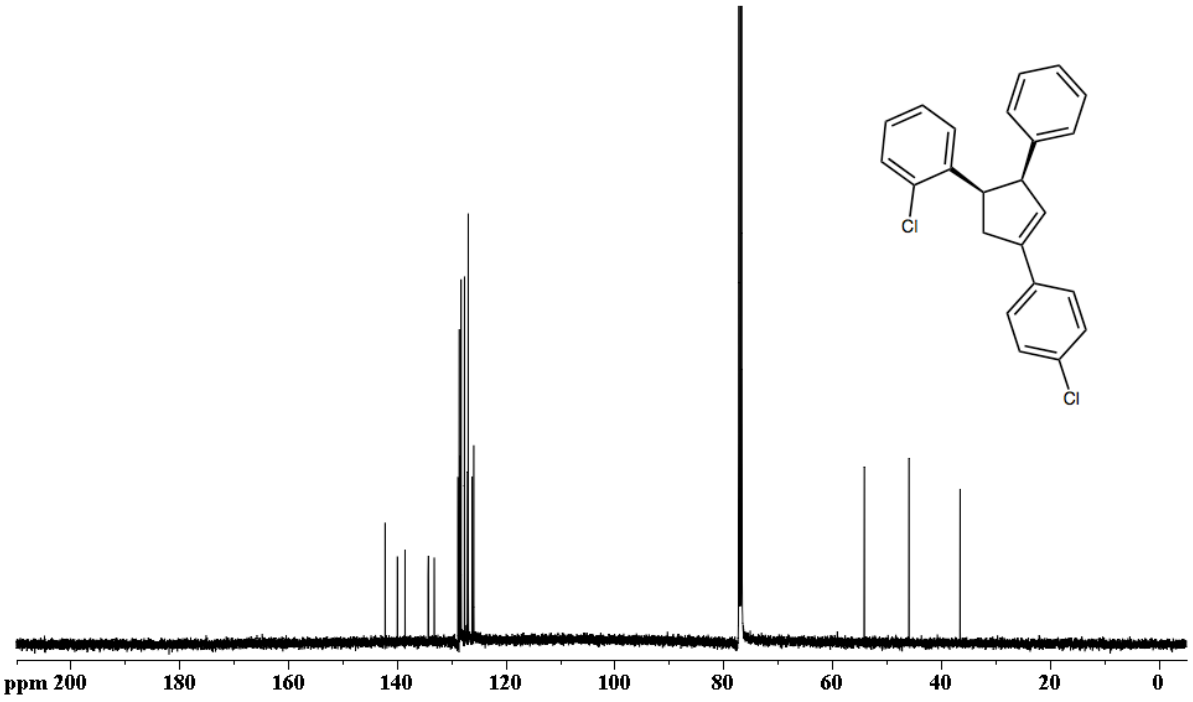
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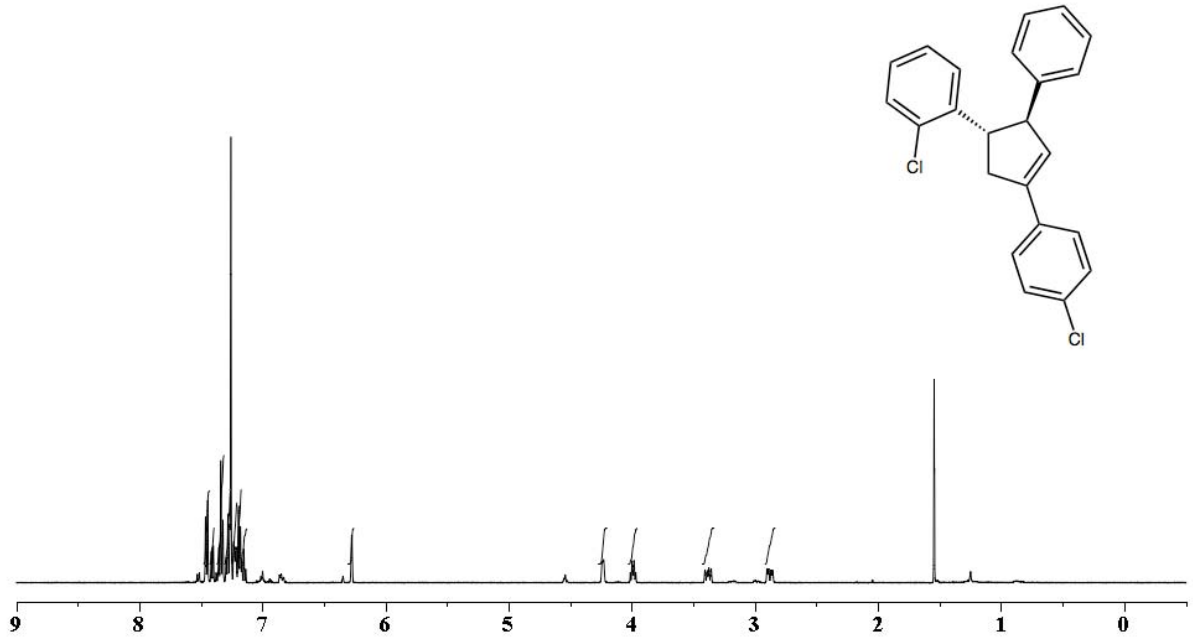
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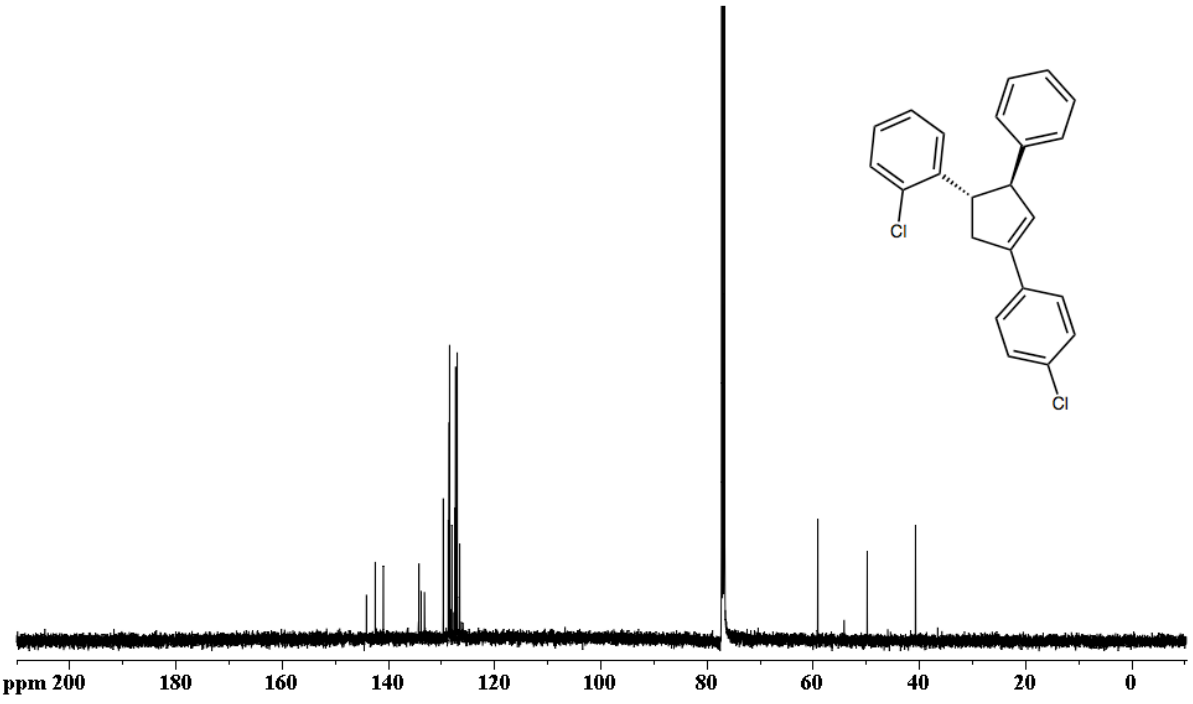
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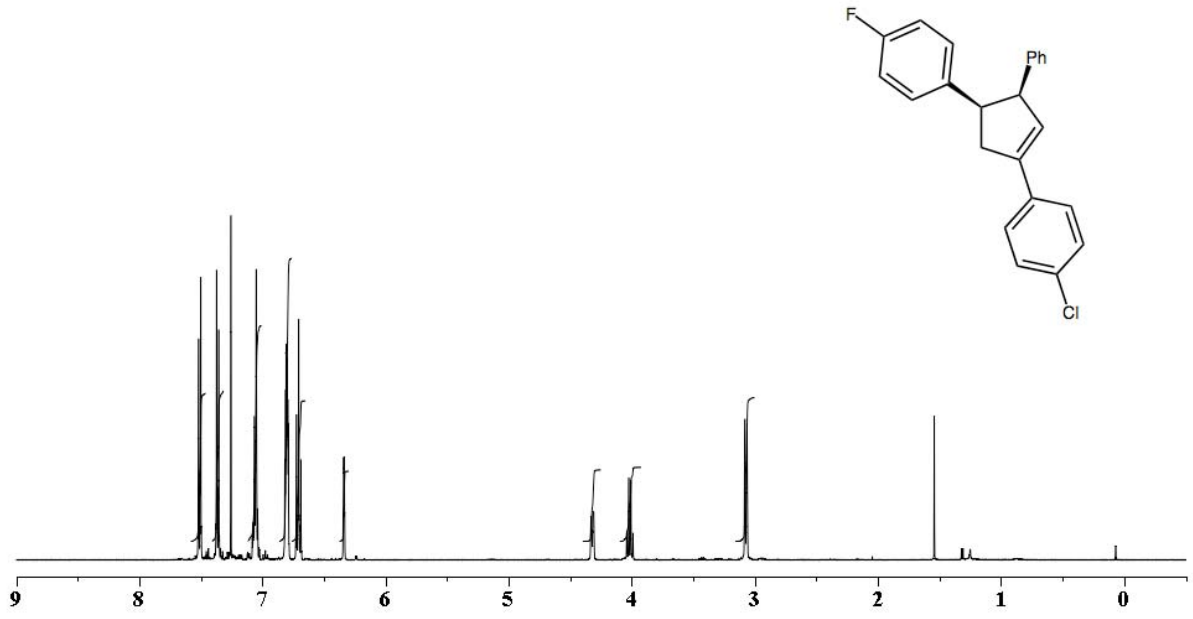
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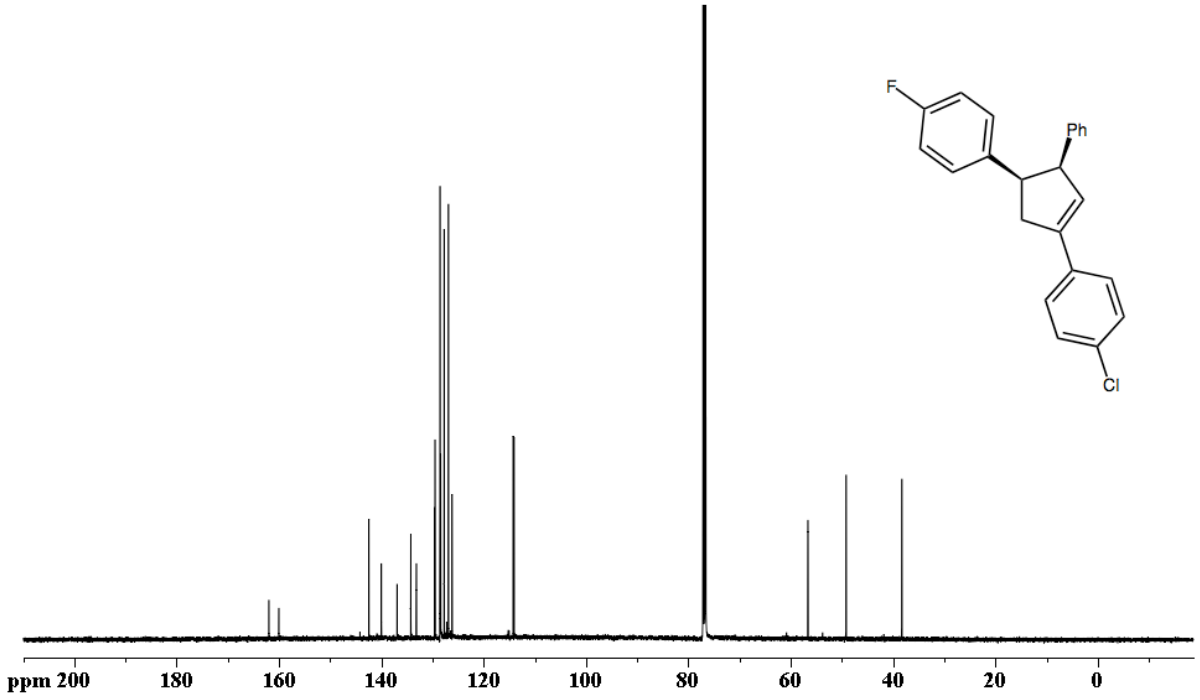
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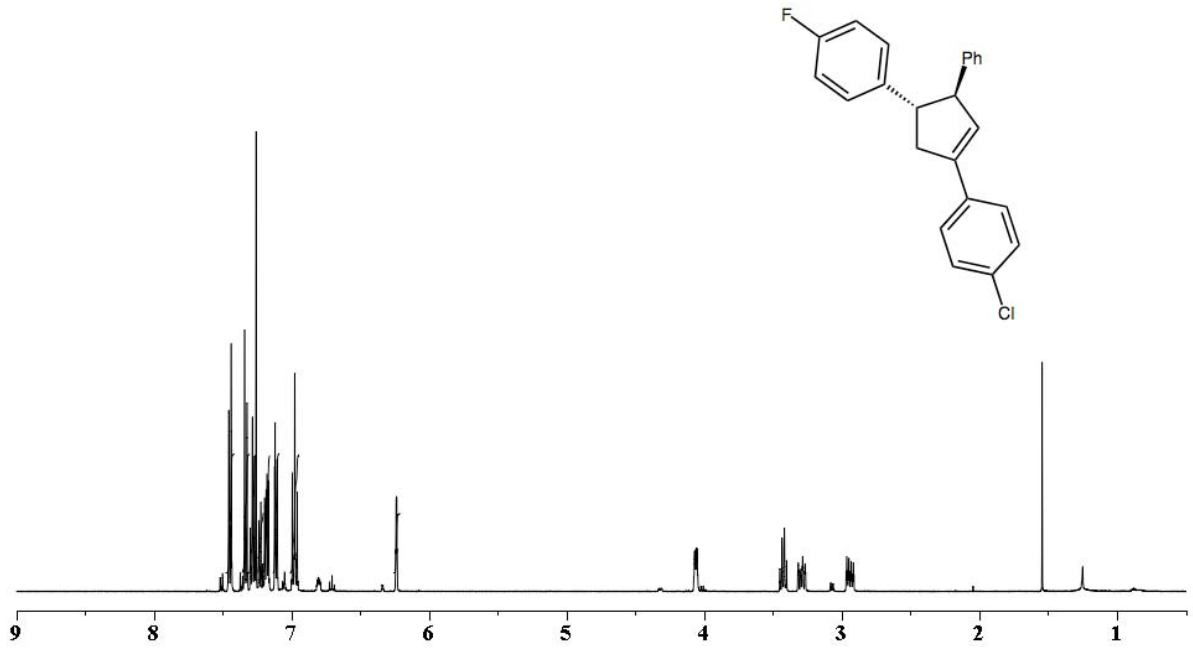
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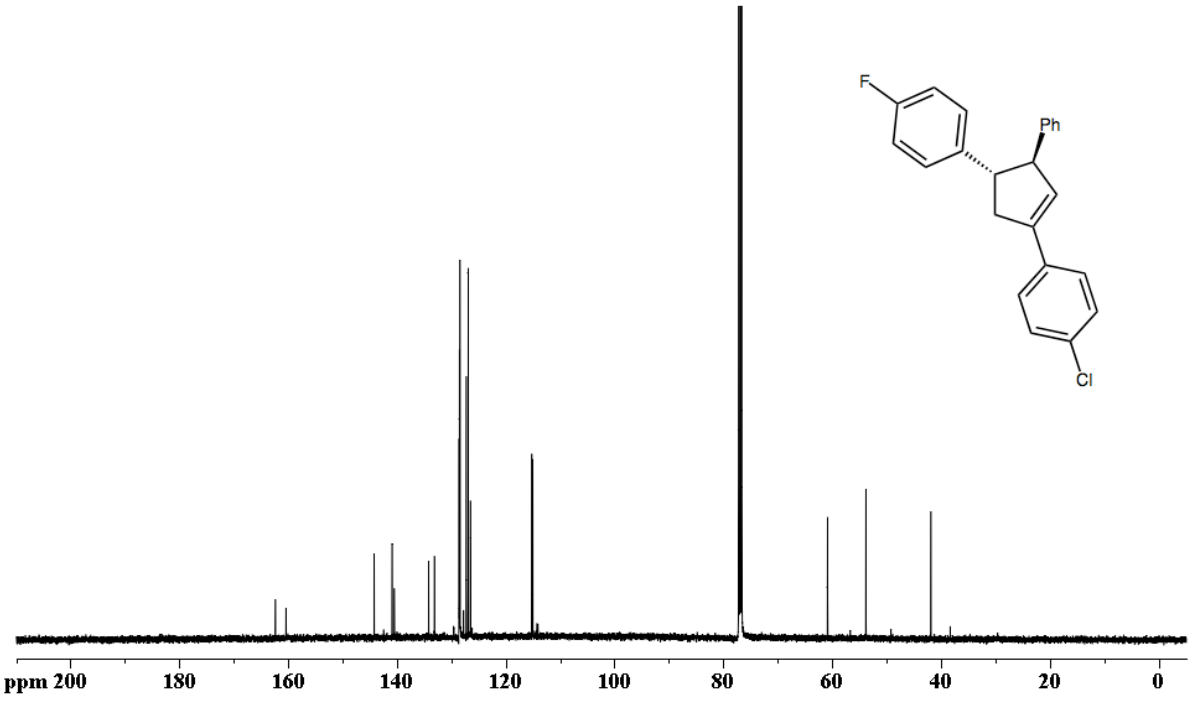
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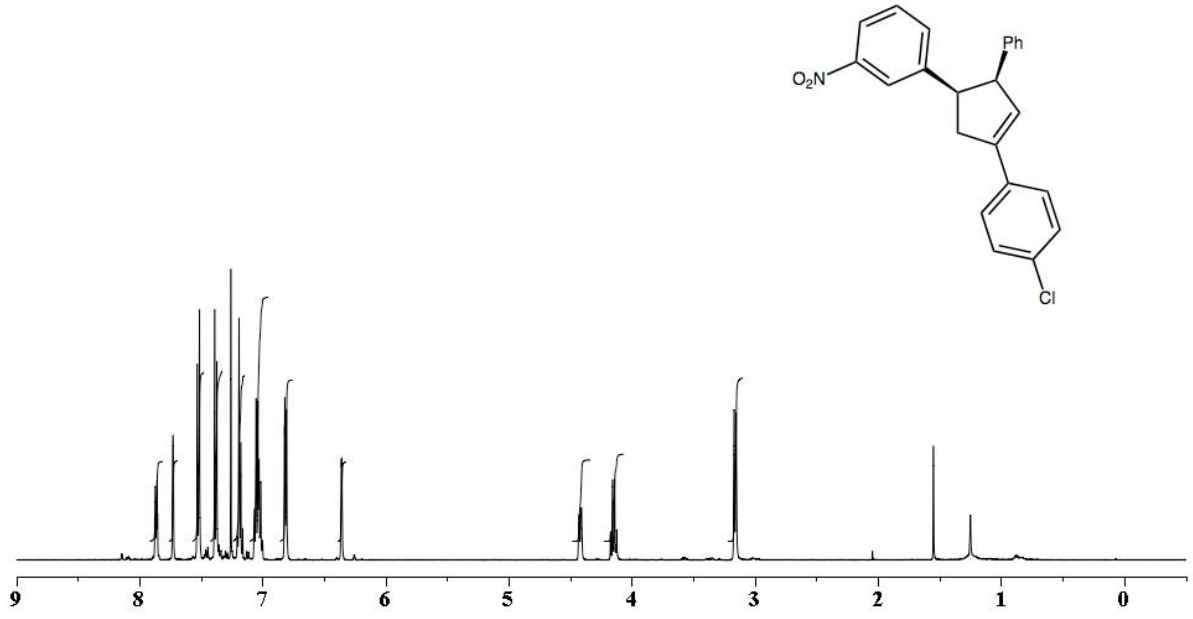
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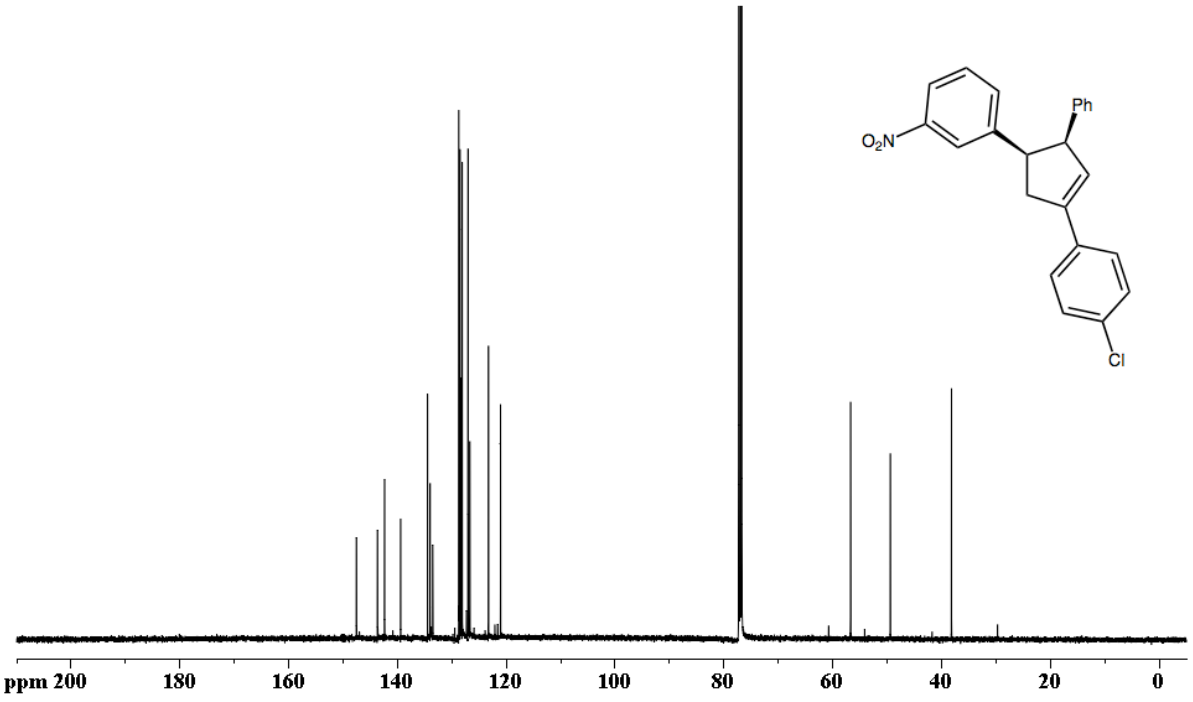
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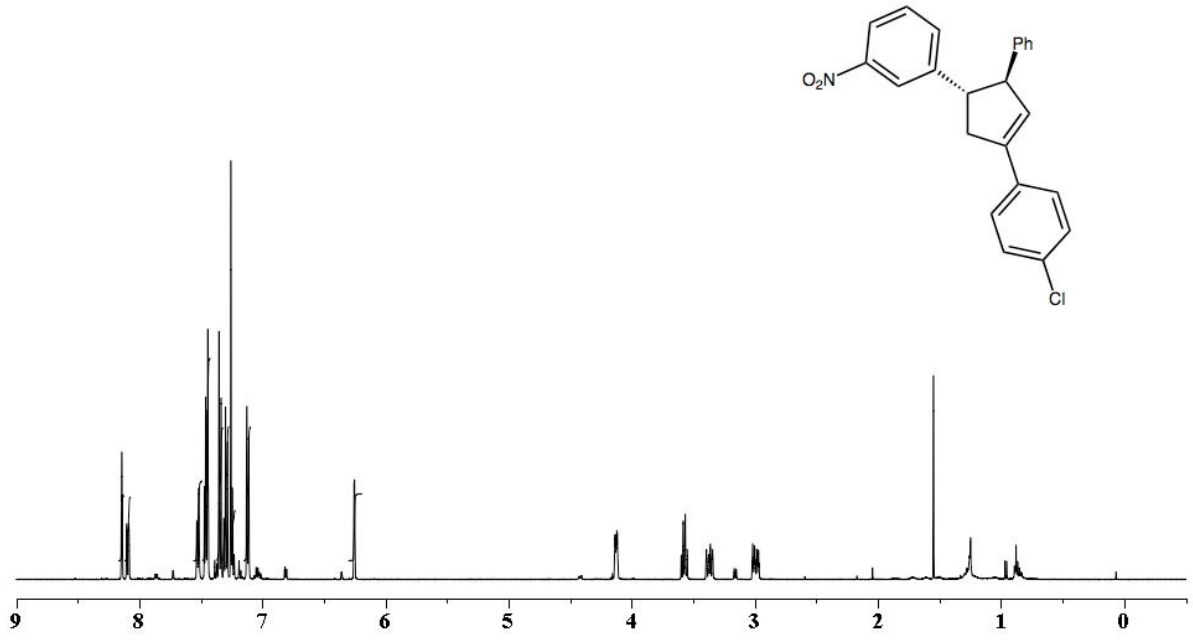
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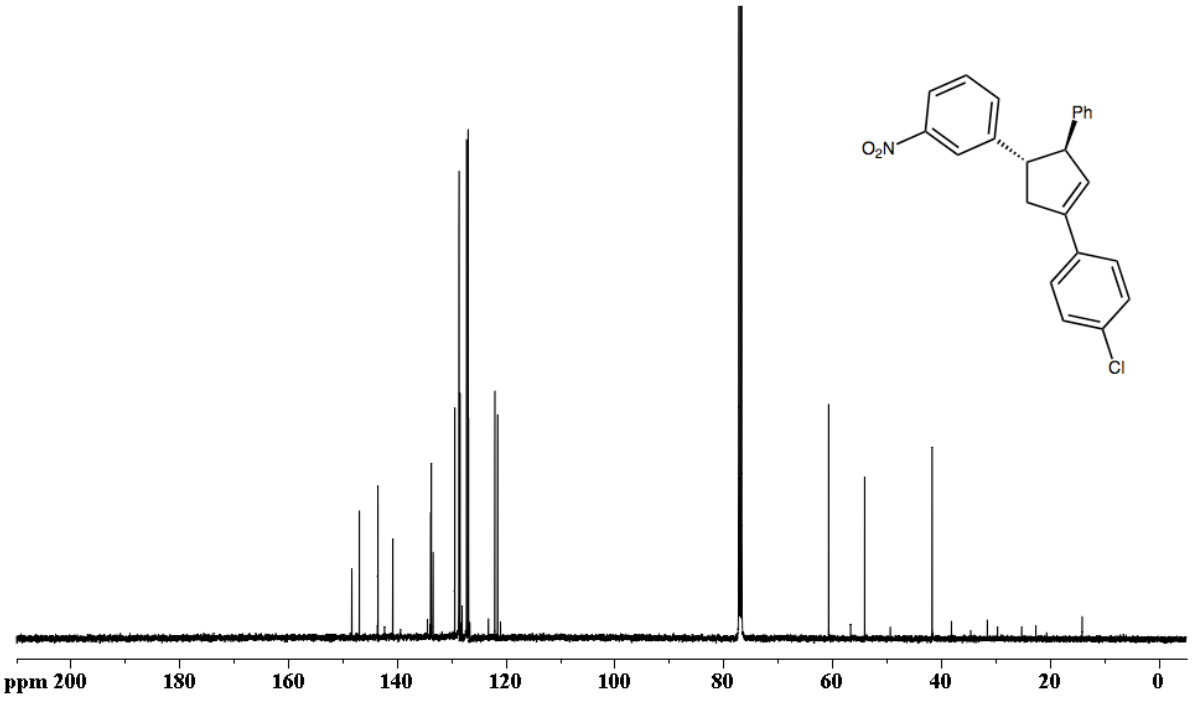
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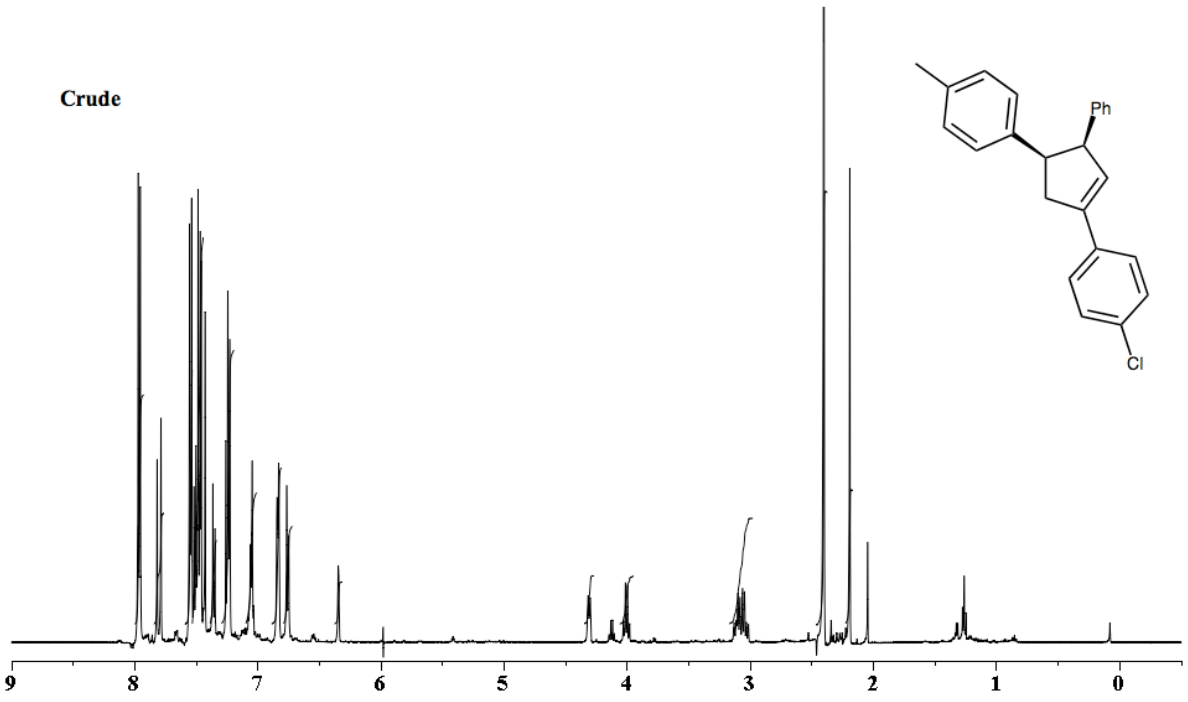
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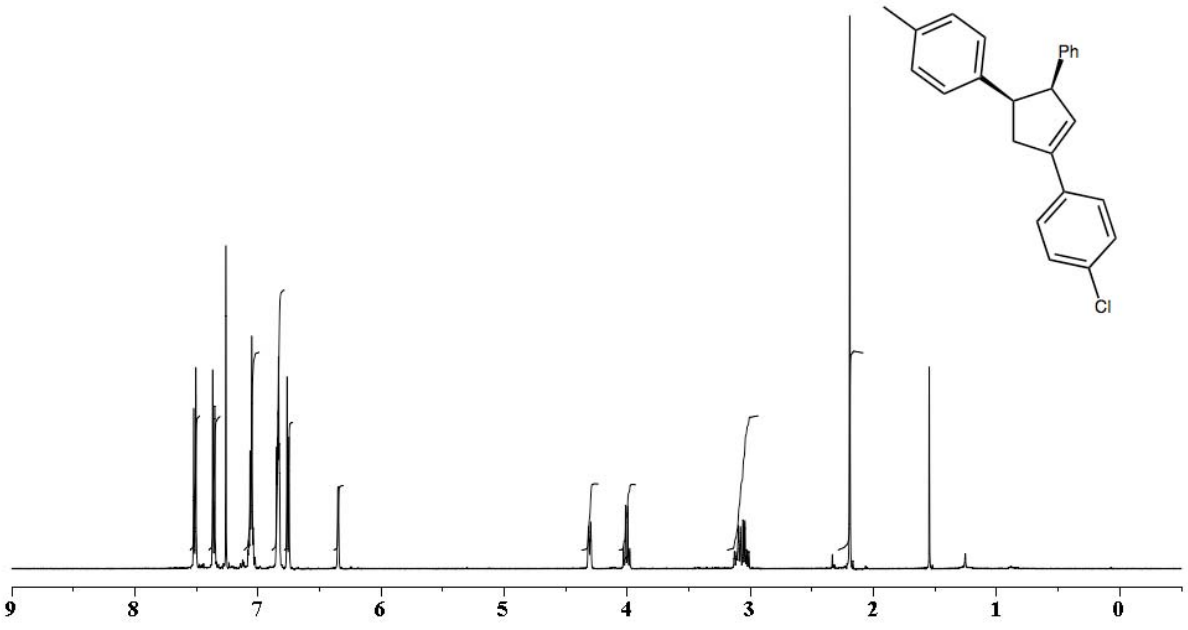
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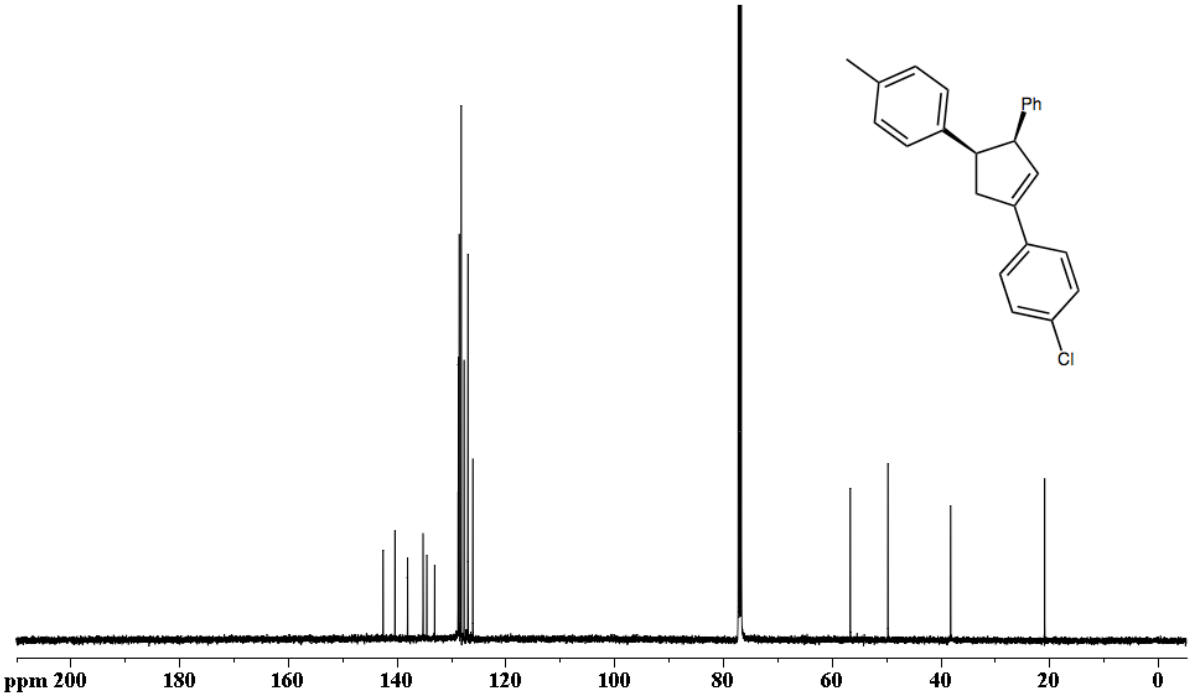
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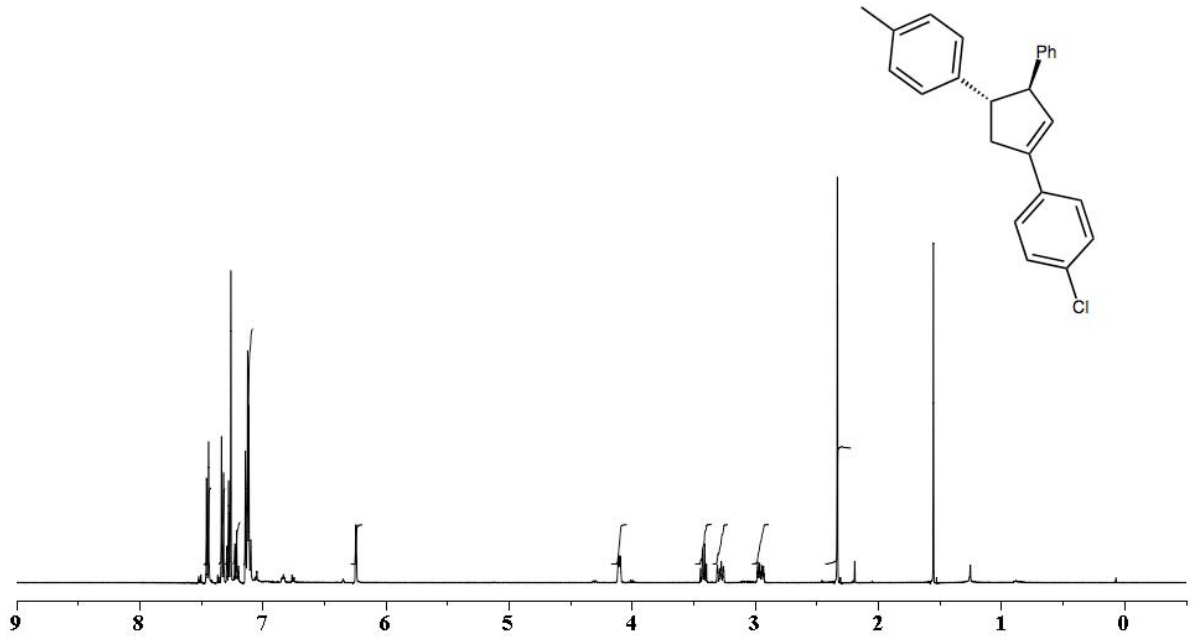
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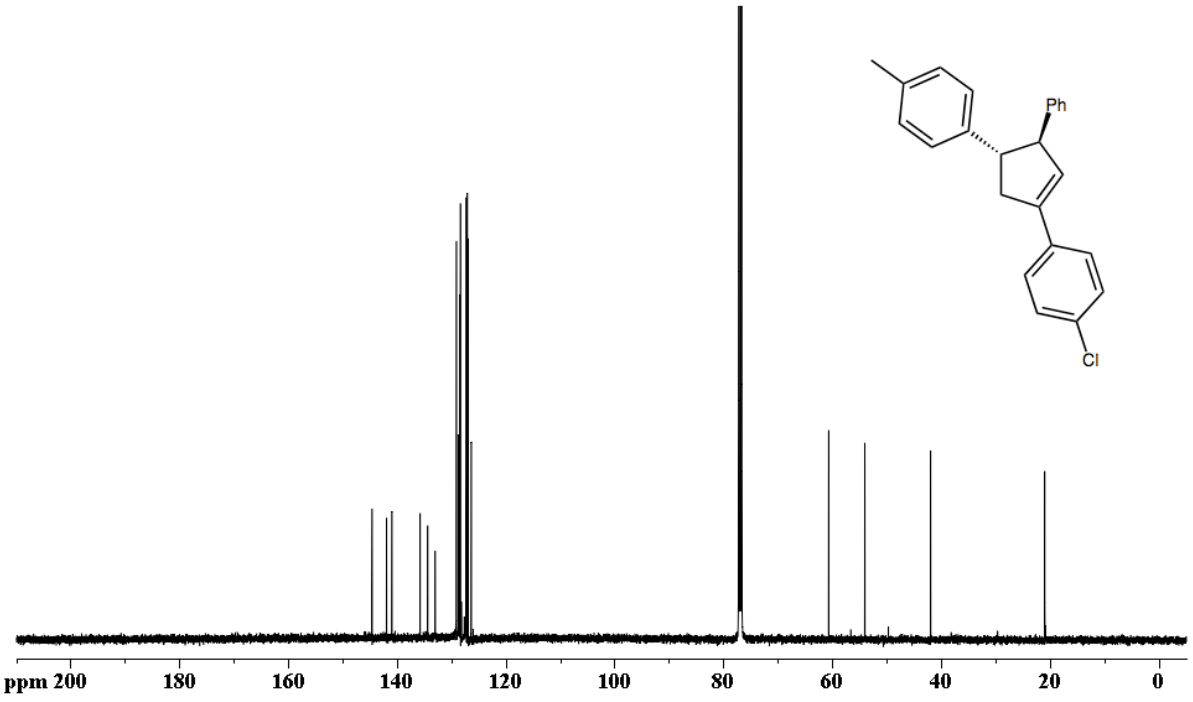
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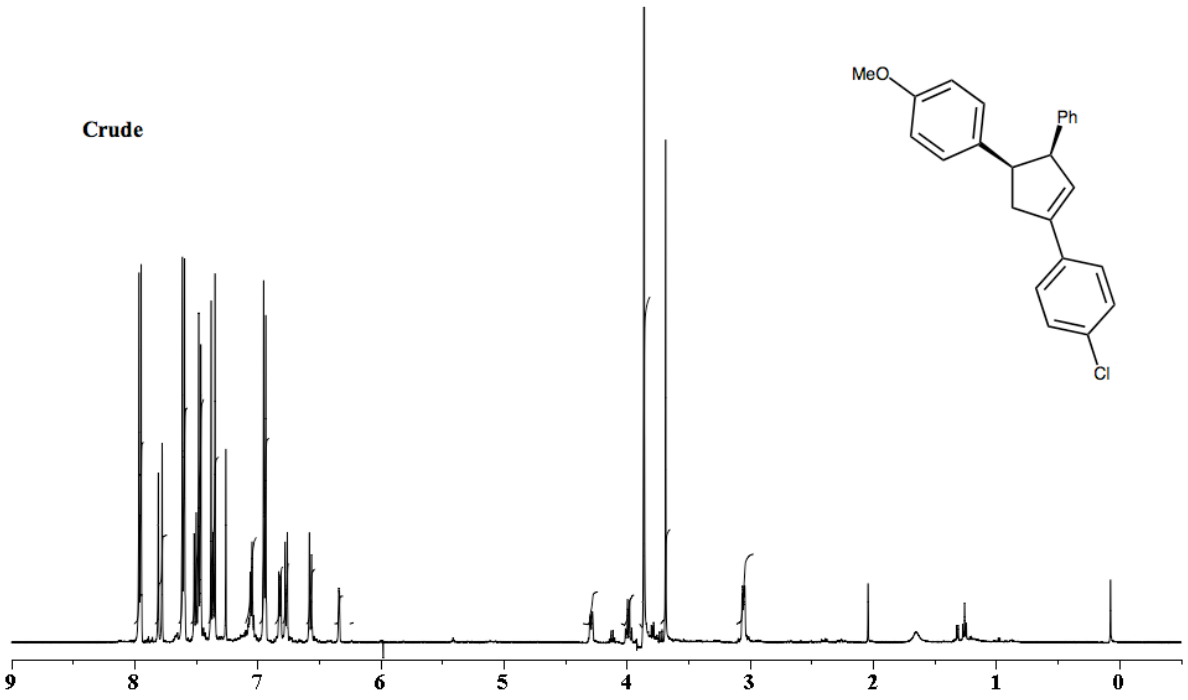
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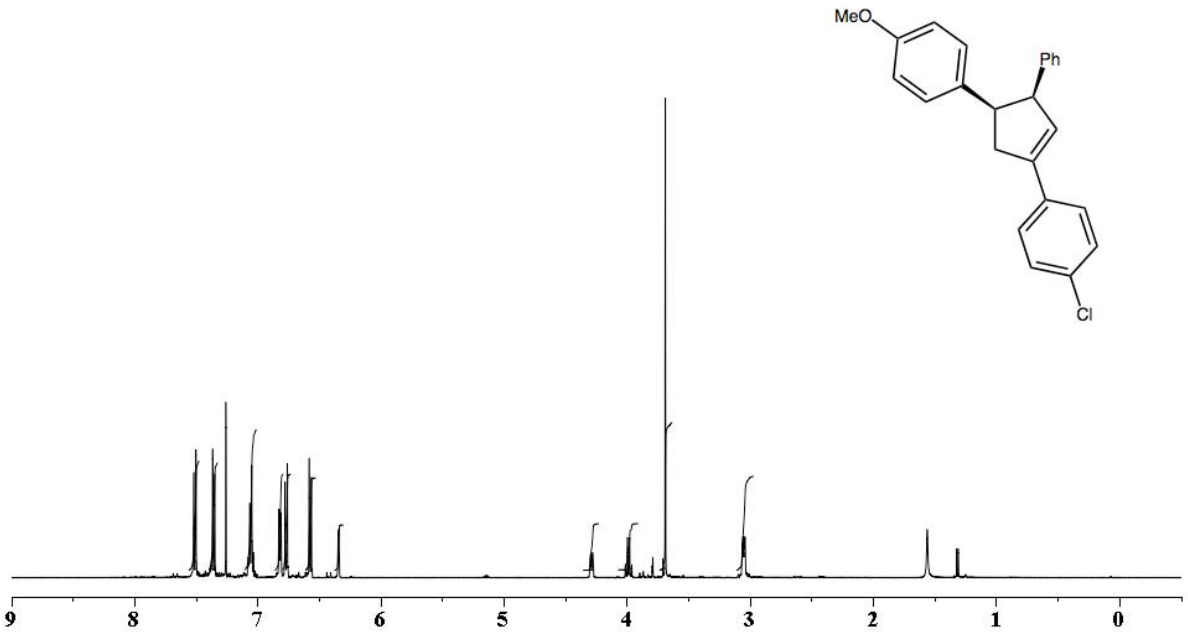
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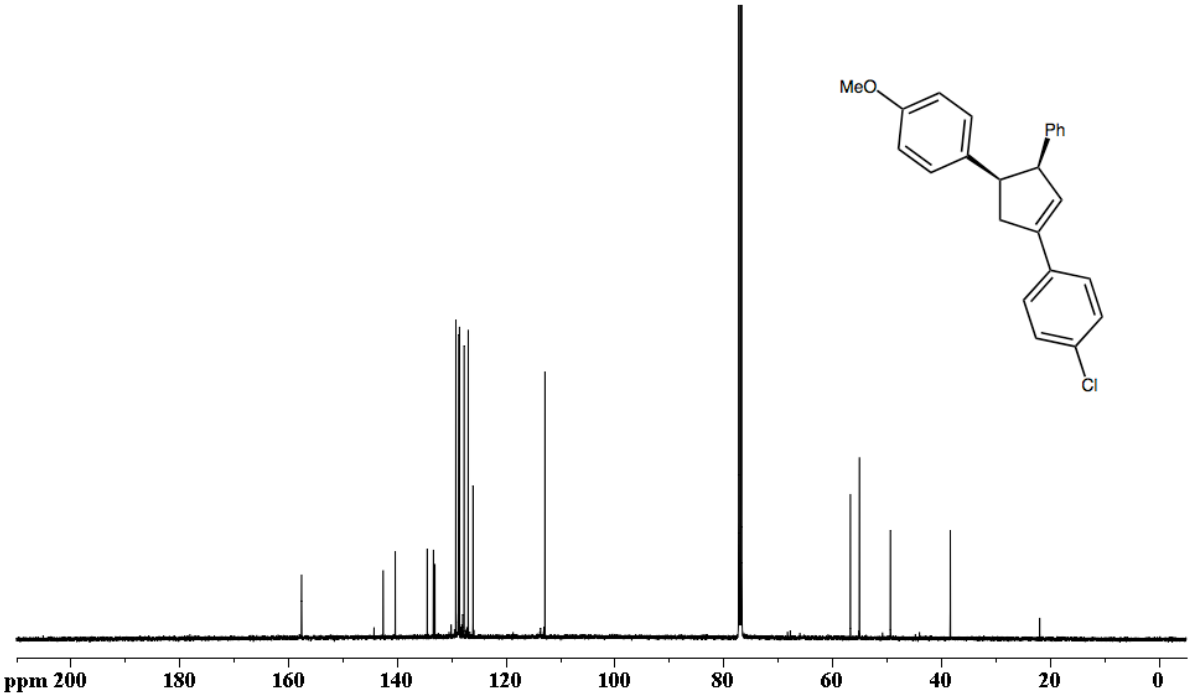
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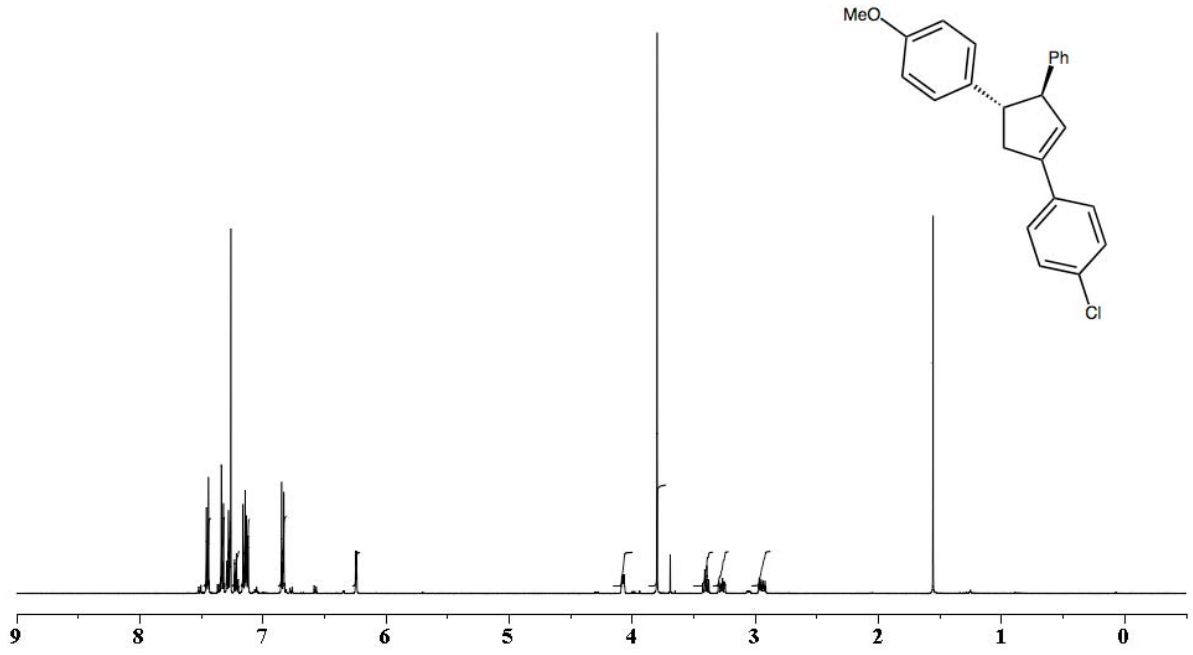
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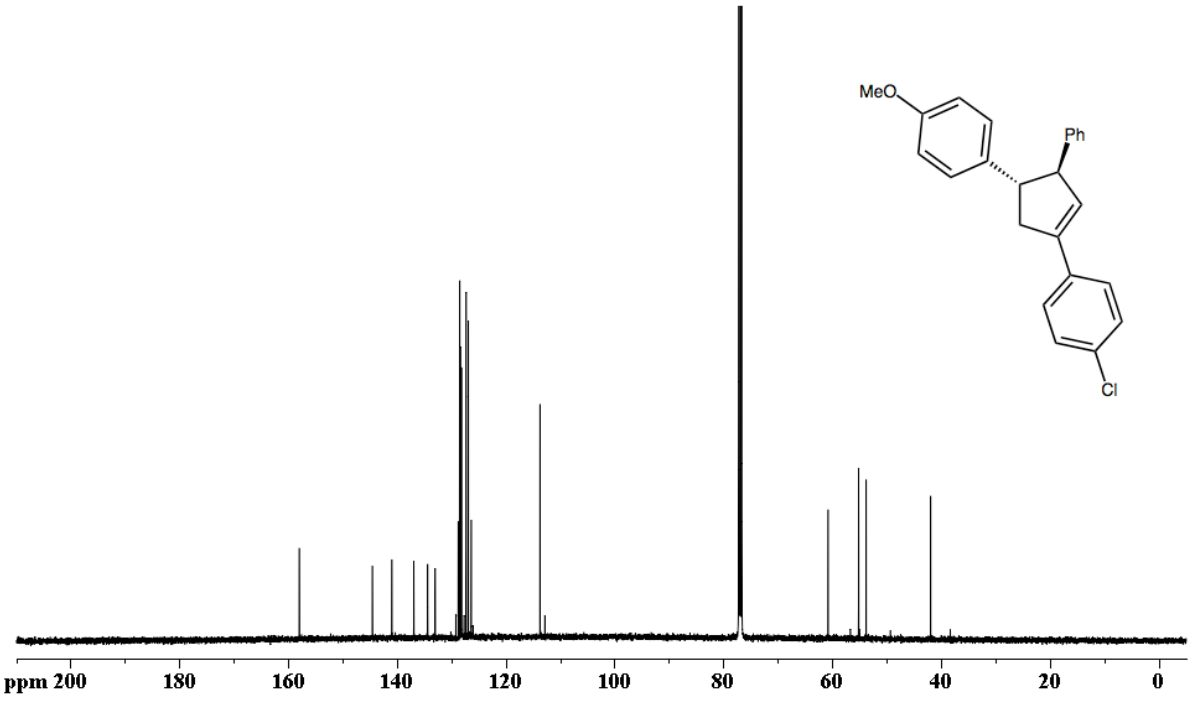
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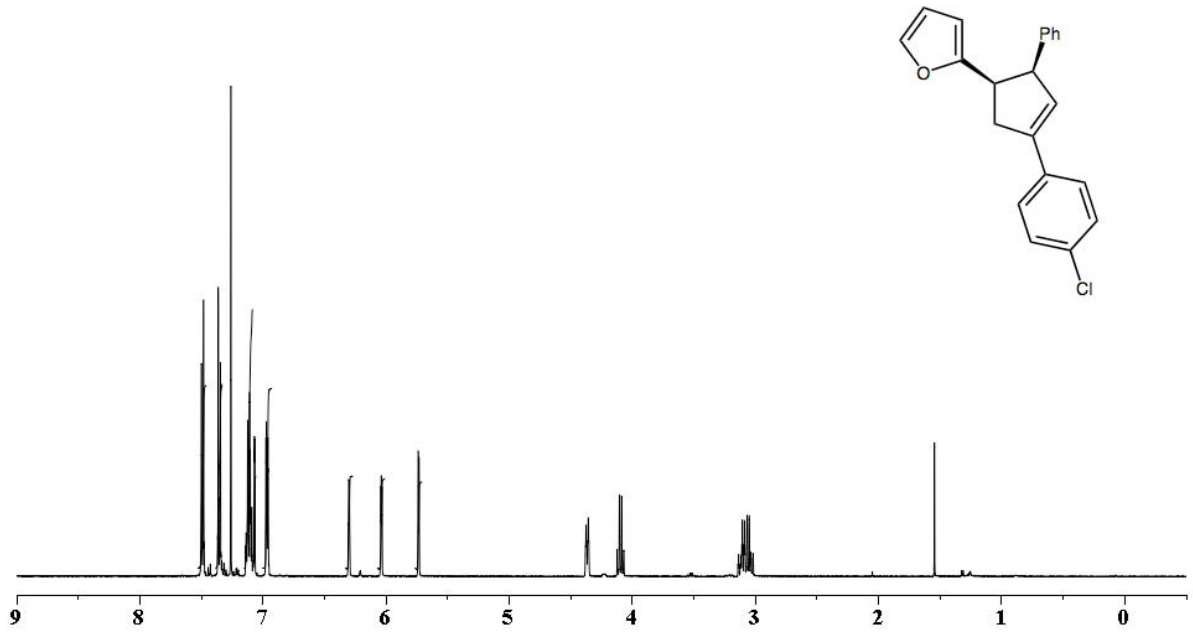
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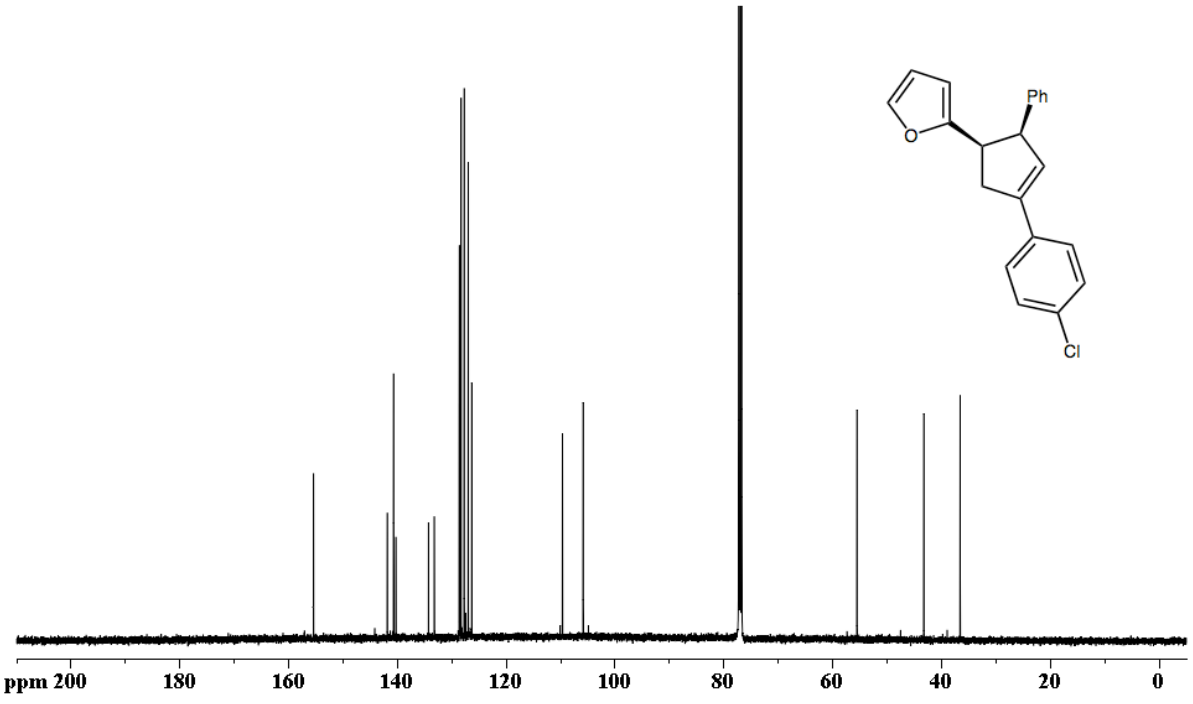
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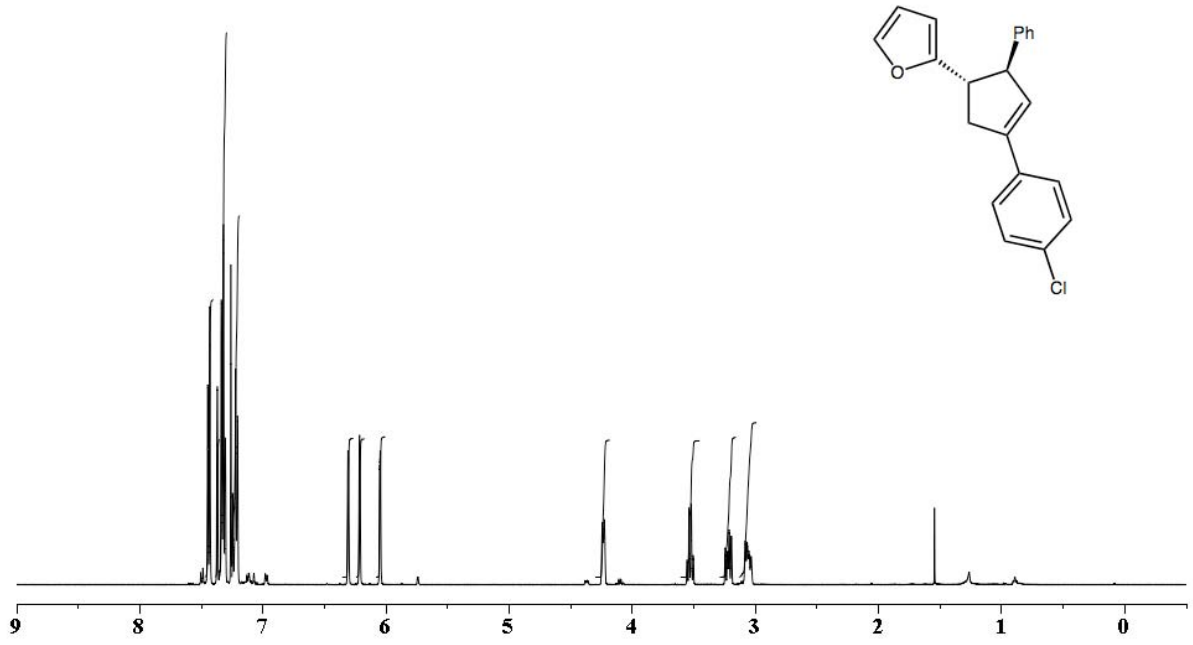
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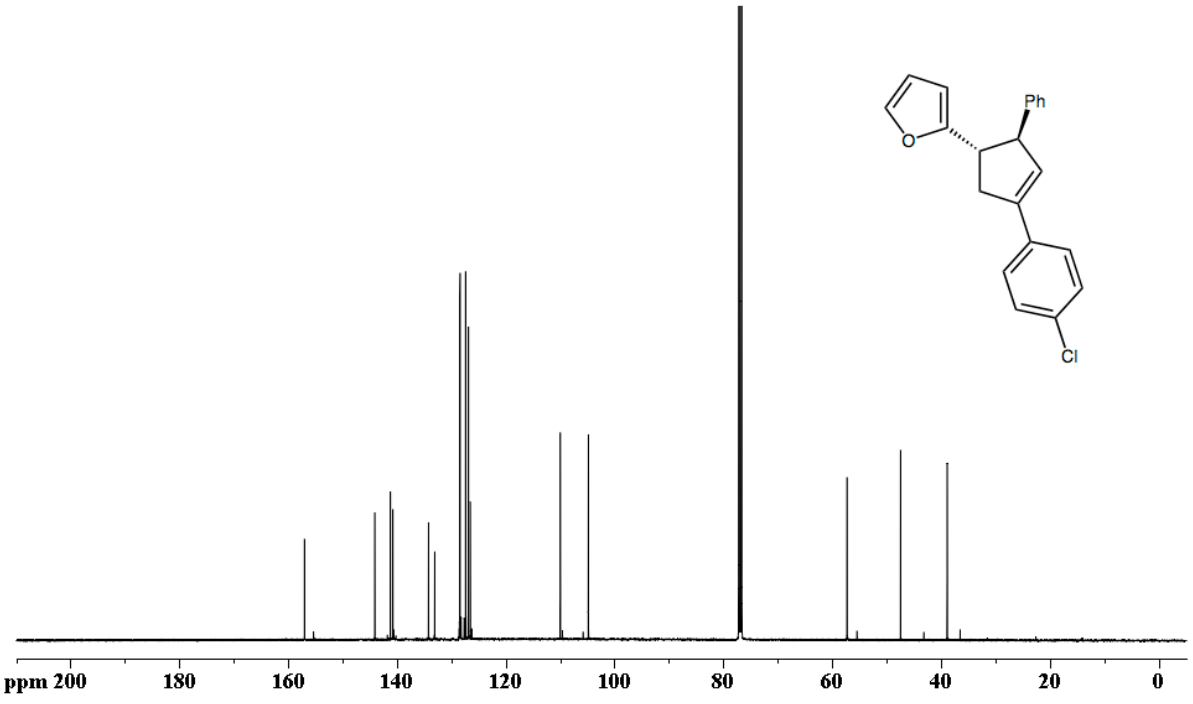
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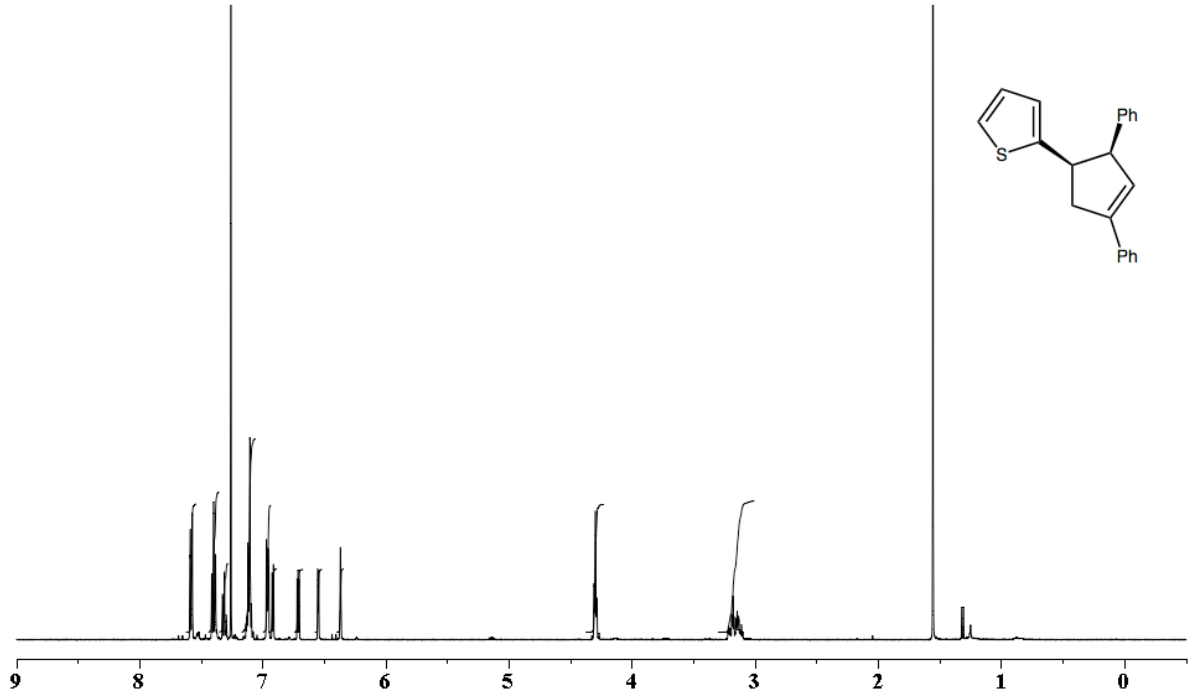
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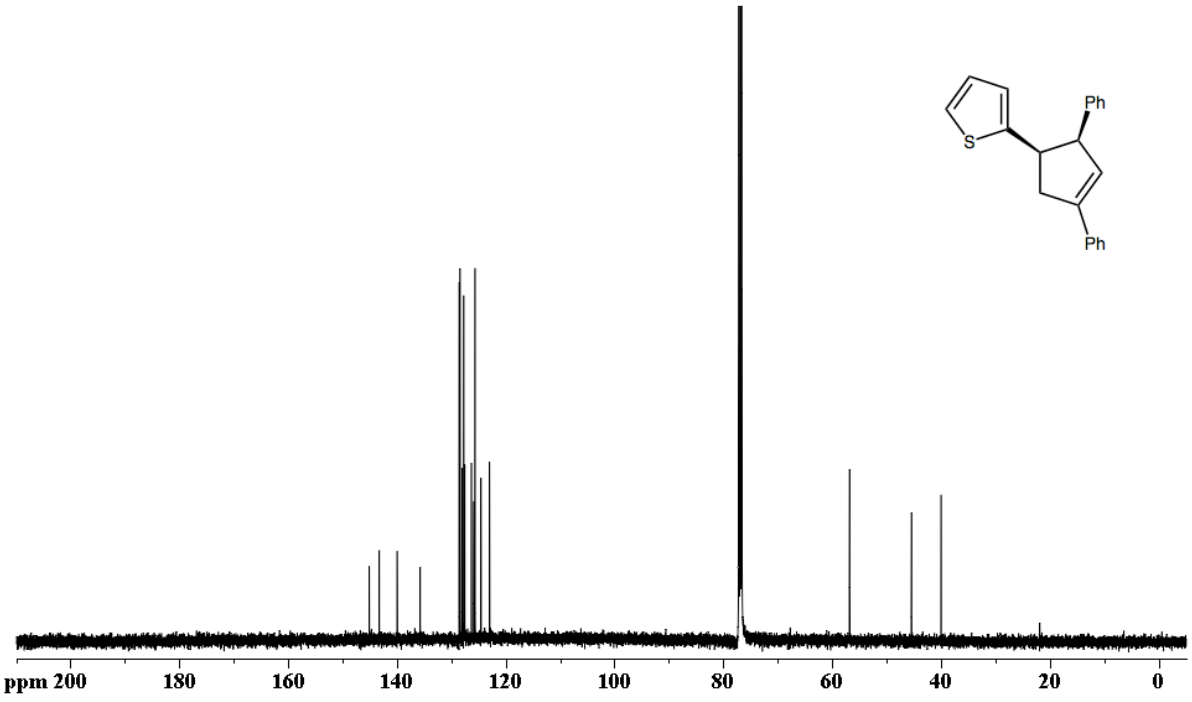
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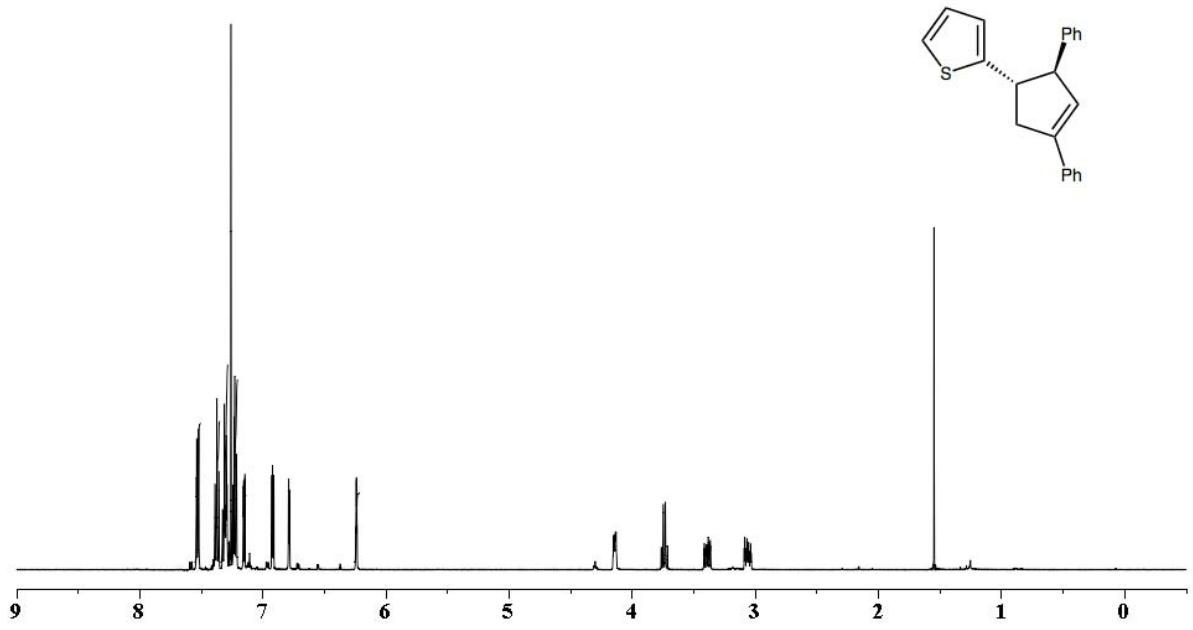
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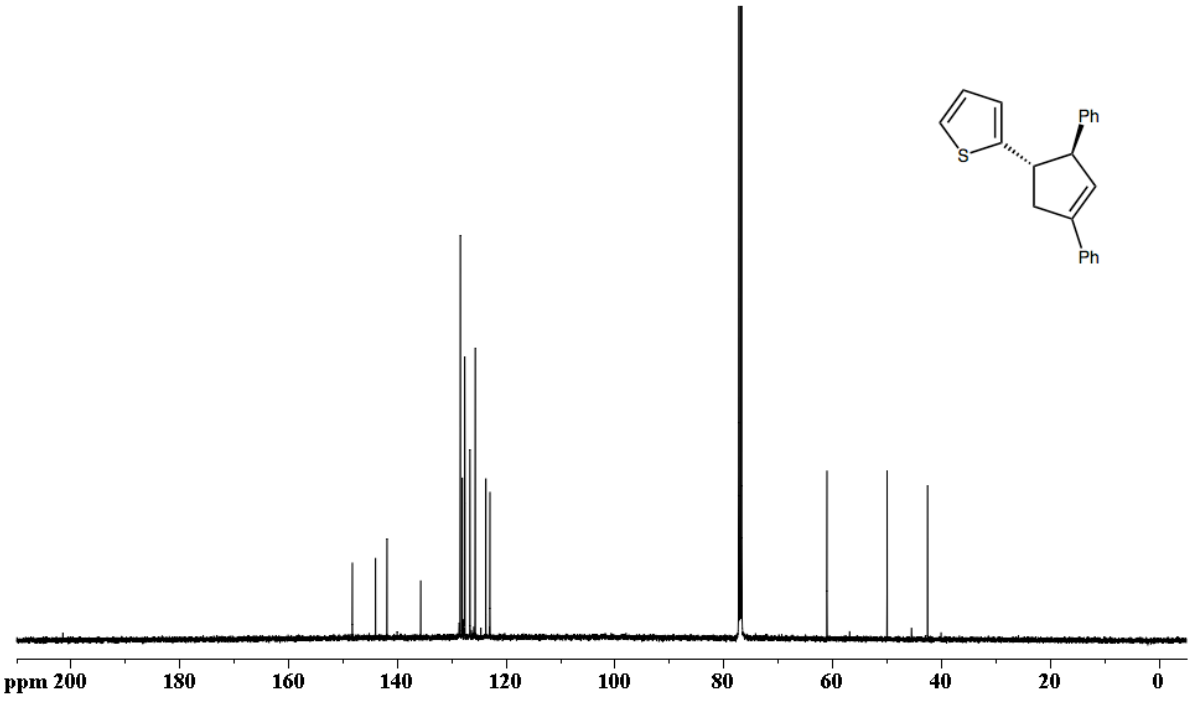
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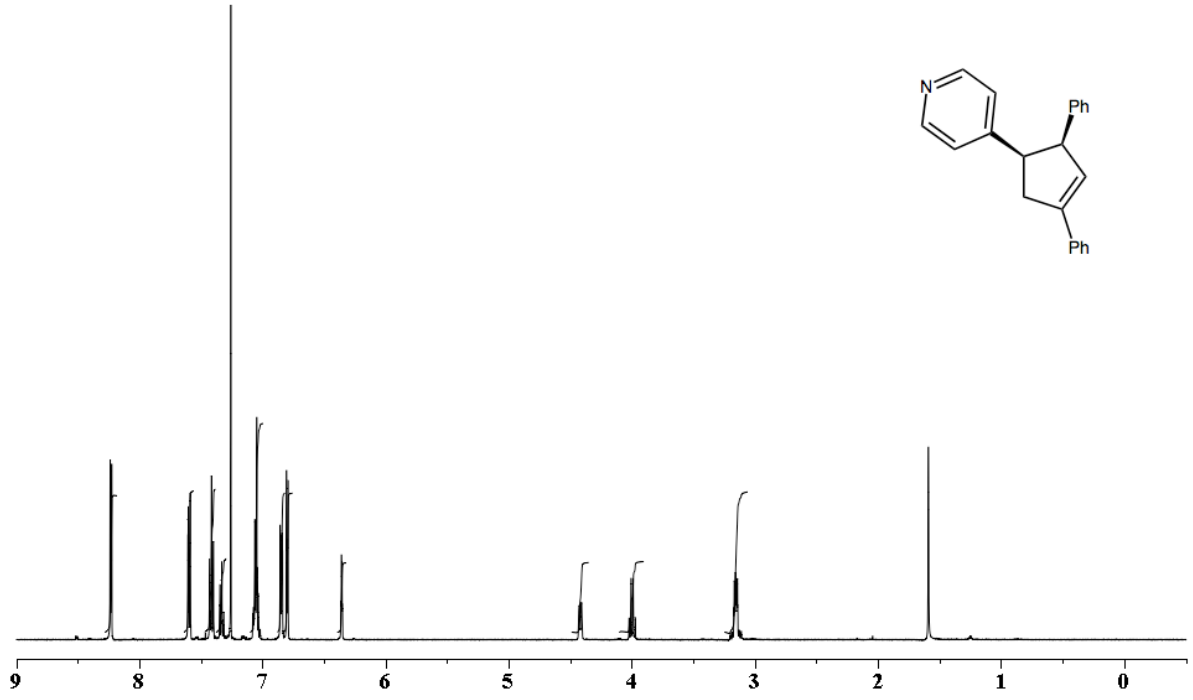
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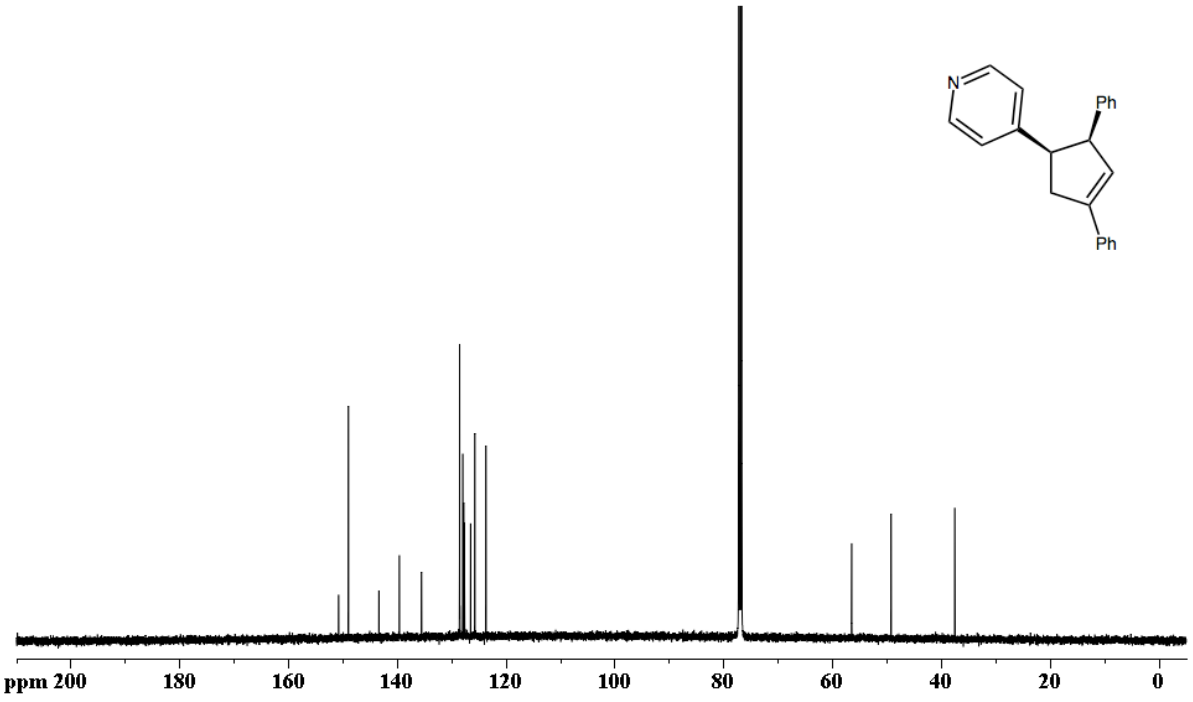
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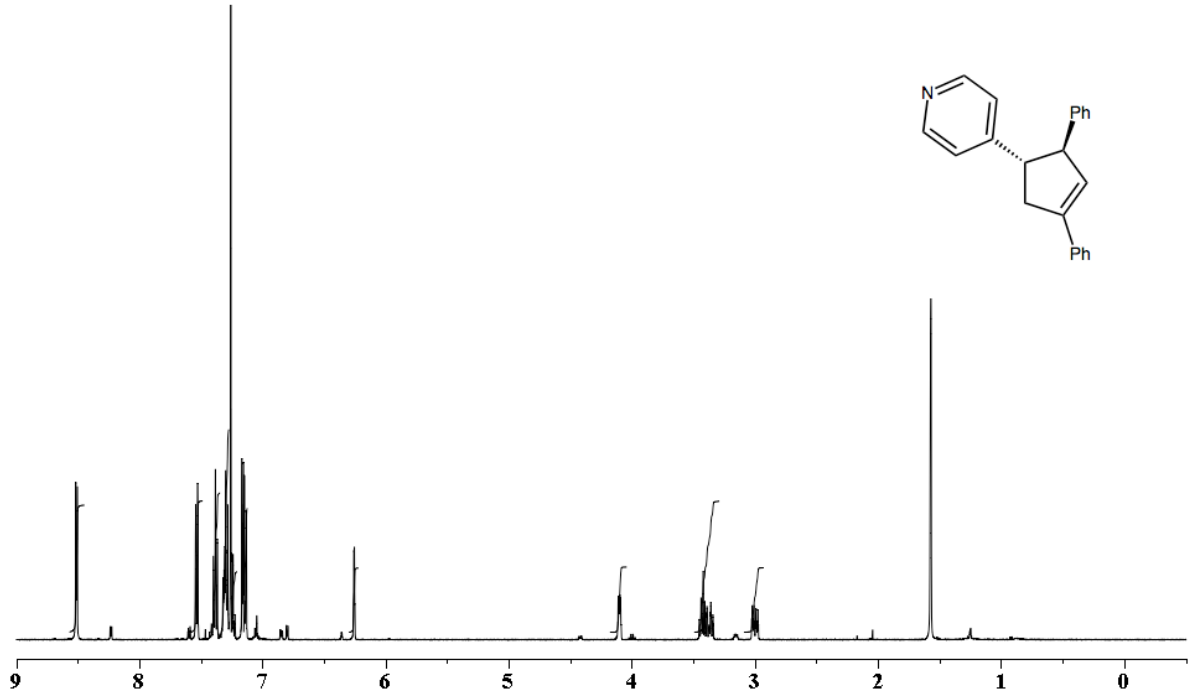
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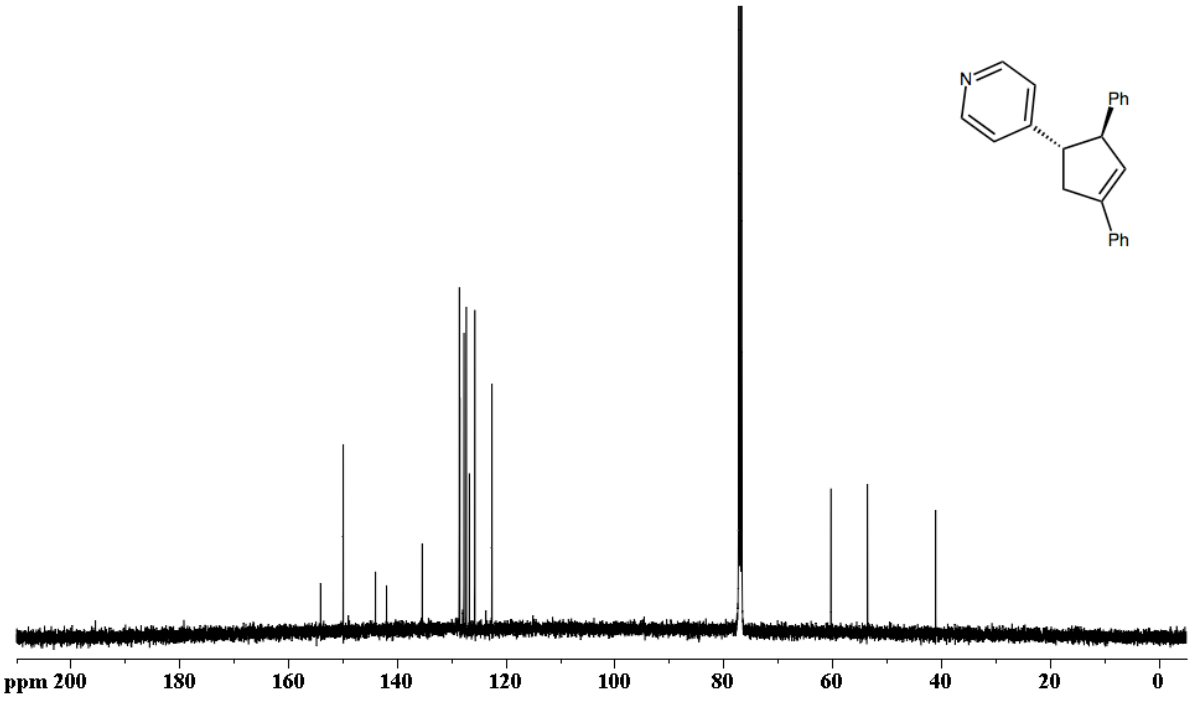
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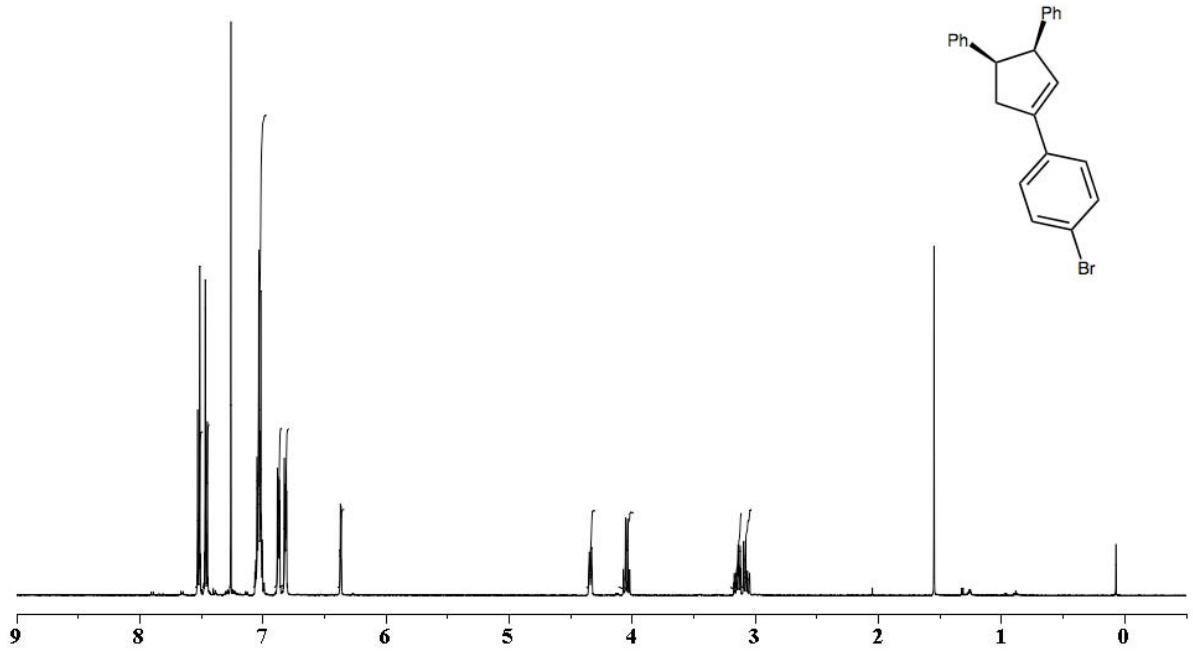
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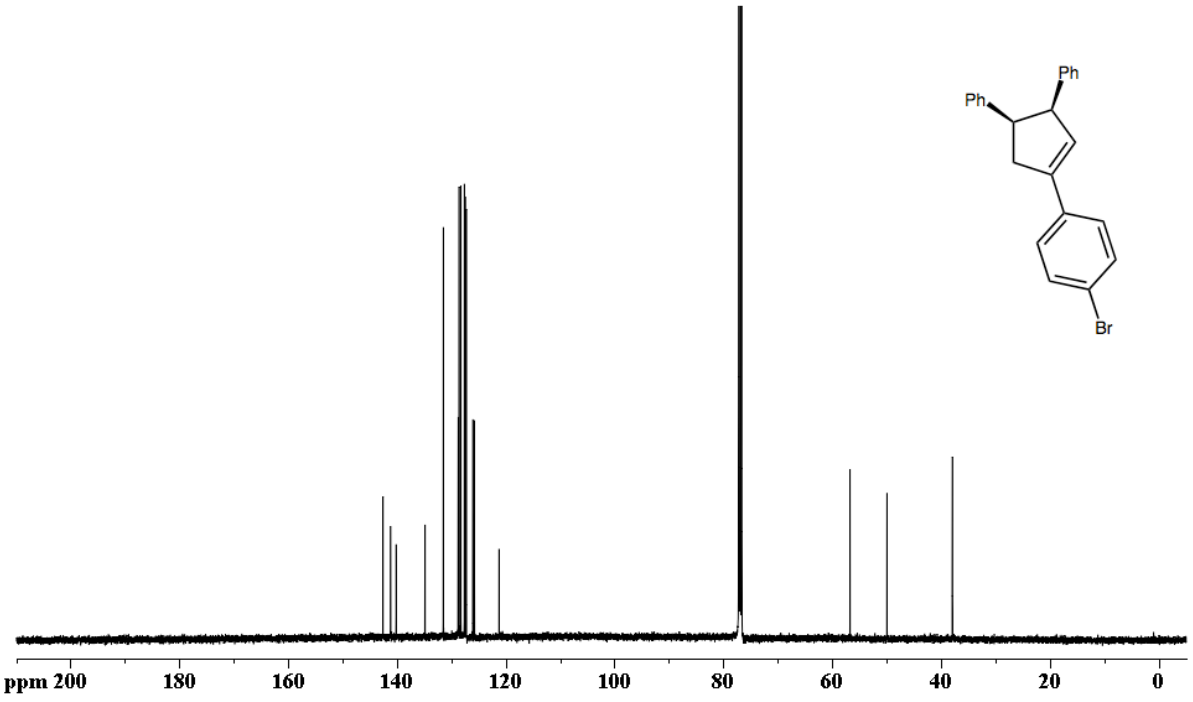
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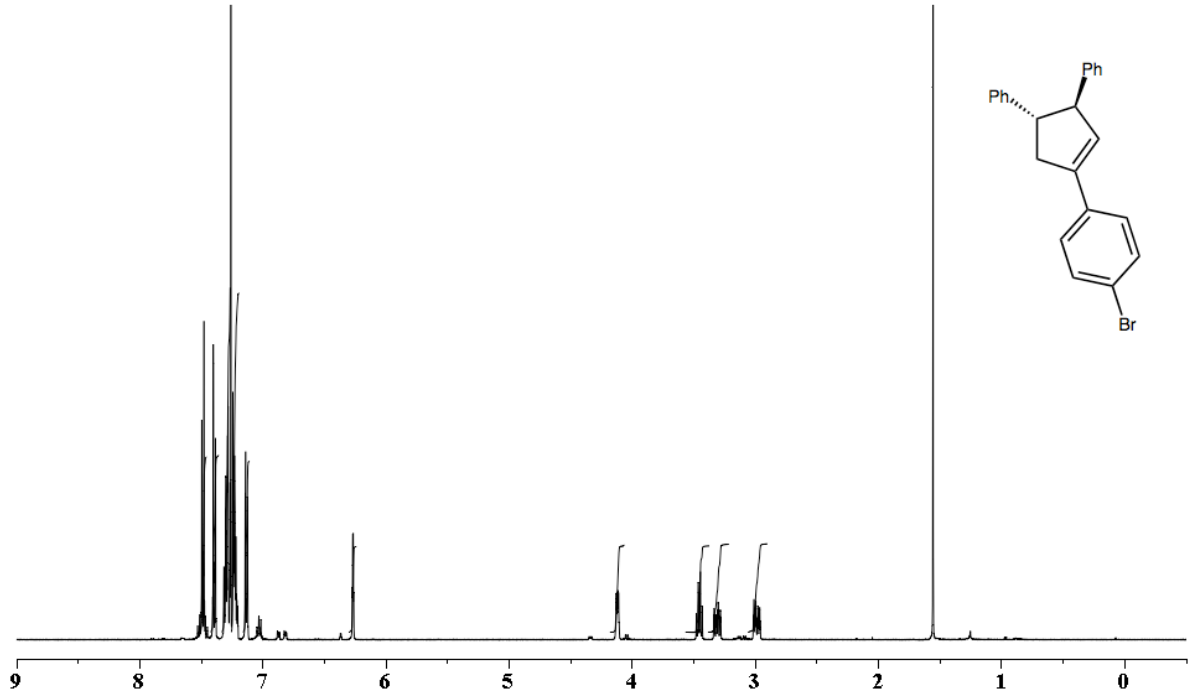
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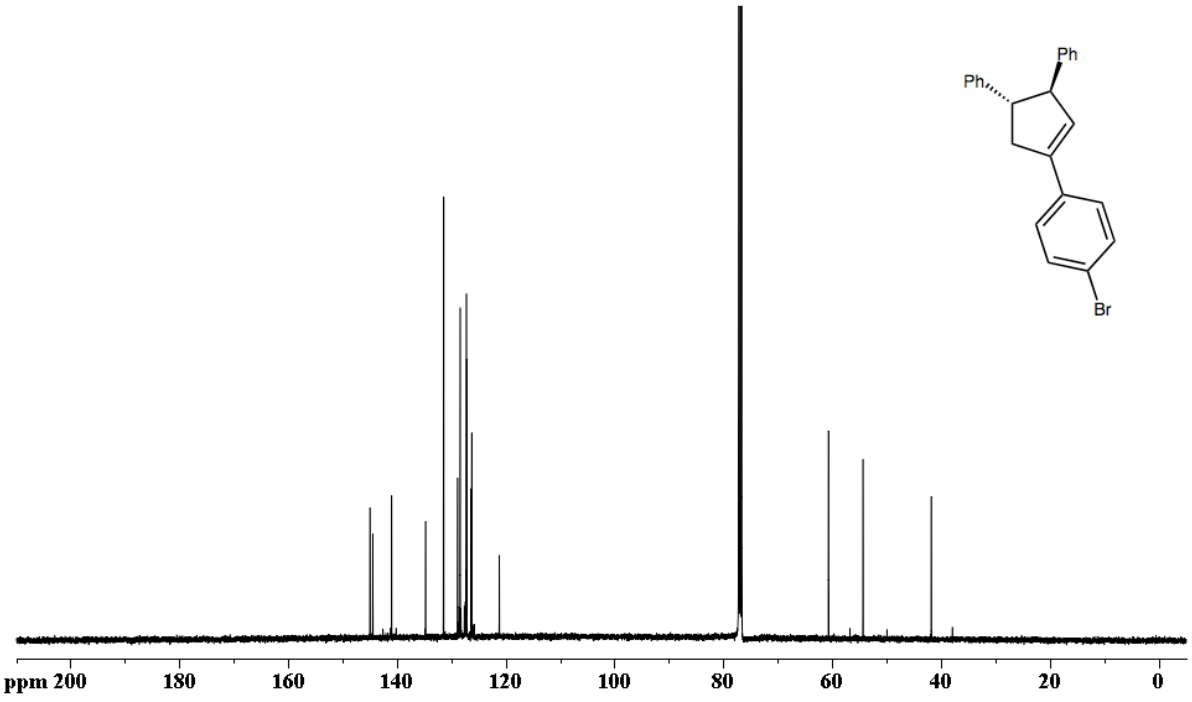
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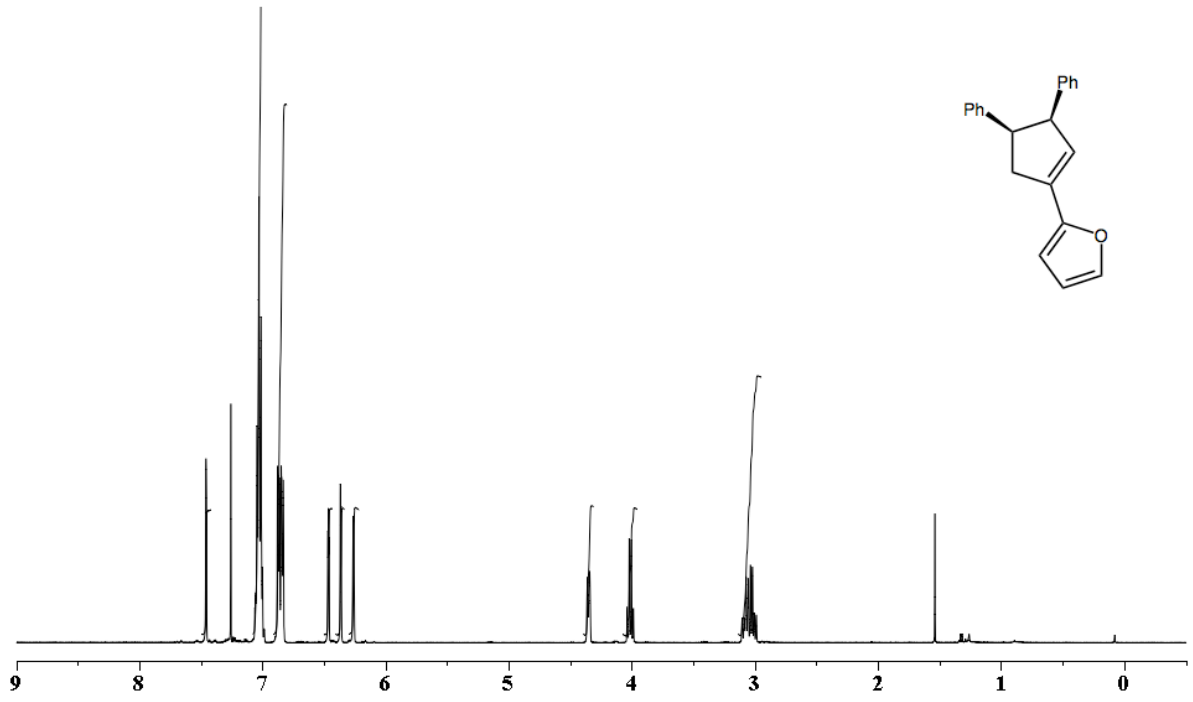
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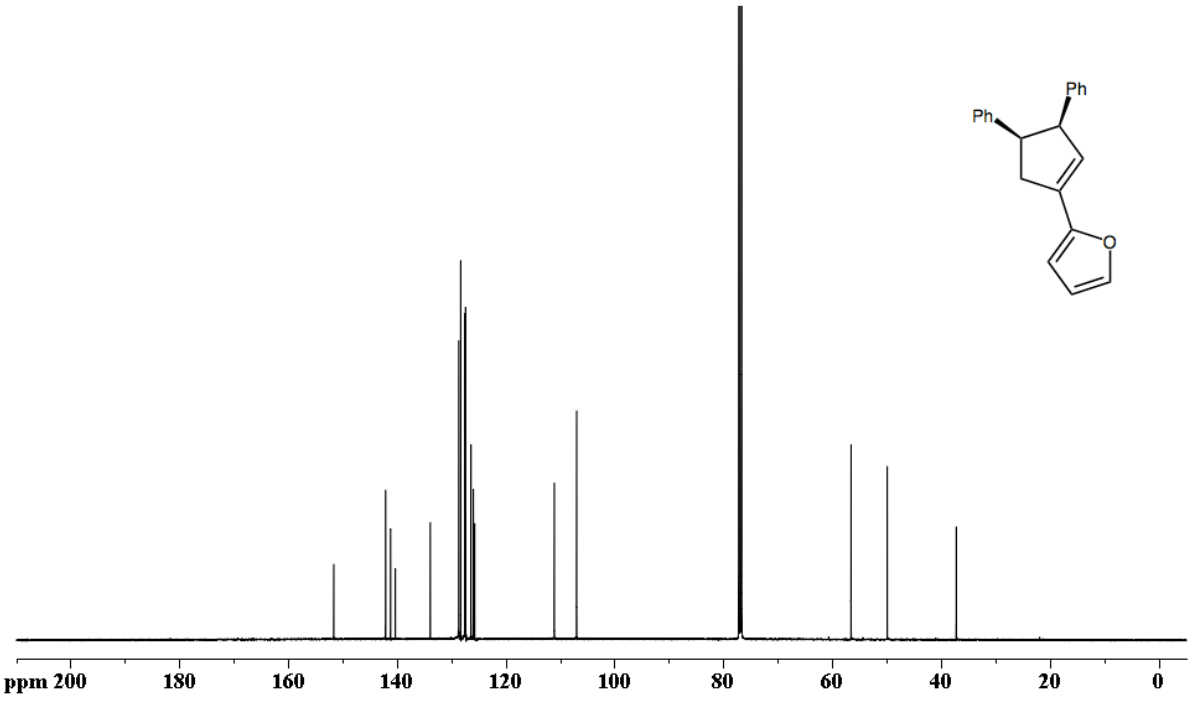
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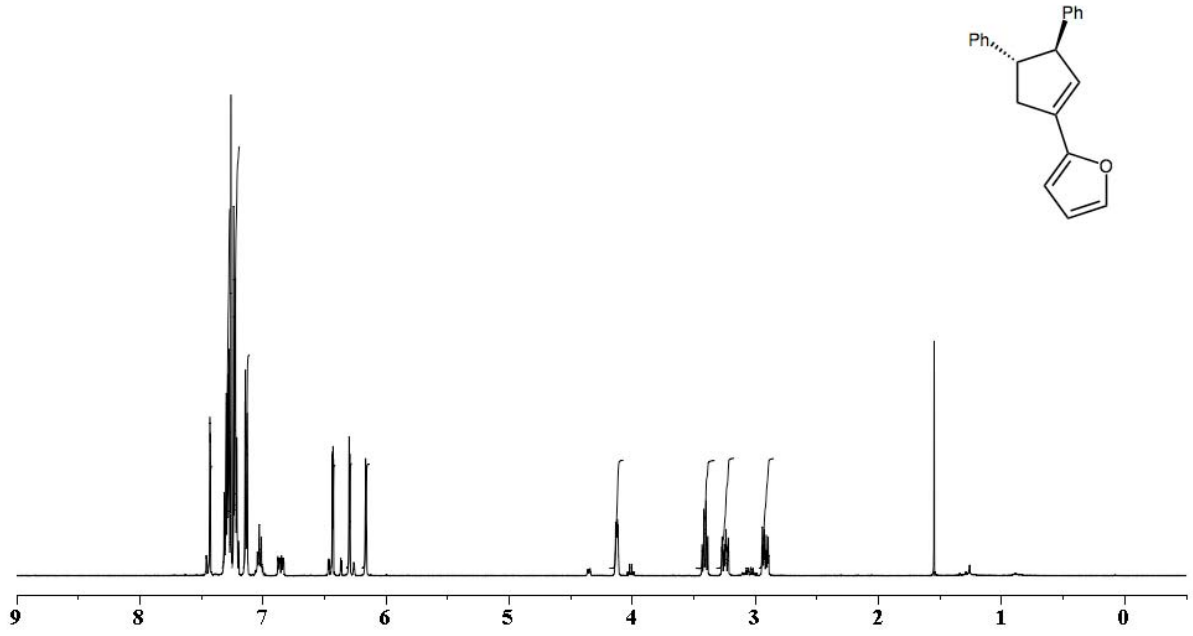
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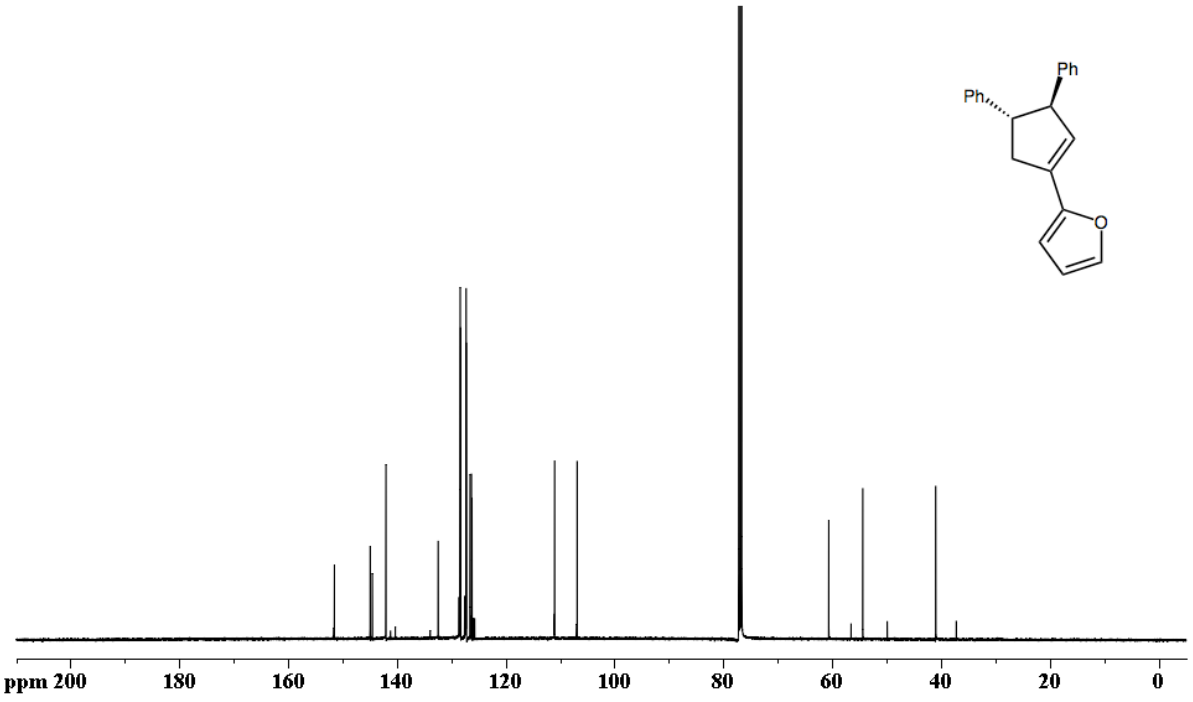
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X-Ray Crystallography of 20

X-ray diffraction was performed at -120 ºC and raw frame data were processed using SAINT. Molecular structure was solved using direct methods and refined by F2 by full-matrix least-squares techniques. The GOF = 1.12 for 217 variables refined to R1 = 0.031 for 4676 reflections with $I>2\alpha(I)$. There was no absorption correction or Flack parameters. Further information is contained in the CIF file.