Supplementary Information

Cis-Enals in *N*-Heterocyclic Carbene-Catalyzed Reactions: Distinct Stereo-Selectivity and Reactivity

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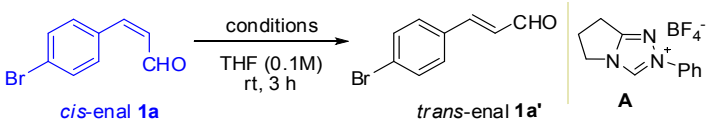
I. General information:

Commercially available materials purchased from Alfa Aesar or Sigma-Aldrich were used as received, except aldehydes that were purified *via* distillation or column chromatography prior to use. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker (400 MHz) spectrometer. Chemical shifts were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ 0.00) or chloroform (δ = 7.26, singlet). ^{1}H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), dd (doublet of doublets), m (multiplets), and etc. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br). Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker (400 MHz) (100 MHz) spectrometer. High resolution mass spectral analysis (HRMS) was performed on Finnigan MAT 95 XP mass spectrometer (Thermo Electron Corporation). The determination of *ee* was performed *via* chiral HPLC analysis using Shimadzu LC-20AD HPLC workstation. X-ray crystallography analysis was performed on Bruker X8 APEX X-ray diffractionmeter. Optical rotations were measured using a 0.5 mL cell with a 10 mm path length on a Jasco P-1030 polarimeter and are reported as follows: $[\alpha]^{rt}_{D}$ (*c* in g per 100 mL solvent). Analytical thin-layer chromatography (TLC) was carried out on Merck 60 F254 pre-coated silica gel plate (0.2 mm thickness). Visualization was performed using a UV lamp.

Summary of the reaction condition optimization:

Table S1. Study on the suppression of *cis*-to-*trans* enal isomerizations.

To a 10 mL Schlenk tube was added *cis*-enal **1a** (0.1 mmol) and THF (1 mL). Catalytic amount (30 mol%) of base or acid–base salt or/and NHC catalyst **A** were added to the reaction mixture under N_2 atmosphere and allowed to stirr at rt for 3 h. The ratios of *trans*- to *cis*-enals were measured by ^{1}H NMR analysis of the crude reaction mixture.

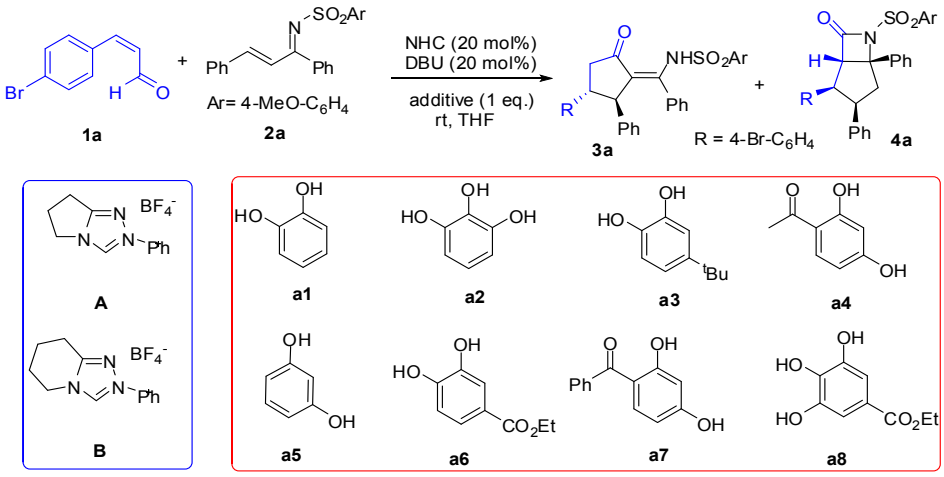


cis-enal **1a** | *trans*-enal **1a'** | **A**

Entry	Conditions	**1a/1a'**[a]
1	DBU (30 mol%)	100:0
2	DBU•HCl (30 mol%)	12:88
3	DBU•HBF_4 (30 mol%)	77:23
4	DBU (30 mol%), HOAc (30 mol%)	24:76
5	**A** (20 mol%), DBU (30 mol%)	79:21

[a] Determined by ^{1}H NMR analysis of unpurified reaction mixtures. DBU=1,8-Diazabicycloundec-7-ene.

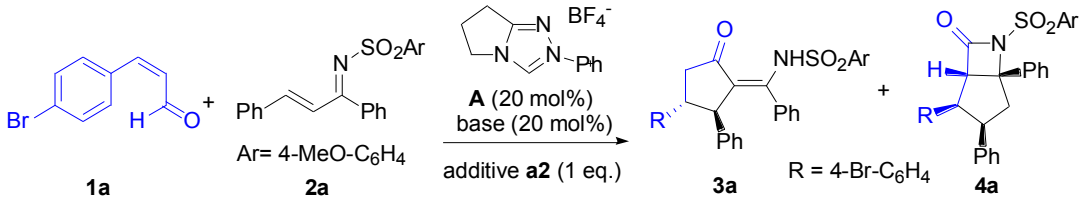
Table S2. Screening of catalysts and additives (selected examples).[a]



Entry	Catalyst	Additive	Conversion [%][b]	**3a**:**4a**[b]
1	**A**	-	74	41:59
2	**A**	**a1**	43	80:20
3	**B**	**a1**	<10%	-
4	**A**	**a2**	**>95**	**94:6**
5	**A**	**a3**	48	79:21
6	**A**	**a4**	89	81:19
7	**A**	**a5**	92	89:11
8	**A**	**a6**	61	80:20
9	**A**	**a7**	86	76:24
10	**A**	**a8**	54	95:5

[a] Reaction condition: **1a** (0.20 mmol), **2a** (0.10 mmol), catalyst (0.02 mmol), DBU (0.02 mmol), additive (0.1 mmol), THF (1 mL) 12h. [b] Determined by ^{1}H NMR analysis of unpurified reaction mixtures.

Table S3. Screening of bases and solvents.[a]



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

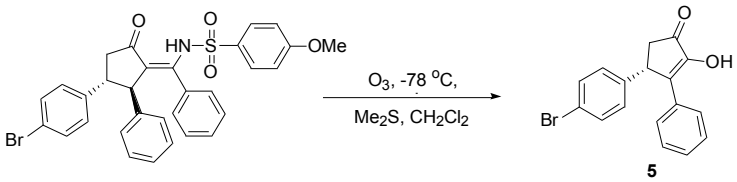
Entry	Base	Solvent	Conversion [%][b]	**3a**:**4a**[b]
1	^{t}BuOK	THF	70	94:6
2	KHMDS	THF	92	94:6
3	KOAc	THF	90	95:5
4	K_3PO_4	THF	81	95:5
5	DIEA	THF	38	99:1
6	DBU	CH_2Cl_2	17	-
7	DBU	EtOAc	33	-
8	DBU	toluene	< 5	-

[a] Reaction condition: **1a** (0.20 mmol), **2a** (0.10 mmol), catalyst **A** (0.02 mmol), base (0.02 mmol), additive **a2** (0.10 mmol), solvent (1 mL), 12 h. [b] Determined *via* ^{1}H NMR analysis of unpurified reaction mixtures.

II. General procedure for the catalytic reaction of *cis*-enal 1 with *α,β*-unsaturated imine 2.

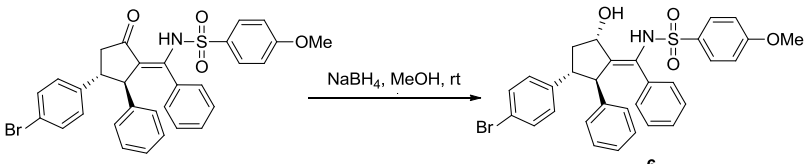
To a 10 mL oven-dried Schlenk tube equipped with a stir bar, was successively added *cis*-enal **1** (0.3 mmol), *α,β*-unsaturated imine **2** (0.1 mmol), triazolium salt **D** (7.2 mg, 0.02 mmol) and pyrogallol **F** (12.6 mg, 0.1 mmol). The tube was closed with a septum, evacuated and refilled with nitrogen. To this mixture was added freshly distilled anhydrous THF (0.5 mL) followed by an injection of DIEA (7.0 μL, 0.04 mmol). The reaction mixture was stirred at rt for 24 h. After complete consumption of **2**, as indicated by TLC and crude ^{1}H NMR analysis, the solvent was removed under reduced pressure. The resulting crude residue was purified by column chromatography on silica gel with hexane/EtOAc (5:1) as eluent to afford the desired product **3**.

Synthetic transformations of 3a.



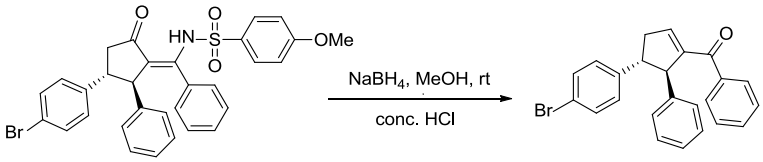
3a **5**
73% yield, 96% ee

A solution of **3a** (58.7 mg, 0.1 mmol) in anhydrous CH_2Cl_2 (5 mL) in a 10 mL Schlenk tube was cooled to -78 ^{o}C. The reaction mixture was slowly bubbled with ozone at the same temperature until it turned to light blue color, followed by nitrogen bubbling for 10 min to remove the dissolved ozone. Dimethyl sulfide (2 mL) was added to the reaction mixture and stirred further for 12 h, simultaneously allowing it to warm up to rt. The resulting mixture was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel with hexane/EtOAc (5:1) as eluent to afford cyclopentene derivative **5** as a white solid (24 mg, 73% yield).



3a **6**
91% yield, 94% ee

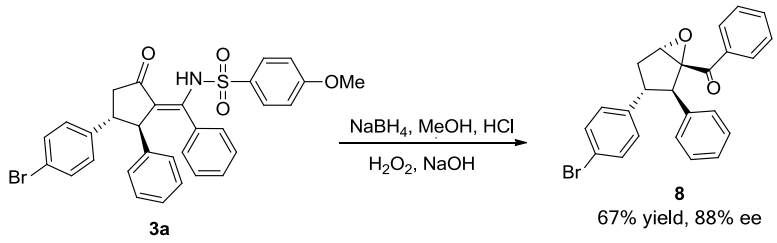
To a solution of **3a** (58.7 mg, 0.1 mmol) in MeOH (2 mL) was added $NaBH_4$ (7.6 mg, 0.2 mmol) at 0 ^{o}C and the mixture was stirred at rt for 2 h. The reaction mixture was quenched with water (0.5 mL) at rt and extracted with EtOAc and the combined organics were dried over anhydrous Na_2SO_4. Solvent was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel with hexane/EtOAc (3:1) as eluent to afford the product **6** as a colorless oil (53 mg, 91% yield).



3a **7**
73% yield, 96% ee

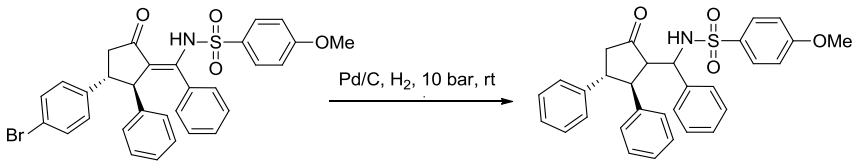
To a solution of **3a** (58.7 mg, 0.1 mmol) in MeOH (2 mL) was added $NaBH_4$ (7.6 mg, 0.2 mmol) at 0 ^{o}C and the mixture was stirred at rt for 3 h. The reaction mixture was acidified with concentrated hydrochloric acid (0.5 mL) at rt and stirred at the same temperature for 5 h. After completion of the reaction, the reaction

mixture was neutralized with aqueous $NaHCO_3$ solution, extracted with EtOAc and the combined organics were dried over anhydrous Na_2SO_4. Solvent was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel with hexane/EtOAc (15:1) as eluent to afford the product **7** as a yellow oil (35 mg, 87% yield).



3a **8**
67% yield, 88% ee

To a solution of **3a** (58.7 mg, 0.1 mmol) in MeOH (2 mL) was added $NaBH_4$ (7.6 mg, 0.2 mmol) at 0 ^oC and the mixture was stirred at rt for 2 h. The reaction mixture was acidified with concentrated hydrochloric acid (0.3 mL) at rt and stirred at the same temperature for 5 h. After completion of the reaction, the reaction mixture pH was adjusted to 7 with 6N NaOH solution, and then charged with 30% H_2O_2 (1.8 mL, 0.3 mmol) at 0 ^oC followed by the solution of 6N NaOH (0.08 mL, 0.48 mmol). The mixture was stirred at room temperature for 4h. The reaction mixture was extracted with EtOAc and the combined organics were dried over anhydrous Na_2SO_4. Solvent was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel with hexane/EtOAc (10:1) as eluent to afford the product **8** as a colorless wax (26 mg, 67% yield).

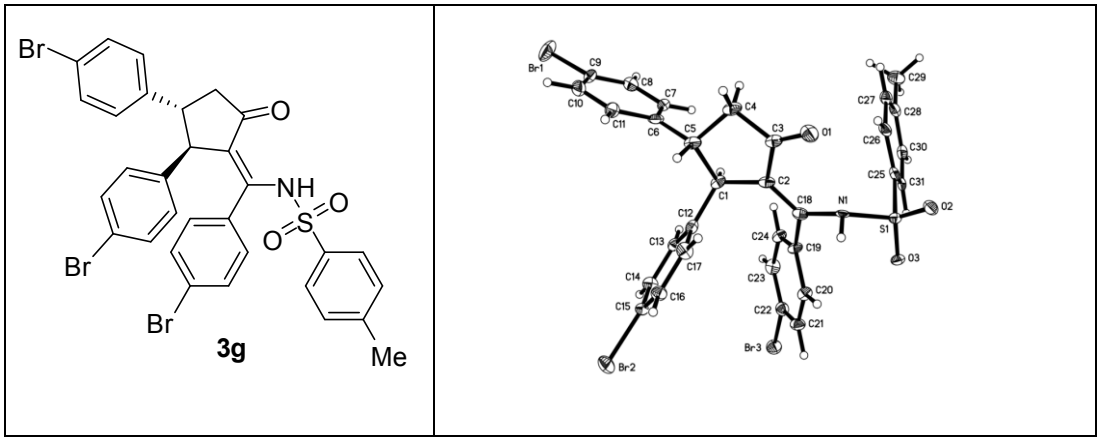


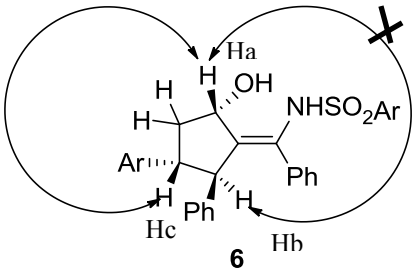
3a **9**
83% yield, 1.5:1 dr

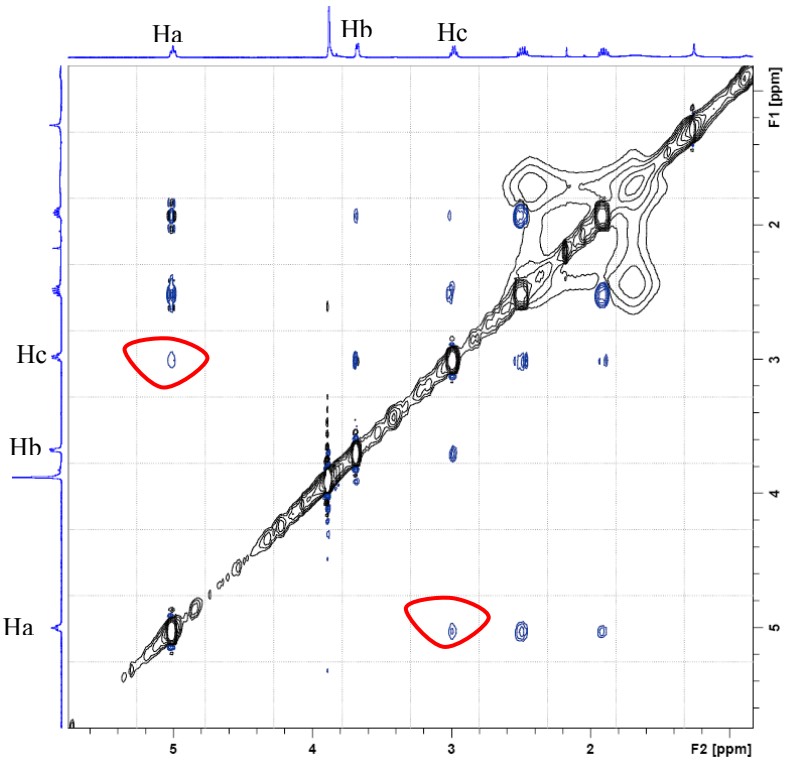
To a solution of **3a** (58.7 mg, 0.1 mmol) in MeOH (2 mL) was added Pd/C (10%, 21.2 mg, 0.02 mmol) at rt. The reaction mixture was stirred under 10 bar of hydrogen at room temperature for 12h. The reaction mixture was diluted with ethyl acetate, and passed through a short silica pad . Solvent was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel with hexane/EtOAc (5:1) as eluent to afford the product **9** as a colorless oil (41 mg, 83% yield, 1.5:1 dr, 93% ee major, 92% ee minor).

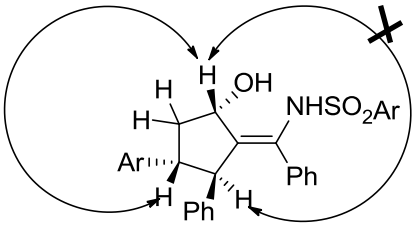
Stereochemistry determination by X-ray crystallographic analysis and 2D NOE analysis.

Absolute configuration of all the products were assigned based on the crystal X-ray structure of **3g**. The crystal (colorless flaky crystal) was obtained by vaporization of a acetone/methanol (1:2) solution of compound **3g**. The CCDC 884437 containes the supplementary crystallographic data. New chiral center for transformation products **6** and **8** were confirmed by 2D NOE analysis.









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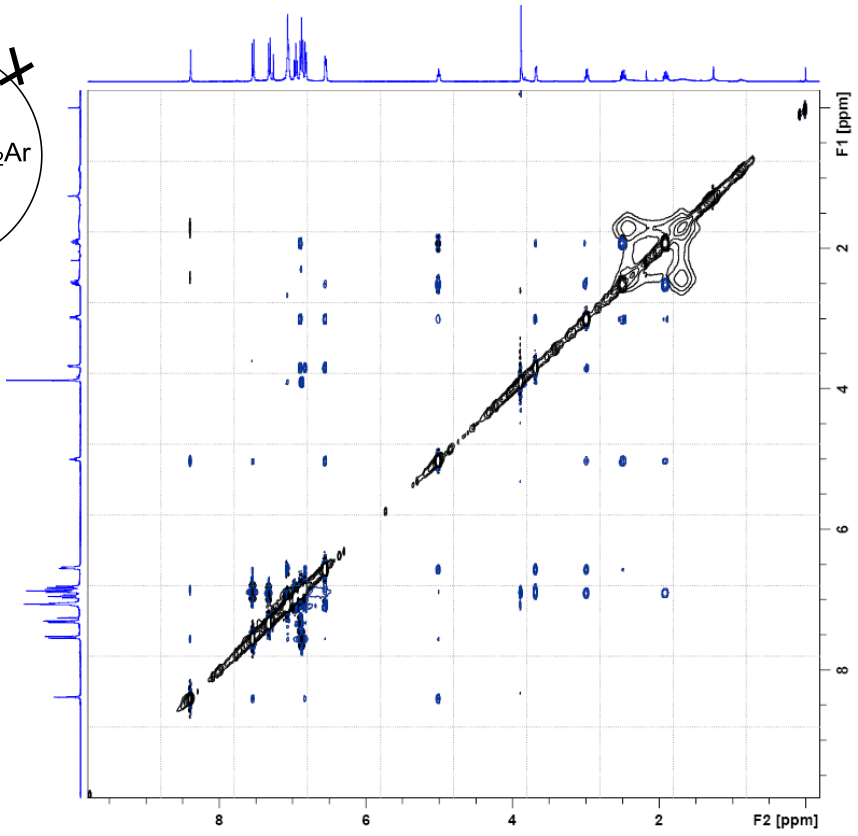

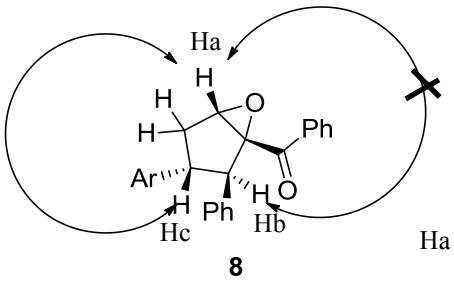

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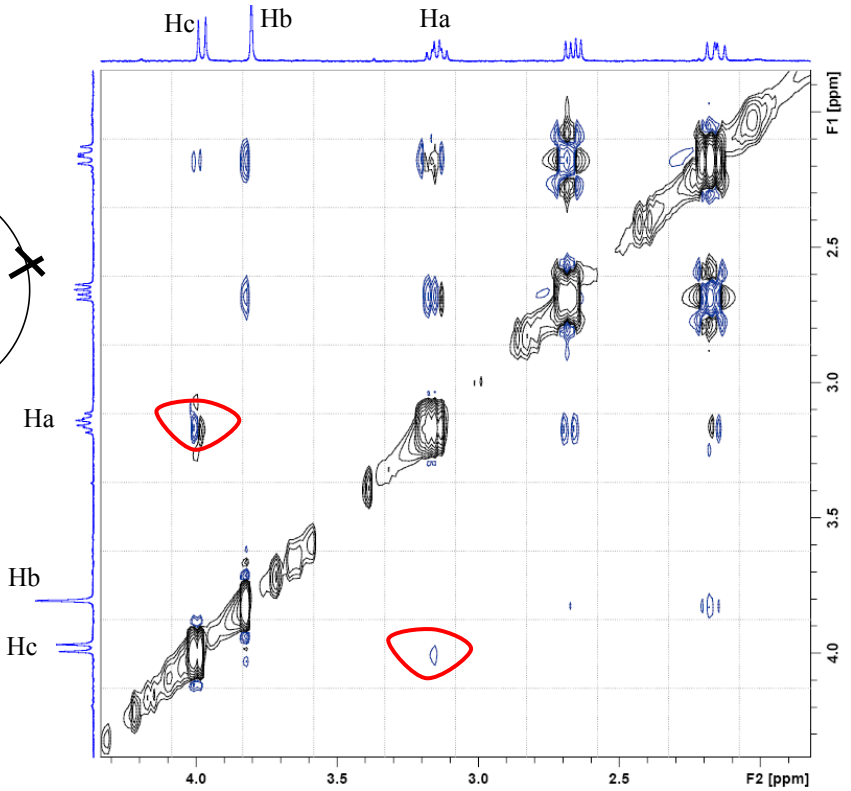
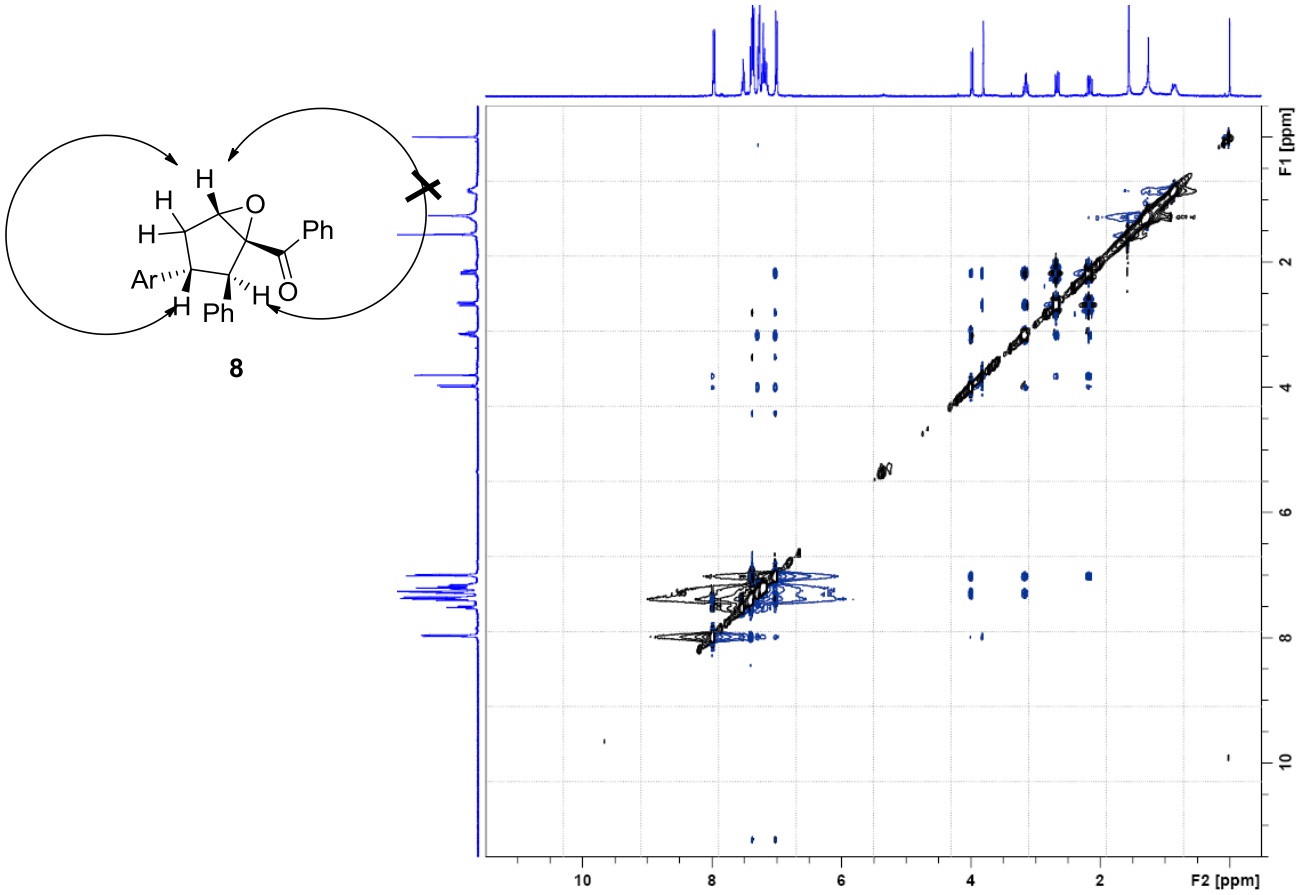
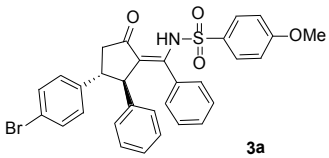
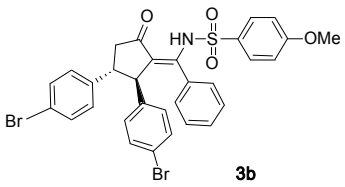




III. Characterization of Products.

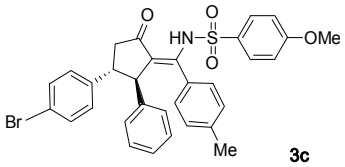


***N*-((*Z*)-((2*R*,3*R*)-3-(4-Bromophenyl)-5-oxo-2-phenylcyclopentylidene)(phenyl)methyl)-4-methoxy benzenesulfonamide (3a)**: Yellowish thick oil, 44 mg, 75% yield, ^{1}H NMR (400 MHz, $CDCl_3$)δ 2.61-2.67 (dd, *J* = 6.0, 6.4 Hz, 1H), 2.94-3.01 (dd, *J* = 8.4, 8.4 Hz, 1H), 3.23 (m, 1H), 3.71 (d, *J* = 4.8 Hz, 1H), 3.85 (s, 3H), 6.60-6.66 (m, 4H), 6.79-6.89 (m, 4H), 6.94-7.02 (m, 5H), 7.11-7.14 (m, 1H), 7.33-7.36 (m, 4H) , 12.05 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 44.9, 48.8, 54.5, 55.7, 113.9, 118.5, 120.6, 126.3, 127.1, 127.4, 128.3, 128.4, 129.0, 129.5, 129.9, 131.0, 131.5, 131.8, 142.6, 143.7, 150.8, 163.3, 207.2; HRMS (ESI, m/z): calcd. for $C_{31}H_{26}BrNO_4S(M+H)^+$: 588.0844, found: 588.0844; $[\alpha]_D^{20}$: -108.0 (*c* 4.3, $CHCl_3$); HPLC analysis: 92% ee (Chiralcel OD-H, 10:90 ^{i}PrOH/Hexane, 0.70 mL/min), R_t (minor) = 39.2 min, R_t (major) = 45.7 min.



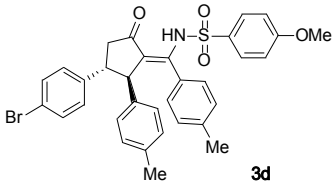
***N*-((*Z*)-((2*R*,3*R*)-2,3-Bis(4-bromophenyl)-5-oxocyclopentylidene)(phenyl)methyl)-4-methoxybenzene sulfonamide (3b)**: Yellowish thick oil, 46.5 mg, 70% yield, ^{1}H NMR (400 MHz, $CDCl_3$)δ 2.65-2.71 (dd, *J* =

6.0, 7.6 Hz, 1H), 2.90-2.97 (dd, *J* = 8.4, 8.4 Hz, 1H), 3.16 (q, *J* = 8.0 Hz, 1H), 3.68 (d, *J* = 5.6 Hz, 1H), 3.85 (s, 3H), 6.46 (d, *J* = 8.4 Hz, 2H), 6.62 (d, *J* = 7.2 Hz, 2H), 6.79-6.85 (dd, *J* = 5.2, 8.4 Hz, 4H), 6.97 (t, *J* = 7.6 Hz, 2H), 7.08-7.16 (m, 3H), 7.30-7.34 (t, *J* = 8.8 Hz, 4H) , 12.09 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 44.9, 48.9, 54.2, 55.7, 114.0, 117.9, 120.0, 120.8, 127.5, 128.5, 128.9(0), 128.9(5), 129.6, 129.9, 130.8, 131.3, 131.5, 131.8, 141.7, 142.5, 151.2, 163.3, 206.4; HRMS (ESI, m/z): calcd. for $C_{31}H_{25}Br_2NO_4S(M+H)^+$: 665.9949, found: 665.9951; $[\alpha]_D^{20}$: -87.2 (*c* 2.1, $CHCl_3$); HPLC analysis: 95% ee (Chiralcel OD-H, 10:90 ^{i}PrOH/Hexane, 0.75 mL/min), R_t (minor) = 39.7 min, R_t (major) = 68.9 min.



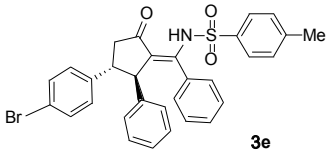
3c

***N*-((*Z*)-((2*R*,3*R*)-3-(4-Bromophenyl)-5-oxo-2-phenylcyclopentylidene)(p-tolyl)methyl)-4-methoxy benzenesulfonamide (3c)**: Yellowish thick oil, 39 mg, 65% yield, ^{1}H NMR (400 MHz, $CDCl_3$)δ 2.21 (s, 3H), 2.55-2.61 (dd, *J* = 5.2, 5.6 Hz, 1H), 2.91-2.98 (dd, *J* = 8.4, 8.4 Hz, 1H), 3.20-3.25 (m, 1H), 3.74 (d, *J* = 4.0 Hz, 1H), 3.87 (s, 3H), 6.58 (d, *J* = 7.6 Hz, 2H), 6.63-6.65 (m, 2H), 6.78-6.85 (m, 6H), 7.03-7.04 (m, 3H), 7.32-7.40 (dd, *J* = 8.4, 9.2 Hz, 4H) , 11.96 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 44.7, 48.5, 54.3, 55.7, 113.9, 118.6, 120.6, 126.3, 127.1, 128.1, 128.2, 128.3, 128.4, 129.0, 129.3, 129.9, 131.8, 139.8, 142.8, 144.0, 151.0, 163.3, 207.2; HRMS (ESI, m/z): calcd. for $C_{32}H_{28}BrNO_4S(M+H)^+$: 602.1001, found: 602.1004; $[\alpha]_D^{20}$: -69.3 (*c* 1.6, $CHCl_3$); HPLC analysis: 96% ee (Chiralcel OD-H, 10:90 ^{i}PrOH/Hexane, 0.70 mL/min), R_t (minor) = 27.4 min, R_t (major) = 28.9 min.



3d

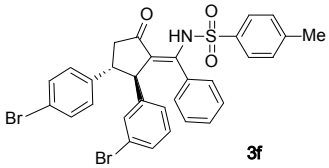
***N*-((*Z*)-((2*R*,3*R*)-3-(4-bromophenyl)-5-oxo-2-(p-tolyl)cyclopentylidene)(p-tolyl)methyl)-4-methoxy benzenesulfonamide (3d):** Yellowish thick oil, 34.5 mg, 56% yield, ^{1}H NMR (400 MHz, $CDCl_3$)δ 2.23 (s, 6H), 2.51-2.57 (dd, *J* = 4.4, 18.4 Hz, 1H), 2.91-2.98 (dd, *J* = 4.4, 18.4 Hz, 1H), 3.19-3.22 (m, 1H), 3.71 (d, *J* = 4.4 Hz, 1H), 3.89 (s, 3H), 6.54 (d, *J* = 8.0 Hz, 2H), 6.60 (d, *J* = 7.6 Hz, 2H), 6.81-6.87 (m, 8H), 7.33 (d, *J* = 8.4 Hz, 2H), 7. 04 (d, *J* = 8.8 Hz, 2H), 11.91 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 21.4, 44.5, 48.4, 53.8, 55.7, 113.9, 118.8, 120.5, 126.9, 128.1, 128.3, 128.5, 129.0(1), 129.0(6), 129.9, 131.4, 131.8, 135.9, 139.9, 141.1, 143.1, 150.7, 163.2, 207.5; HRMS (ESI, m/z): calcd. for $C_{33}H_{30}BrNO_4S(M+H)^+$: 616.1157, found: 616.1155; $[\alpha]_D^{20}$: -58.6 (*c* 1.7, $CHCl_3$); HPLC analysis: 90% ee (Chiralcel AS-H, 10:90 ^{i}PrOH/Hexane, 0.75 mL/min), R_t (minor) = 55.7 min, R_t (major) =44.4 min.



3e

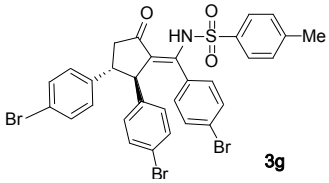
***N*-((*Z*)-((2*R*,3*R*)-3-(4-Bromophenyl)-5-oxo-2-phenylcyclopentylidene)(phenyl)methyl)-4-methylbenzene sulfonamide (3e)**: Yellowish thick oil, 39.4 mg, 69% yield, ^{1}H NMR (400 MHz, $CDCl_3$)δ 2.42 (s, 3H), 2.61-2.67 (dd, *J* = 6.4, 6.4 Hz, 1H), 2.94-3.00 (dd, *J* = 8.4, 8.4 Hz, 1H), 3.21-3.26 (m, 1H), 3.71 (d, *J* = 4.8 Hz, 1H),

6.60-6.63 (m, 4H), 6.86 (d, *J* = 6.8 Hz, 2H), 6.95 (t, *J* = 8.0 Hz, 3H), 7.00 (d, *J* = 4.8 Hz, 2H), 7.11-7.17 (m, 3H), 7.32 (t, *J* = 8.8 Hz, 4H), 11.09 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 44.8, 48.6, 54.5, 118.6, 120.6, 126.3, 127.1, 127.4, 127.6, 128.3, 128.4, 129.0, 129.4, 129.5, 130.9, 131.8, 136.9, 142.5, 143.7, 144.0, 150.7, 207.2; HRMS (ESI, m/z): calcd. for $C_{31}H_{26}BrNO_3S(M+H)^+$: 572.0895, found: 572.0894; $[\alpha]_D^{20}$: -78.4 (*c* 1.7, $CHCl_3$); HPLC analysis: 97% ee (Chiralcel OD-H, 10:90 ^{i}PrOH/Hexane, 0.75 mL/min), R_t (minor) = 19.9 min, R_t (major) = 23.3 min.



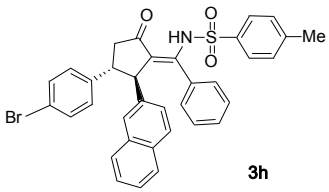
3f

***N*-((*Z*)-((2*R*,3*R*)-2-(3-Bromophenyl)-3-(4-bromophenyl)-5-oxocyclopentylidene)(phenyl)methyl)-4-methylbenzenesulfonamide (3f):** Yellowish thick oil, 43 mg, 66% yield, ^{1}H NMR (400 MHz, $CDCl_3$)δ 2.41 (s, 3H), 2.67-2.73 (dd, *J* = 8.0, 18.0 Hz, 1H), 2.94-3.00 (dd, *J* = 8.4, 18.0 Hz, 1H), 3.18-3.24 (m, 1H), 3.66 (d, *J* = 6.0 Hz, 1H), 6.52-6.60 (dd, *J* = 7.6, 7.6 Hz, 3H), 6.68 (s, 1H), 6.83-6.87 (m, 3H), 6.96 (t, *J* = 7.6 Hz, 2H), 7.10-7.16 (m, 4H), 7.29 (d, *J* = 8.4 Hz, 4H), 7.34 (d, *J* = 8.4 Hz, 4H), 12.15 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 45.1, 48.8, 54.3, 117.8, 120.8, 122.3, 125.8, 127.4, 127.6, 128.4, 128.9, 129.3, 129.4, 129.6, 129.7, 130.4, 130.5, 131.8, 136.9, 141.5, 144.2, 145.6, 151. 3, 206.3; HRMS (ESI, m/z): calcd. for $C_{31}H_{25}Br_2NO_3S(M+H)^+$: 650.0000, found: 649.9997; $[\alpha]_D^{20}$: -128.2 (*c* 1.7, $CHCl_3$); HPLC analysis: 91% ee (Chiralcel OD-H, 10:90 ^{i}PrOH/Hexane, 0.75 mL/min), R_t (minor) = 26.9 min, R_t (major) =32.4 min.



3g

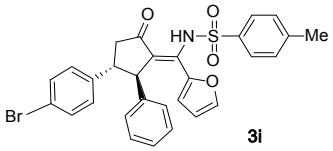
***N*-((*Z*)-((2*R*,3*R*)-2,3-bis(4-Bromophenyl)-5-oxocyclopentylidene)(4-bromophenyl)methyl)-4-methyl benzenesulfonamide (3g)**: Yellowish semi-solid, 46.5 mg, 64% yield, ^{1}H NMR (400 MHz, $CDCl_3$)δ 2.44 (s, 3H), 2.65-2.72 (dd, *J* = 8.0, 8.0 Hz, 1H), 2.89-2.96 (dd, *J* = 8.0, 8.4 Hz, 1H), 3.19 (q, *J* = 8.0 Hz,1H), 3.62 (d, *J* = 4.8 Hz, 1H), 6.46-6.49 (dd, *J* = 6.0, 6.0 Hz, 4H), 6.83 (d, *J* = 8.4 Hz, 2H), 7.09-7.20 (m, 6H), 7.31-7.35 (dd, *J* = 5.2, 5.2 Hz, 4H), 12.02 (s, 1H); ^{13}C NMR (100 MHz, CDCl3) δ 21.7, 44.8, 48.9, 54.1, 118.4, 120.3, 120.9, 124.2, 127.6, 128.4, 128.9, 129.5, 129.6, 130.5, 130.7, 131.4, 131.9, 136.8, 141.3, 142.1, 144.4, 149.6, 206.5; HRMS (ESI, m/z): calcd. for $C_{31}H_{24}Br_3NO_3S(M+H)^+$: 727.9105, found: 727.9108; $[\alpha]_D^{20}$: -59.1 (*c* 2.1, $CHCl_3$); HPLC analysis: 92% ee (Chiralcel OD-H, 10:90 ^{i}PrOH/Hexane, 0.75 mL/min), R_t (minor) = 37.5 min, R_t (major) =54.1 min.



3h

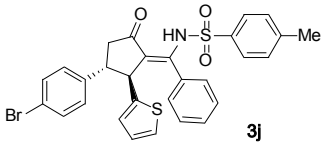
***N*-((*Z*)-((2*R*,3*R*)-3-(4-Bromophenyl)-2-(naphthalen-2-yl)-5-oxocyclopentylidene)(phenyl)methyl)-4-methylbenzenesulfonamide (3h):** Yellowish thick oil, 37.9 mg, 61% yield, ^{1}H NMR (400 MHz, $CDCl_3$)δ 2.41 (s, 3H), 2.65-2.72 (dd, *J* = 6.4, 18.4 Hz, 1H), 2.99-3.06 (dd, *J* = 8.4, 18.4 Hz, 1H), 3.32-3.36 (m, 1H),

3.86 (d, *J* = 4.8 Hz, 1H), 6.60 (d, *J* = 7.6 Hz, 2H), 6.82 (t, *J* = 7.2 Hz, 2H), 6.88-6.94 (m, 4H), 6.99 (t, *J* = 7.2 Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.30-7.33 (m, 4H), 7.35-7.41 (m, 2H), 7.48-7.50 (m, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.69-7.72 (m, 1H), 12.15 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 44.8, 48.3, 54.6, 118.3, 120.6, 125.3, 125.6, 125.8, 126.0, 127.3, 127.4, 127.5, 127.7, 128.3, 128.4, 128.9, 129.4, 129.5, 130.7, 131.8, 132.0, 133.0, 137.0, 140.9, 142.5, 144.1, 150.9, 207.2; HRMS (ESI, m/z): calcd. for $C_{35}H_{29}BrNO_3S(M+H)^+$: 622.1051, found: 622.1050; $[\alpha]_D^{20}$: -35.1 (*c* 1.9, $CHCl_3$); HPLC analysis: 92% ee (Chiralcel OD-H, 10:90 ^{i}PrOH/Hexane, 0.75 mL/min), R_t (minor) = 26.7 min, R_t (major) =34.8 min.



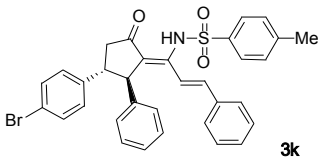
3i

***N*-((*Z*)-((2*R*,3*R*)-3-(4-Bromophenyl)-5-oxo-2-phenylcyclopentylidene)(furan-2-yl)methyl)-4-methyl benzenesulfonamide (3i):** Yellowish thick oil, 32.6 mg, 58% yield, ^{1}H NMR (400 MHz, $CDCl_3$)δ 2.47 (s, 3H), 2.50-2.56 (dd, *J* = 5.6, 18.0 Hz, 1H), 2.85-2.92 (dd, *J* = 8.4, 18.0 Hz, 1H), 3.17-3.21 (m, 1H), 4.23 (d, *J* = 4.4 Hz, 1H), 6.24-6.25 (dd, *J* = 1.6, 3.6 Hz, 1H), 6.63 (d, *J* = 3.6 Hz, 1H), 6.75-6.77 (m, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 7.10-7.12 (m, 3H), 7.20 (d, *J* = 1.2 Hz, 1H), 7.27 (d, *J* = 6.4 Hz, 3H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 11.56 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 44.9, 48.7, 54.7, 112.0, 118.6, 119.6, 120.6, 126.5(3), 126.5(8), 127.7, 128.4, 128.5, 129.6, 131.8, 136.1, 138.3, 142.7, 143.6, 144.2, 144.8, 145.0, 207.8; HRMS (ESI, m/z): calcd. for $C_{29}H_{24}BrNO_4S(M+H)^+$: 562.0688, found: 562.0687; $[\alpha]_D^{20}$: -92.3 (*c* 1.4, $CHCl_3$); HPLC analysis: 93% ee (Chiralcel OD-H, 10:90 ^{i}PrOH/Hexane, 0.75 mL/min), R_t (minor) = 21.4 min, R_t (major) =26.6 min.



3j

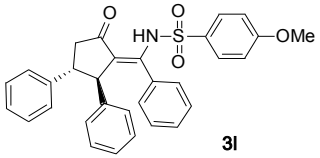
***N*-((*Z*)-((2*S*,3*R*)-3-(4-Bromophenyl)-5-oxo-2-(thiophen-2-yl)cyclopentylidene)(phenyl)methyl)-4-methyl benzenesulfonamide (3j):** Yellowish thick oil, 32.9 mg, 57% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44 (s, 3H), 2.59-2.65 (dd, *J* = 4.8, 18.4 Hz, 1H), 3.02-3.08 (dd, *J* = 8.4, 18.4 Hz, 1H), 3.34-3.38 (m, 1H), 3.97 (d, *J* = 3.7 Hz, 1H), 6.14 (d, *J* = 3.4 Hz, 1H), 6.61-6.63 (dd, *J* = 3.5, 5.2 Hz, 1H), 6.72 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 6.99-7.18 (m, 3H), 7.16-7.26 (m, 3H), 7.31-7.36 (m, 4H), 12.02 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 44.3, 48.7, 49.4, 118.4, 120.8, 123.8, 124.5, 126.4, 127.6, 128.3, 128.9, 129.5, 129.7, 130.7, 131.8, 136.9, 142.3, 144.1, 147.3, 151.1, 206.5; HRMS (ESI, m/z): calcd. for $C_{29}H_{24}BrNO_3S_2(M+H)^+$: 578.0459, found: 578.0455; $[\alpha]_D^{20}$: -113.1 (*c* 1.4, $CHCl_3$); HPLC analysis: 91% ee (Chiralcel AS-H, 5:5:90 MeOH/^{i}PrOH/Hexane, 0.50 mL/min), R_t (minor) = 24.7 min, R_t (major) =26.9 min.



3k

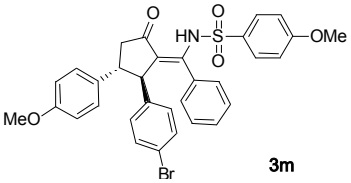
***N*-((1*Z*,2*E*)-1-((2*R*,3*R*)-3-(4-Bromophenyl)-5-oxo-2-phenylcyclopentylidene)-3-phenylallyl)-4-methyl benzenesulfonamide (3k):** Yellowish thick oil, 37.6 mg, 63% yield, ^{1}H NMR (400 MHz, $CDCl_3$)δ 2.47 (s, 3H), 2.52-2.58 (dd, *J* = 6.0, 18.4 Hz, 1H), 2.86-2.93 (dd, *J* = 8.4, 18.4 Hz, 1H), 3.19-3.23 (m, 1H), 3.99 (d, *J* = 4.4 Hz, 1H), 6.31 (d, *J* = 16.0 Hz, 1H), 6.76-6.88 (m, 4H), 7.03-7.05 (dd, *J* = 2.0, 7.6 Hz, 2H), 7.18-7.28 (m,

9H), 7.36 (d, *J* = 6.4 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 11.60 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 44.8, 48.9, 55.3, 119.2, 119.3, 120.7, 127.0, 127.1, 127.5, 127.8, 128.5, 128.7, 129.0, 129.6, 129.7, 131.9, 135.2, 136.5, 142.4, 142.8, 143.5, 144.1, 147.3, 207.1; HRMS (ESI, m/z): calcd. for $C_{33}H_{29}BrNO_3S(M+H)^+$: 598.1051, found: 598.1052; $[\alpha]_D^{20}$: -56.0 (*c* 0.9, $CHCl_3$); HPLC analysis: 89% ee (Chiralcel OD-H, 10:90 ^{i}PrOH/Hexane, 0.75 mL/min), R_t (minor) = 22.6 min, R_t (major) =25.8 min.



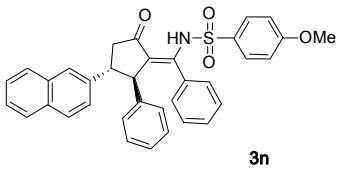
3l

4-Methoxy-*N*-((*Z*)-((2*R*,3*R*)-5-oxo-2,3-diphenylcyclopentylidene)(phenyl)methyl)benzenesulfonamide (3l): Yellowish thick oil, 37 mg, 73% yield, ^{1}H NMR (400 MHz, $CDCl_3$)δ 2.65-2.71 (dd, *J* = 6.0, 5.6 Hz, 1H), 2.97-3.03 (dd, *J* = 8.8, 8.8 Hz, 1H), 3.25-3.30 (m, 1H), 3.78 (d, *J* = 4.4 Hz, 1H), 3.86 (s, 3H), 6.63-6.68 (m, 4H), 6.82 (d, *J* = 7.2 Hz, 2H), 6.94-7.03 (m, 7H), 7.11-7.23 (m, 4H), 7.36 (d, *J* = 8.8 Hz, 2H) , 12.06 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 45.1, 49.0, 54.4, 55.7, 113.9, 119.0, 126.2, 126.6, 126.8, 127.1, 127.4, 128.2, 128.7, 129.0, 129.4, 129.8, 131.2, 131.5, 143.7, 144.3, 150.4, 163.2, 207.8; HRMS (ESI, m/z): calcd. for $C_{31}H_{27}NO_4S(M+H)^+$: 510.1739, found: 510.1738; $[\alpha]_D^{20}$: -30.0 (*c* 2.1, $CHCl_3$); HPLC analysis: 96% ee (Chiralcel OD-H, 10:90 ^{i}PrOH/Hexane, 0.75 mL/min), R_t (minor) = 22.9 min, R_t (major) = 26.2 min.



3m

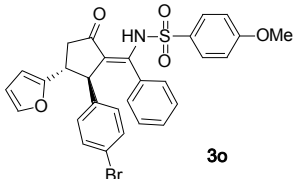
***N*-((*Z*)-((2*R*,3*R*)-2-(4-Bromophenyl)-3-(4-methoxyphenyl)-5-oxocyclopentylidene)(phenyl)methyl)-4-methoxybenzenesulfonamide (3m)**: Yellowish thick oil, 41.8 mg, 68% yield, ^{1}H NMR (400 MHz, $CDCl_3$)δ 2.65-2.72 (dd, *J* = 7.6, 7.6 Hz, 1H), 2.89-2.96 (dd, *J* = 8.4, 8.4 Hz, 1H), 3.15 (q, *J* = 8.0 Hz, 1H), 3.69 (d, *J* = 6.0 Hz, 1H), 3.75 (s, 3H), 3.85 (s, 3H), 6.46-6.49 (m, 2H), 6.64 (d, *J* = 7.2 Hz, 2H), 6.76 (d, *J* = 6.8 Hz, 2H), 6.80 (d, *J* = 7.2 Hz, 2H), 6.88 (d, *J* = 6.8 Hz, 4H), 6.97 (t, *J* = 7.6 Hz, 2H), 7.06-7.16 (m, 5H), 7.31 (d, *J* = 7.2 Hz, 2H) , 12.09 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 45.3, 48.6, 54.4, 55.2, 55.7, 113.9, 114.1, 118.5, 119.8, 127.4, 127.7, 128.9, 129.0, 129.5, 129.8, 130.9, 131.1, 131.5, 134.7, 142.9, 150.7, 158.4, 163.2, 207.2; HRMS (ESI, m/z): calcd. for $C_{32}H_{28}BrNO_5S(M+H)^+$: 618.0950, found: 618.0952; $[\alpha]_D^{20}$: -58.4 (*c* 2.0, $CHCl_3$); HPLC analysis: 93% ee (Chiralcel OD-H, 10:90 ^{i}PrOH/Hexane, 0.75 mL/min), R_t (minor) = 49.7 min, R_t (major) = 70.3 min.



3n

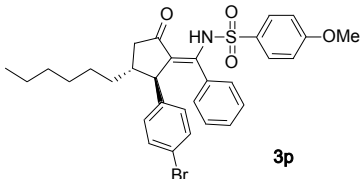
***N*-((*Z*)-((2*R*,3*R*)-2-Phenyl-3-(naphthalen-2-yl)-5-oxocyclopentylidene)(phenyl)methyl)-4-methoxy benzenesulfonamide (3n):** Yellowish thick oil, 39.6 mg, 71% yield, ^{1}H NMR (400 MHz, $CDCl_3$)δ 2.77-2.83 (dd, *J* = 6.4, 18.4 Hz, 1H), 3.04-3.11 (dd, *J* = 8.4, 18.4 Hz, 1H), 3.42-3.47 (m, 1H), 3.85 (s, 3H), 3.88 (d, *J* = 4.4 Hz, 1H), 6.75 (t, *J* = 3.6 Hz, 4H), 6.81 (d, *J* = 8.8 Hz, 2H), 6.95 (t, *J* = 7.6 Hz, 2H), 7.03 (d, *J* = 2.0 Hz, 3H), 7.10-7.16 (m, 2H), 7.36 (d, *J* = 8.8 Hz, 2H), 7.43-7.45 (m, 3H), 7.68-7.77 (m, 3H), 12.10 (s, 1H); ^{13}C

NMR (100 MHz, $CDCl_3$) δ 45.0, 49.1, 54.3, 55.7, 113.9, 118.9, 125.0, 125.1, 125.8, 126.2, 126.3, 127.1, 127.4, 127.6, 127.7, 128.3, 128.6, 129.0, 129.4, 129.8, 131.1, 131.5, 132.3, 133.3, 141.1, 144.3, 150.6, 163.2, 207.7; HRMS (ESI, m/z): calcd. for $C_{35}H_{29}NO_4S(M+H)^+$: 560.1896, found: 560.1894; $[\alpha]_D^{20}$: -143.2 (*c* 1.5, $CHCl_3$); HPLC analysis: 92% ee (Chiralcel AS-H, 10:90 ^{i}PrOH/Hexane, 0.75 mL/min), R_t (minor) = 65.2 min, R_t (major) =92.0 min.



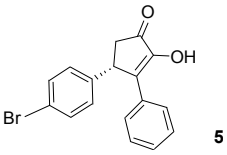
3o

***N*-((*Z*)-((2*R*,3*R*)-2-(4-bromophenyl)-3-(furan-2-yl)-5-oxocyclopentylidene)(phenyl)methyl)-4-methoxy benzenesulfonamide (3o)**: Yellowish thick oil, 35.7 mg, 62% yield, ^{1}H NMR (400 MHz, $CDCl_3$)δ 2.69-2.75 (dd, *J* = 6.4, 18.4 Hz, 1H), 2.83-2.89 (dd, *J* = 8.4, 8.4 Hz, 1H), 3.24-3.29 (m, 1H), 3.85 (s, 3H), 3.86 (d, *J* = 5.2 Hz, 1H), 5.84 (d, *J* = 3.2 Hz, 1H), 6.22 (d, *J* = 2.0 Hz, 1H), 6.57 (d, *J* = 8.4 Hz, 2H), 6.66 (d, *J* = 7.6 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 2H), 7.02 (t, *J* = 7.6 Hz, 2H), 7.14-7.19 (m, 3H), 7.26-7.32 (m, 3H), 11.97 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.5, 42.6, 50.8, 55.7, 105.6, 110.2, 113.9, 117.7, 120.1, 127.5, 128.9, 129.0, 129.6, 129.8, 130.9, 131.3, 131.4, 141.9, 142.6, 150.9, 155.3, 163.3, 206.3; HRMS (ESI, m/z): calcd. for $C_{29}H_{24}BrNO_5S(M+H)^+$: 578.0637, found: 578.0635; $[\alpha]_D^{20}$: +22.6 (*c* 1.7, $CHCl_3$); HPLC analysis: 90% ee (Chiralcel OD-H, 10:90 ^{i}PrOH/Hexane, 0.75 mL/min), R_t (minor) = 26.1 min, R_t (major) = 47.5 min.



3p

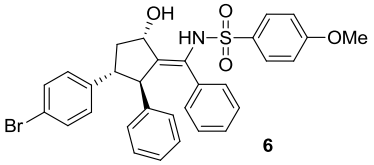
***N*-((*Z*)-((2*R*,3*R*)-2-(4-Bromophenyl)-3-hexyl-5-oxocyclopentylidene)(phenyl)methyl)-4-methoxybenzene sulfonamide (3p)**: Yellowish thick oil, 32.5 mg, 55% yield, ^{1}H NMR (400 MHz, $CDCl_3$)δ 0.83 (t, *J* = 7.2 Hz, 3H), 1.16-1.37 (m, 10H), 1.94-1.98 (m, 1H), 2.15-2.21 (dd, *J* = 6.8, 6.8 Hz, 1H), 2.64-2.71 (dd, *J* = 7.6, 8.0 Hz, 1H), 3.34 (d, *J* = 5.2 Hz, 1H), 3.85 (s, 3H), 6.50 (d, *J* = 8.4 Hz, 2H), 6.65 (d, *J* = 7.2 Hz, 2H), 6.79 (d, *J* = 6.8 Hz, 2H), 7.01 (t, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 6.8 Hz, 2H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.26-7.32 (m, 2H), 11.98 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 22.5, 27.4, 29.1, 31.6, 34.9, 43.9, 51.8, 55.7, 113.9, 119.0, 119.6, 127.4, 128.9, 129.0, 129.4, 129.8, 131.1, 131.5, 143.8, 150.3, 163.2, 208.0; HRMS (ESI, m/z): calcd. for $C_{31}H_{34}BrNO_4S(M+H)^+$: 596.1470, found: 596.1473; $[\alpha]_D^{20}$: +261.9 (*c* 1.1, $CHCl_3$); HPLC analysis: 92% ee (Chiralcel OD-H, 10:90 ^{i}PrOH/Hexane, 0.75 mL/min), R_t (minor) = 13.4 min, R_t (major) = 22.2 min.



5

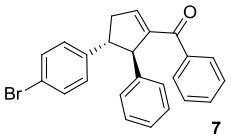
(*S*)-4-(4-Bromophenyl)-2-hydroxy-3-phenylcyclopent-2-enone (5): White solid, 24 mg, 73% yield, ^{1}H NMR (400 MHz, $CDCl_3$)δ 2.32-2.37 (dd, *J* = 1.2, 19.2 Hz, 1H), 3.07-3.14 (dd, *J* = 6.8, 19.2 Hz, 1H), 4.47-4.49 (dd, *J* = 1.2, 6.8 Hz, 1H), 6.42 (s, 1H), 7.06 (d, *J* = 8.4 Hz, 2H), 7.30-7.39 (m, 5H), 7.74-7.76 (dd, *J* = 1.2, 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 41.1, 42.3, 120.7, 128.5, 128.7, 128.8, 129.3, 132.2, 132.5, 138.9, 142.4, 149.2, 201.5; HRMS (ESI, m/z): calcd. for $C_{17}H_{13}BrO_2(M+H)^+$: 329.0177, found: 329.0174; $[\alpha]_D^{20}$:

+152.1 (*c* 1.0, $CHCl_3$); HPLC analysis: 96% ee (Chiralcel IA, 10:90 ^{i}PrOH/Hexane, 0. 50 mL/min), R_t (minor) = 17.8 min, R_t (major) =25.5 min.



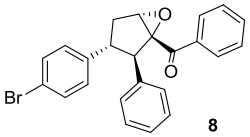
6

***N*-((*Z*)-((2*R*,3*R*,5*S*)-3-(4-bromophenyl)-5-hydroxy-2-phenylcyclopentylidene)(phenyl)methyl)-4-methoxybenzenesulfonamide (6):** Colorless oil, 53 mg, 91% yield, ^{1}H NMR (400 MHz, $CDCl_3$)δ 1.87-1.94 (m, 1H), 2.43 (s, br, 1H), 2.46-2.52 (m, 1H), 2.96-3.00 (m, 1H), 3.68 (d, *J* = 4.4 Hz, 1H), 3.88 (s, 3H), 5.00 (s, 1H), 6.54-6.56 (m, 2H), 6.83-7.07 (m, 12H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.8 Hz, 2H), 8.38 (s, br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 41.8, 51.2, 55.4, 55.7, 74.9, 113.9, 120.3, 126.0, 127.4, 127.5, 128.1, 128.2, 128.8, 129.3, 129.7, 131.6, 131.9, 134.7, 134.9, 135.2, 142.5, 144.8, 162.9; HRMS (ESI, m/z): calcd. for $C_{31}H_{29}BrNO_4S(M+H)^+$: 590.1001, found: 590.1005; $[\alpha]_D^{20}$: -190.8 (*c* 1.25, $CHCl_3$); HPLC analysis: 94% ee (Chiralcel OD-H, 20:80 ^{i}PrOH/Hexane, 0.60 mL/min), R_t (minor) = 20.8 min, R_t (major) =19.2 min.



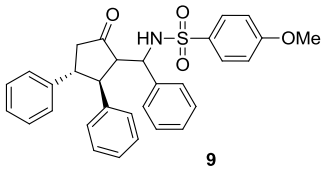
7

(3*S*,4*R*)-2-Benzoyl-4-(4-bromophenyl)-3-phenylcyclopentanone (7): Yellowish thick oil, 35 mg, 87% yield, ^{1}H NMR (400 MHz, $CDCl_3$)δ 2.72-2.79 (m, 1H), 2.21-2.28 (m, 1H), 3.42-3.46 (m, 1H), 4.42-4.44 (m, 1H), 6.67 (d, *J* = 2.0 Hz, 1H), 7.06 (d, *J* = 7.2 Hz, 2H), 7.11-7.17 (m, 3H), 7.21-7.24 (m, 2H), 7.40-7.47 (m, 4H), 7.54 (t, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 41.6, 53.5, 59.9, 120.3, 126.6, 127.2, 128.3, 128.6, 128.9, 129.1, 131.7, 132.4, 138.2, 143.2, 143.4, 143.7, 146.0, 192.9; HRMS (ESI, m/z): calcd. for $C_{24}H_{19}BrO(M+H)^+$: 403.0698, found: 403.0698; $[\alpha]_D^{20}$: -144.6 (*c* 0.7, $CHCl_3$); HPLC analysis: 90% ee (Chiralcel OD-H, 10:90 ^{i}PrOH/Hexane, 0.50 mL/min), R_t (minor) = 16.2 min, R_t (major) =13.5 min.



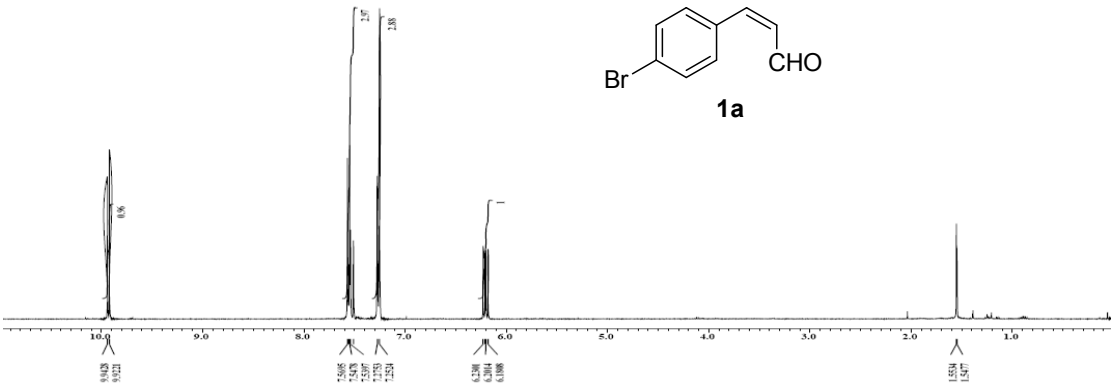
8

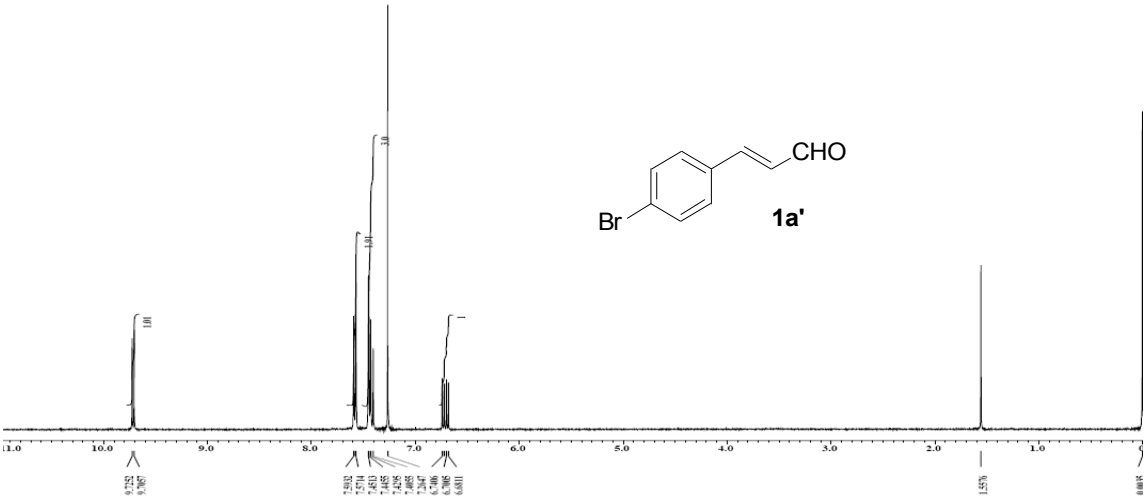
((1*R*,2*R*,3*R*,5*S*)-3-(4-bromophenyl)-2-phenyl-6-oxabicyclo[3.1.0]hexan-1-yl)(phenyl)methanone (8): Colorless wax, 26 mg, 67% yield, ^{1}H NMR (400 MHz, $CDCl_3$)δ 2.16 (dd, *J* = 10.8, 15.6 Hz, 1H), 2.66 (dd, *J* = 7.2, 15.6 Hz, 1H), 3.11-3.18 (m, 1H), 3.80 (s, 1H), 3.98 (d, *J* = 10.8 Hz, 1H), 7.00 (d, *J* = 4.0 Hz, 2H), 7.15-7.28 (m, 5H), 7.35-7.53 (m, 5H), 7.96 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 36.2, 46.5, 53.7, 60.6, 72.4, 120.6, 127.2, 128.1, 128.3, 128.5, 129.3, 129.6, 131.5, 133.3, 135.3, 138.1, 139.6, 196.3; HRMS (ESI, m/z): calcd. for $C_{24}H_{20}BrO_2(M+H)^+$: 419.0647, found: 419.0644; $[\alpha]_D^{20}$: -98.6 (*c* 0.6, $CHCl_3$); HPLC analysis: 88% ee (Chiralcel IC, 10:90 ^{i}PrOH/Hexane, 0.60 mL/min), R_t (minor) = 18.6 min, R_t (major) =17.5 min.

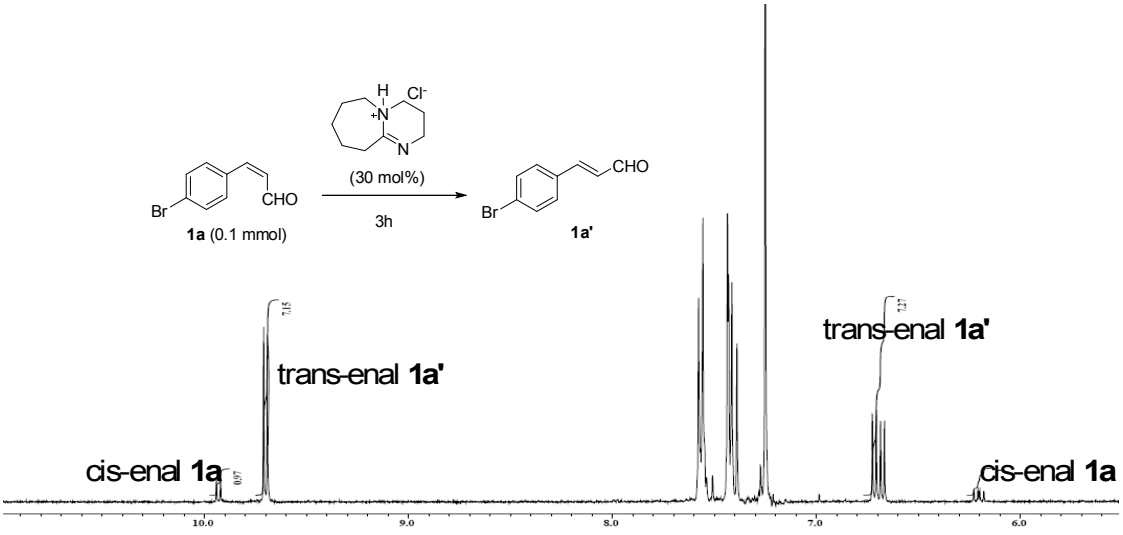


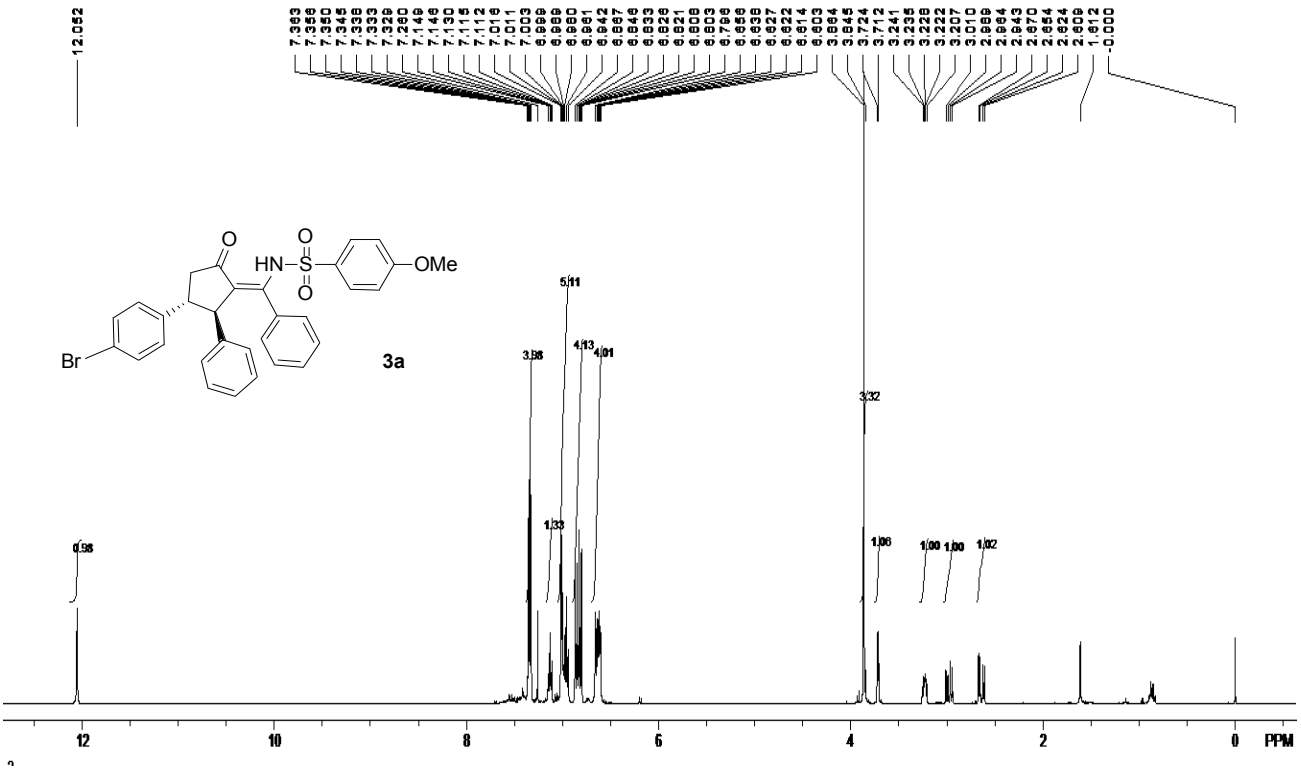
9

4-methoxy-N-(((2*S*,3*R*)-5-oxo-2,3-diphenylcyclopentyl)(phenyl)methyl)benzenesulfonamide (9): Colorless oil, 41 mg, 83% yield, ^{1}H NMR (400 MHz, $CDCl_3$)δ 2.19 (dd, *J* = 12.8, 19.2 Hz, 1H major), 2.42 (dd, *J* = 11.6, 19.2 Hz, 1H major), 2.72-2.88 (m, 1H major, 0.68x2H minor), 2.99 (d, *J* = 7.6 Hz, 1H major), 3.07 (dd, *J* = 4.8, 12.4 Hz, 0.68x1H minor), 3.17-3.36 (m, 1H major, 0.68x3H minor), 3.77 (s, 3H major), 3.80 (s, 0.68x3H minor), 4.41 (dd, *J* = 4.8, 9.2 Hz, 0.68x1H minor), 4.63 (dd, *J* = 2.4, 9.2 Hz, 1H major), 5.34 (d, *J* = 9.6 Hz, 1H major), 6.67-6.74 (m, 3H major, 0.68x3H minor), 6.88-6.96 (m, 7.3H major+minor), 7.05-7.08 (m, 6.7H major+minor), 7.13-7.24 (m, 8.2H major+minor), 7.43 (d, *J* = 8.8 Hz, 0.68x2H minor), 7.50 (d, *J* = 7.2 Hz, 1H major); ^{13}C NMR (100 MHz, $CDCl_3$) δ 46.5, 47.3, 48.1, 48.7, 53.2, 53.3, 55.5, 55.9, 56.8, 60.1, 63.4, 113.8, 113.9, 126.9(1), 126.9(7), 127.0, 127.2, 127.3, 127.4, 127.5, 127.6, 127.8, 127.9, 128.3, 128.4, 128.5, 128.6, 128.8, 128.9, 129.2, 131.9, 132.6, 137.4, 138.2, 138.9, 139.2, 139.6, 140.0, 162.4, 162.7, 214.8, 217.8; HRMS (ESI, m/z): calcd. for $C_{31}H_{30}NO_4S(M+H)^+$: 512.1896, found: 512.1894; $[\alpha]_D^{20}$: -57.9 (*c* 0.7, $CHCl_3$); HPLC analysis: (Chiralcel AD-H, 20:80 ^{i}PrOH/Hexane, 0.6 mL/min), 93% ee (major), R_t (minor) = 41.5 min, R_t (major) =61.0 min; 92% ee (minor), R_t (minor) = 71.6 min, R_t (major) =87.1 min.





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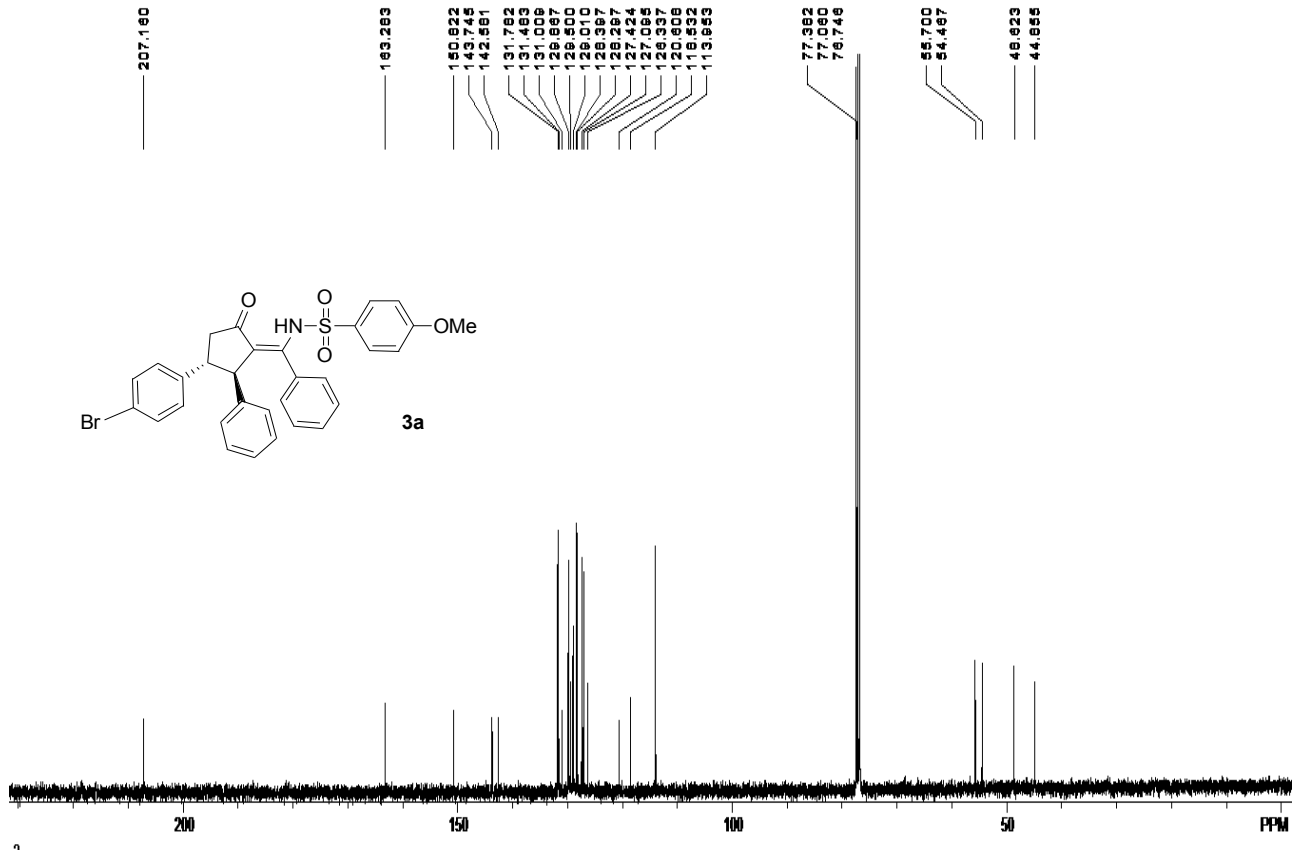
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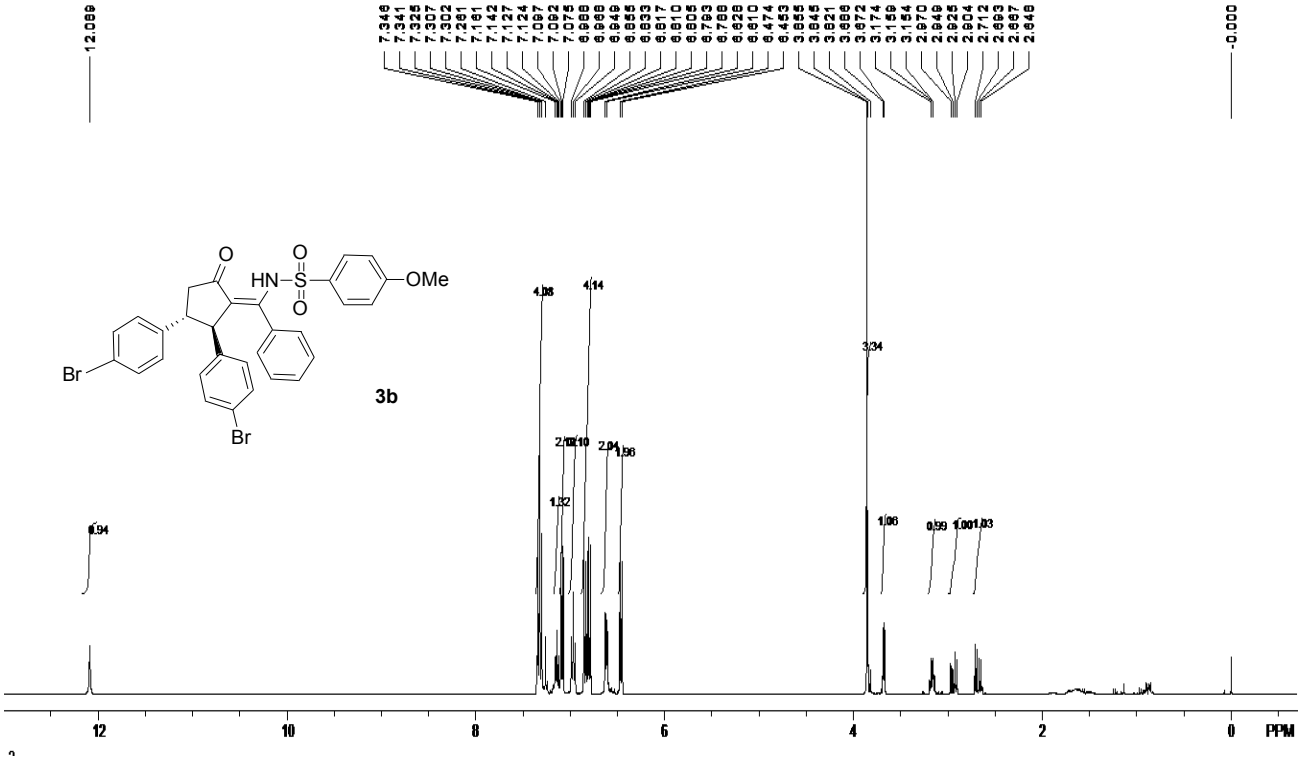
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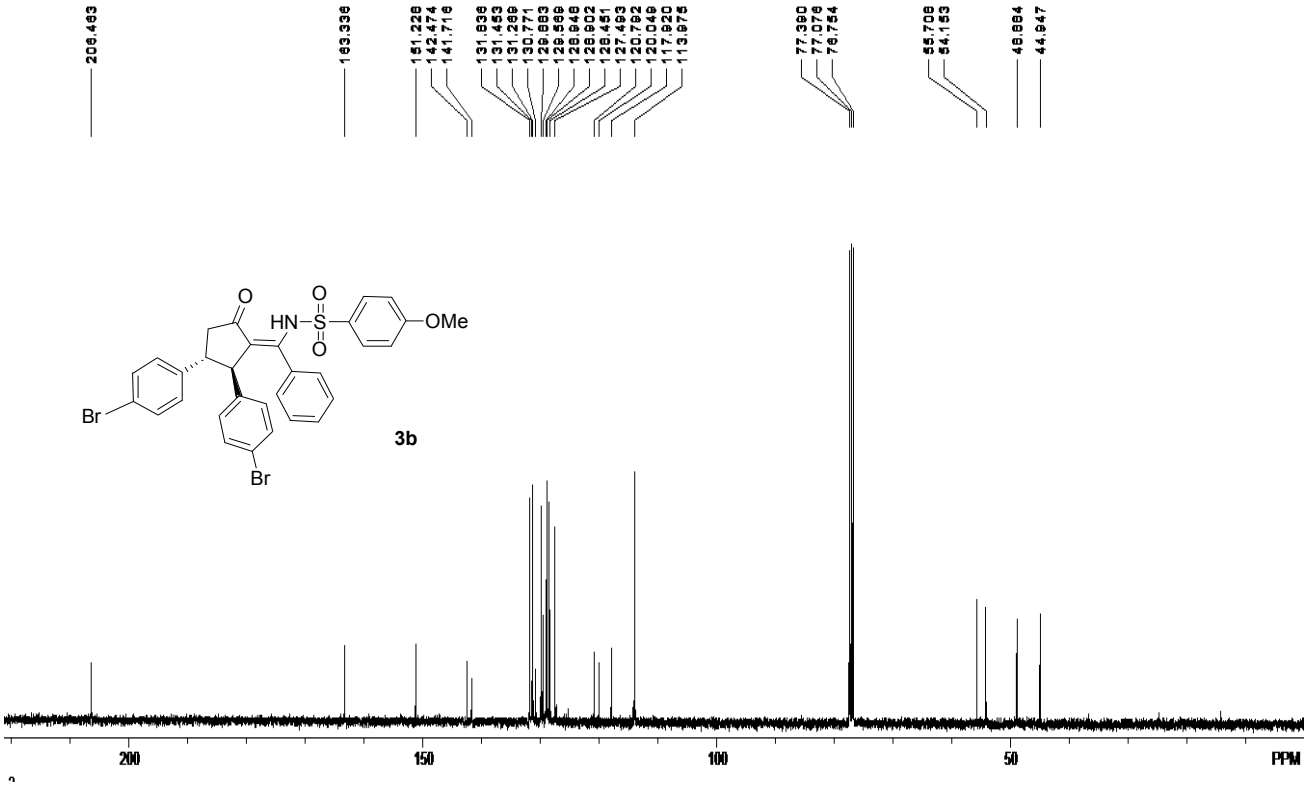
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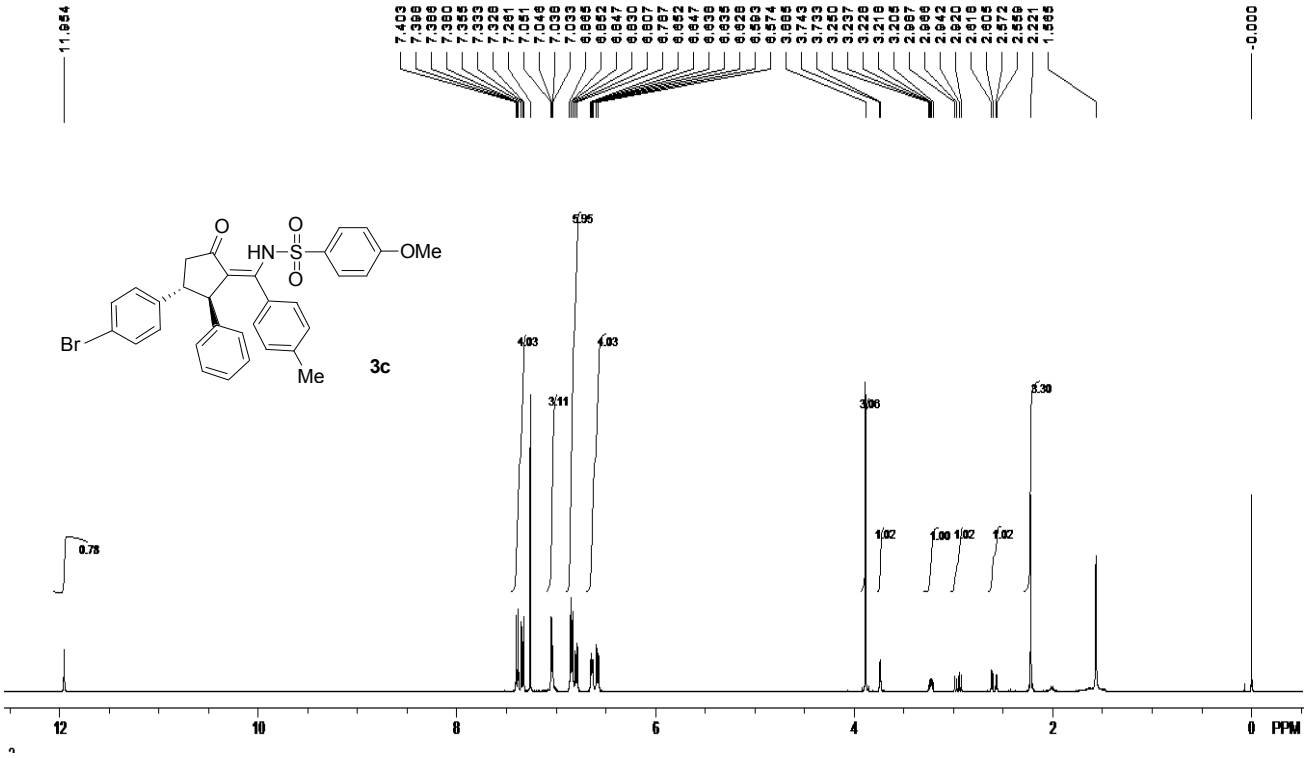
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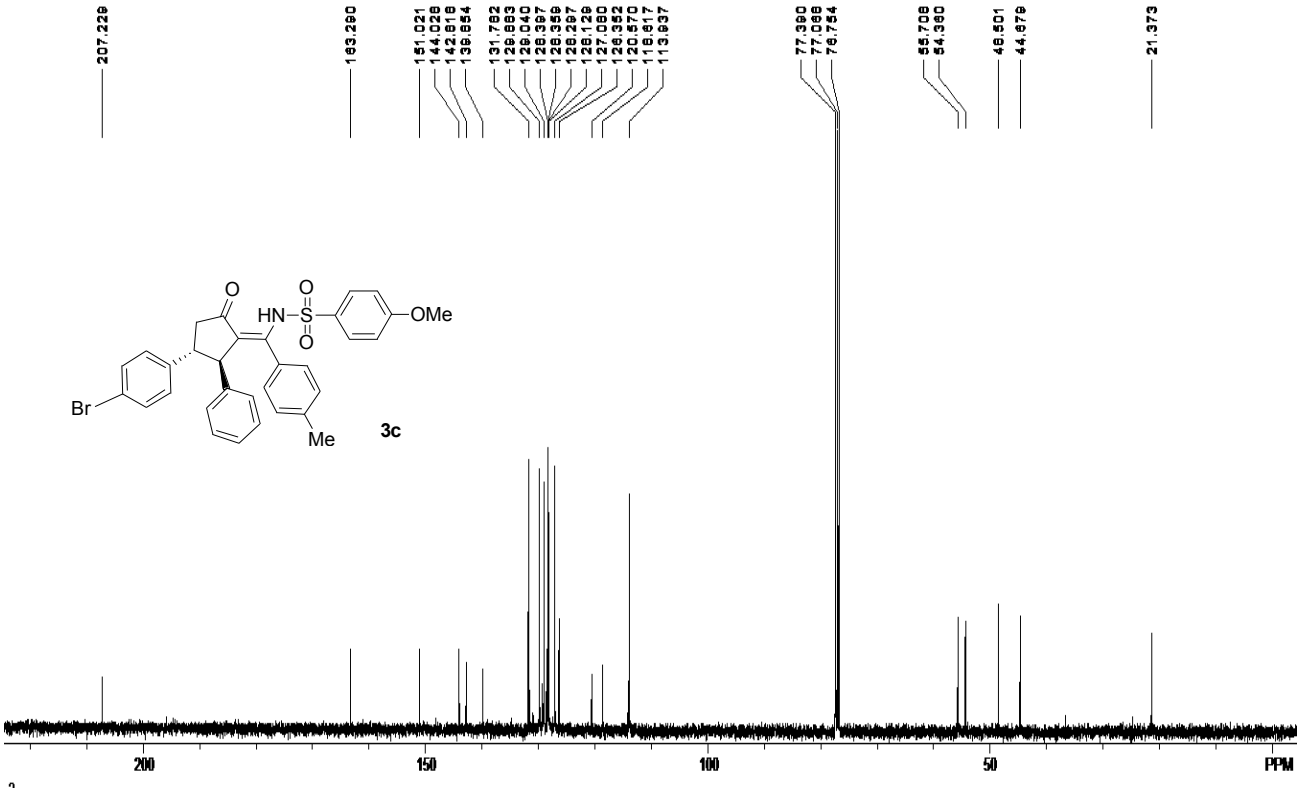
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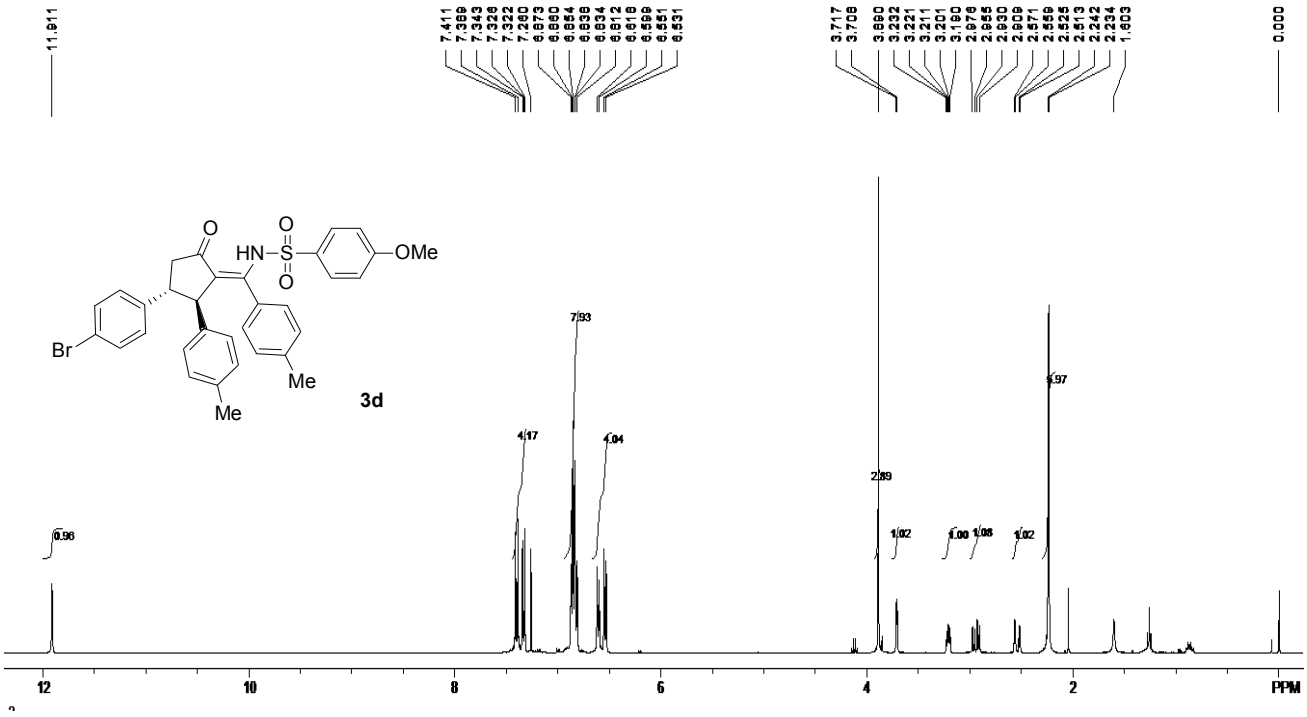
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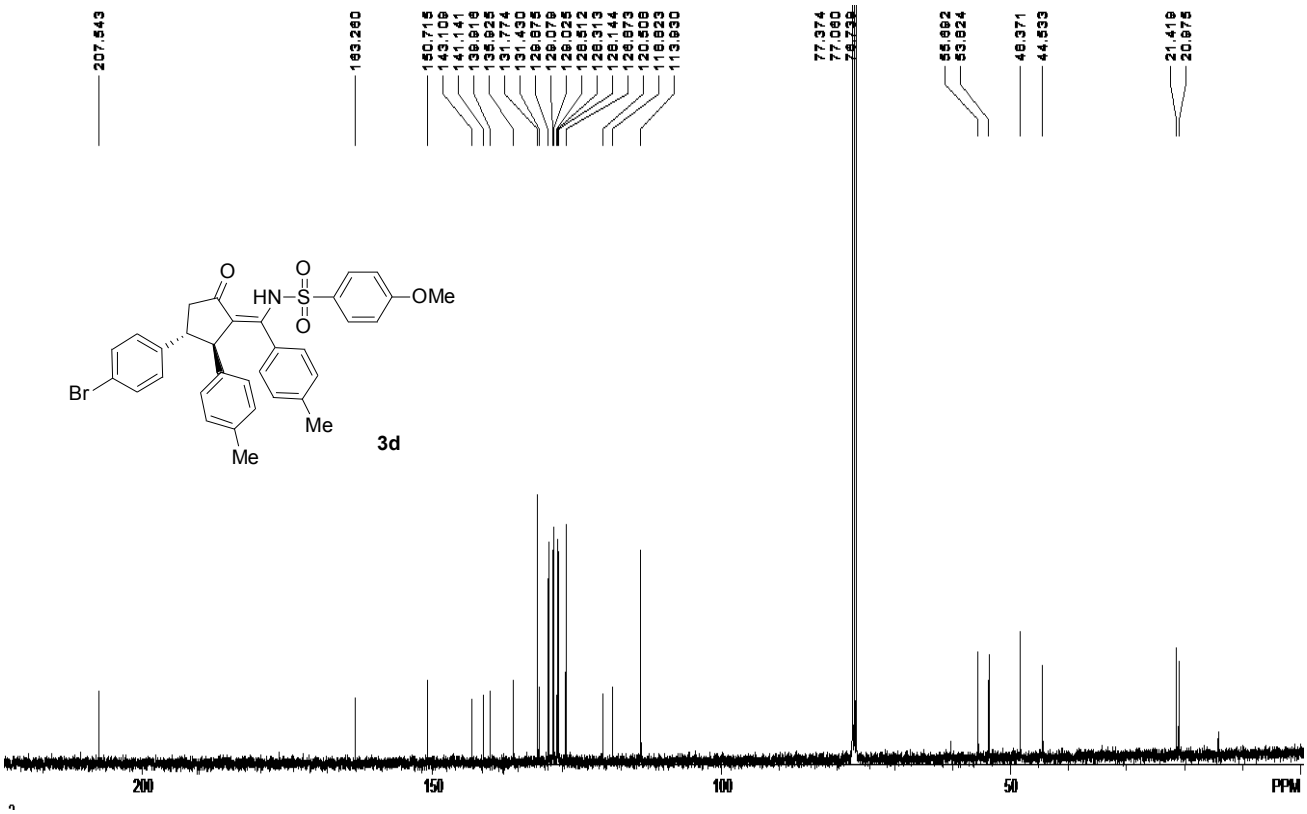
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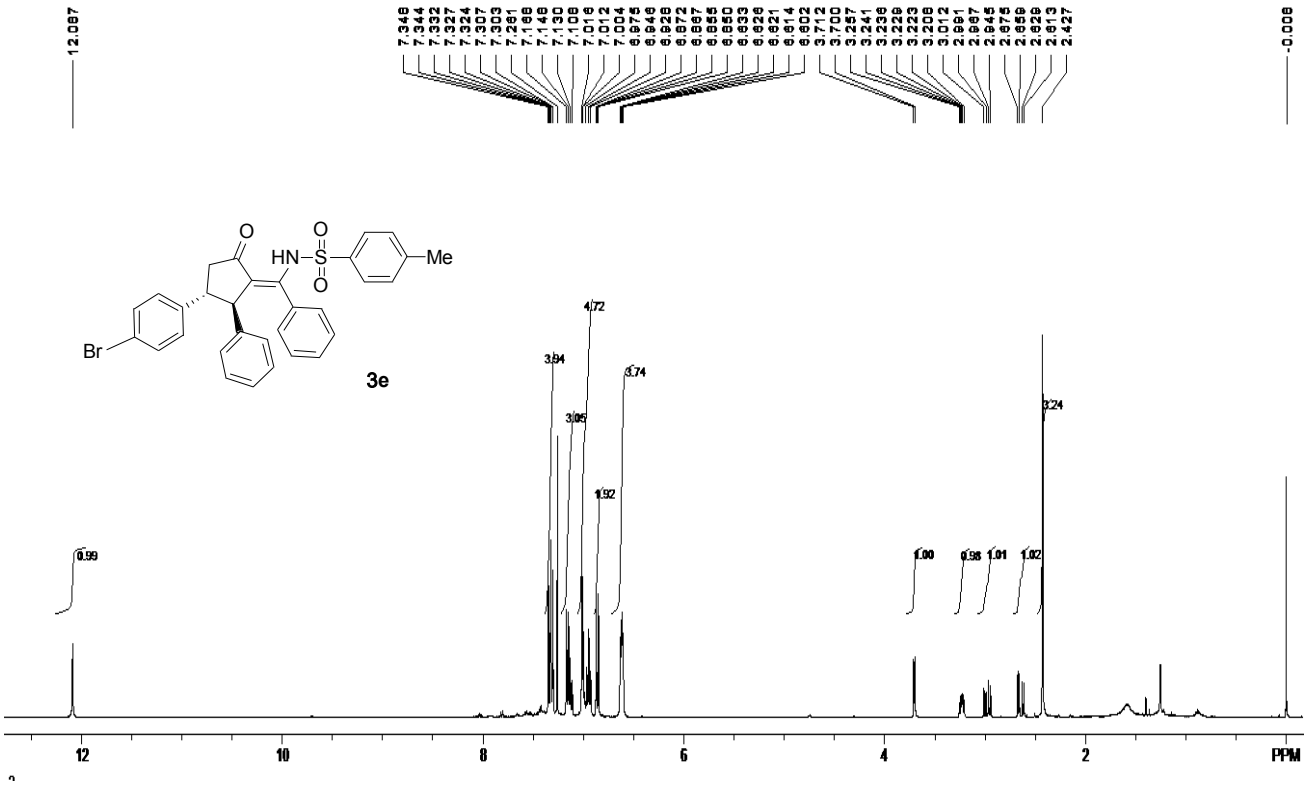

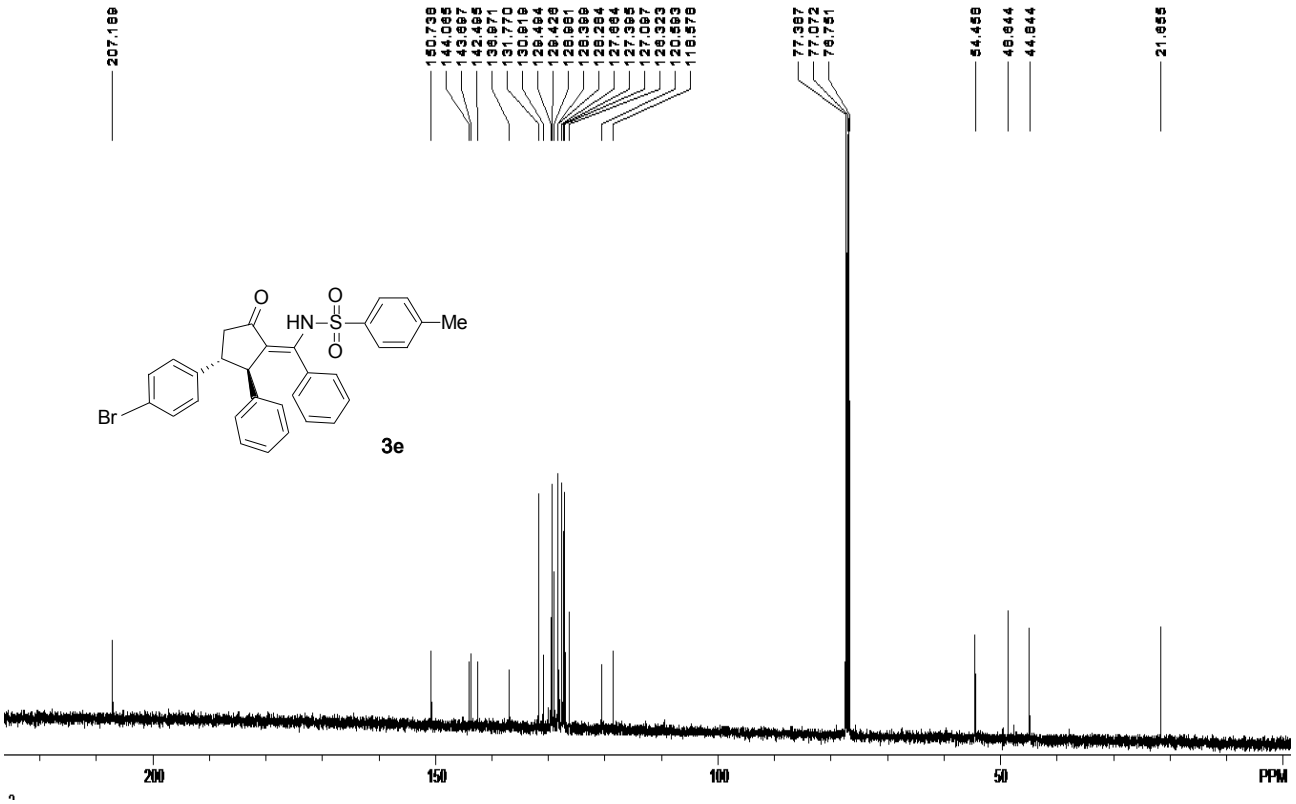

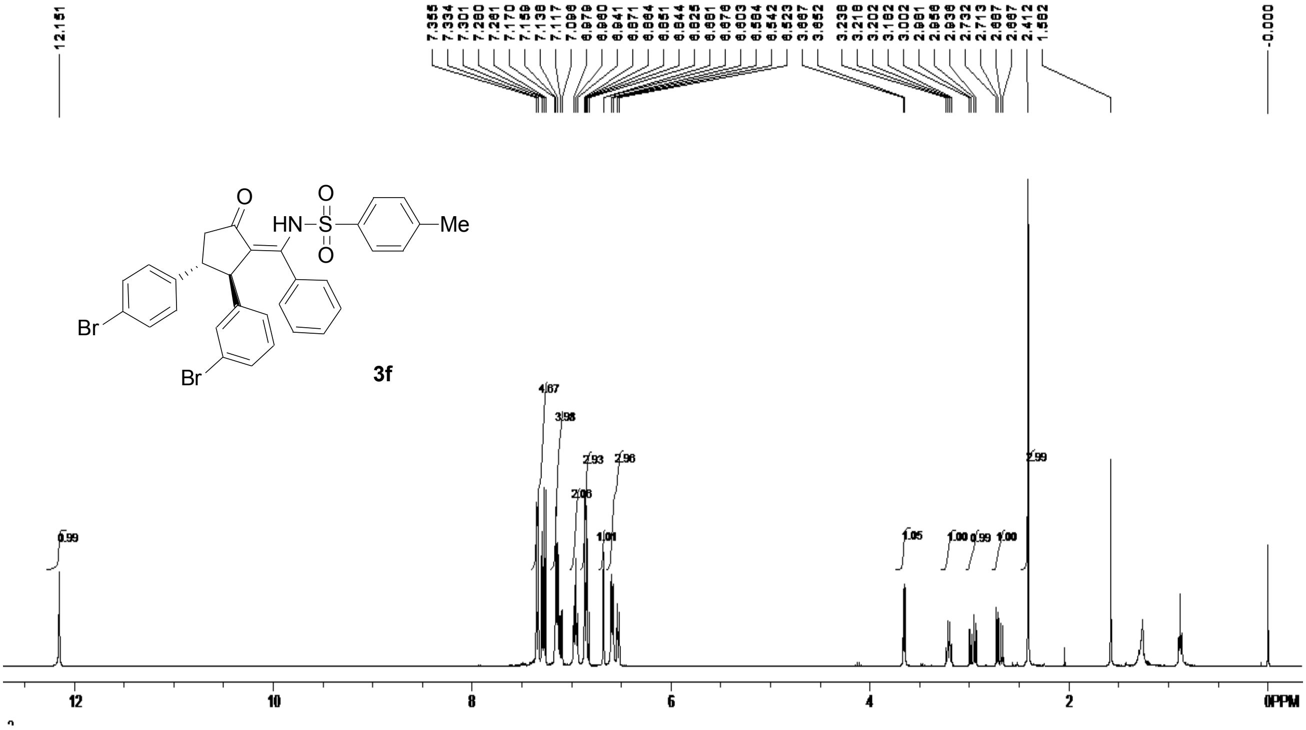
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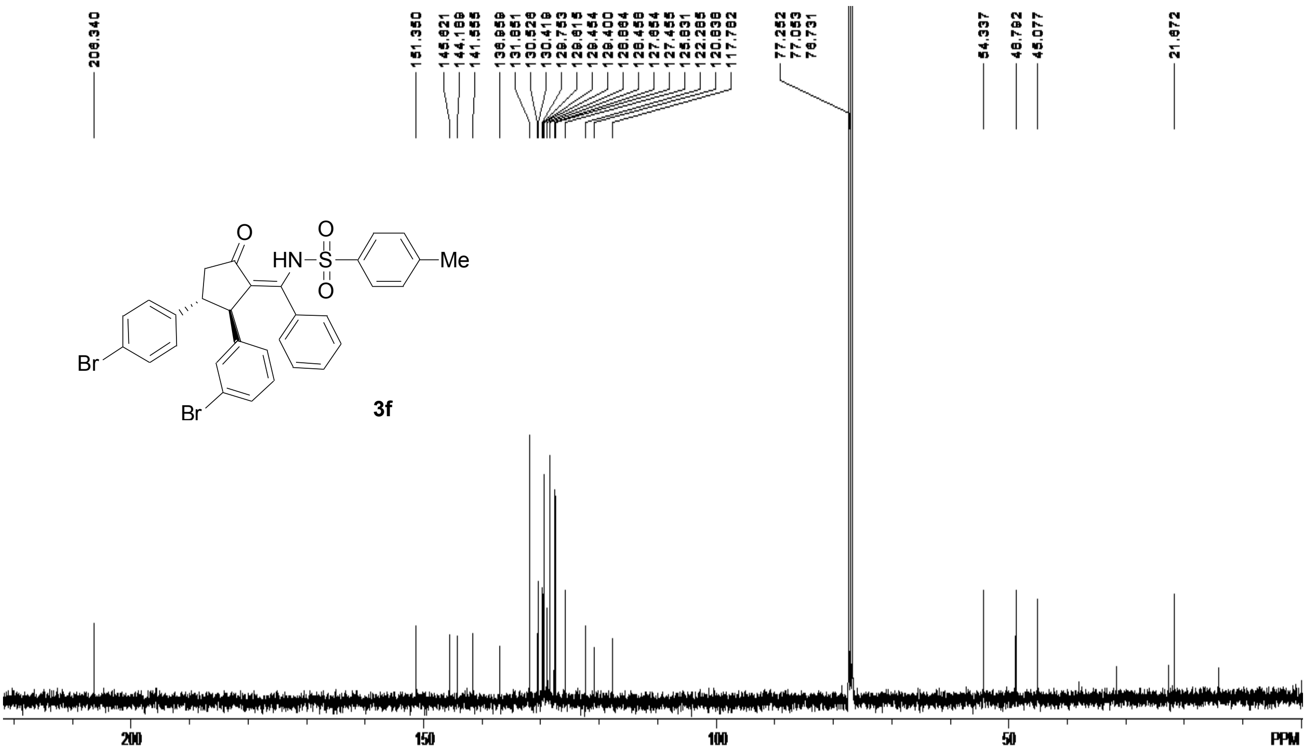
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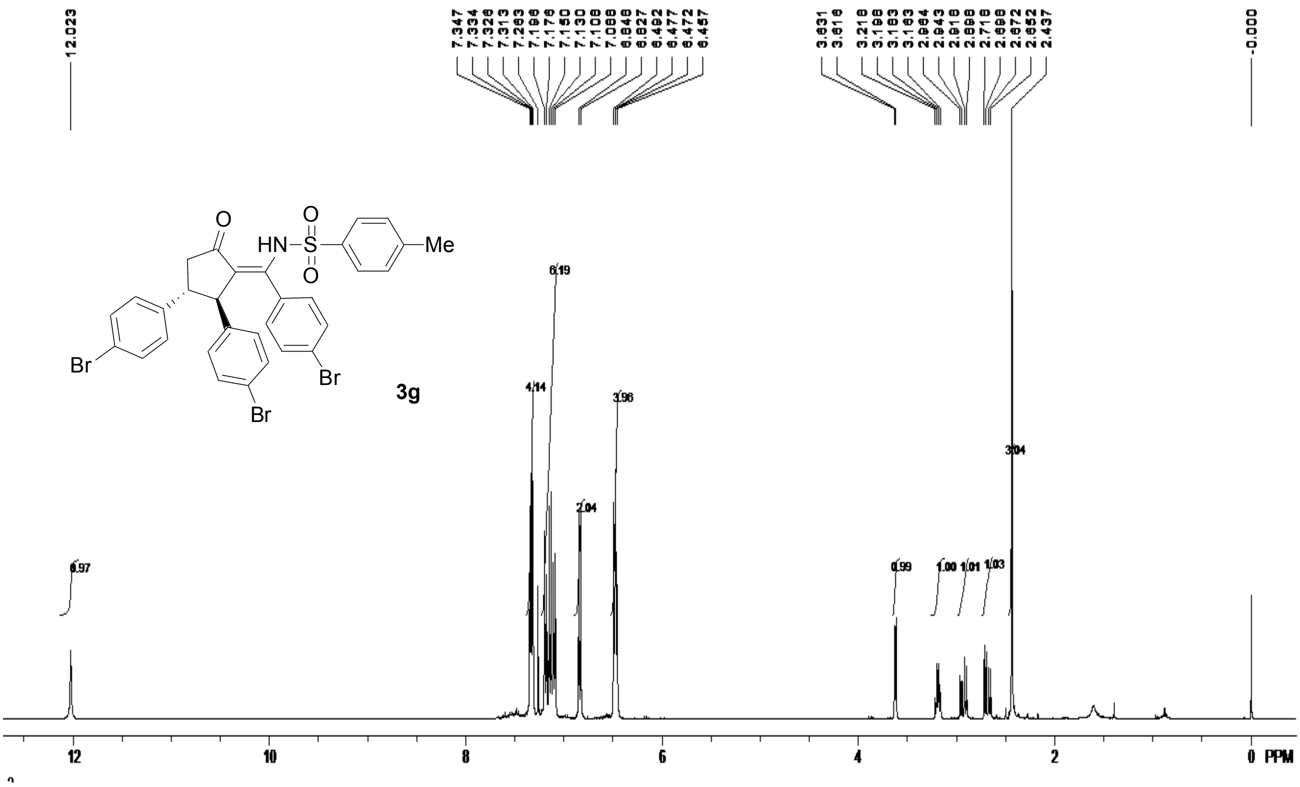
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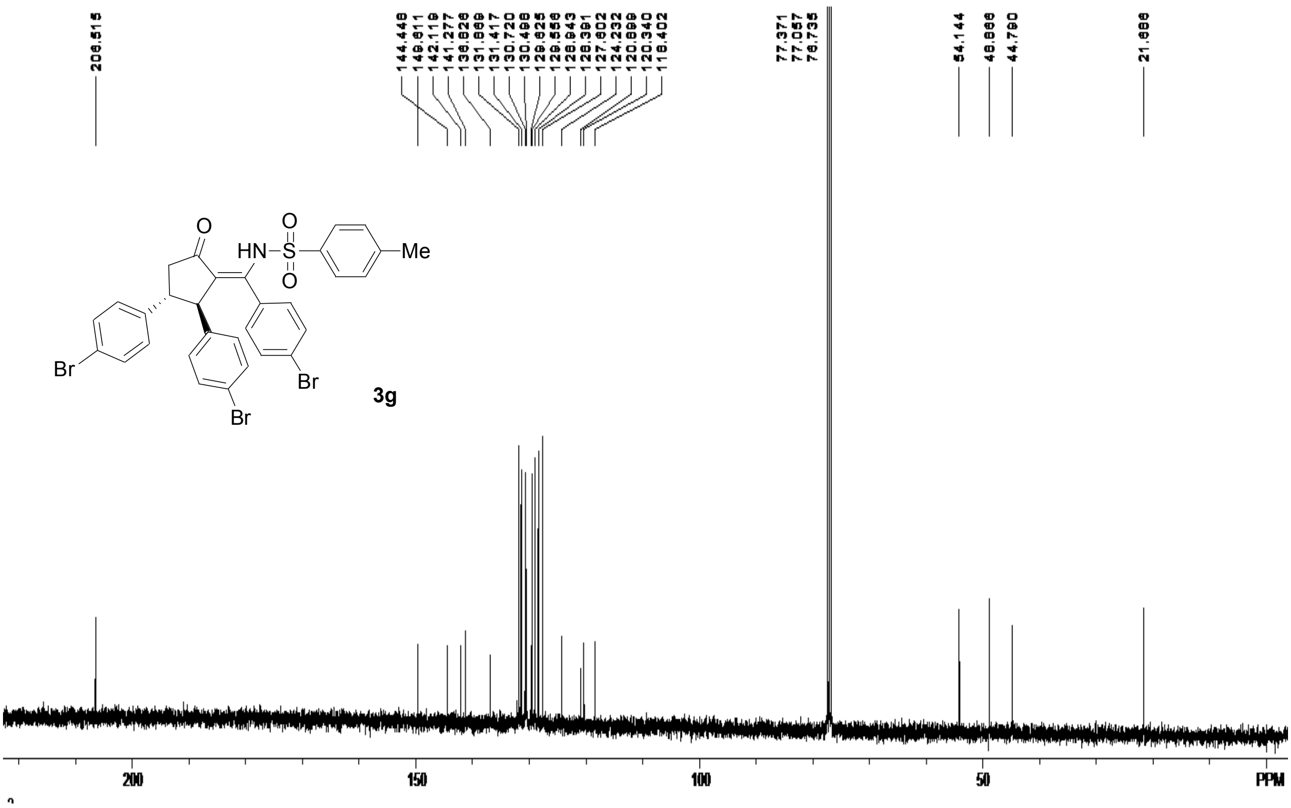
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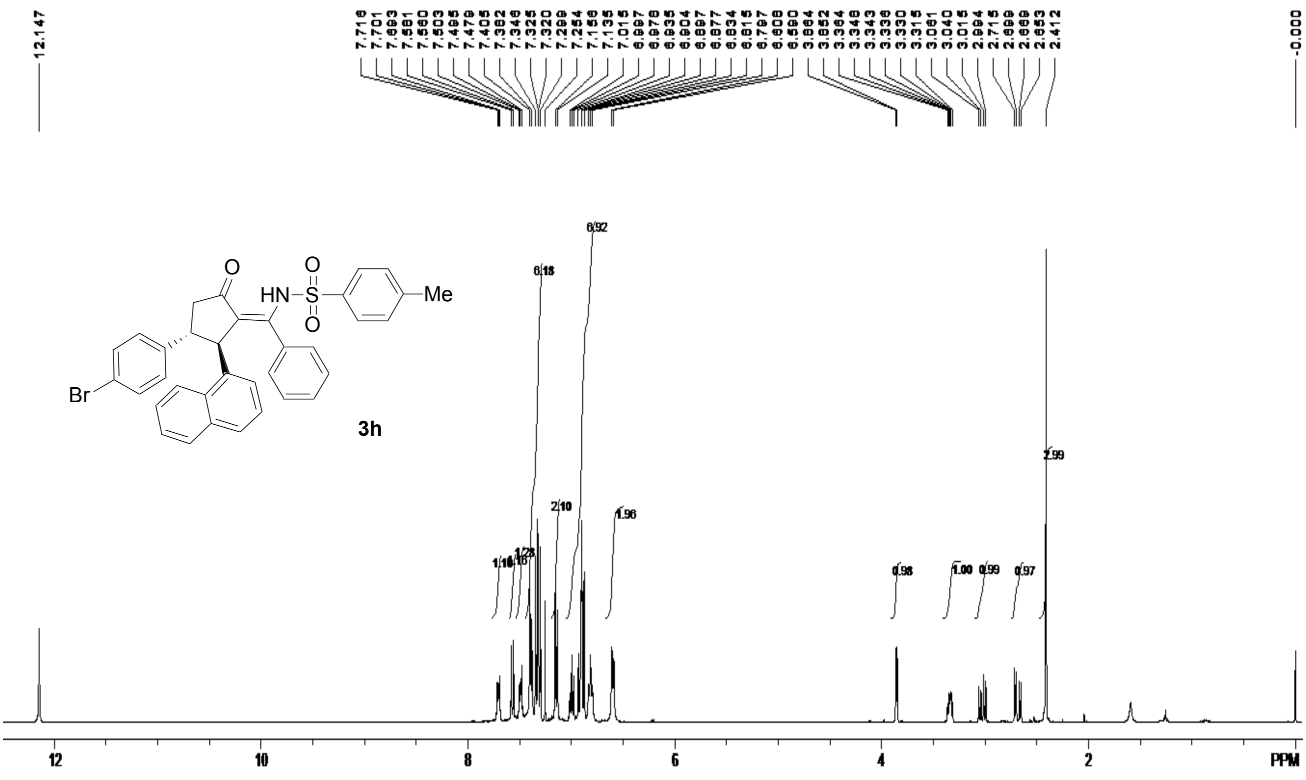
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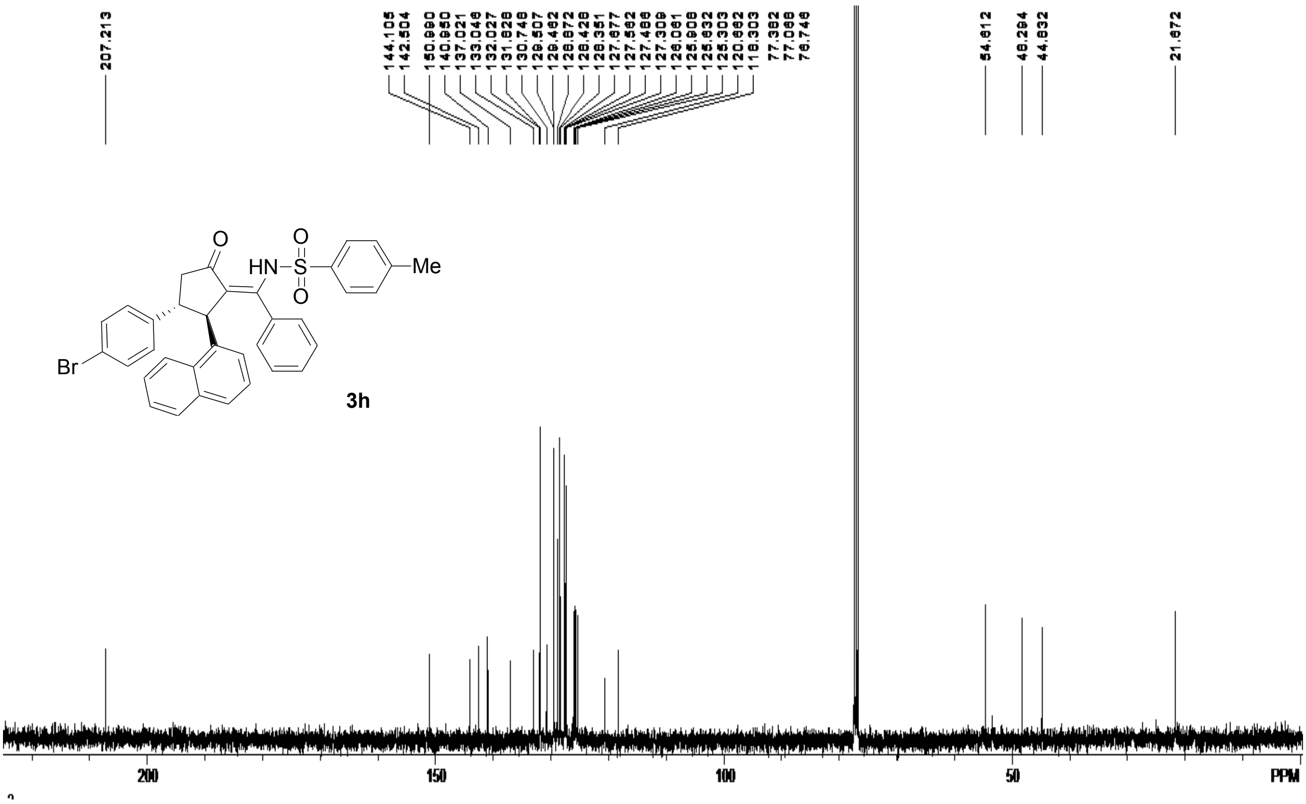
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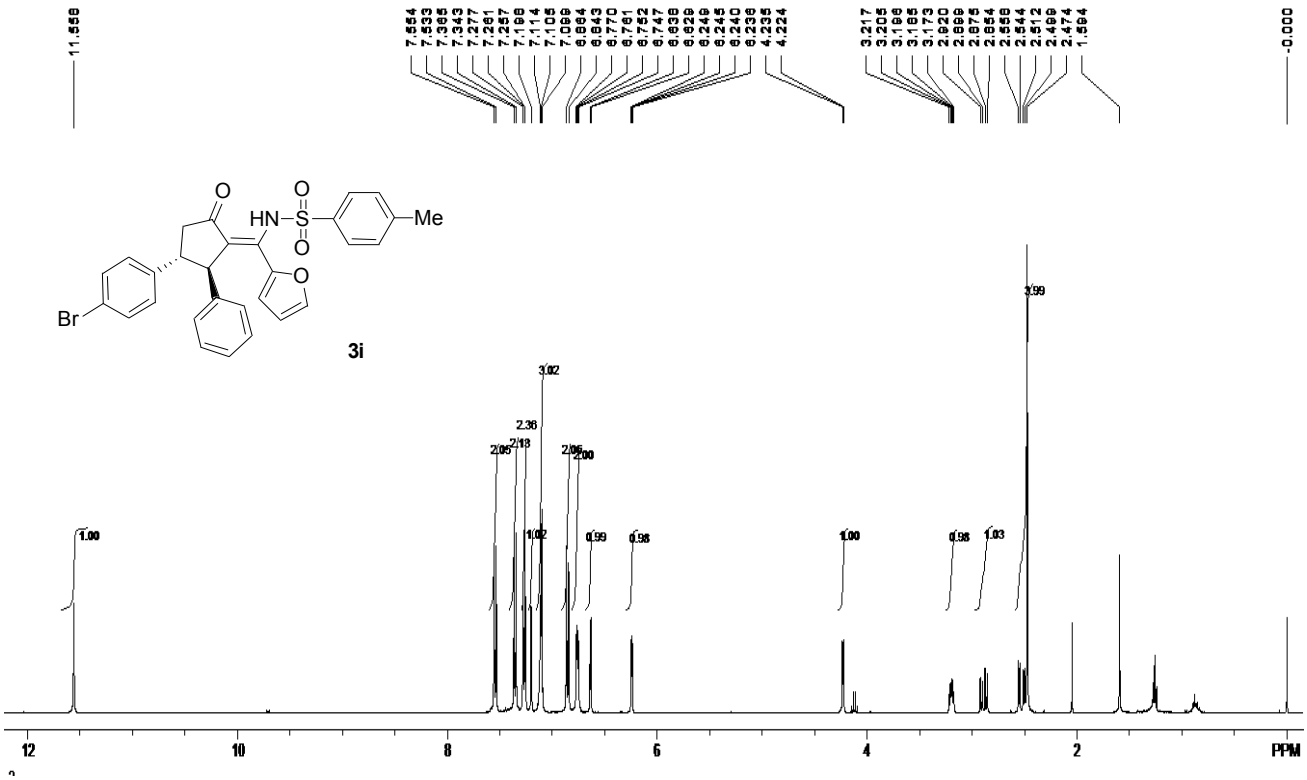
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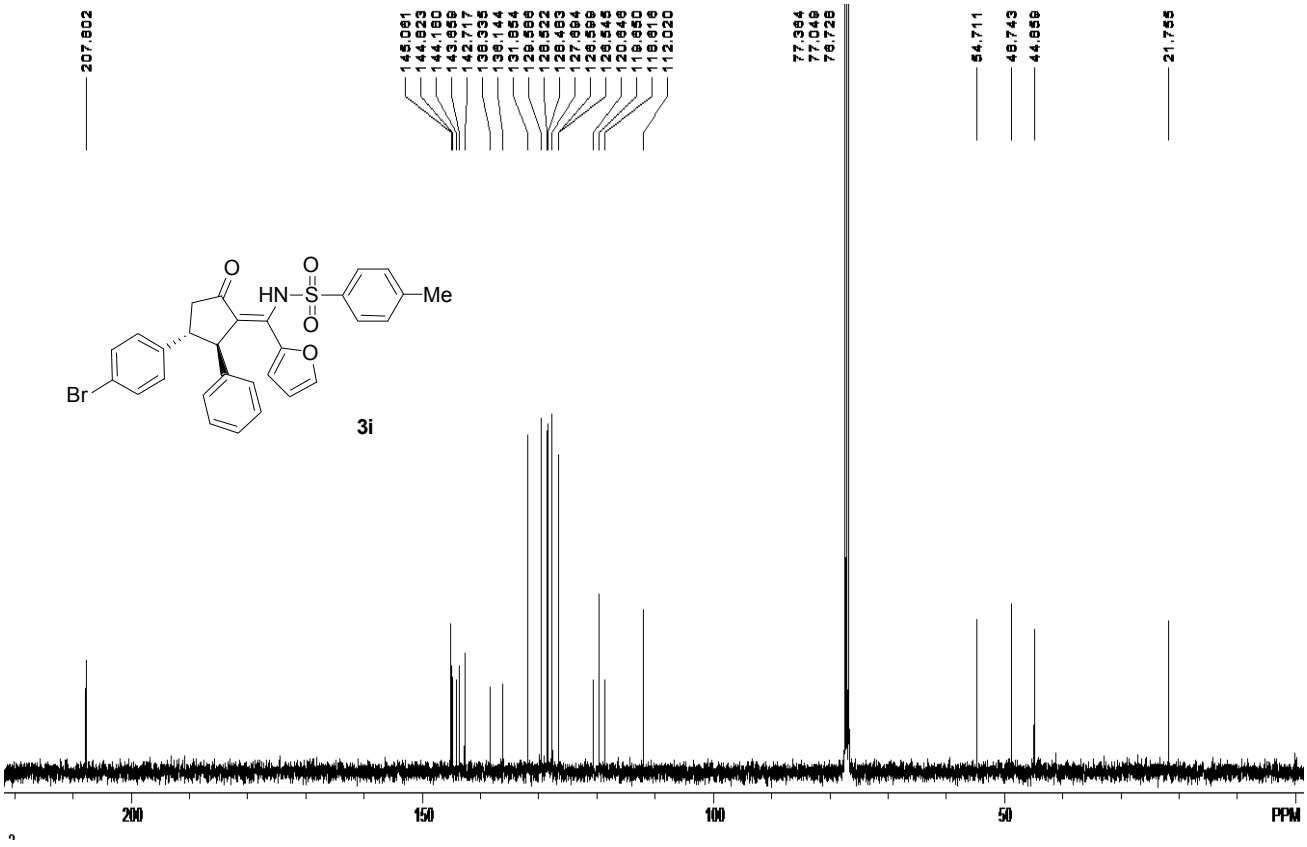
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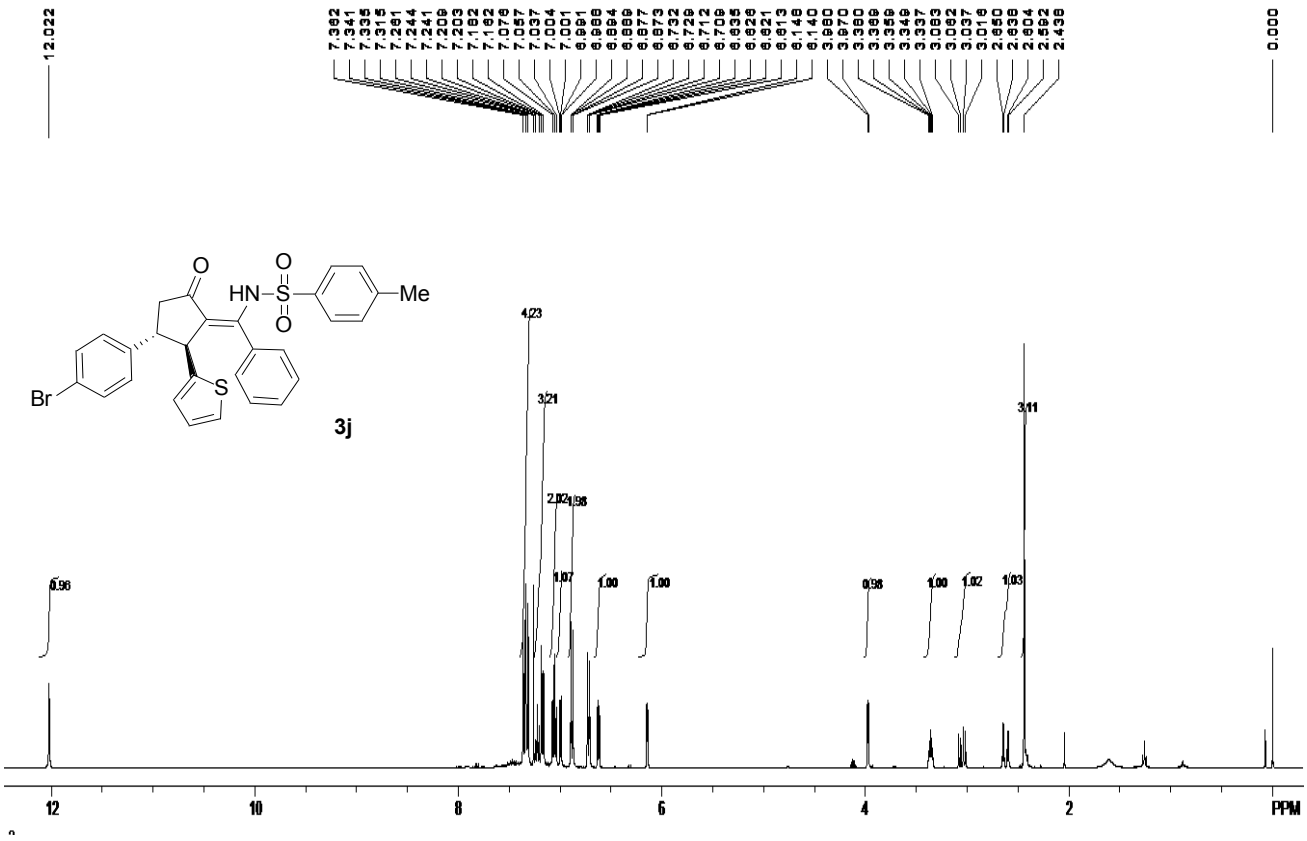
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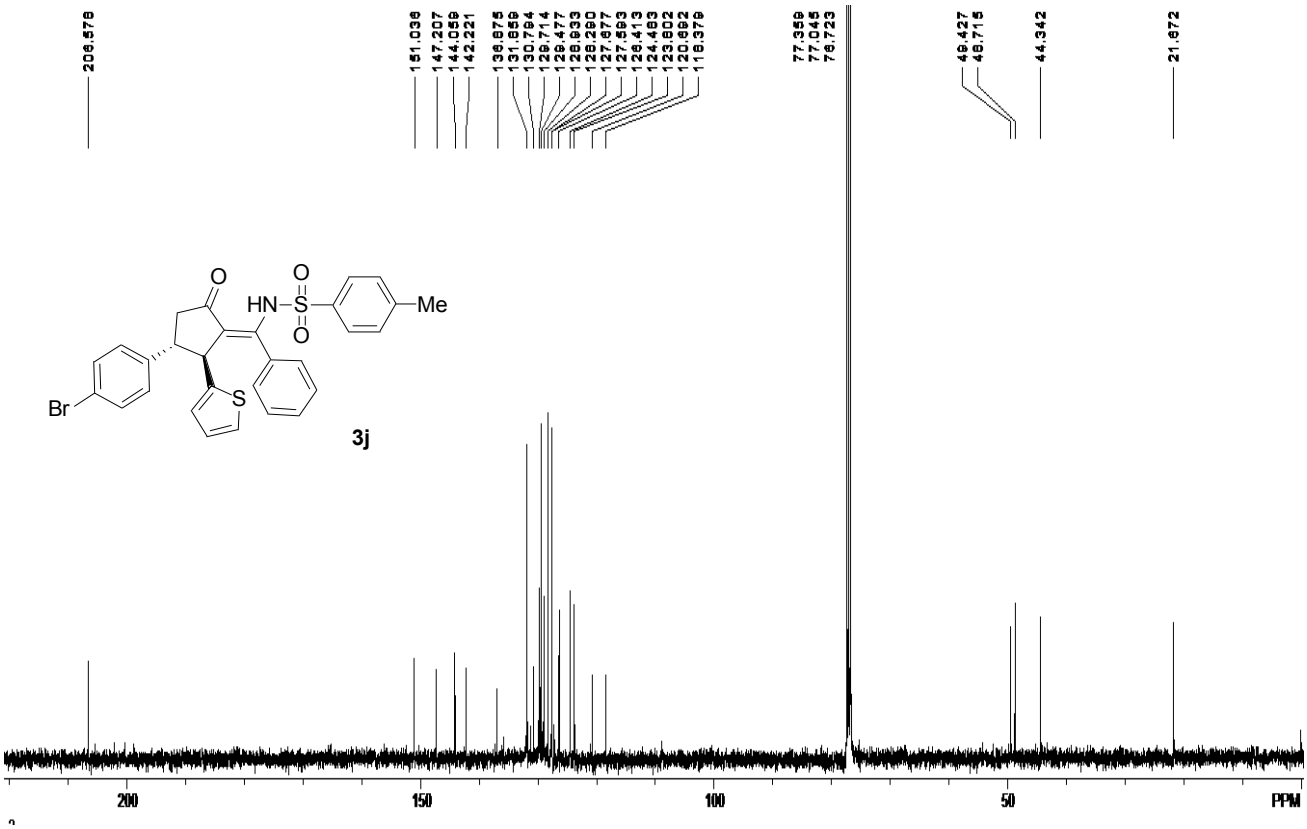
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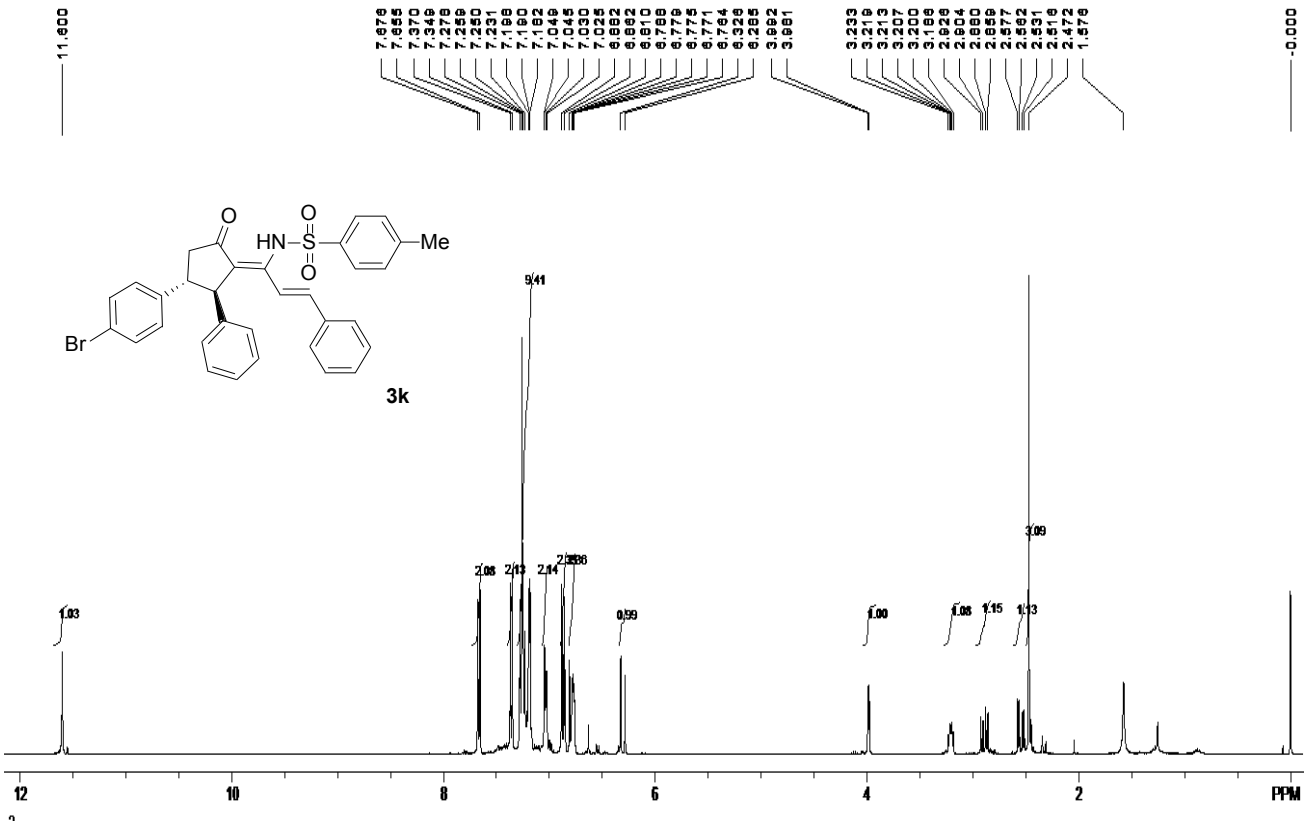
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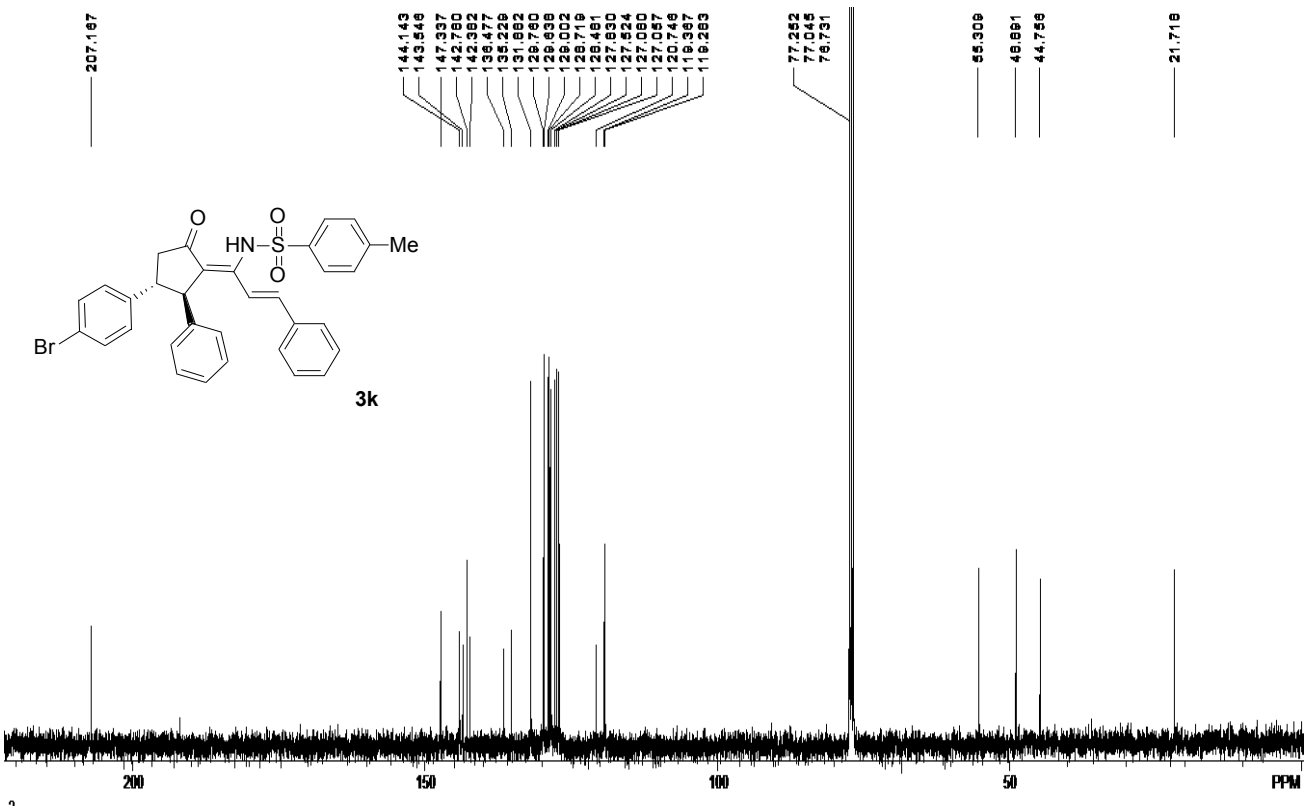
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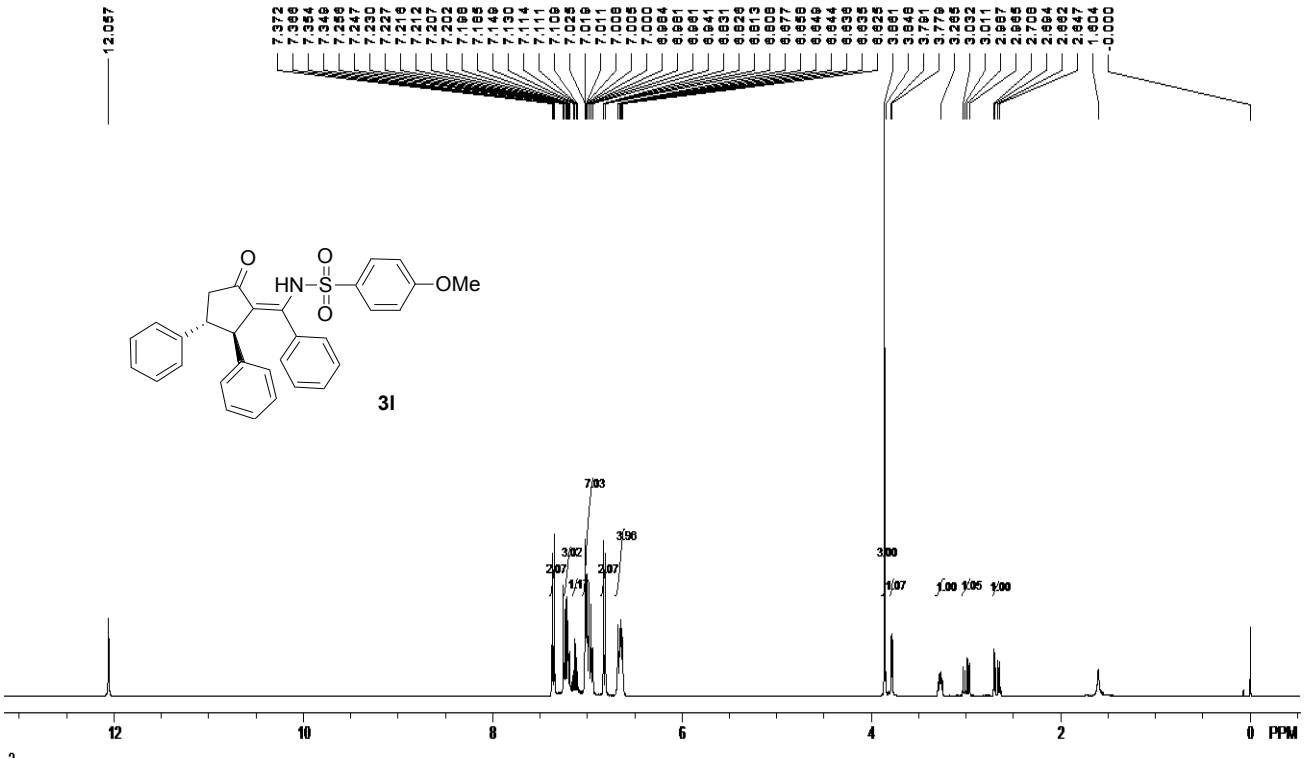
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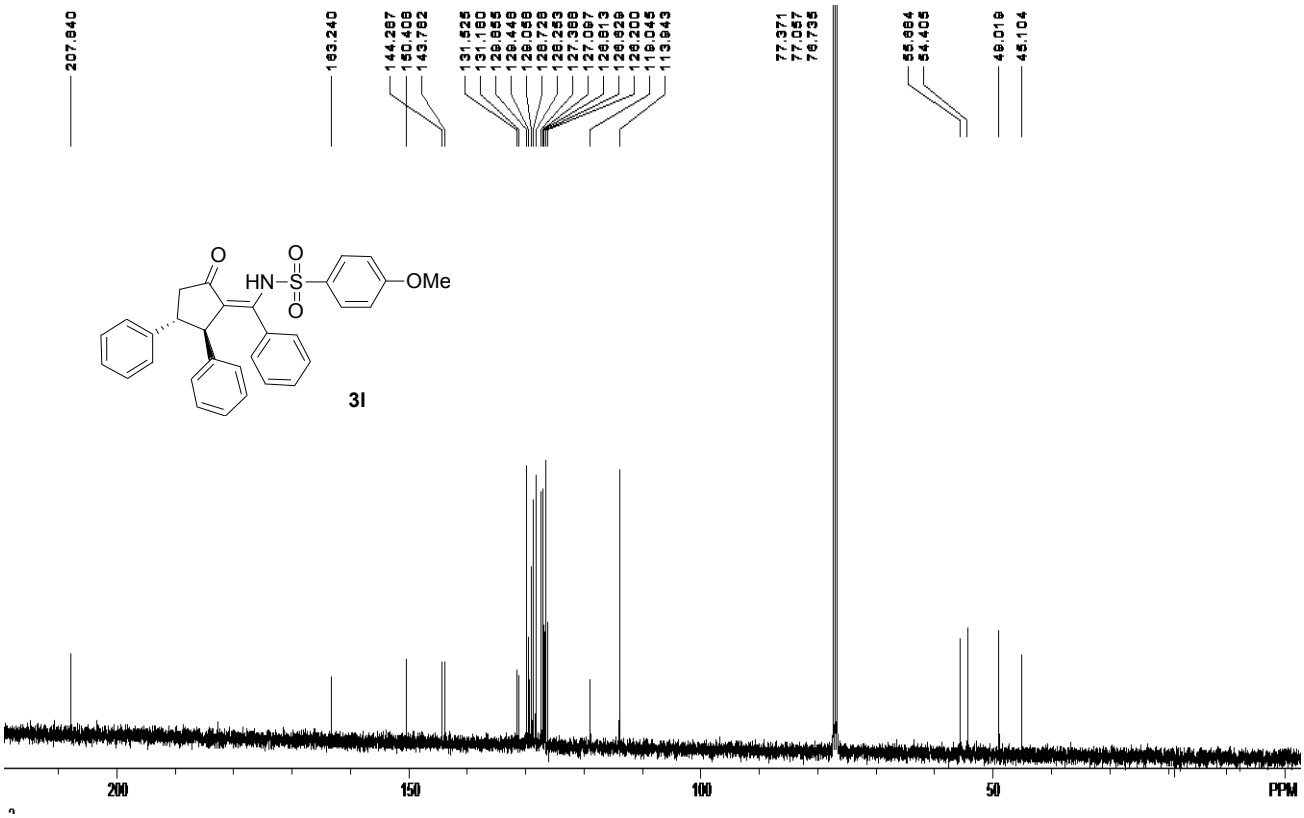
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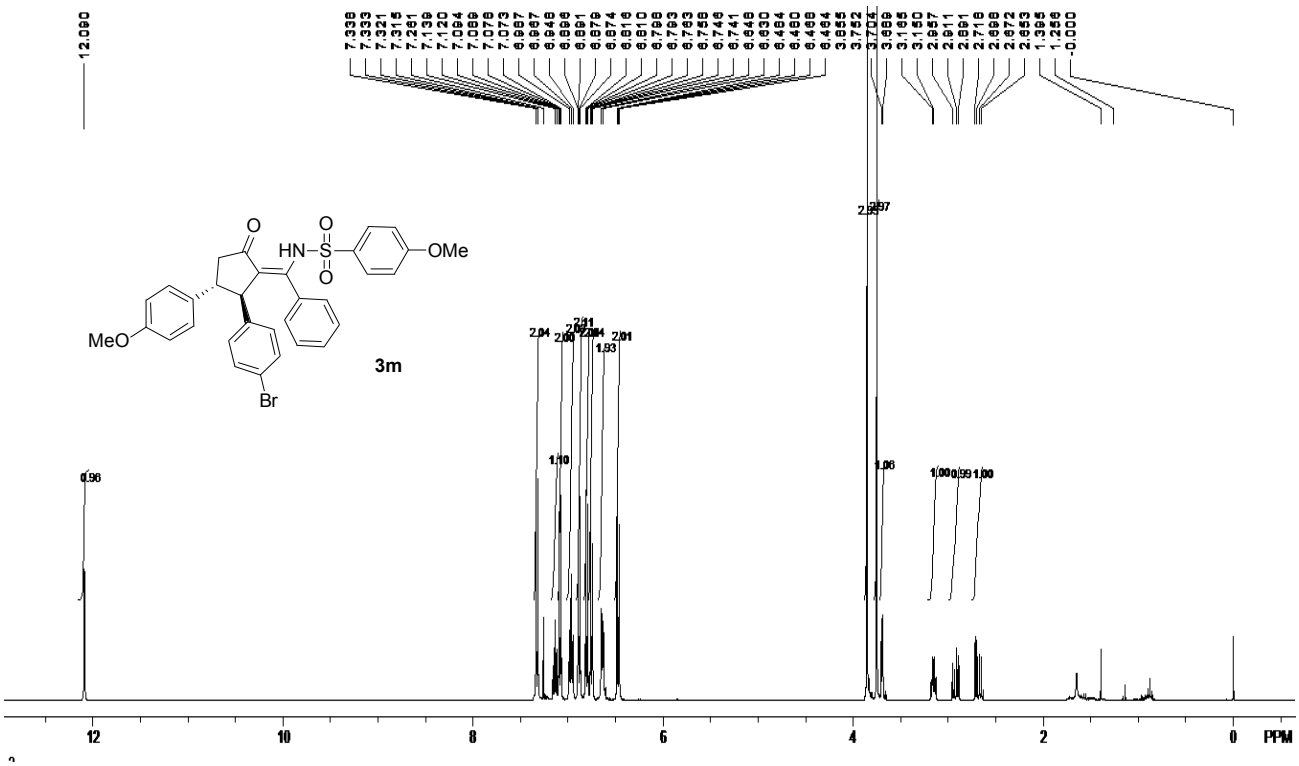
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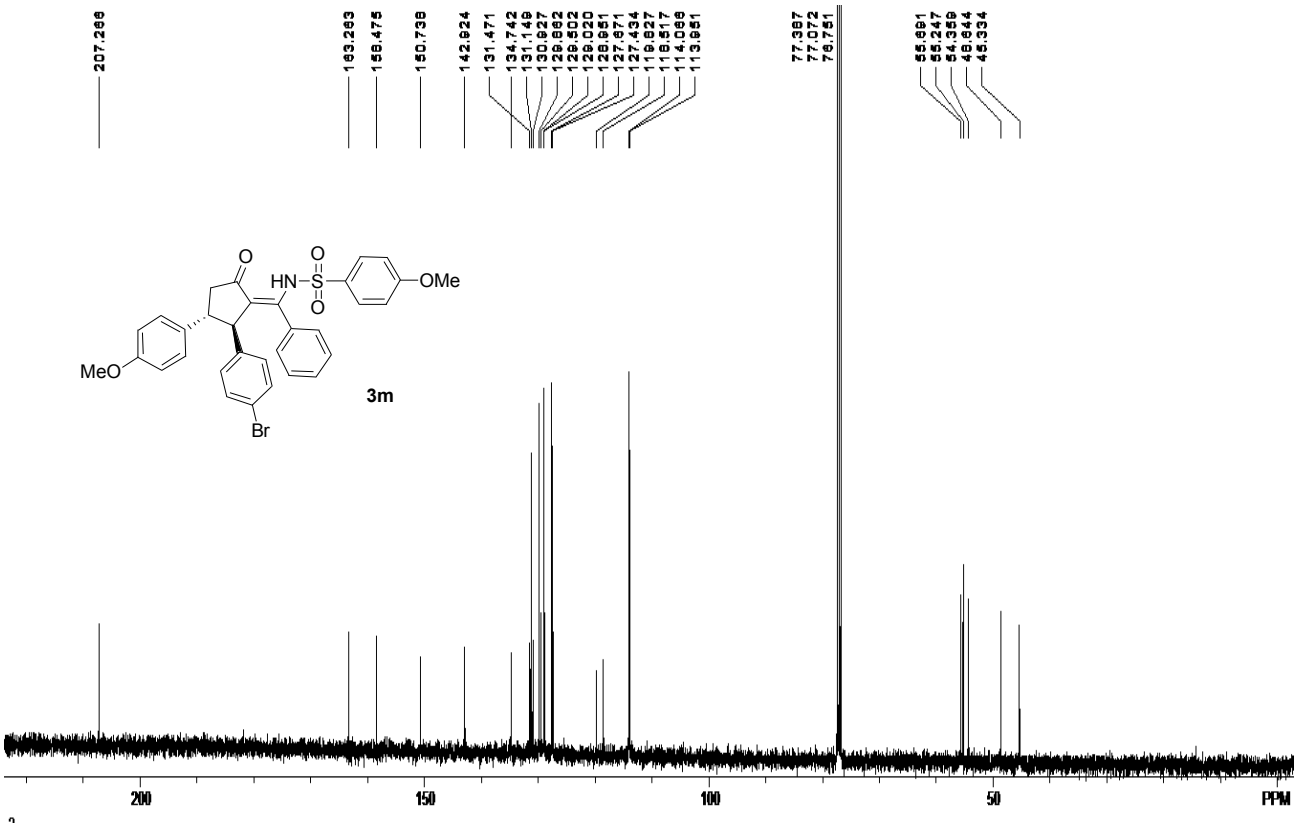
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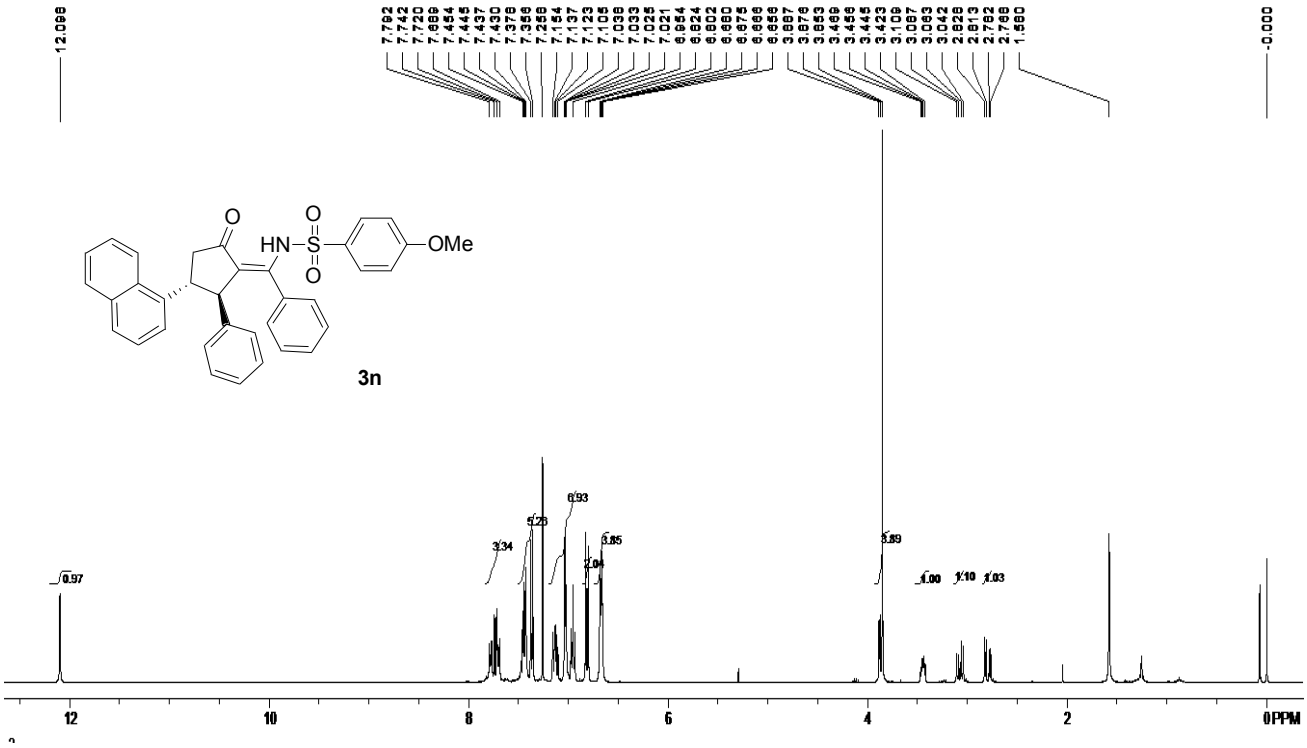
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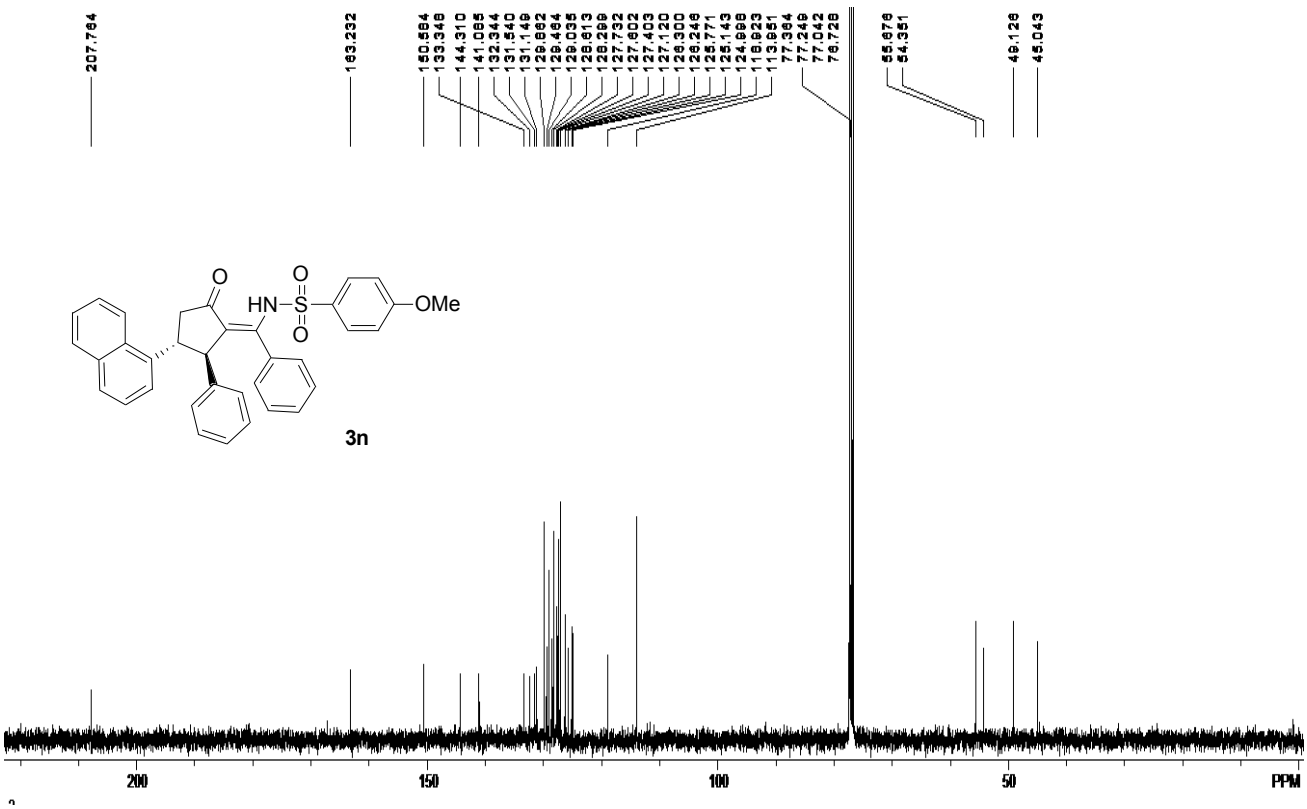
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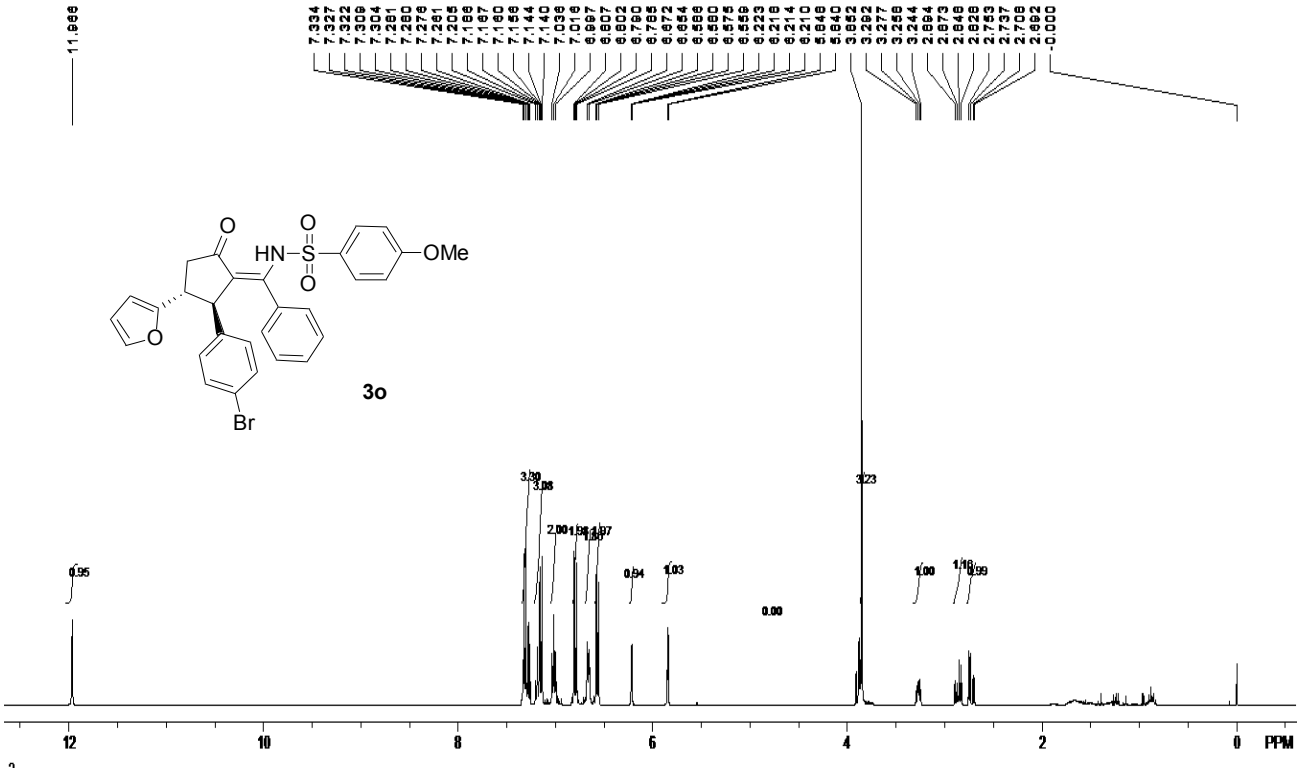
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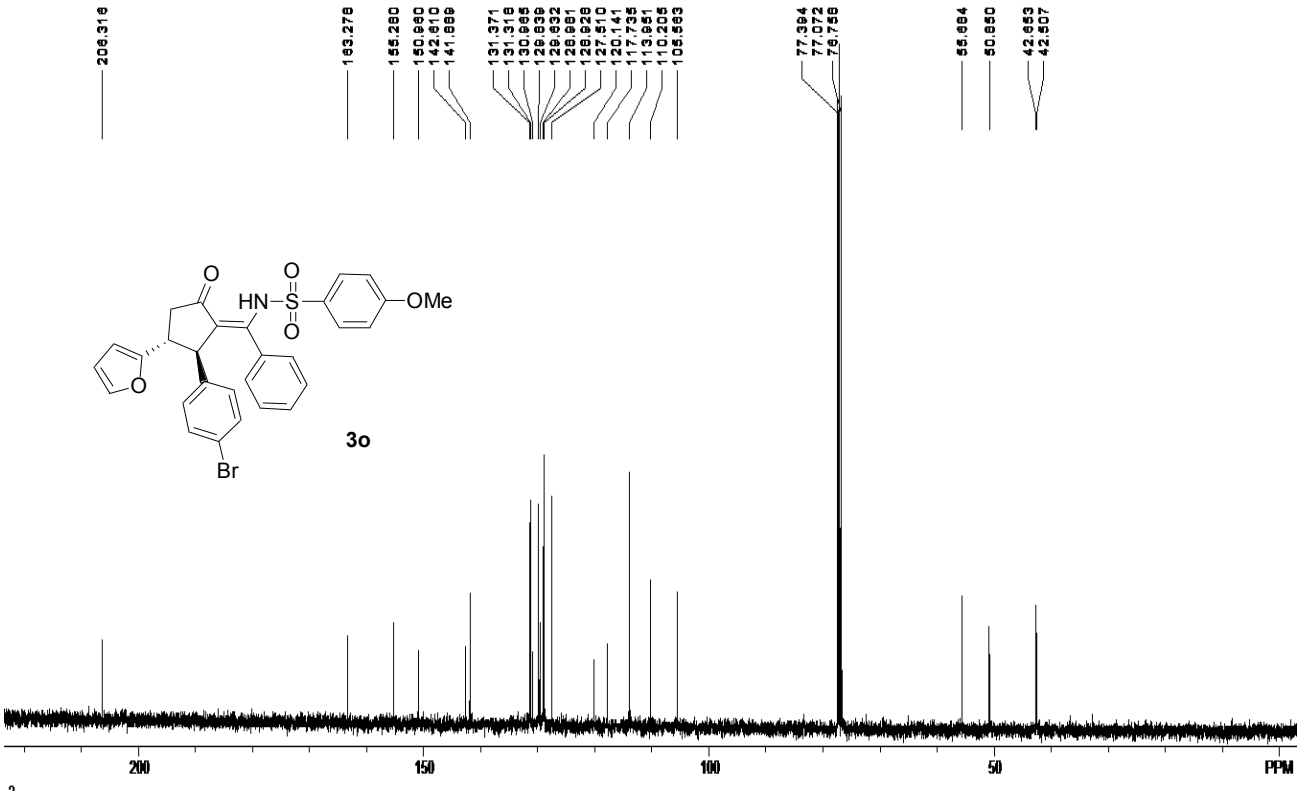
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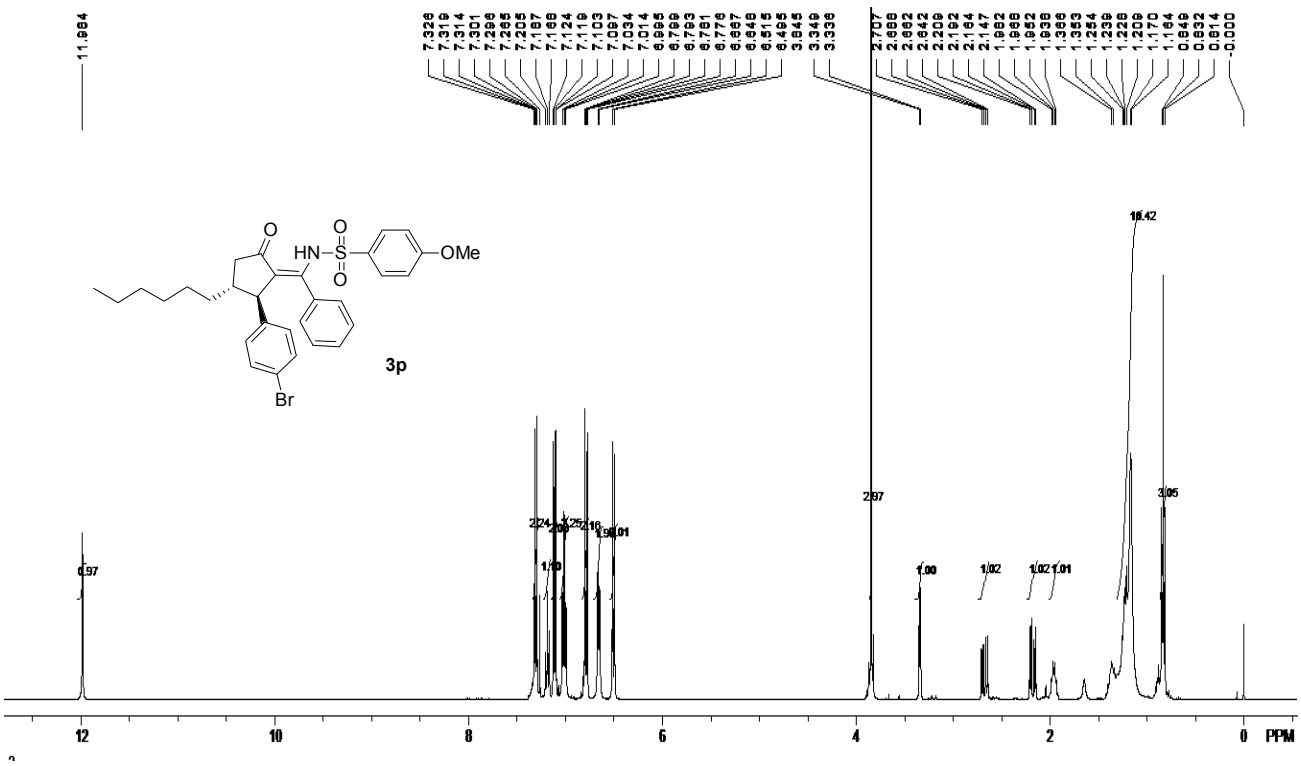
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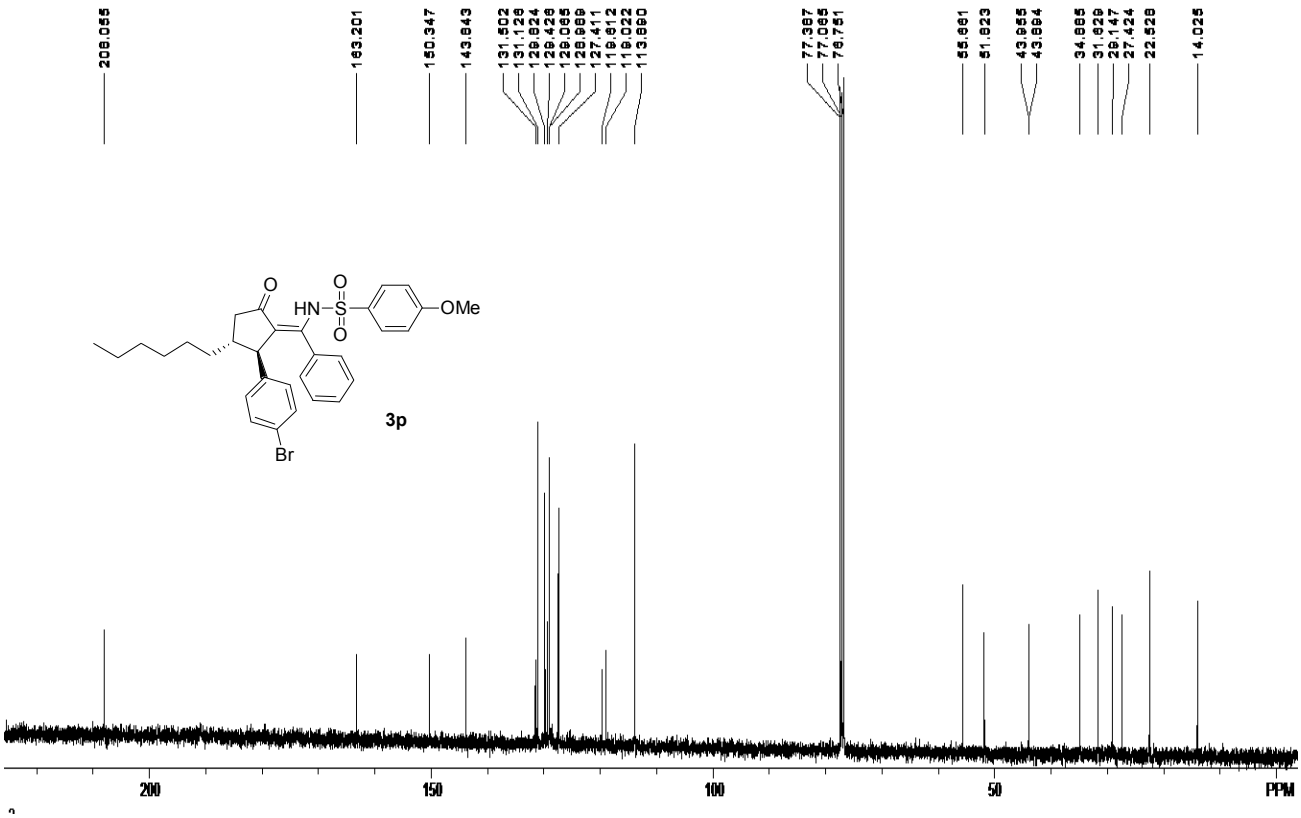
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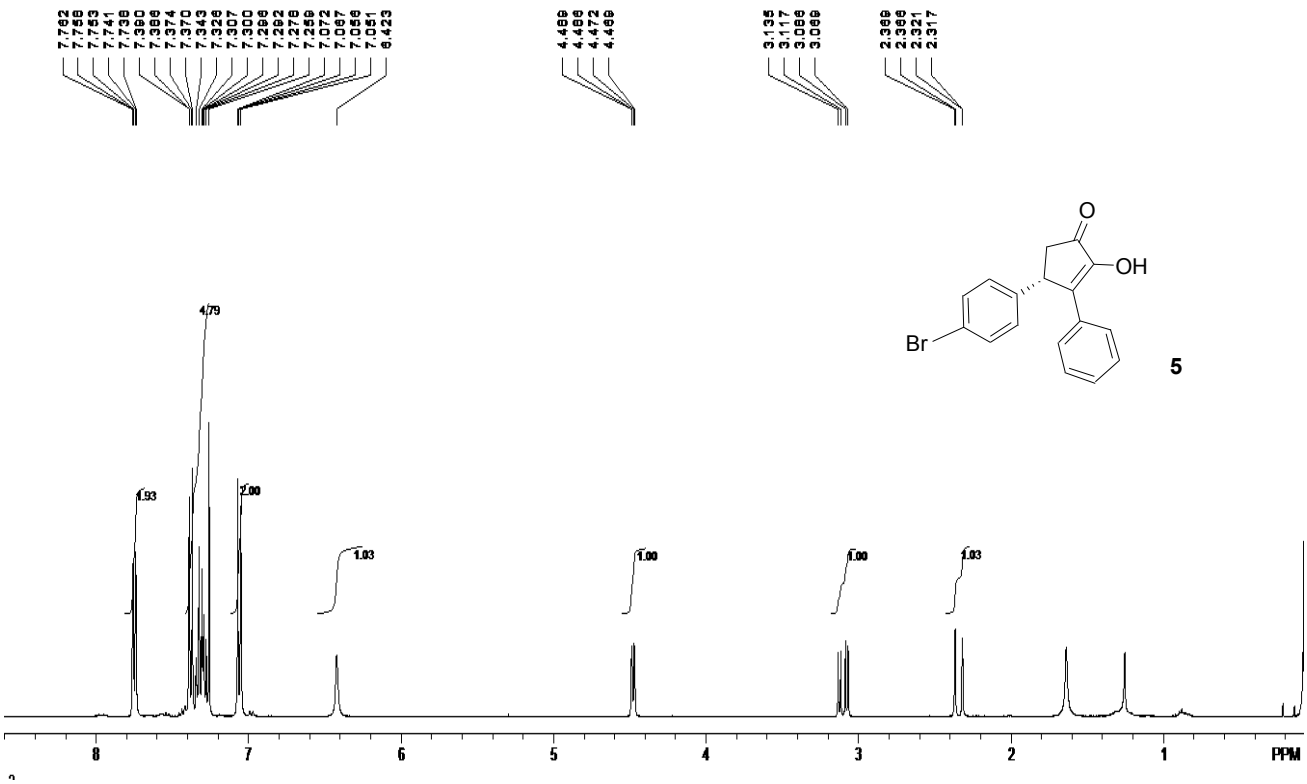
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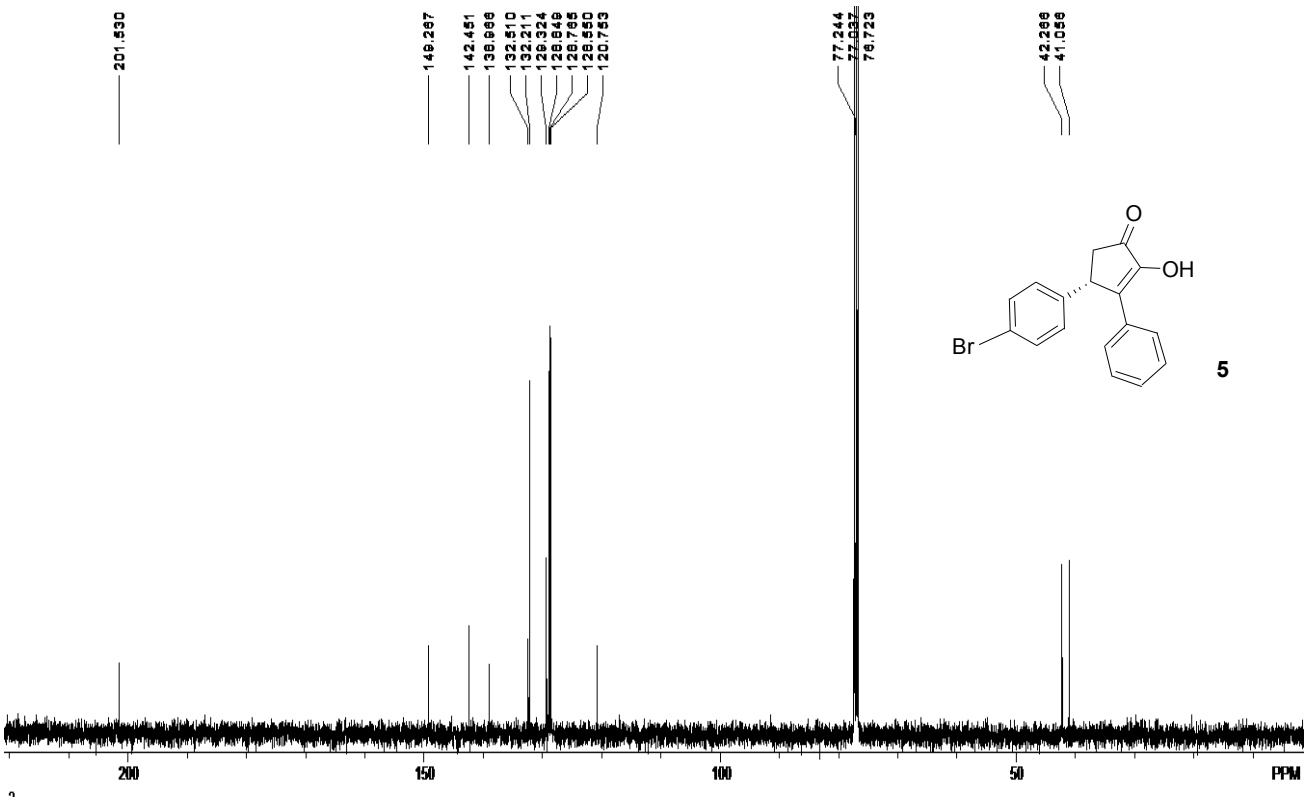
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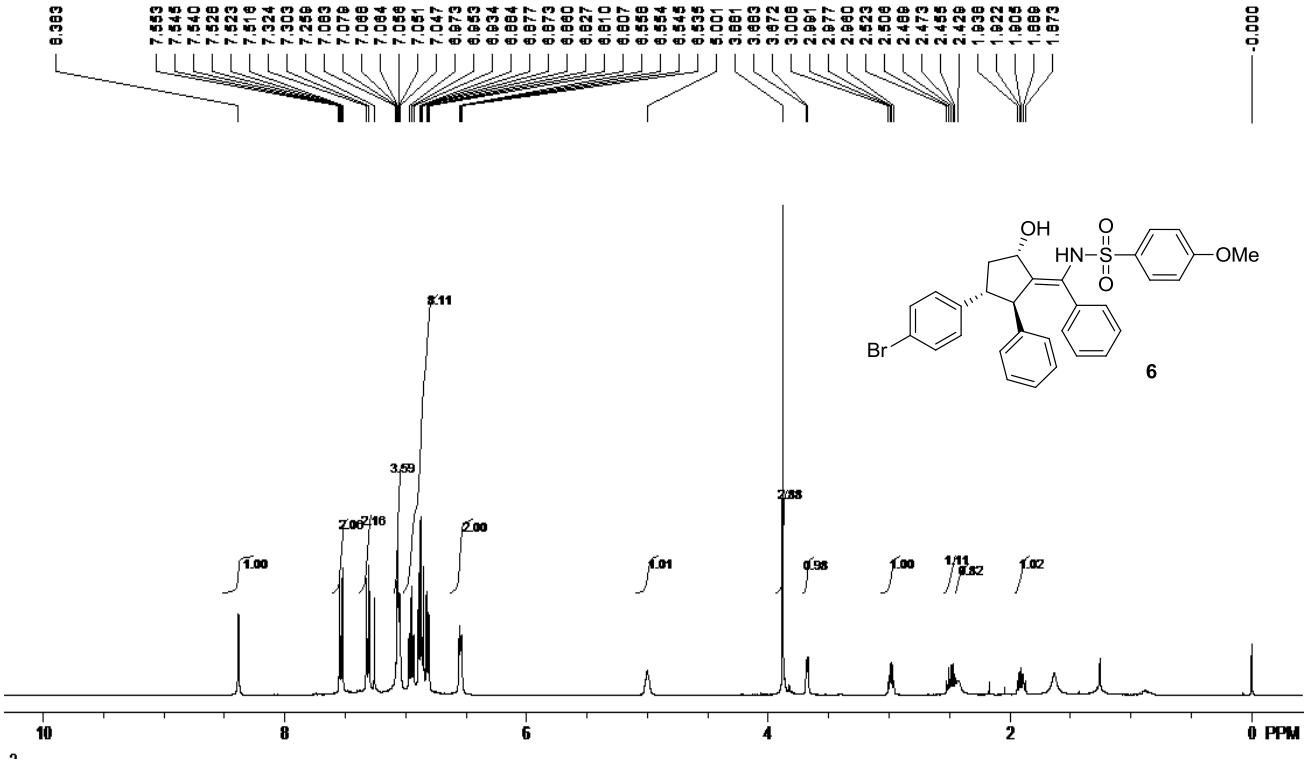
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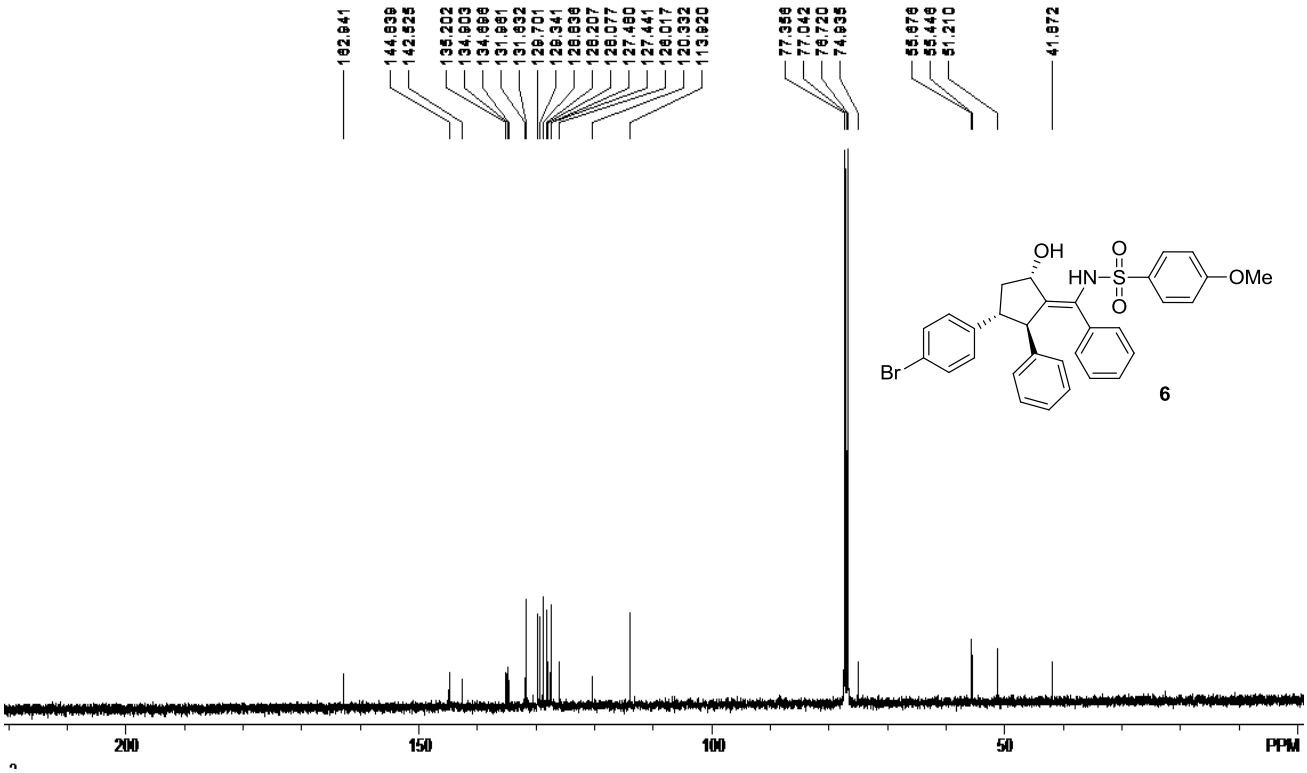
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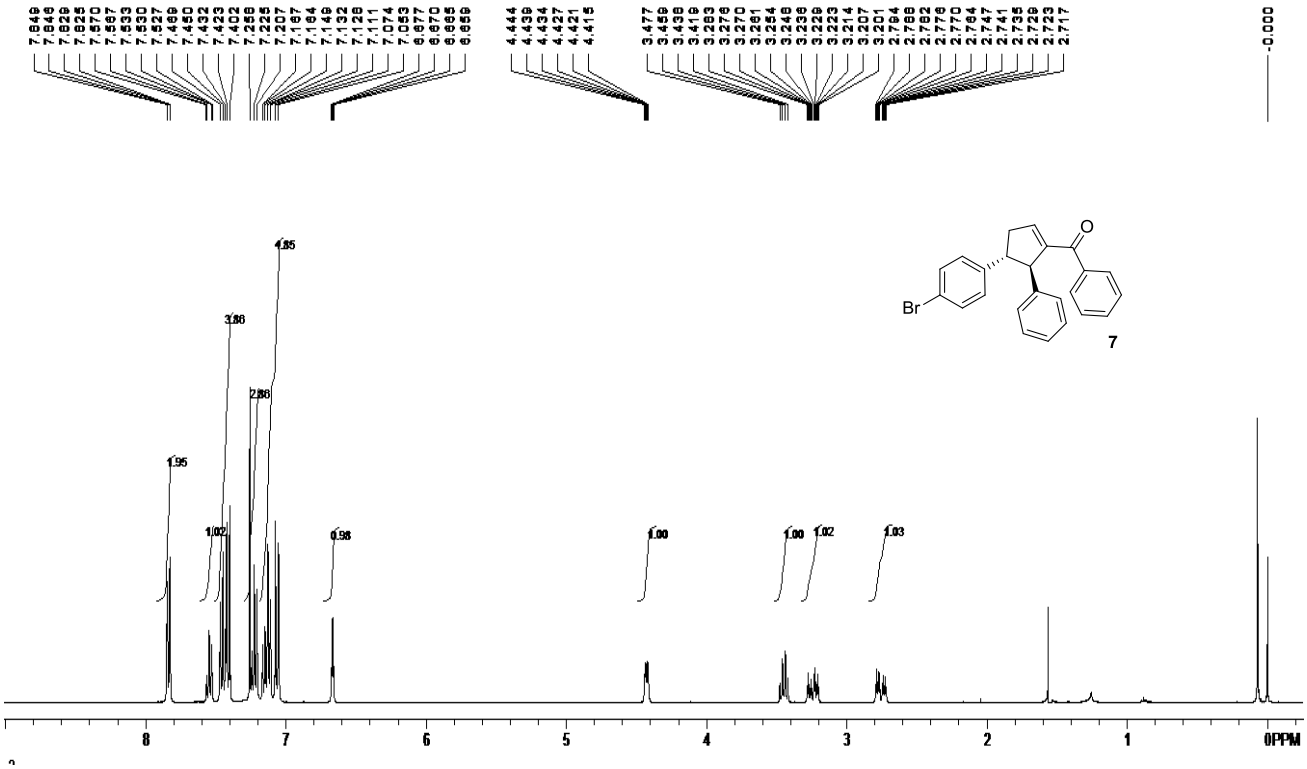
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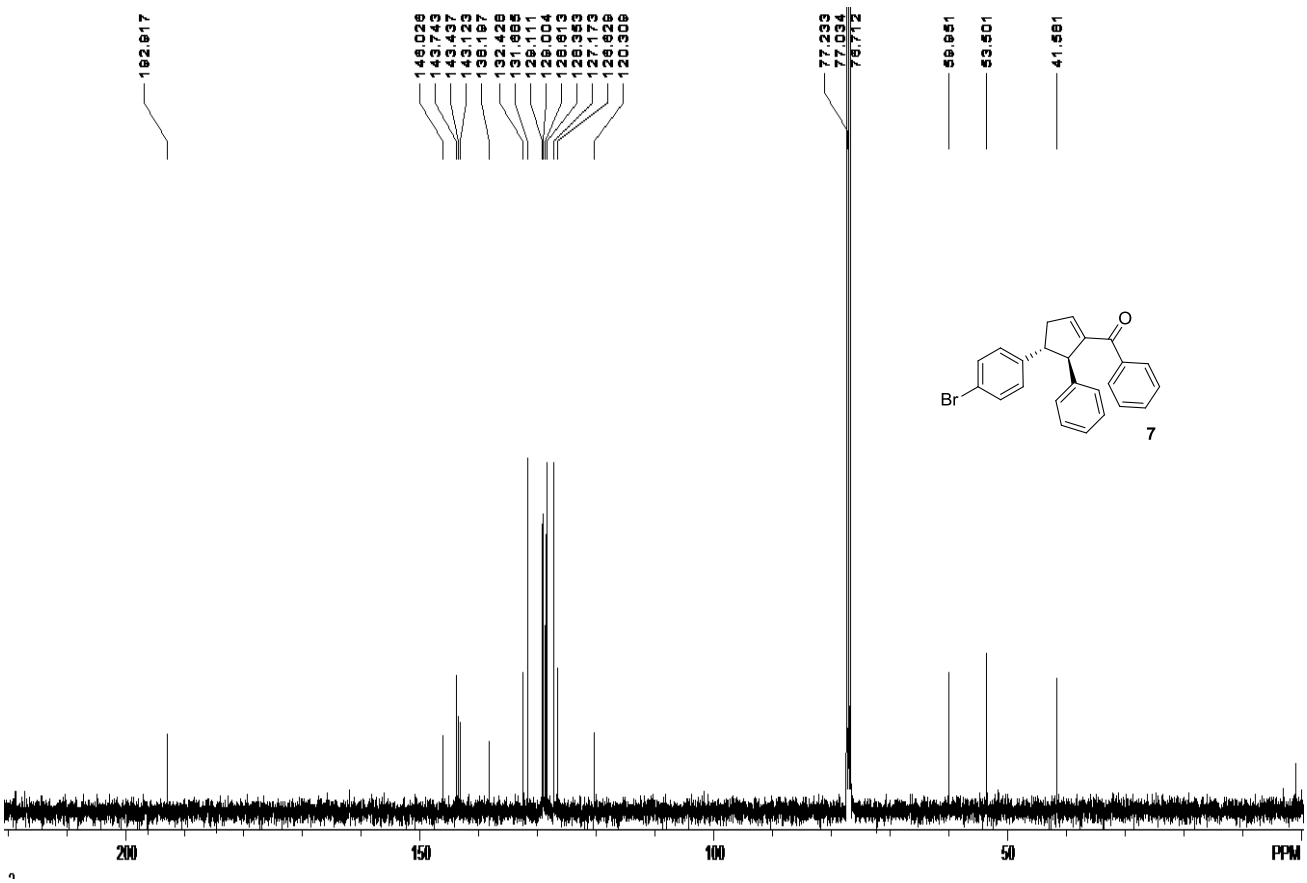
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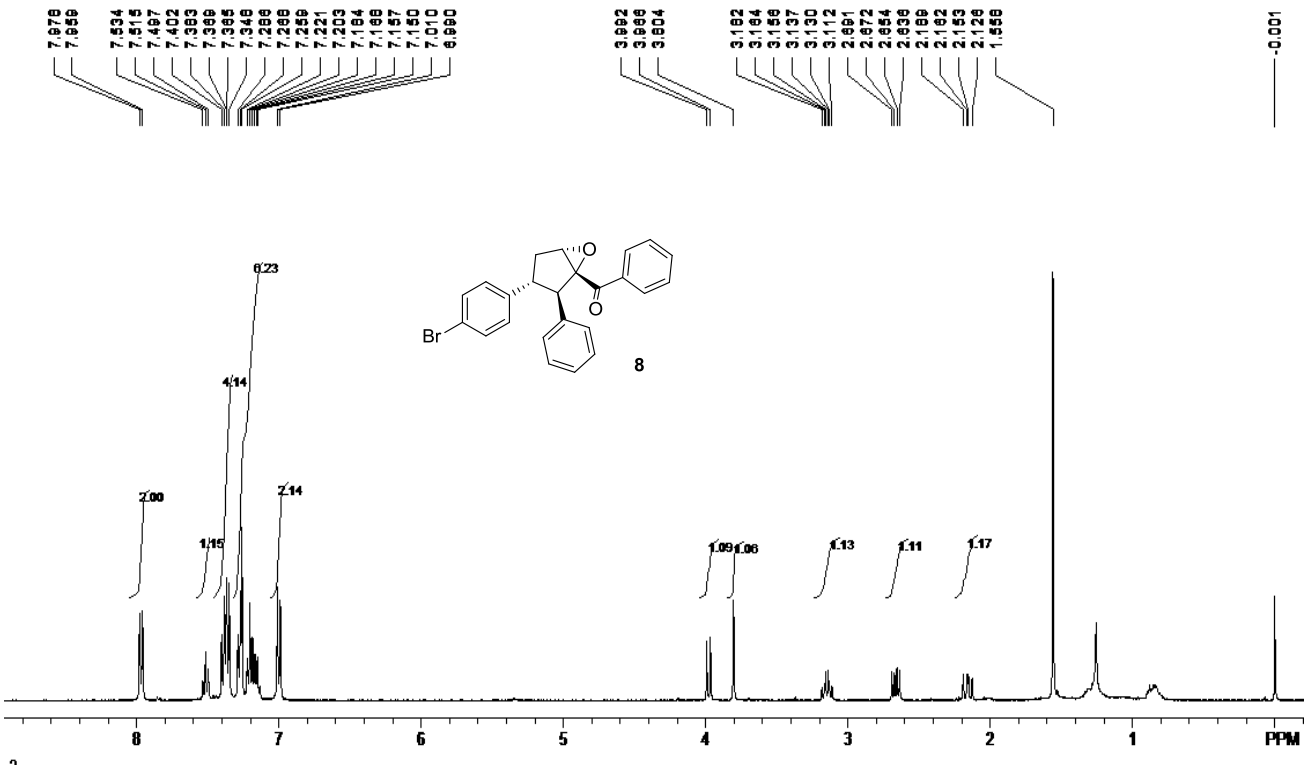

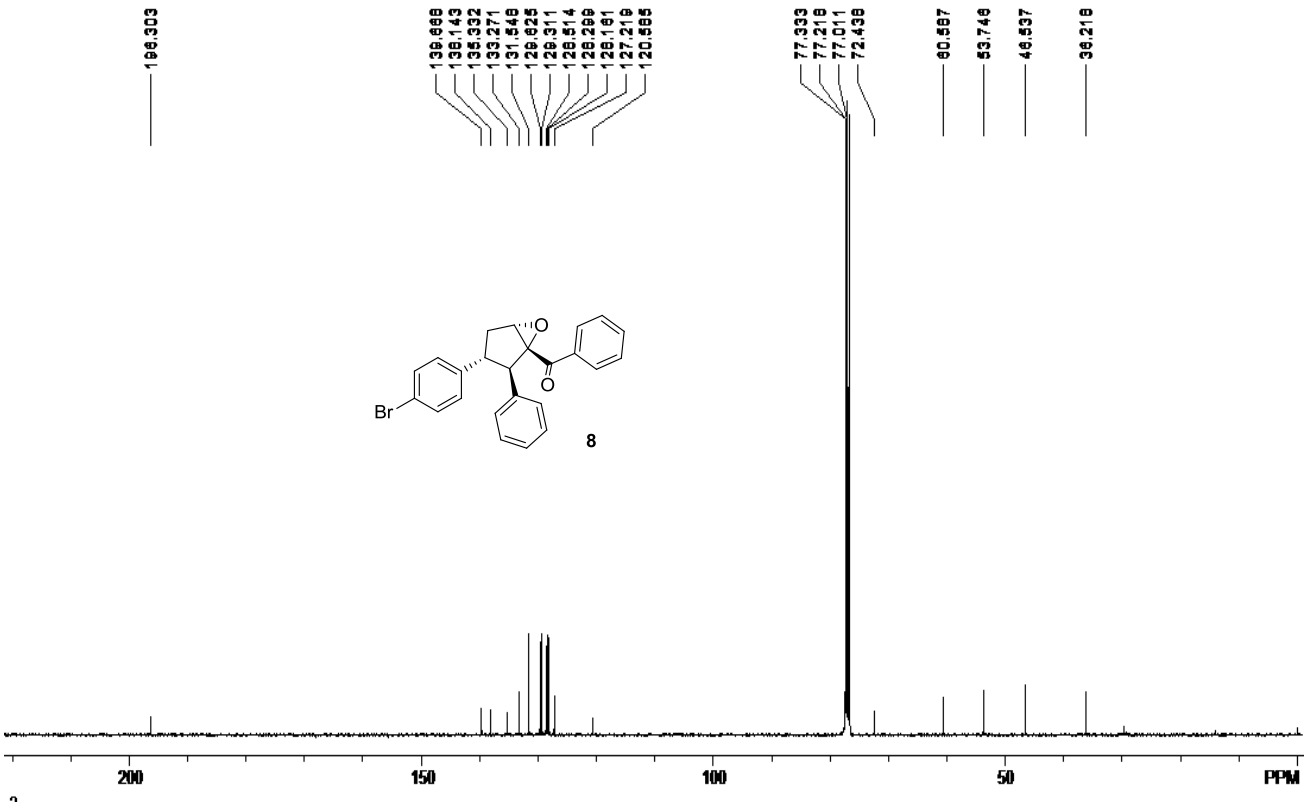

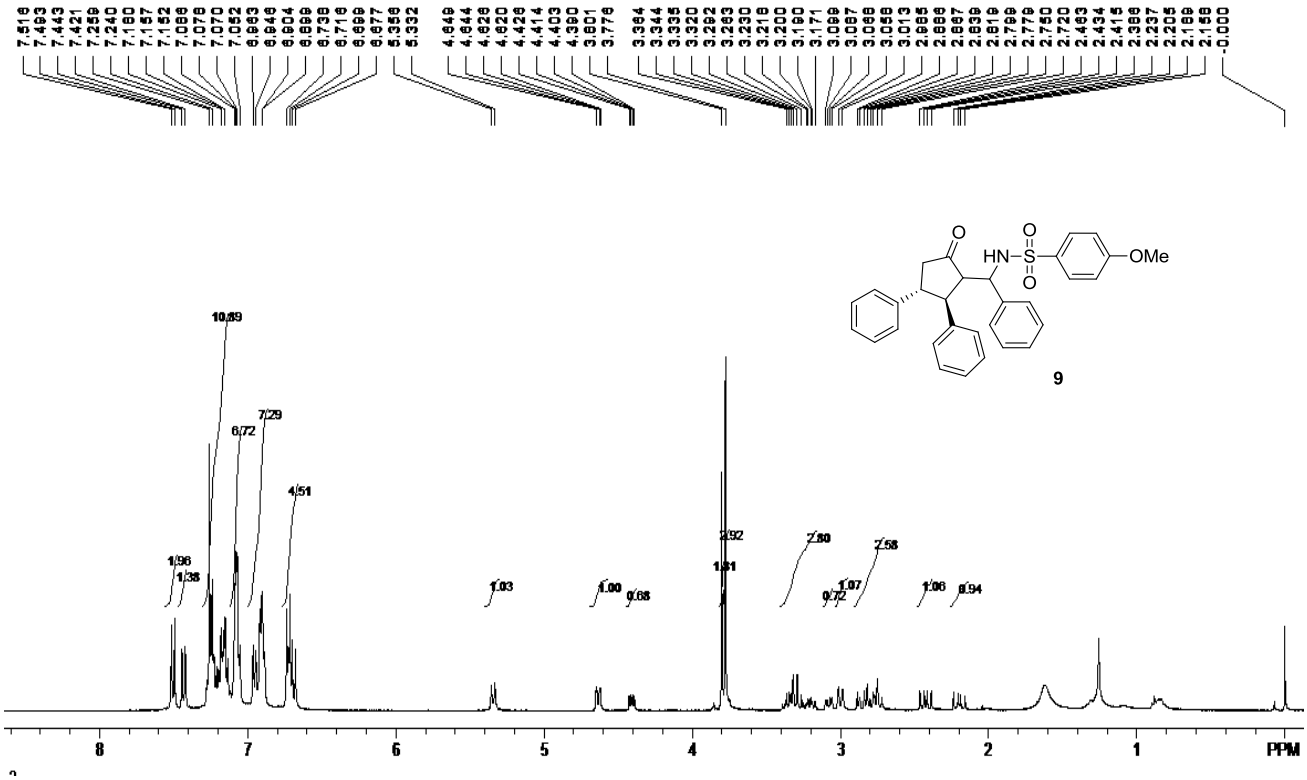
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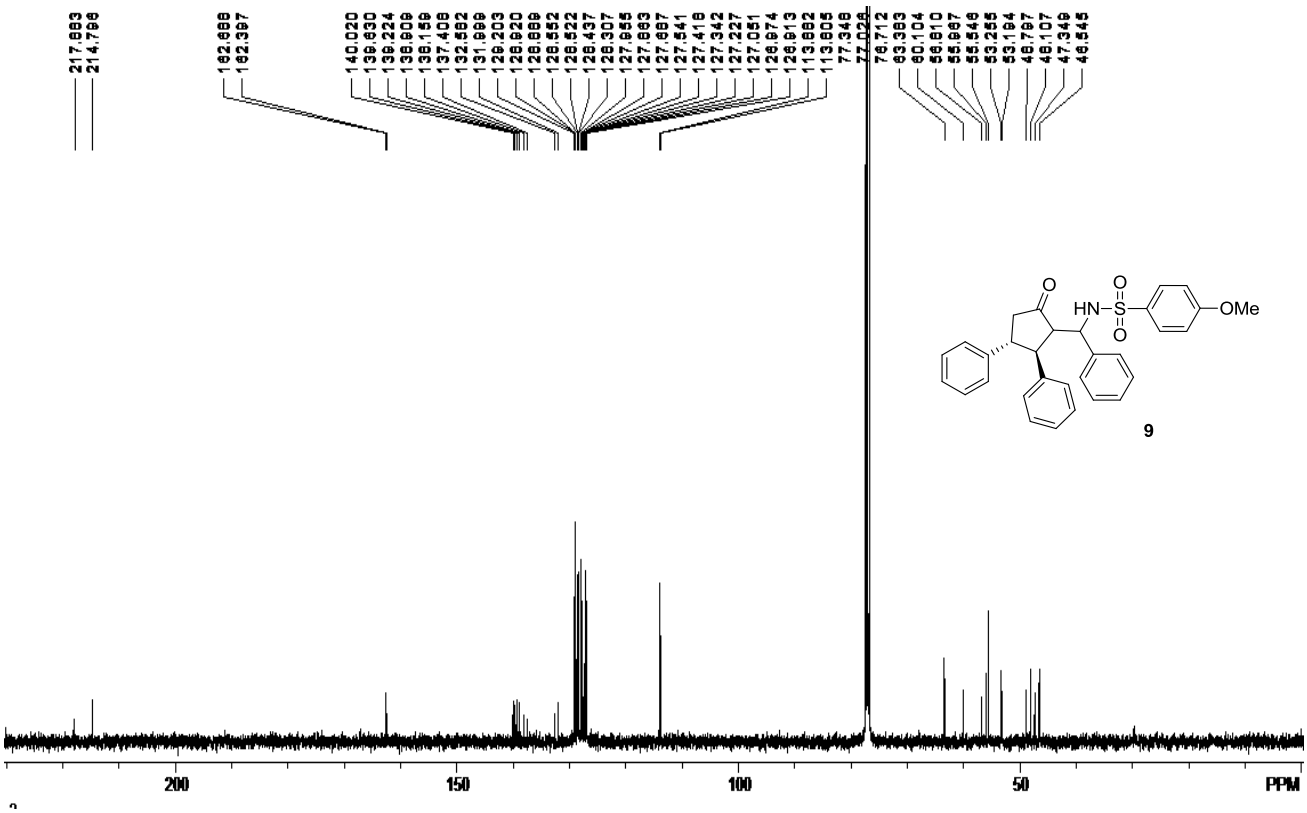
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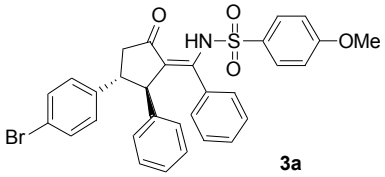

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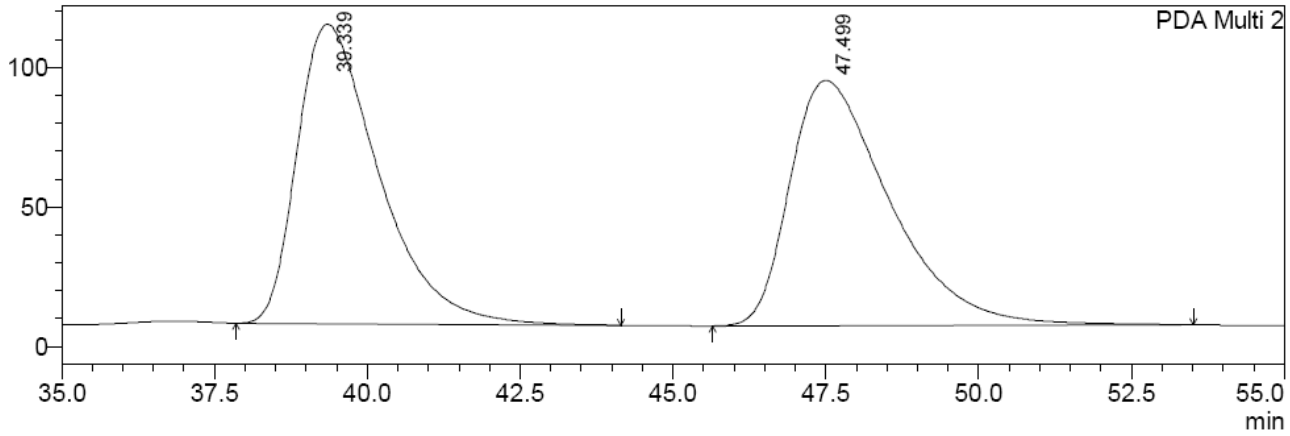
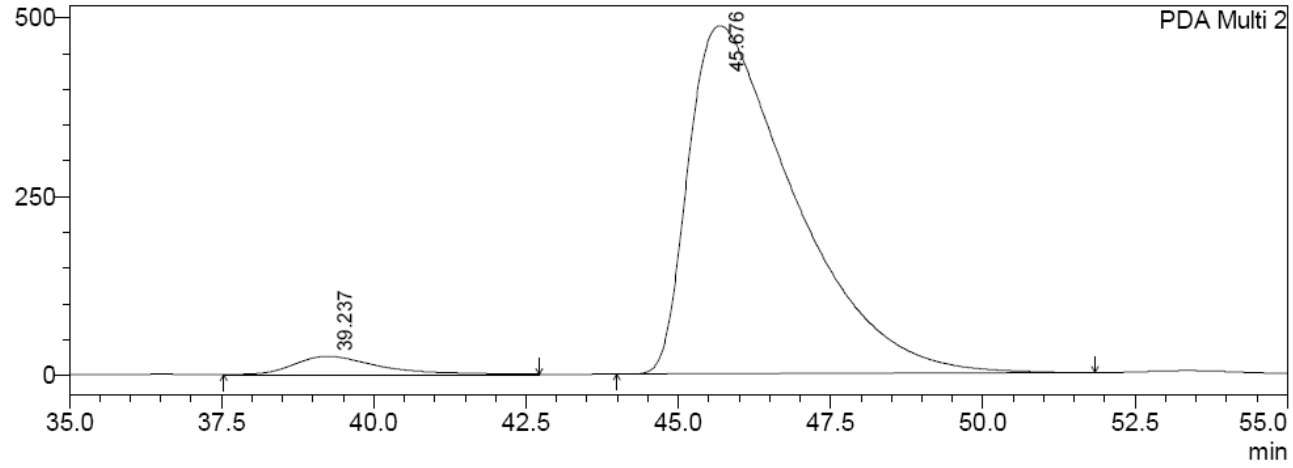


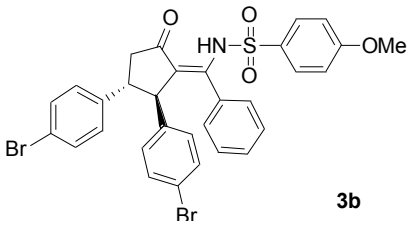
PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	39.339	9957784	107091	49.902	54.972
2	47.499	9996917	87721	50.098	45.028
Total		19954701	194812	100.000	100.000



PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	39.237	2392067	25140	3.882	4.912
2	45.676	59233055	486657	96.118	95.088
Total		61625122	511797	100.000	100.000



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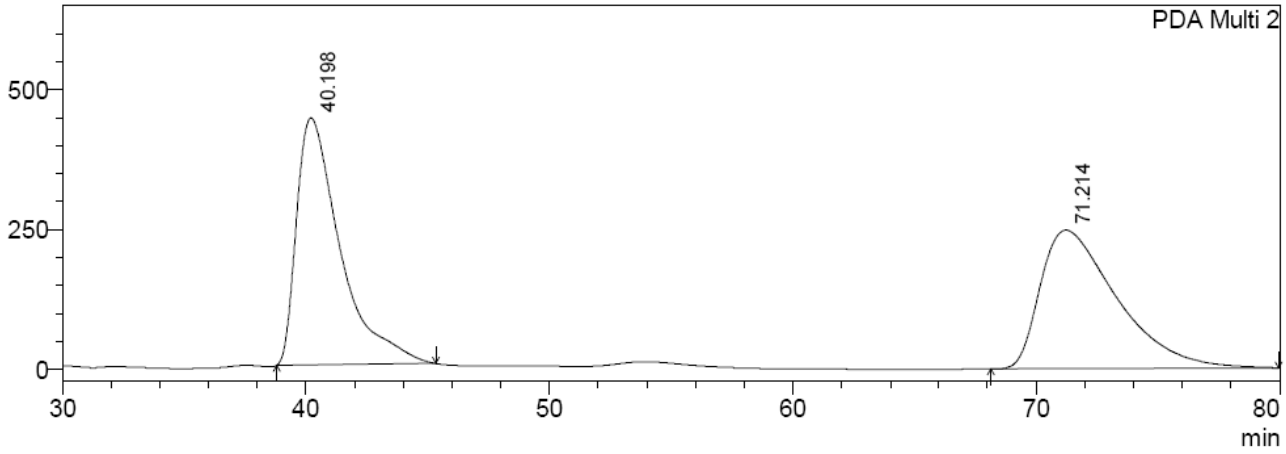
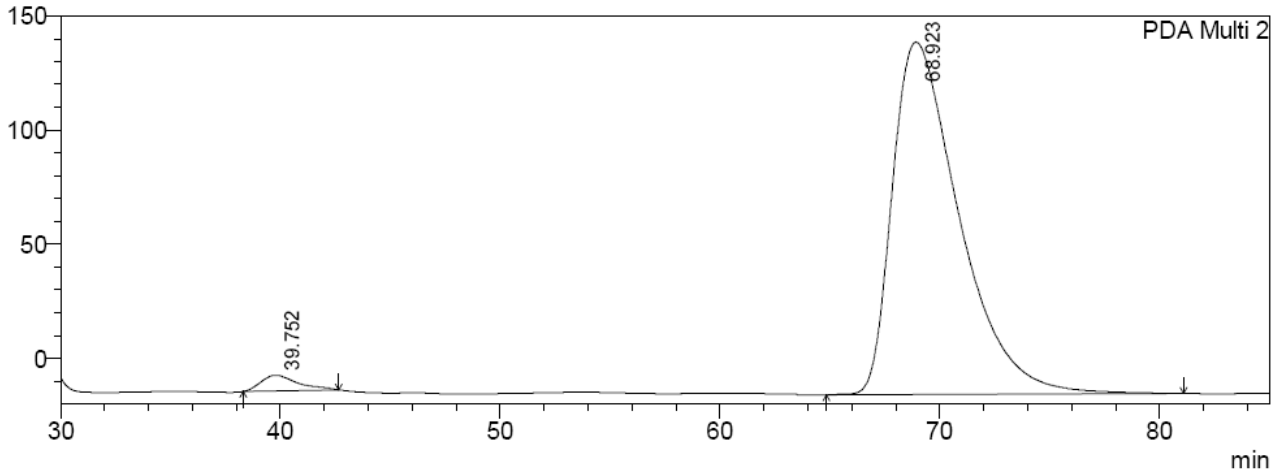


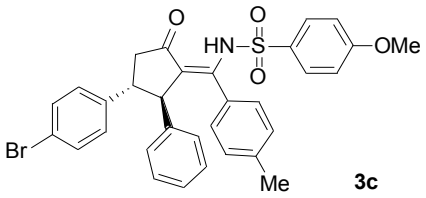
PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	40.198	55071218	441181	50.445	64.093
2	71.214	54099806	247161	49.555	35.907
Total		109171024	688343	100.000	100.000



PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	39.747	266029	2192	2.470	4.229
2	68.926	10505512	49645	97.530	95.771
Total		10771540	51838	100.000	100.000



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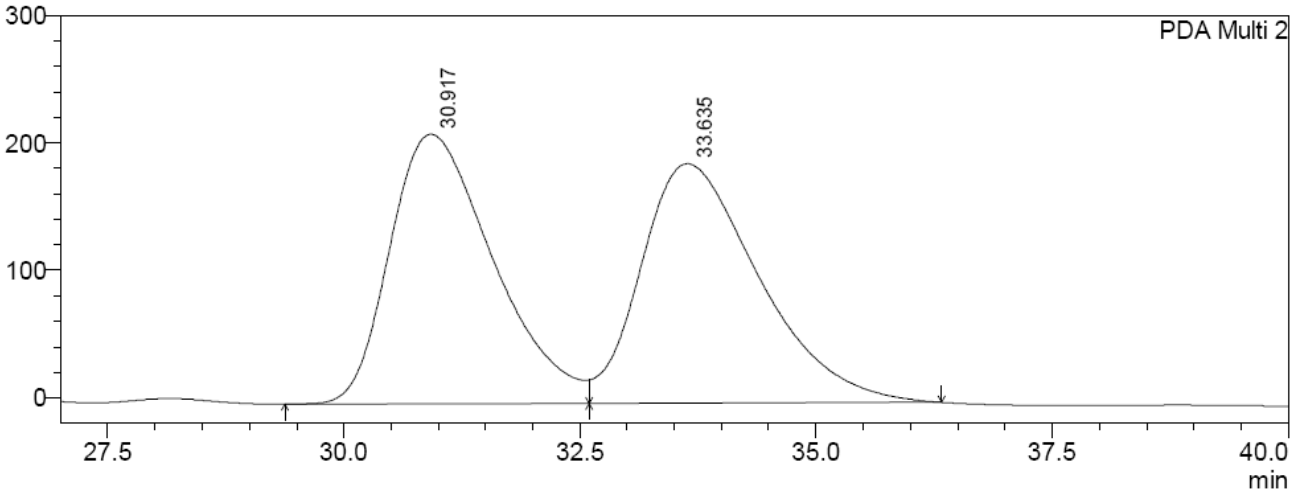
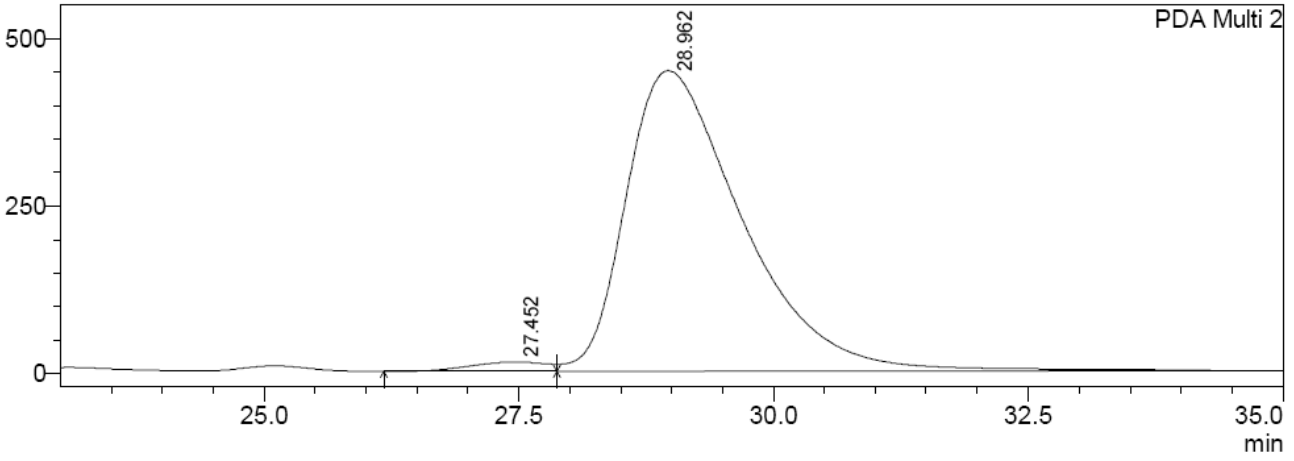


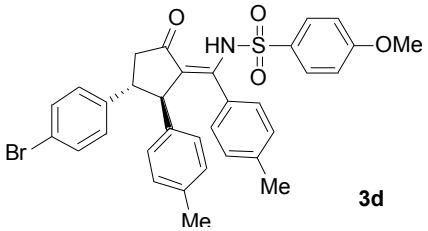
PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	30.917	16154163	211663	49.713	52.958
2	33.635	16340829	188015	50.287	47.042
Total		32494993	399678	100.000	100.000



PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.452	731405	13768	2.000	2.976
2	28.962	35843807	448929	98.000	97.024
Total		36575212	462696	100.000	100.000



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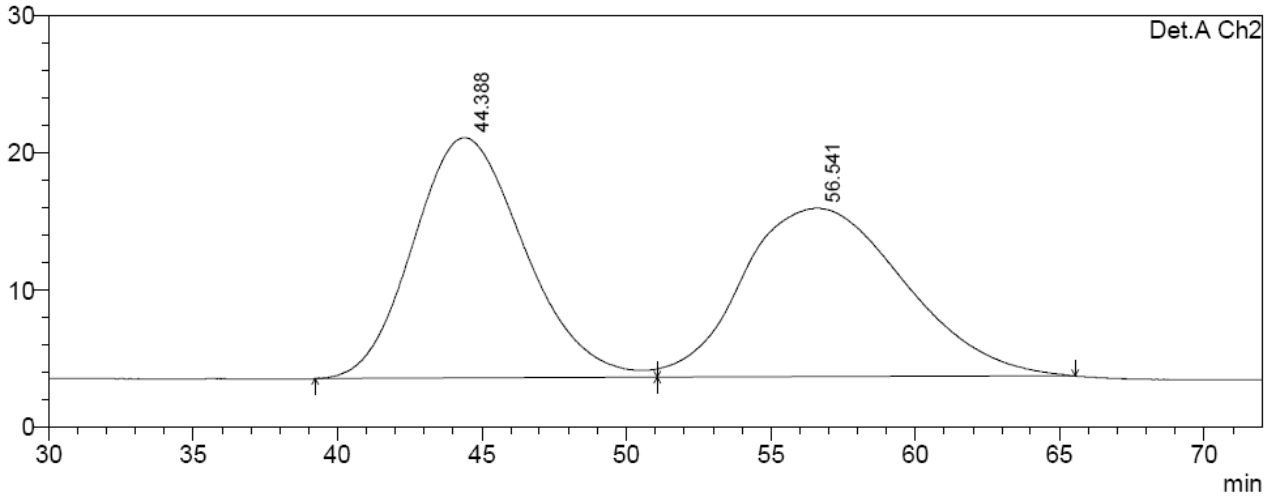
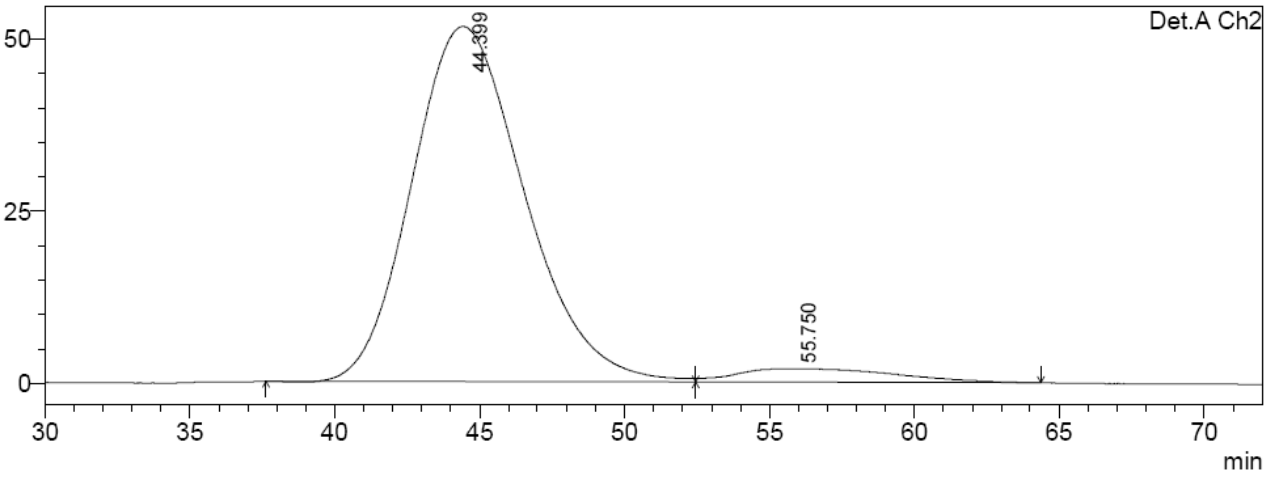


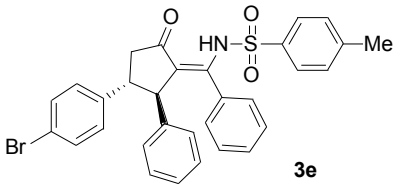
UV Detector Ch2 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	44.388	4713645	17546	49.561	58.770
2	56.541	4797223	12309	50.439	41.230
Total		9510868	29855	100.000	100.000



UV Detector Ch2 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	44.399	13875250	51488	94.827	96.305
2	55.750	756853	1975	5.173	3.695
Total		14632103	53464	100.000	100.000



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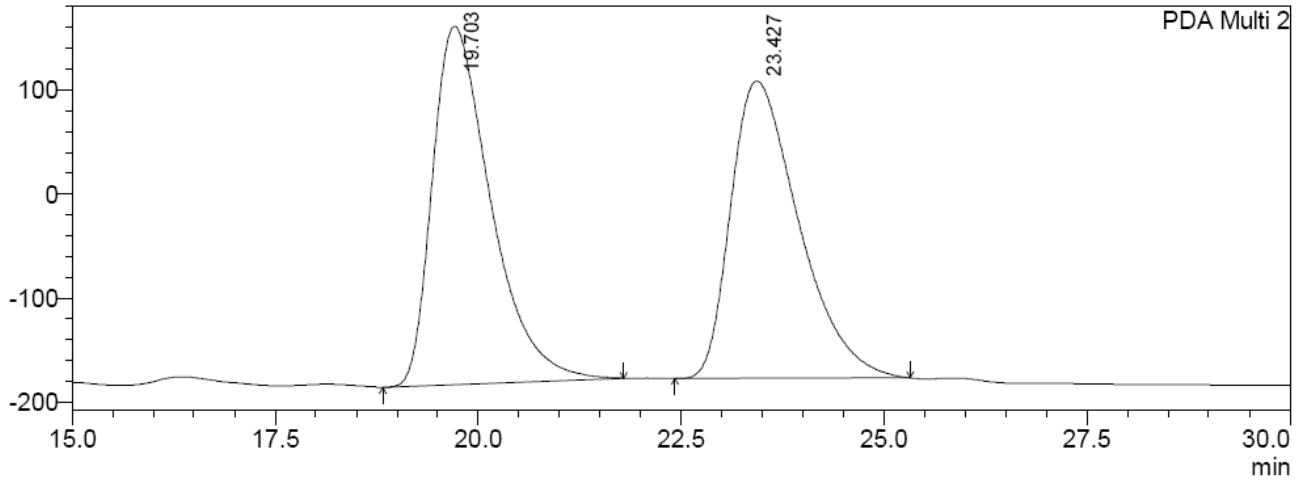
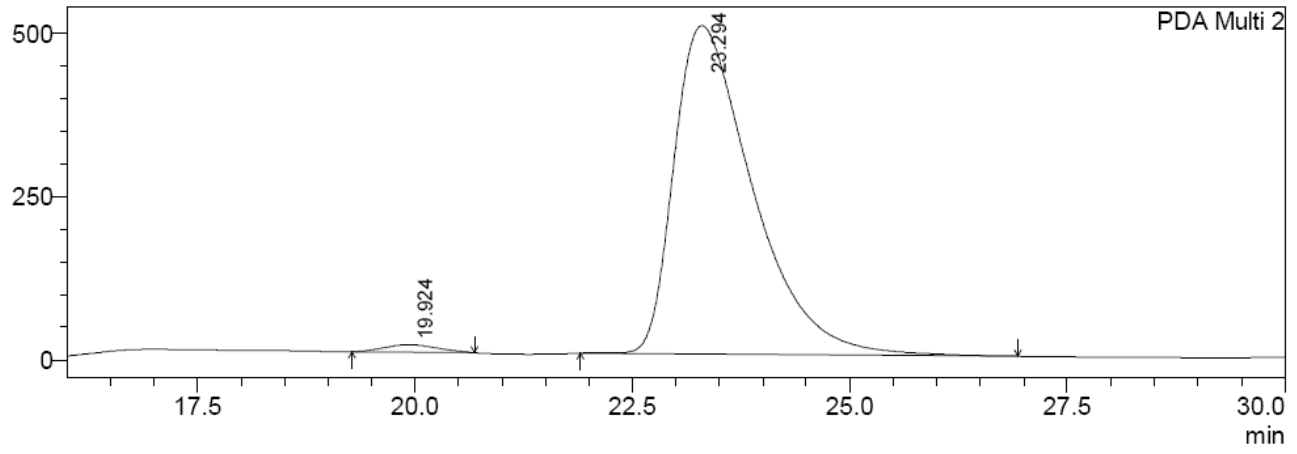


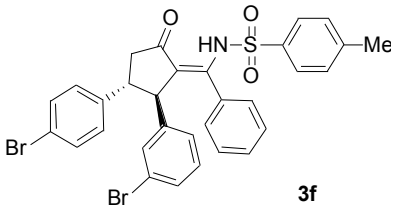
PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.703	17244035	344072	50.822	54.644
2	23.427	16686178	285595	49.178	45.356
Total		33930213	629667	100.000	100.000



PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.924	482756	11251	1.498	2.189
2	23.294	31748848	502822	98.502	97.811
Total		32231604	514073	100.000	100.000



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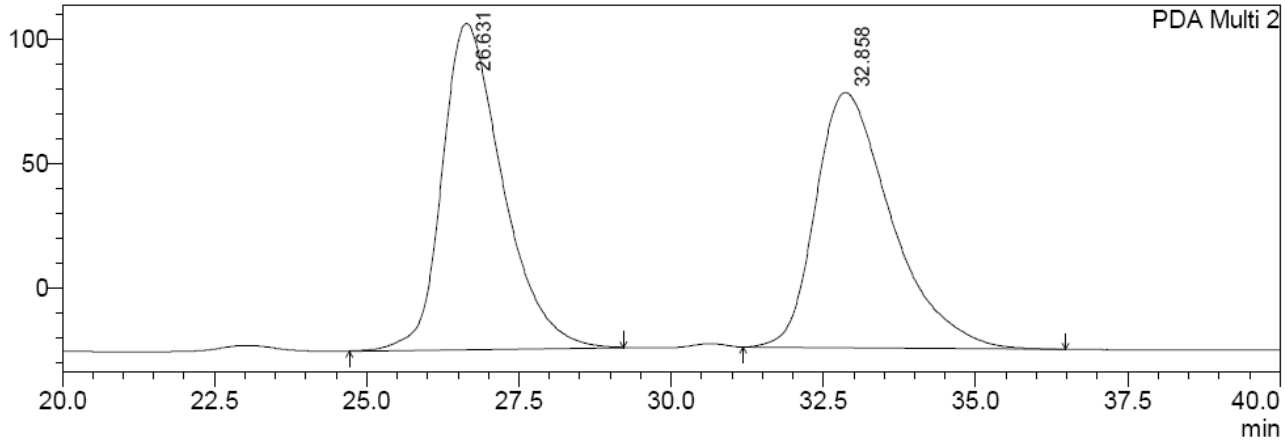
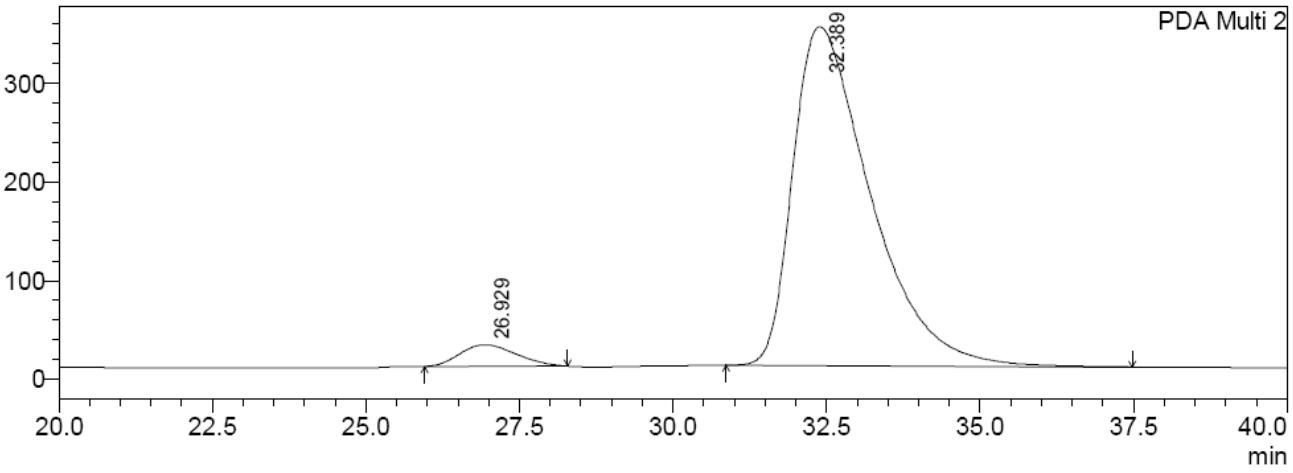


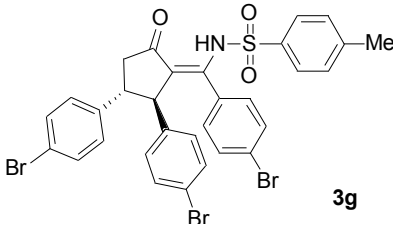
PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.631	9074398	131244	50.375	56.080
2	32.858	8939311	102788	49.625	43.920
Total		18013709	234032	100.000	100.000



PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.929	1398315	21929	4.431	6.007
2	32.389	30159444	343159	95.569	93.993
Total		31557759	365088	100.000	100.000



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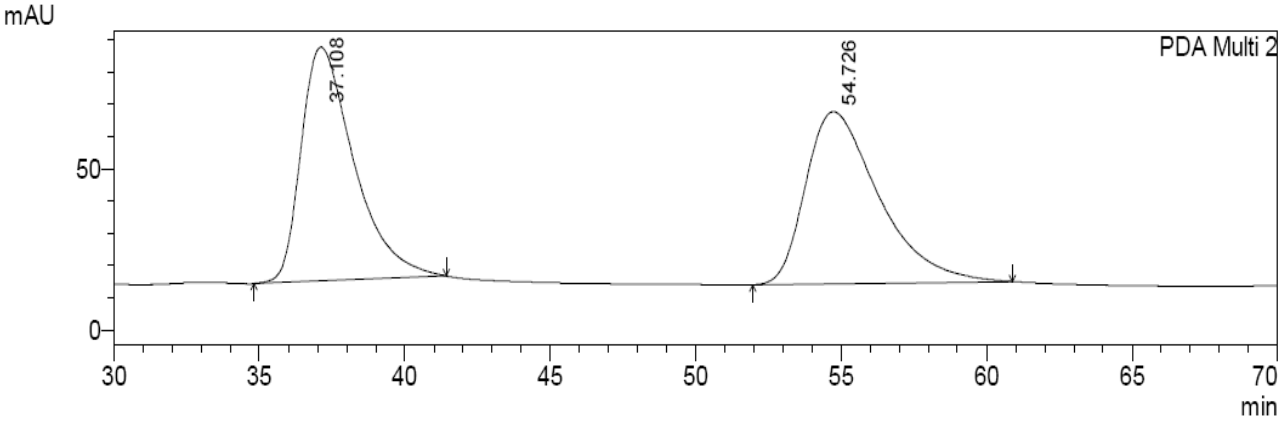
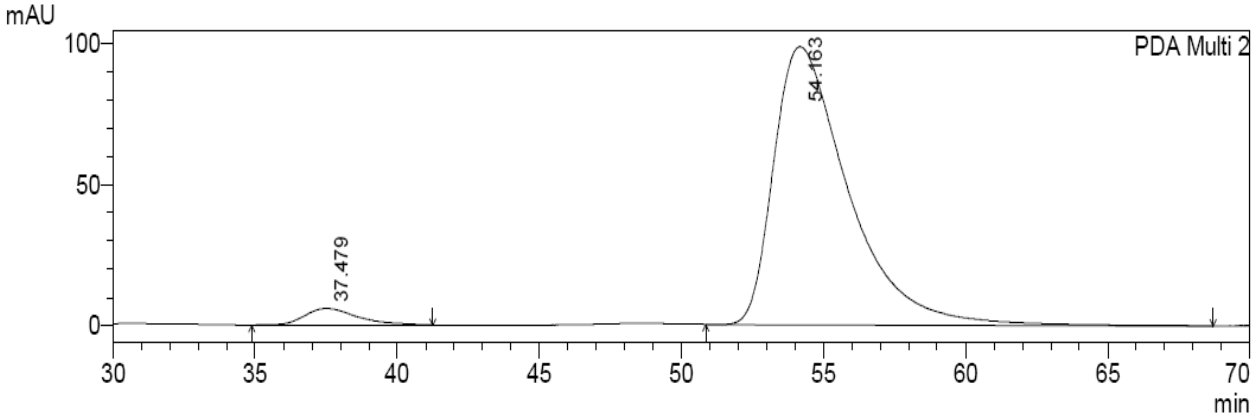


PeakTable

PDA Ch2 220nm 4nm

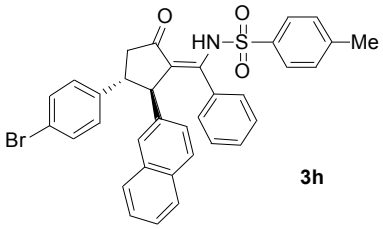
Peak#	Ret. Time	Area	Height	Area %	Height %
1	37.108	9197731	72622	49.500	57.612
2	54.726	9383664	53430	50.500	42.388
Total		18581394	126052	100.000	100.000



PeakTable

PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	37.479	774475	5941	4.125	5.684
2	54.163	17999234	98575	95.875	94.316
Total		18773709	104517	100.000	100.000



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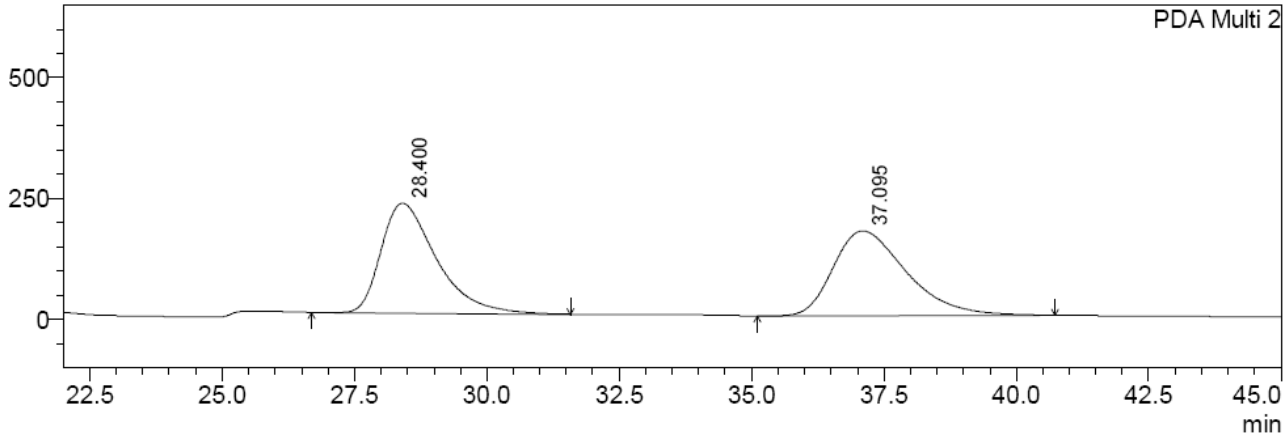
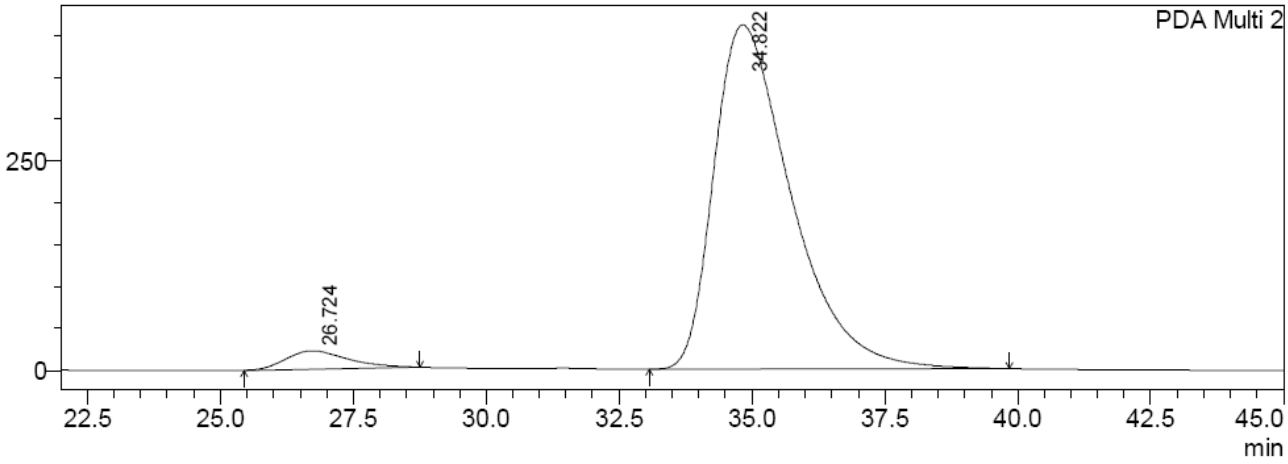


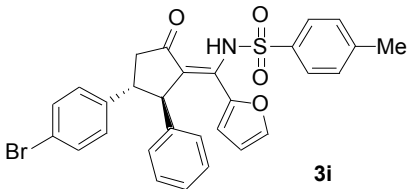
PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.400	16544280	227277	49.495	56.392
2	37.095	16881651	175755	50.505	43.608
Total		33425930	403032	100.000	100.000



PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.724	1776916	21836	4.099	5.047
2	34.822	41570379	410857	95.901	94.953
Total		43347295	432693	100.000	100.000



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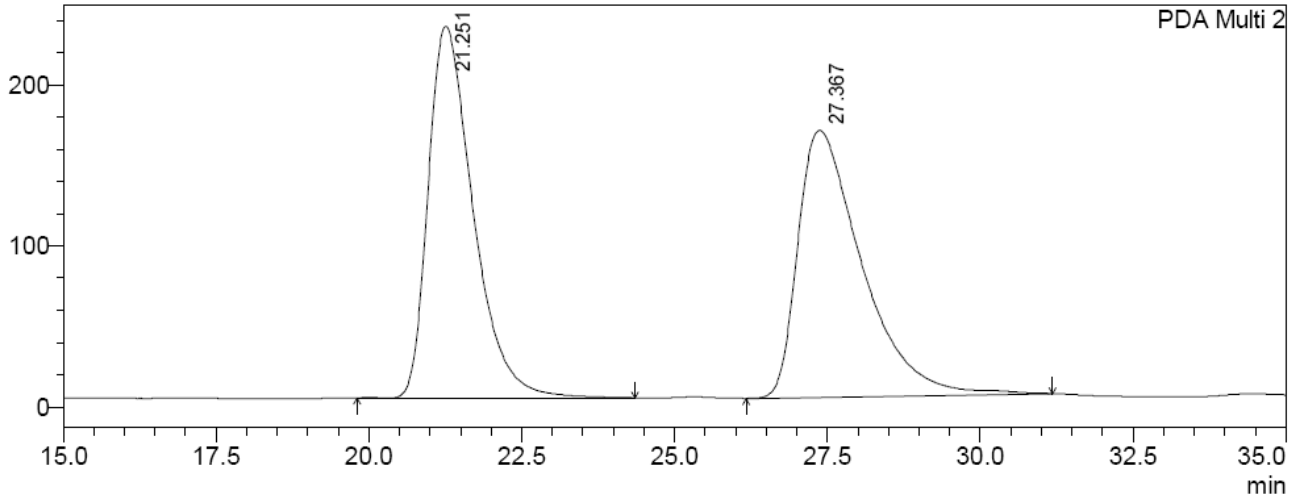
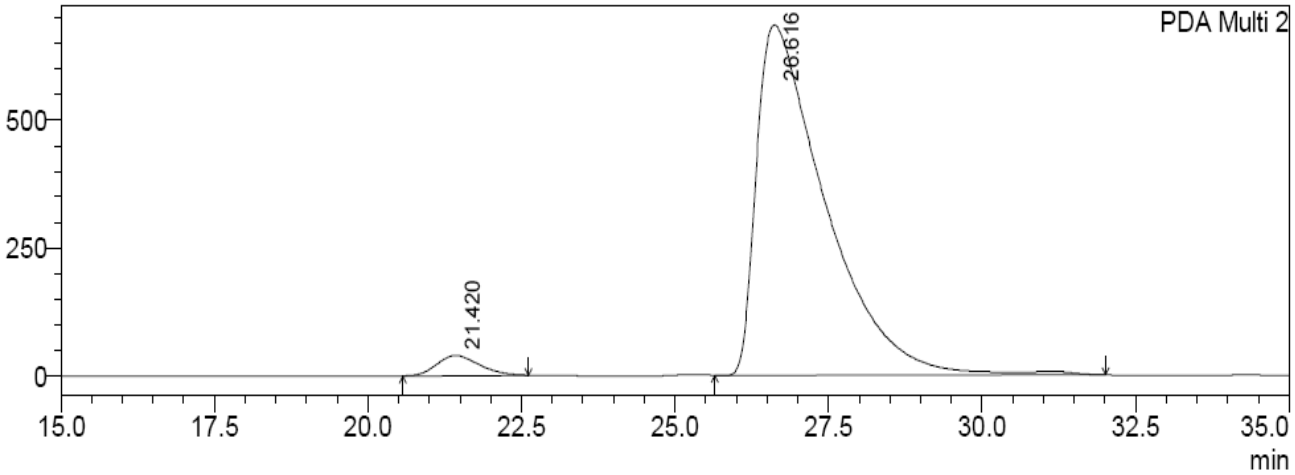


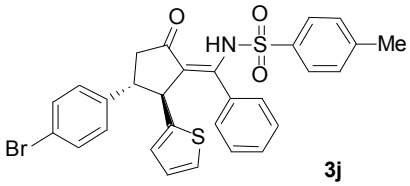
PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.251	11792799	230633	49.343	58.165
2	27.367	12106847	165881	50.657	41.835
Total		23899646	396514	100.000	100.000



PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.420	1892251	39185	3.409	5.417
2	26.616	53609608	684195	96.591	94.583
Total		55501860	723380	100.000	100.000



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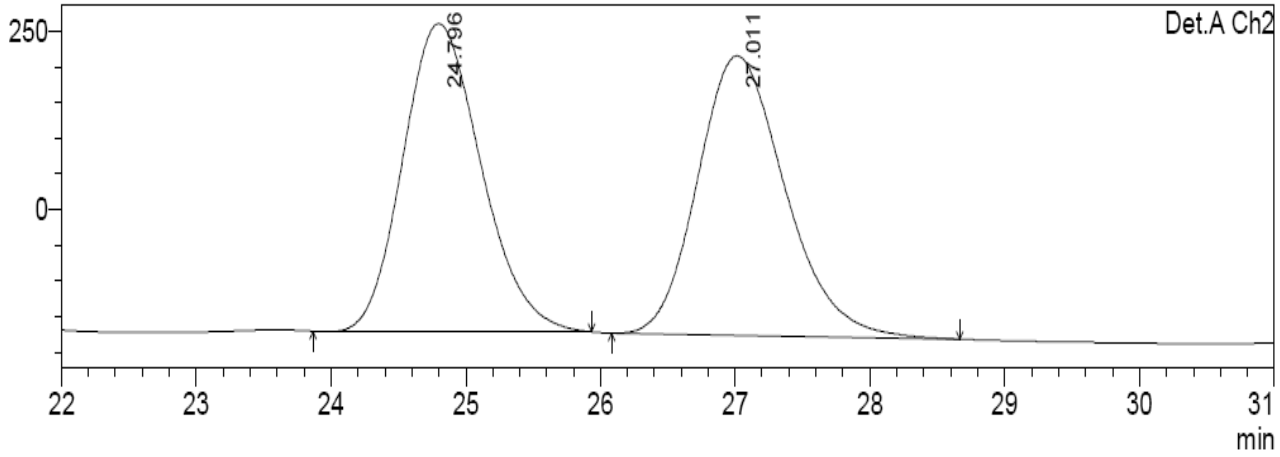
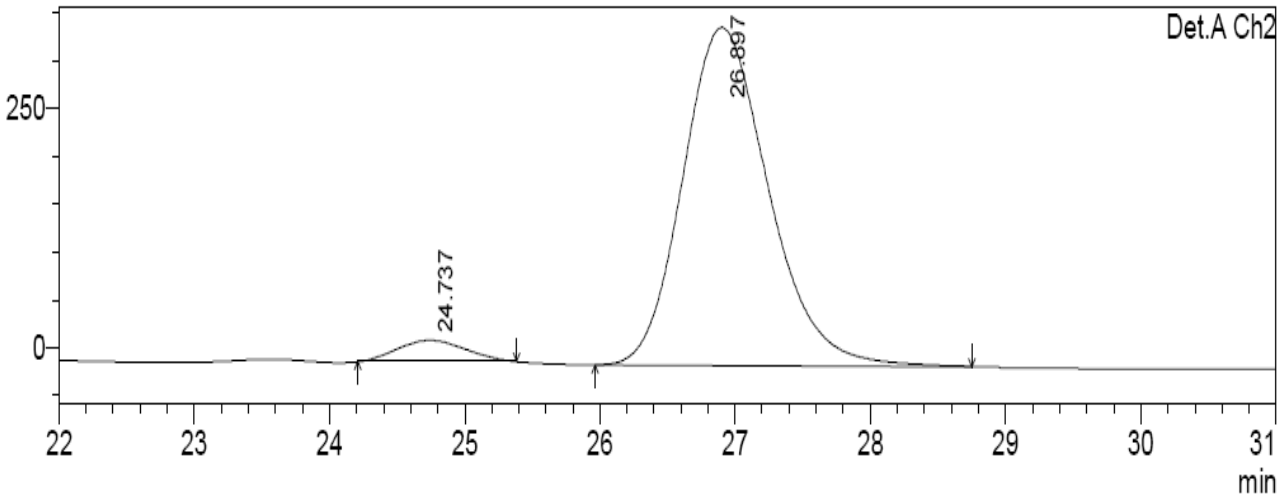


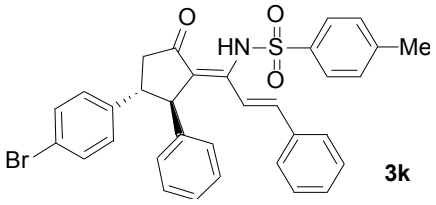
UV Detector Ch2 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.796	17430568	432117	49.617	52.417
2	27.011	17699514	392267	50.383	47.583
Total		35130082	824384	100.000	100.000



UV Detector Ch2 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.737	781985	22086	4.788	5.892
2	26.897	15551524	352762	95.212	94.108
Total		16333509	374848	100.000	100.000



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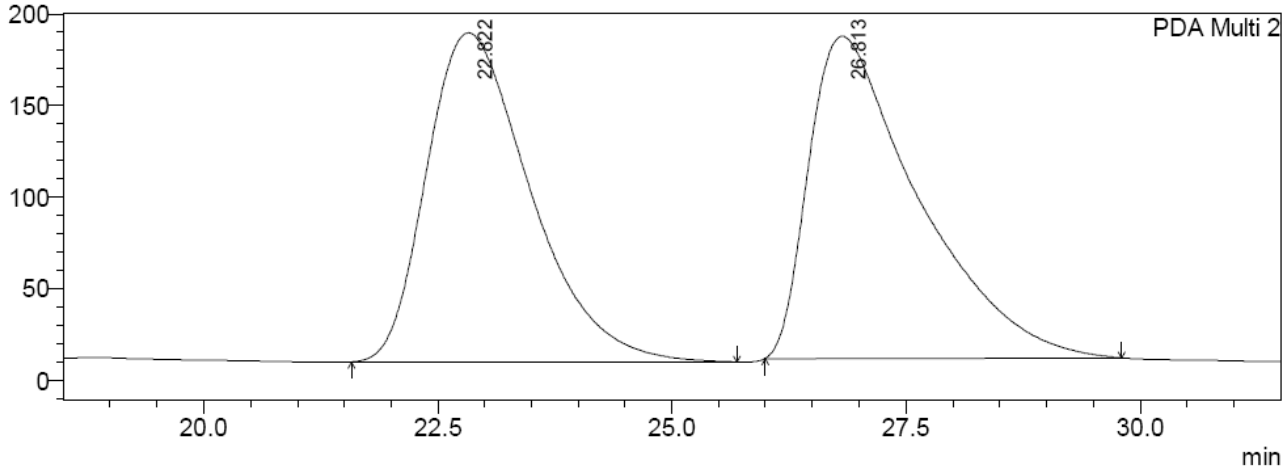
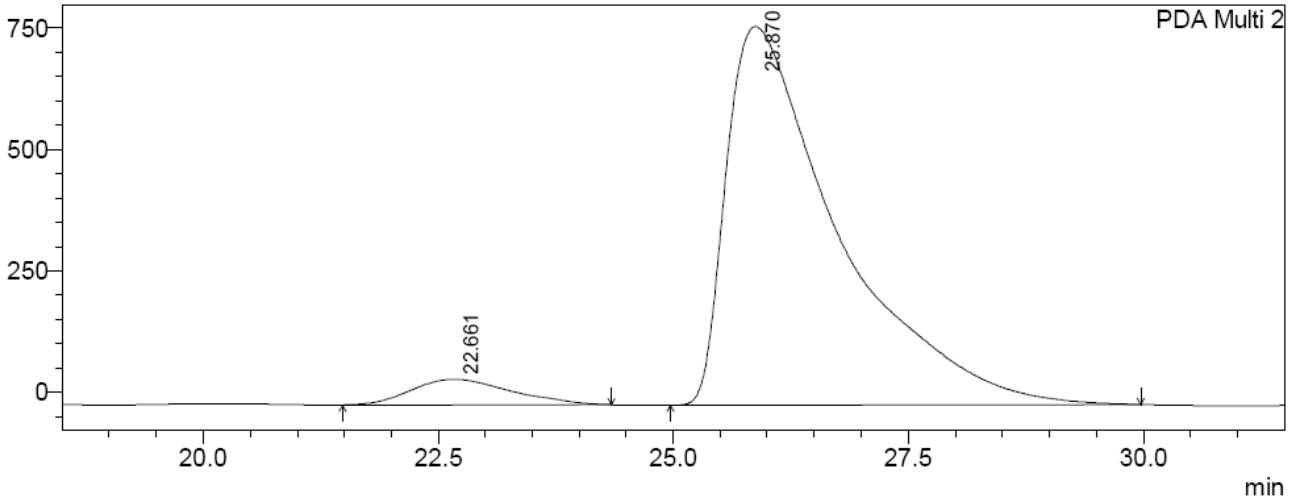


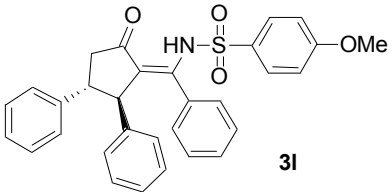
PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.822	13836994	179350	49.181	50.526
2	26.813	14297921	175618	50.819	49.474
Total		28134915	354968	100.000	100.000



PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.661	3919285	52512	5.739	6.310
2	25.870	64372249	779750	94.261	93.690
Total		68291534	832262	100.000	100.000



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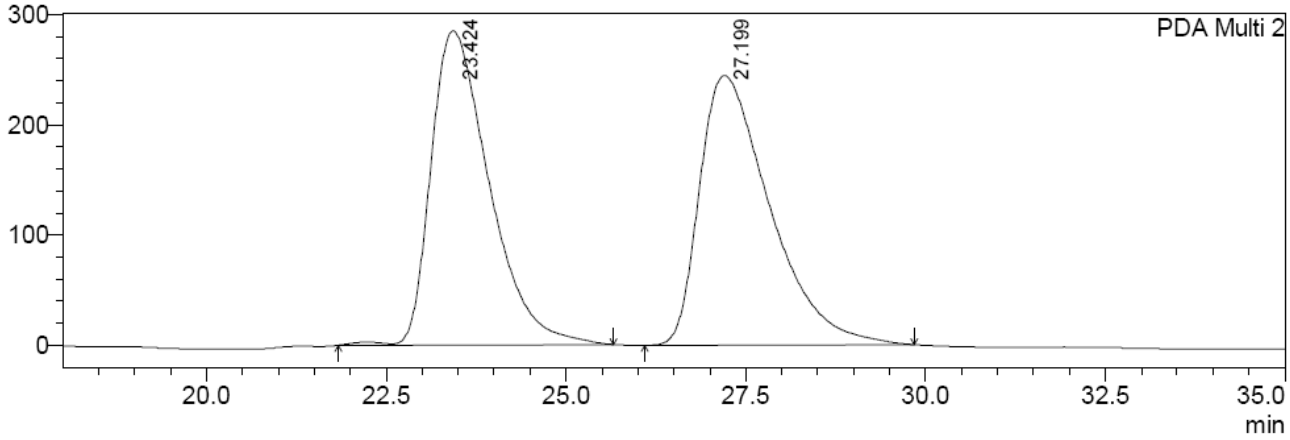
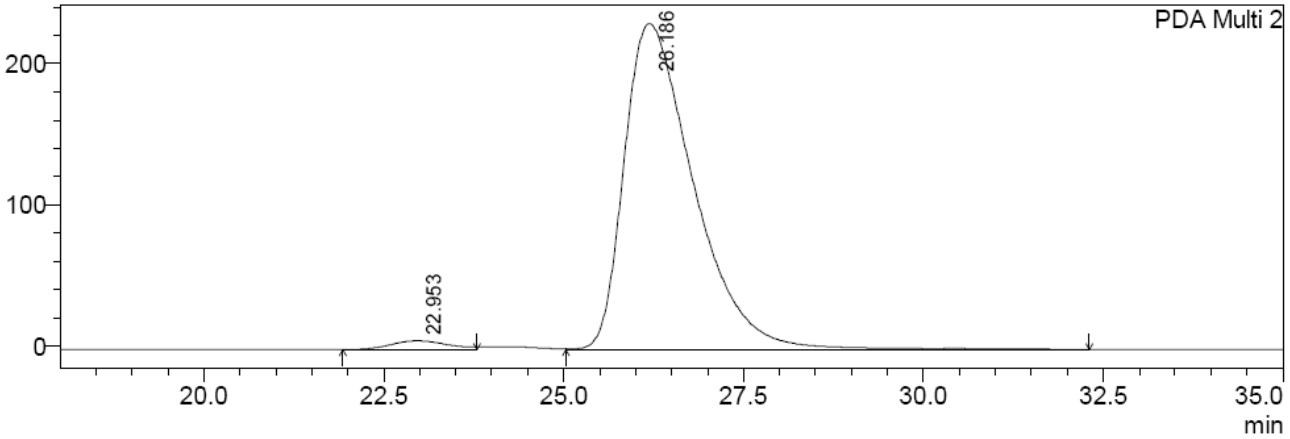


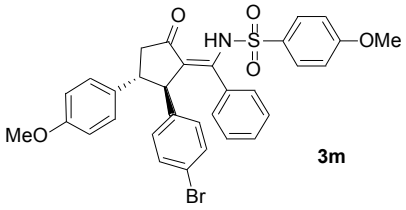
PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.424	16105192	284665	49.137	53.796
2	27.199	16671233	244487	50.863	46.204
Total		32776424	529152	100.000	100.000

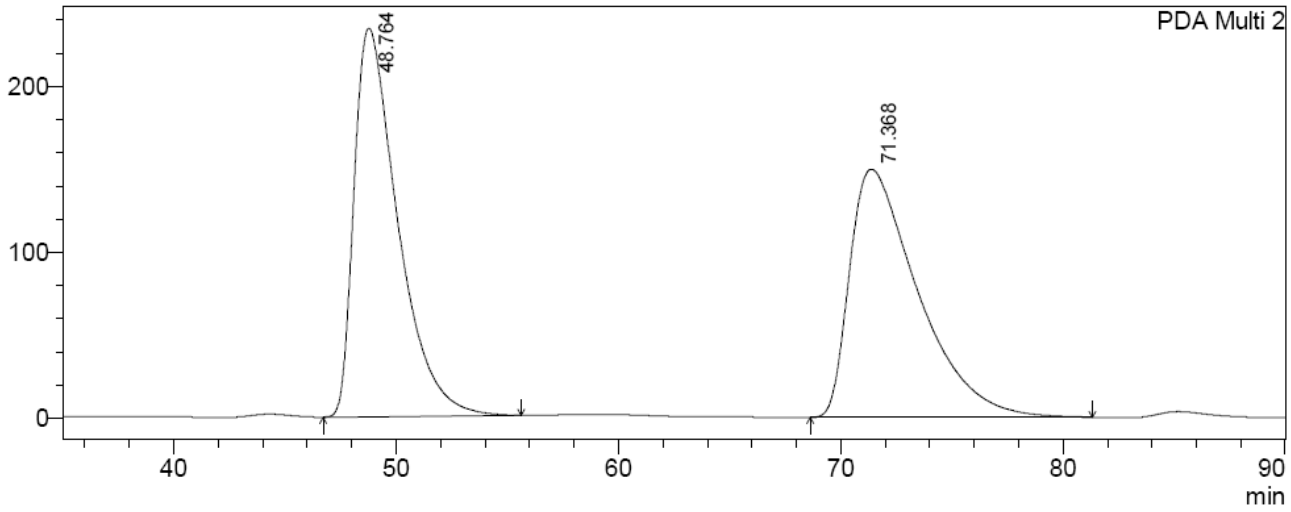


PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.953	340747	6175	2.141	2.604
2	26.186	15572491	230904	97.859	97.396
Total		15913238	237078	100.000	100.000

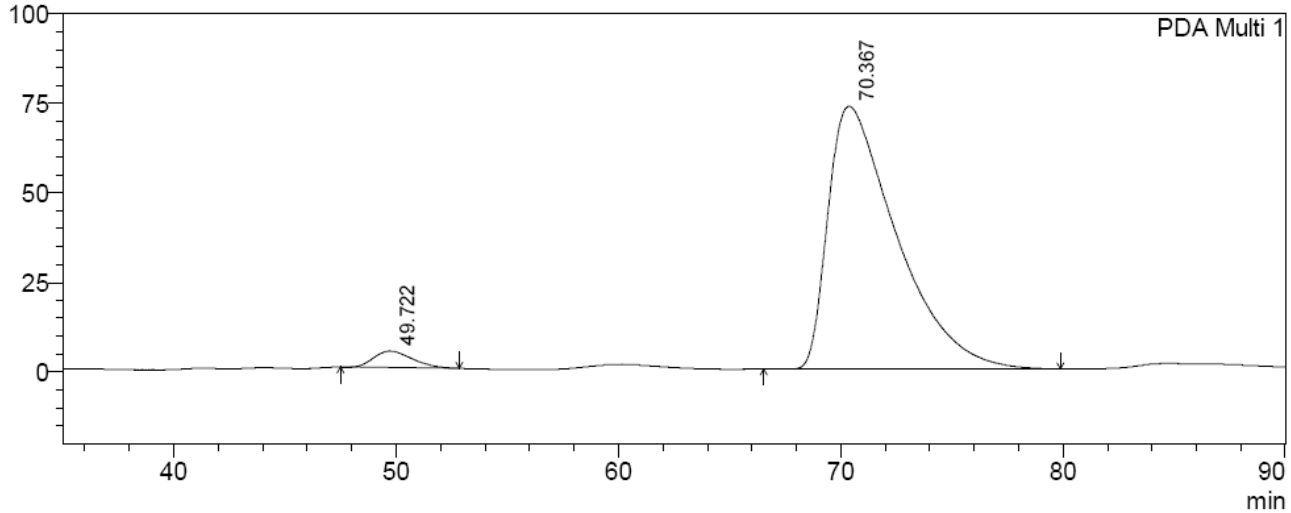


3m



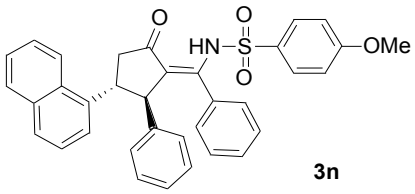
PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	48.764	32062734	234251	49.999	60.995
2	71.368	32063818	149796	50.001	39.005
Total		64126552	384047	100.000	100.000

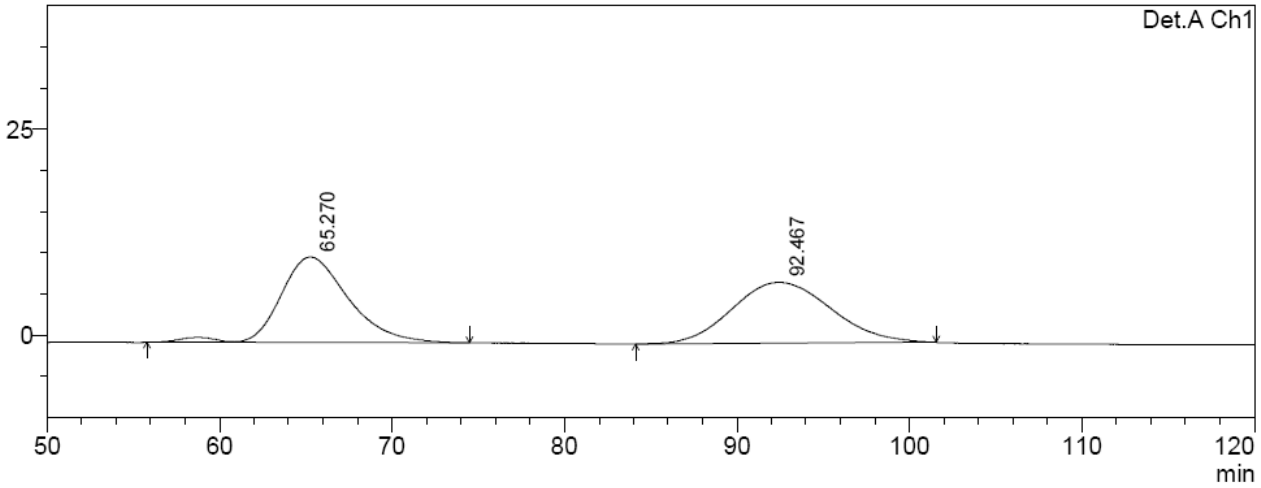


PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	49.722	561624	4622	3.436	5.922
2	70.367	15785013	73419	96.564	94.078
Total		16346637	78041	100.000	100.000

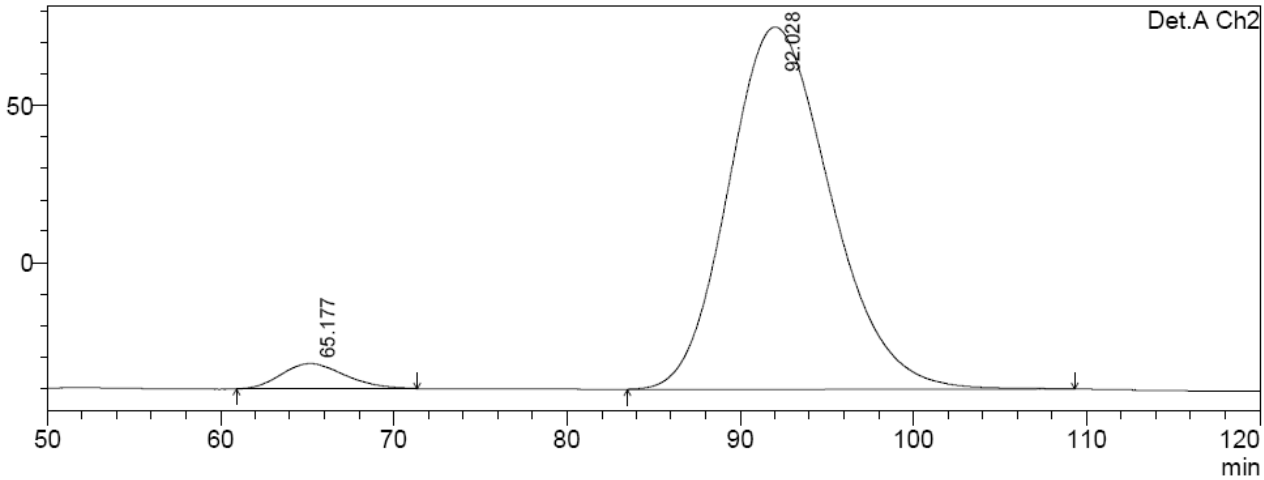


3n



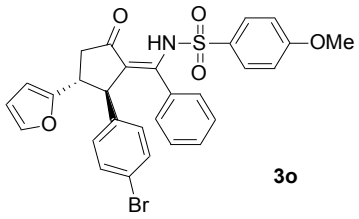
UV Detector Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	65.270	2894021	10384	49.565	58.461
2	92.467	2944844	7378	50.435	41.539
Total		5838865	17762	100.000	100.000

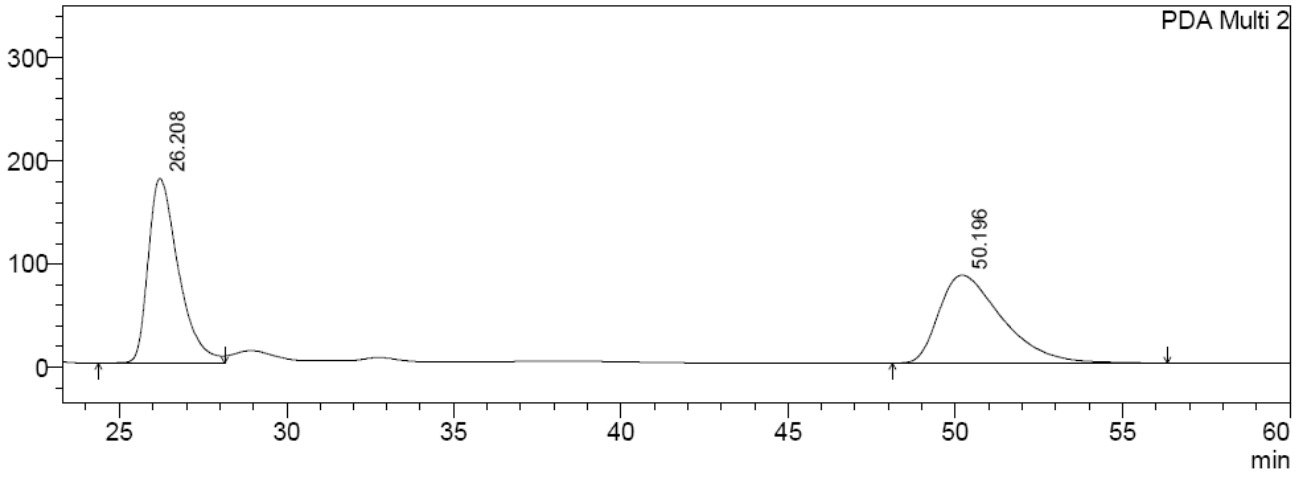


UV Detector Ch2 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	65.177	2063359	8029	4.185	6.518
2	92.028	47234537	115156	95.815	93.482
Total		49297896	123185	100.000	100.000

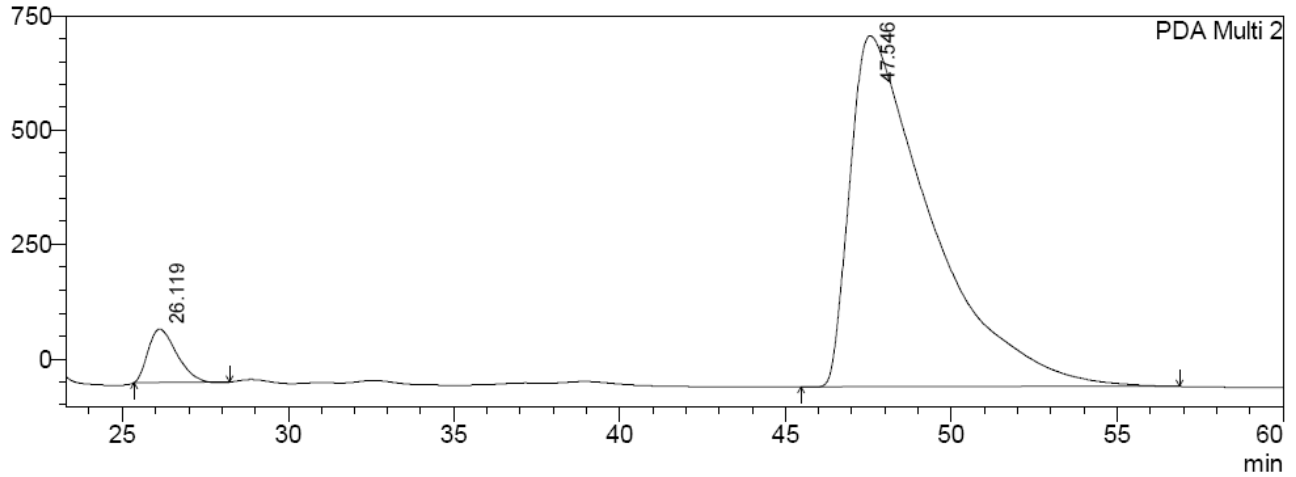


3o



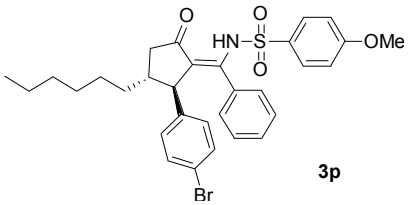
PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.208	11300438	179182	50.118	67.716
2	50.196	11247096	85426	49.882	32.284
Total		22547534	264608	100.000	100.000

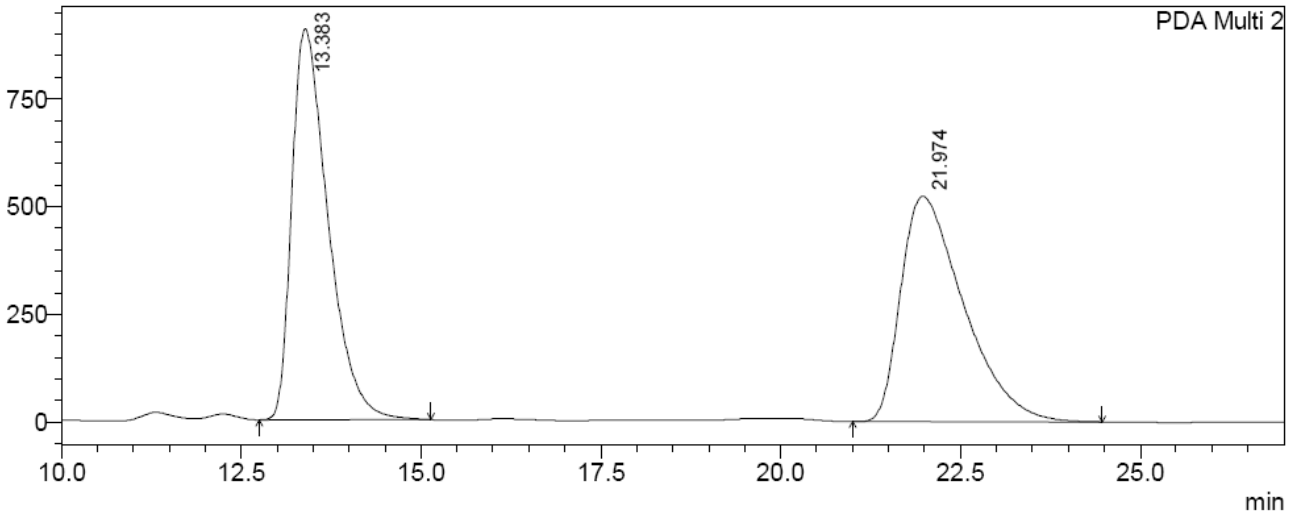


PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.119	6946912	116838	5.039	13.214
2	47.546	130912789	767392	94.961	86.786
Total		137859702	884230	100.000	100.000

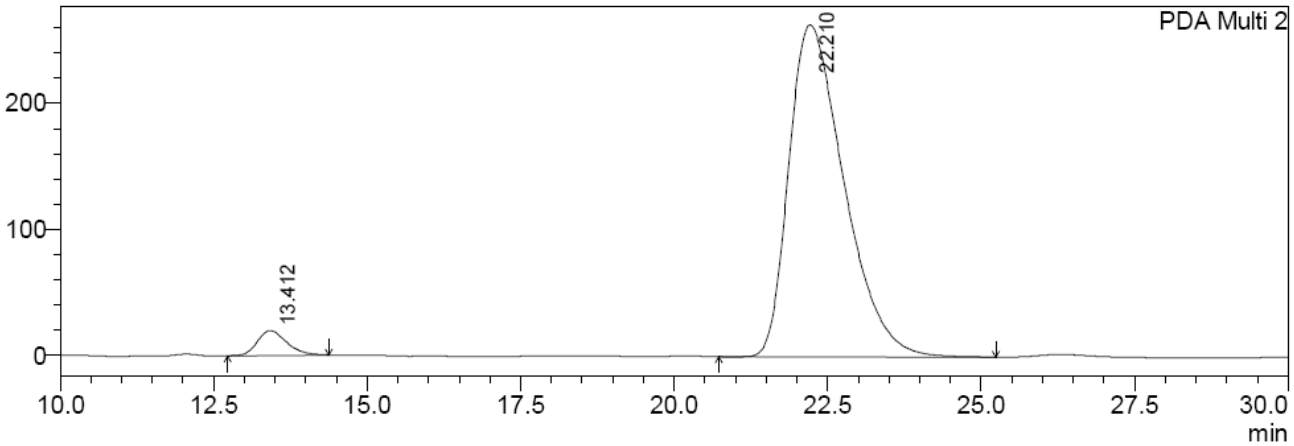


3p



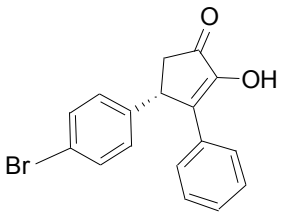
PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.383	31827698	907224	50.014	63.427
2	21.974	31810462	523113	49.986	36.573
Total		63638160	1430337	100.000	100.000

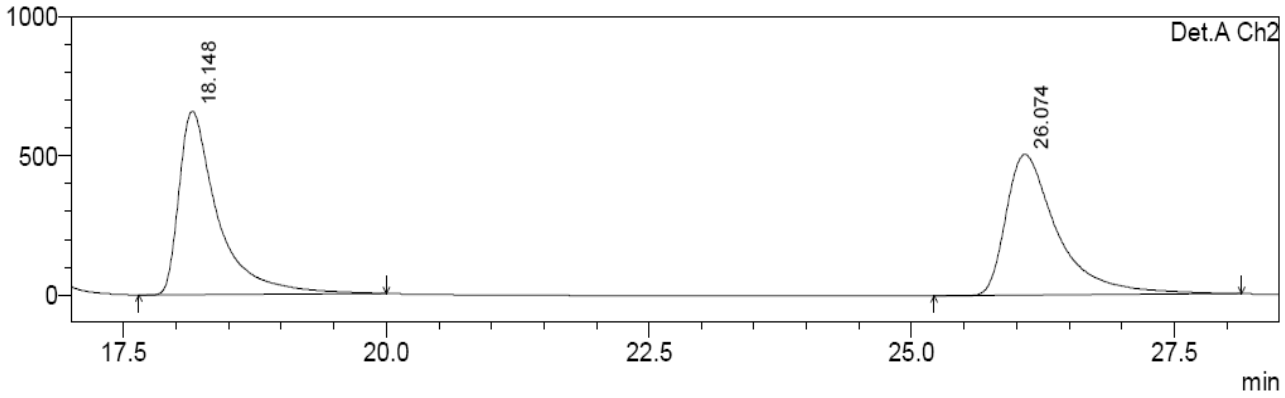


PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.412	656427	19658	3.817	6.935
2	22.210	16541195	263815	96.183	93.065
Total		17197622	283473	100.000	100.000

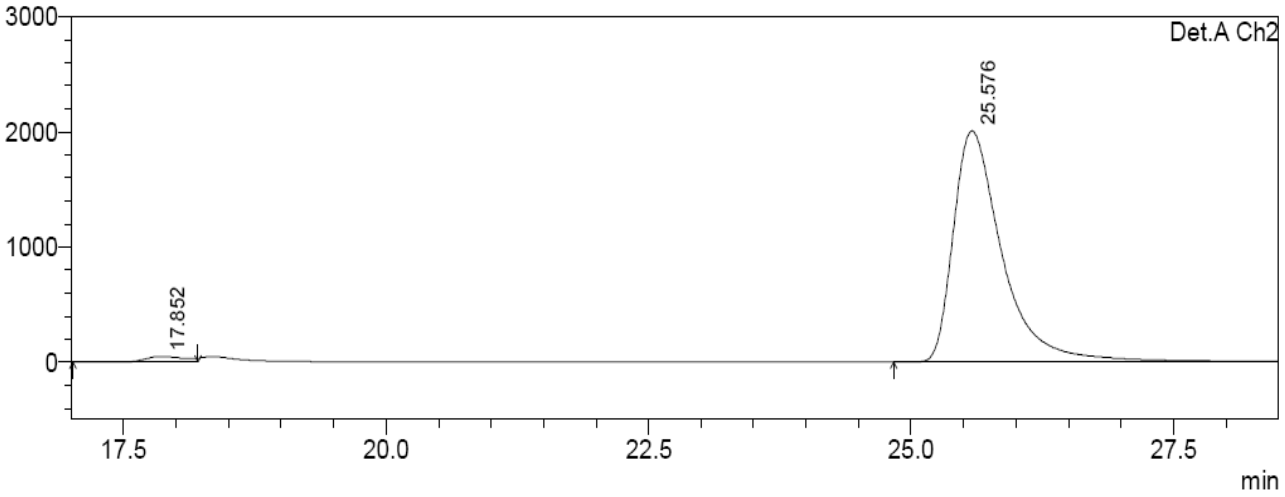


5



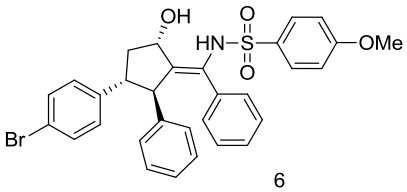
UV Detector Ch2 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.148	17026599	660299	49.522	56.564
2	26.074	17355297	507044	50.478	43.436
Total		34381896	1167343	100.000	100.000

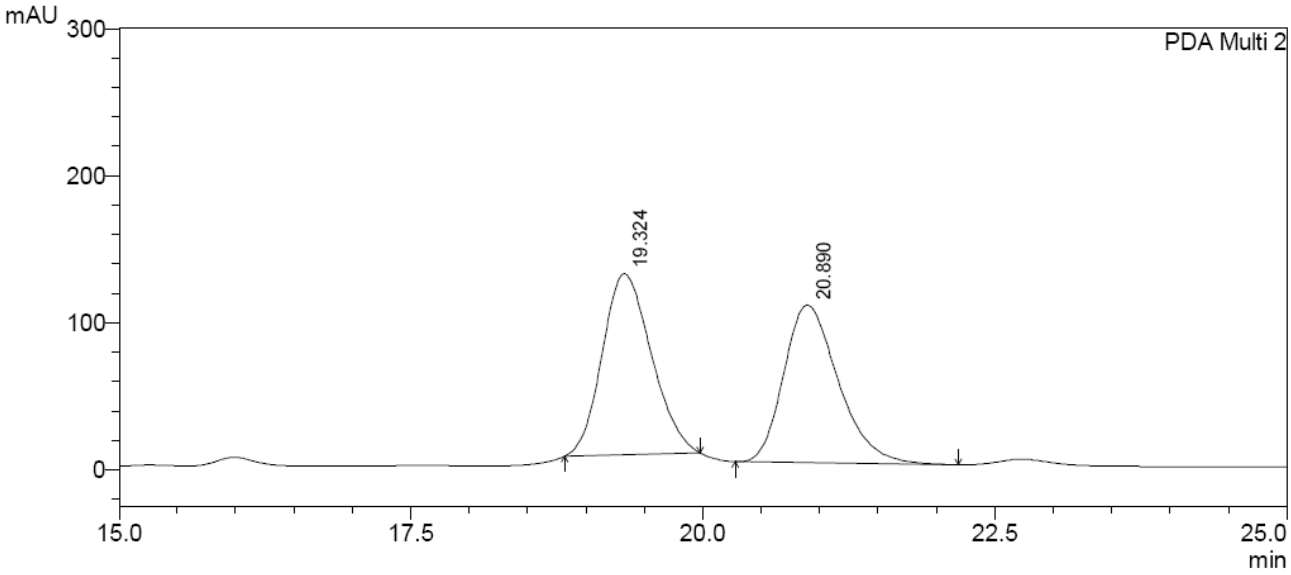


UV Detector Ch2 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.852	1357385	48892	2.035	2.379
2	25.576	65348183	2006227	97.965	97.621
Total		66705568	2055119	100.000	100.000

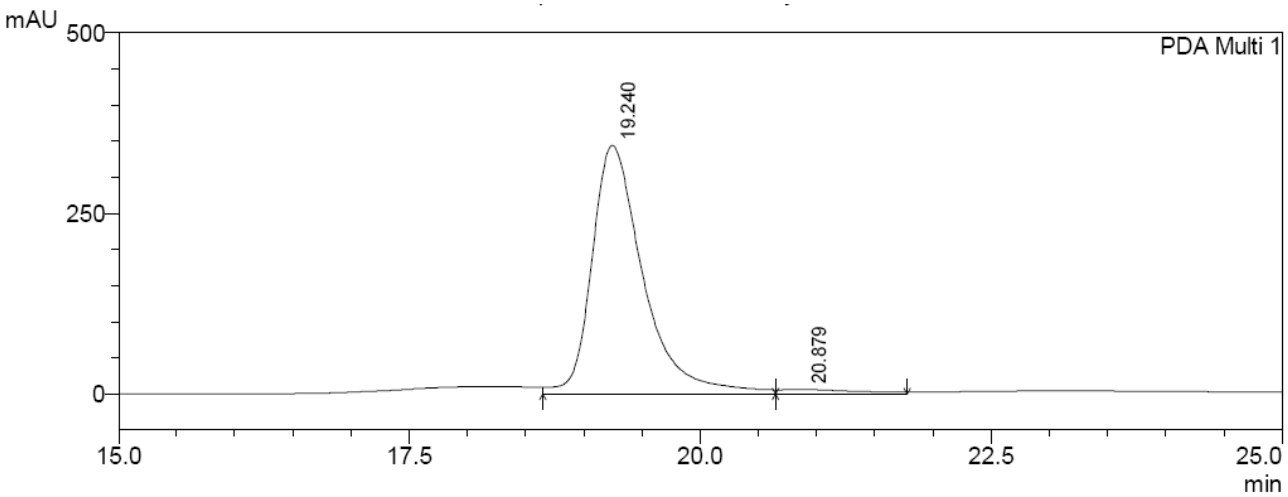


6



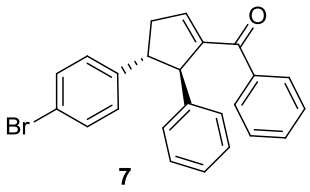
PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.324	3623827	123241	50.911	53.455
2	20.890	3494088	107311	49.089	46.545
Total		7117915	230552	100.000	100.000

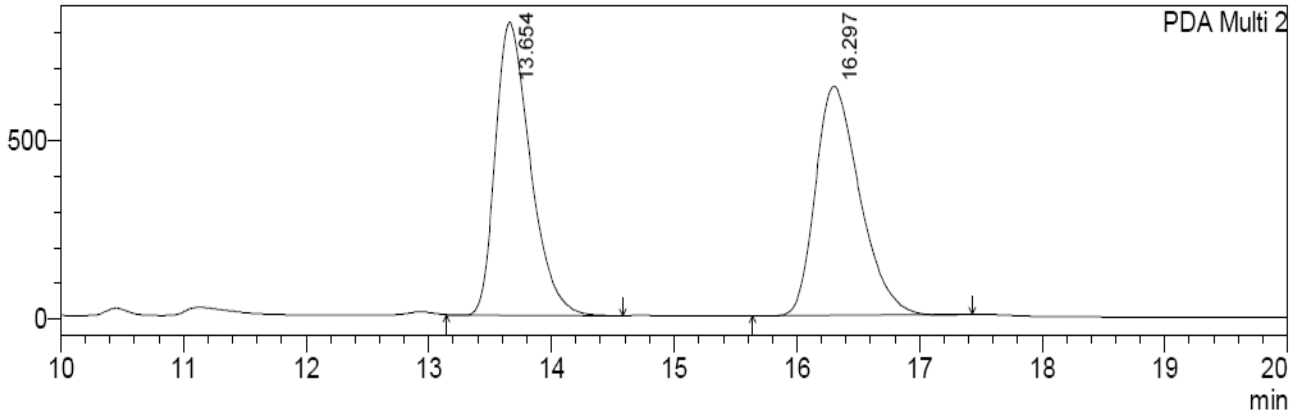


PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.240	10624722	344378	97.137	98.178
2	20.879	313151	6393	2.863	1.822
Total		10937873	350771	100.000	100.000

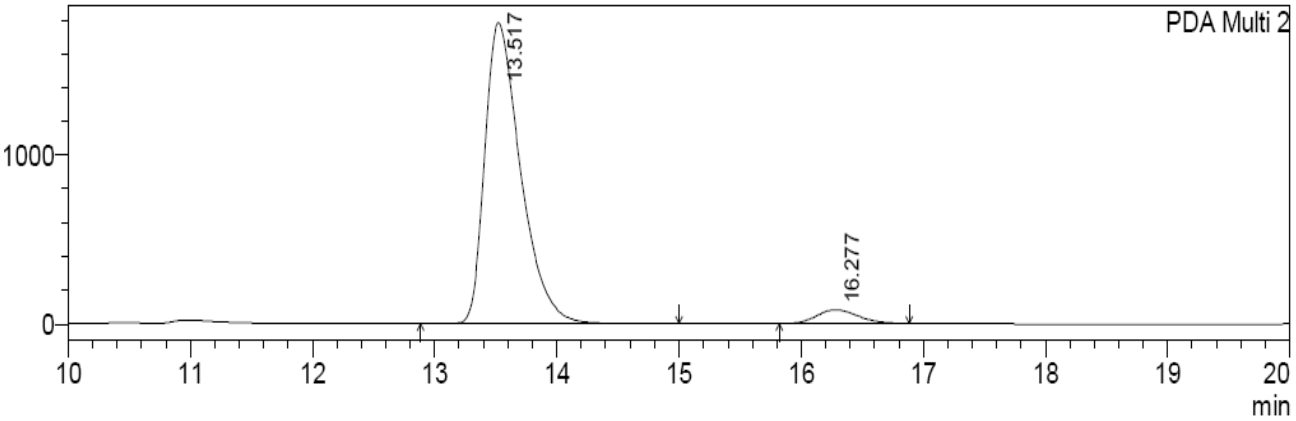


7



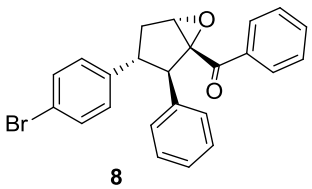
PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.654	16177125	817683	50.271	56.093
2	16.297	16002559	640053	49.729	43.907
Total		32179684	1457736	100.000	100.000

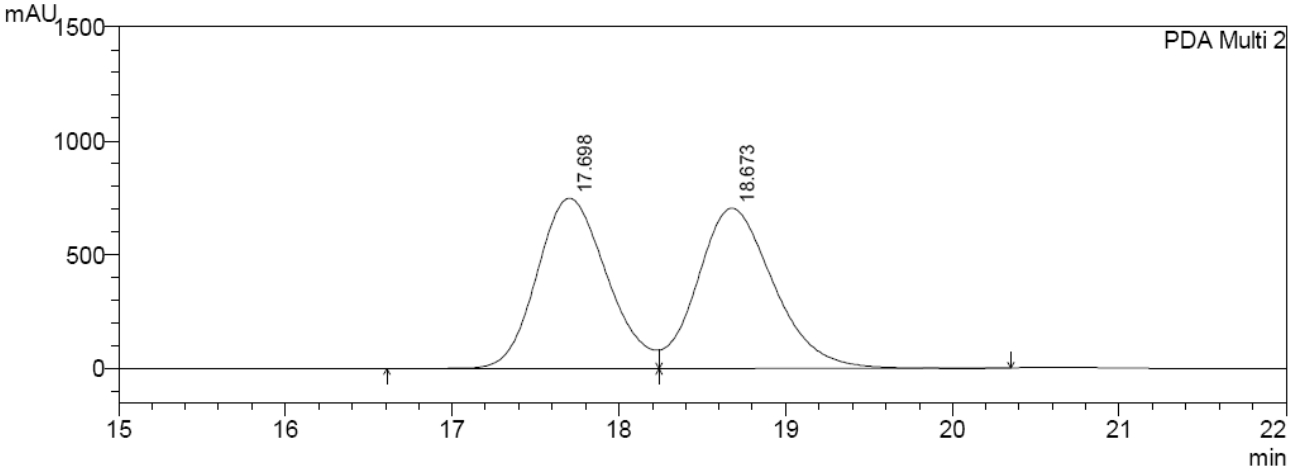


PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.517	36328223	1781775	94.787	95.524
2	16.277	1997852	83492	5.213	4.476
Total		38326075	1865268	100.000	100.000

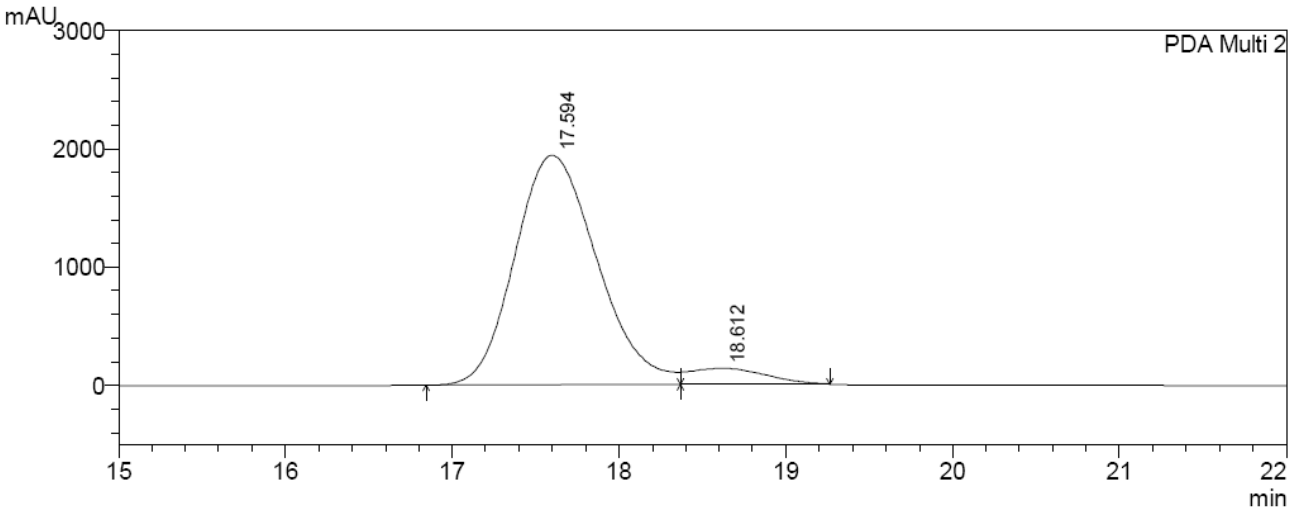


8



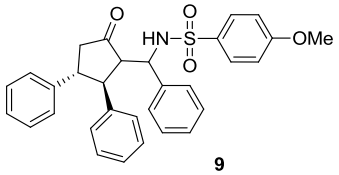
PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.698	21812339	747755	49.701	51.577
2	18.673	22074373	702023	50.299	48.423
Total		43886712	1449777	100.000	100.000

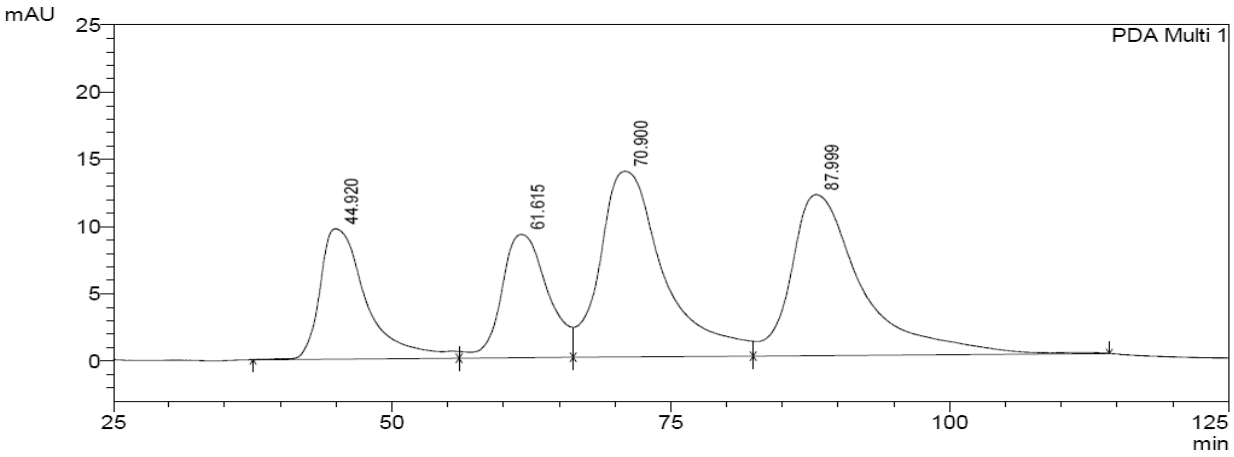


PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.594	66748312	1940332	93.963	93.470
2	18.612	4288378	135560	6.037	6.530
Total		71036690	2075892	100.000	100.000

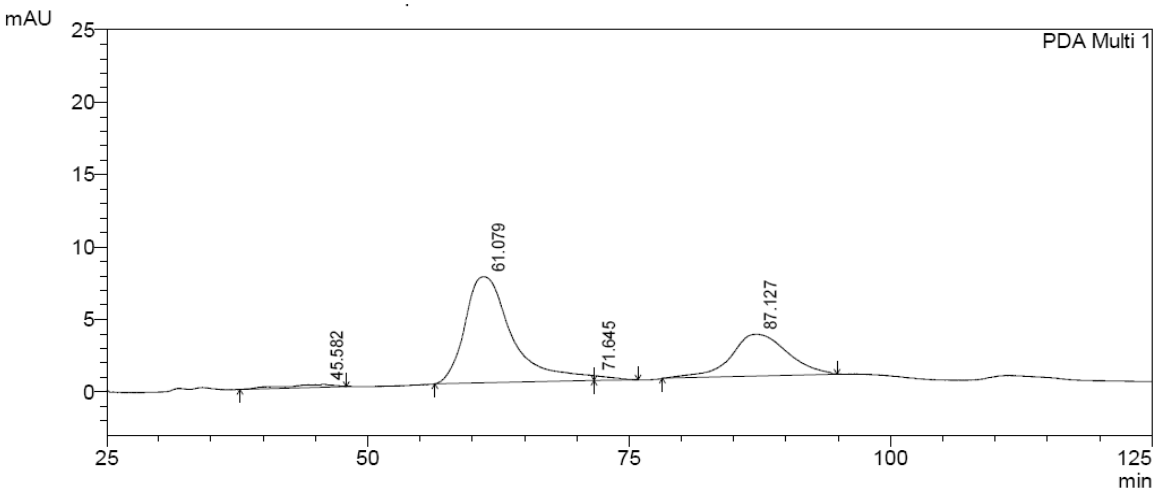


9



PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	44.920	2819073	9712	17.260	21.721
2	61.615	2651294	9184	16.233	20.540
3	70.900	5518406	13833	33.788	30.937
4	87.999	5343868	11984	32.719	26.802
Total		16332641	44713	100.000	100.000



PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	45.582	69823	199	1.996	1.847
2	61.079	2299988	7331	65.765	68.015
3	71.645	38085	349	1.089	3.235
4	87.127	1089380	2900	31.149	26.904
Total		3497275	10779	100.000	100.000