

**Bifunctional Thiourea-Promoted Cascade
aza-Michael-Henry-Dehydration Reactions:
Asymmetric Synthesis of 3-Nitro-1, 2-dihydroquinolines**

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Supporting Information

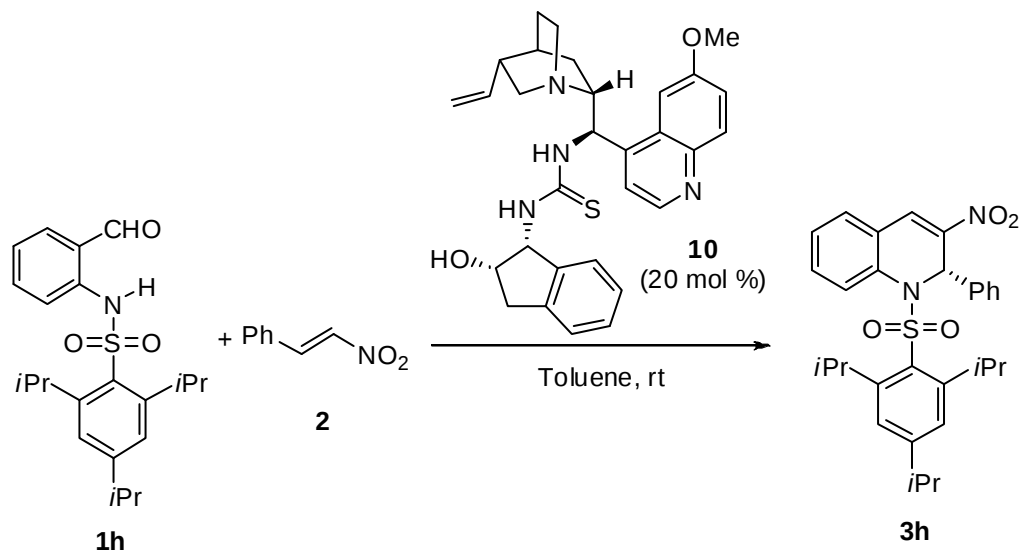
A. General information	S2
B. Representative Procedure for Cascade aza-Michael-Henry-Dehydration Reaction	S3
C. Representative Procedure for the Reductive Desulfonation	S3
D. Determination of the Absolute Configurations of Products	S4
E. Analytical Data and HPLC Chromatogram of the Substrates and Products	S5
F. NMR Spectra of Products	S25

A. General information

Chemicals and solvents were purchased from commercial suppliers and used as received. ^1H and ^{13}C NMR spectra were recorded on a Bruker ACF300 or DPX300 (300 MHz) or AMX500 (500 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.26), carbon (chloroform δ 77.0). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), br s (broad singlet). Coupling constants were reported in Hertz (Hz). Low resolution mass spectra were obtained on a Finnigan/MAT LCQ spectrometer in ESI mode, and a Finnigan/MAT 95XL-T mass spectrometer in FAB mode and mass spectrometer in EI mode. All high resolution mass spectra were obtained on a Finnigan/MAT 95XL-T spectrometer. For thin-layer chromatography (TLC), Merck pre-coated TLC plates (Merck 60 F₂₅₄) were used, and compounds were visualized with a UV light at 254 nm. Flash chromatography separations were performed on Merck 60 (0.040 - 0.063 mm) mesh silica gel.

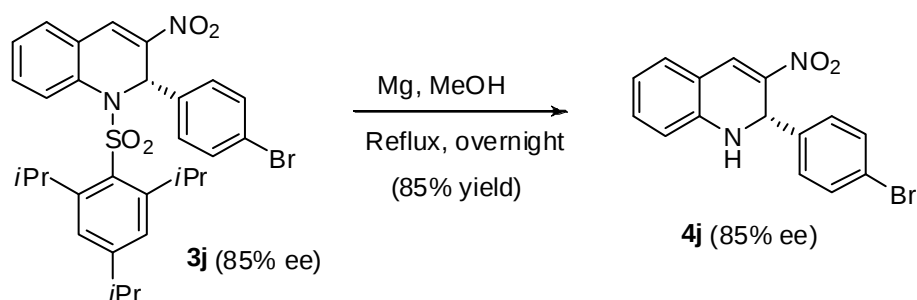
Different sulfonamide-containing 2-aminobenzaldehydes were synthesized according to the literature procedure,¹ and the thiourea catalysts were prepared following the literature procedures.²

B. Representative Procedure for Cascade aza-Michael-Henry-Dehydration Reaction



A solution of *N*-(2-formylphenyl)-2,4,6-triisopropylbenzenesulfonamide **1h** (9.7 mg, 0.025 mmol), (*E*)-(2-nitrovinyl)benzene **2** (11.2 mg, 0.075 mmol) and thiourea **10** (2.6 mg, 0.005 mmol) in toluene (200 μ L) was stirred at room temperature for 72 hrs. The mixture was then diluted with water, and extracted with CH_2Cl_2 several times. The combined organic layers were dried over anhydrous Na_2SO_4 . After concentration, the residue was purified by flash chromatographic column (EtOAc: Hexanes = 1: 10) to afford **3h** as a light yellow solid (10.5 mg, 81% yield).

C. Representative Procedure for the Reductive Desulfonation

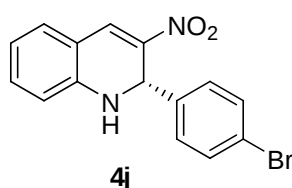


To a mixture of **3j** (44.7 mg, 0.075 mmol) and activated Mg (18 mg, 0.75 mmol) in a 25 mL round bottom flask was added anhydrous methanol (10 mL). The reaction solution was brought to reflux overnight. After cooling down to room temperature, the reaction mixture was quenched by adding 1 M aqueous HCl, and extracted by CH₂Cl₂ several times. The combined organic layers were dried over anhydrous Na₂SO₄. After concentration, the residue was purified by flash chromatographic column (EtOAc: hexanes = 1: 8) to afford **4j** as a dark red solid (21 mg, 85% yield).

D. Determination of the Absolute Configurations of Products

The absolute configuration of **4j** was determined by comparing the HPLC traces of **4j** with those reported in the literature,³ and the absolute configuration of **3j** was deduced accordingly. The configurations of other quinolines were assigned by analogy.

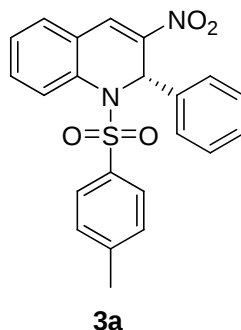
(S)-2-(4-Bromophenyl)-3-nitro-1,2-dihydroquinoline **4j**



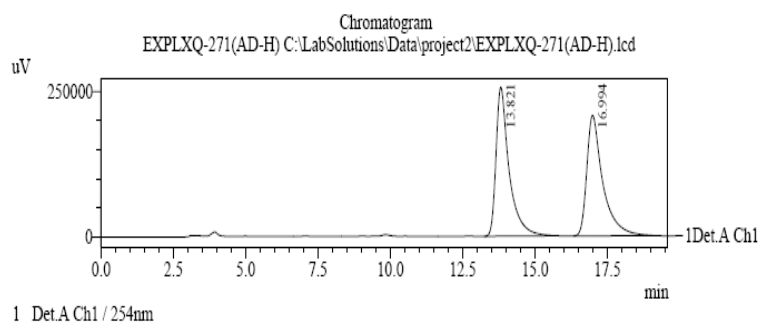
HRMS (EI) m/z calcd for C₁₅H₁₁O₂N₂⁷⁹Br₁ [M]⁺ = 330.0004, found = 329.9994; C₁₅H₁₁O₂N₂⁸¹Br₁ [M]⁺ = 331.9983, found = 331.9989. The NMR spectra of **4j** were consistent with the literature data.³ The enantiomers of **4j** were analyzed by chiral phase HPLC using OD-H column at 254 nm (2-propanol/hexane = 15/85), flow rate = 1.0 mL/min; major enantiomer: t_R = 19.8 min, minor enantiomer: t_R = 15.9 min (literature:³ major enantiomer: t_R = 21.0 min, minor enantiomer: t_R = 15.6 min).

E. Analytical Data and HPLC Chromatogram of the Substrates and Products

(S)-3-Nitro-2-phenyl-1-tosyl-1,2-dihydroquinoline 3a



A yellow solid; Isolated in 95% yield after flash column chromatographic purification (hexane: ethyl acetate = 10: 1 to 5: 1); ^1H NMR (300 MHz, CDCl_3) δ 2.38 (s, 3H), 6.90 (s, 1H), 7.11-7.14 (d, $J = 8.4$ Hz, 2H), 7.28-7.32 (m, 4H), 7.48 (m, 1H), 7.57 (s, 1H), 7.77-7.79 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 21.5, 55.5, 125.1, 126.6, 126.8, 127.6, 128.5, 128.6, 128.7, 128.8, 129.6, 129.8, 132.5, 134.2, 134.8, 135.1, 144.0, 144.6. The enantiomers were analyzed by HPLC using an AD-H column at 254 nm (2-propanol: hexane = 10: 90), 1.0 mL/min; Major enantiomer: $t_R = 15.8$ min, minor enantiomer: $t_R = 13.0$ min. HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{18}\text{O}_4\text{N}_2^{23}\text{Na}_1^{32}\text{S}_1$ $[\text{M}+\text{Na}]^+ = 429.0880$, found = 429.0894.

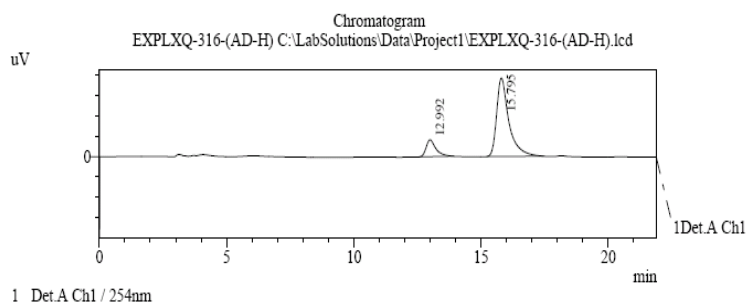


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.821	8061457	256637	50.156	55.278
2	16.994	8011205	207632	49.844	44.722
Total		16072662	464269	100.000	100.000

Racemic **3a**



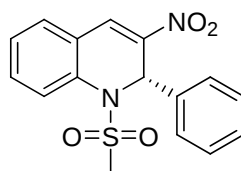
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.992	440655	16504	14.628	17.649
2	15.795	2571702	77008	85.372	82.351
Total		3012357	93512	100.000	100.000

Enantiomeric enriched **3a**

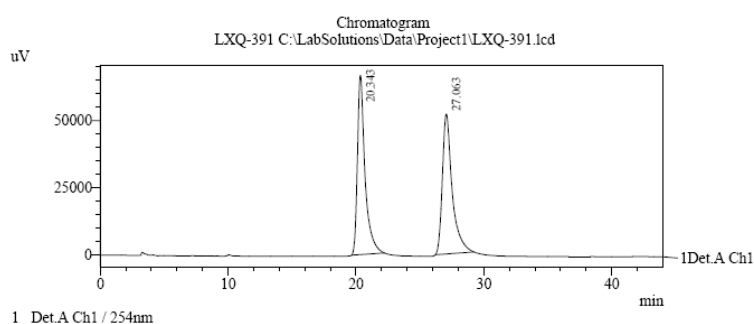
(S)-1-(Methylsulfonyl)-3-nitro-2-phenyl-1,2-dihydroquinoline **3b**



3b

A yellow oil; Isolated in 95% yield after flash column chromatographic purification (hexane: ethyl acetate = 10: 1 to 5: 1); ¹H NMR (300 MHz, CDCl₃) δ 2.78

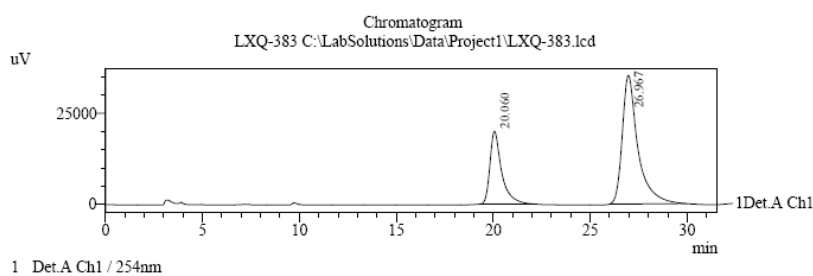
(s, 3H), 6.88 (s, 3H), 7.25-7.34 (m, 6H), 7.44-7.52 (m, 2H), 7.65-7.66 (d, $J = 8.2$ Hz, 1H), 8.15(s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 38.6, 55.7, 124.0, 126.3, 126.6, 127.1, 128.8, 129.0, 129.2, 130.5, 133.0, 134.4, 135.4, 144.7; The enantiomers were analyzed by HPLC using an AD-H column at 254 nm (2-propanol: hexane = 10: 90), 1.0 mL/min; Major enantiomer: $t_R = 26.9$ min, minor enantiomer: $t_R = 20.0$ min. HRMS (EI) m/z calcd for $\text{C}_{16}\text{H}_{14}\text{O}_4\text{N}_2$ $^{32}\text{S}_1$ $[\text{M}]^+ = 330.0674$, found = 330.0672.



PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.343	2747016	66633	49.745	56.164
2	27.063	2775201	52008	50.255	43.836
Total		5522217	118641	100.000	100.000

Racemic **3b**

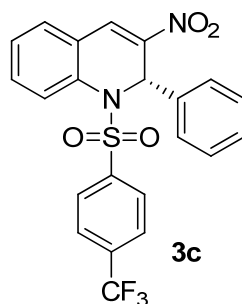


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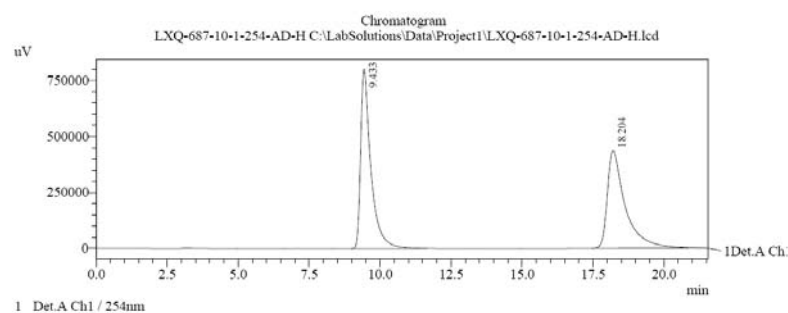
Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.060	835145	19909	29.642	36.104
2	26.967	1982328	35234	70.358	63.896
Total		2817473	55143	100.000	100.000

Enantiomeric enriched **3b**

(S)-3-Nitro-2-phenyl-1-(4-(trifluoromethyl)phenylsulfonyl)-1,2-dihydroquinoline 3c

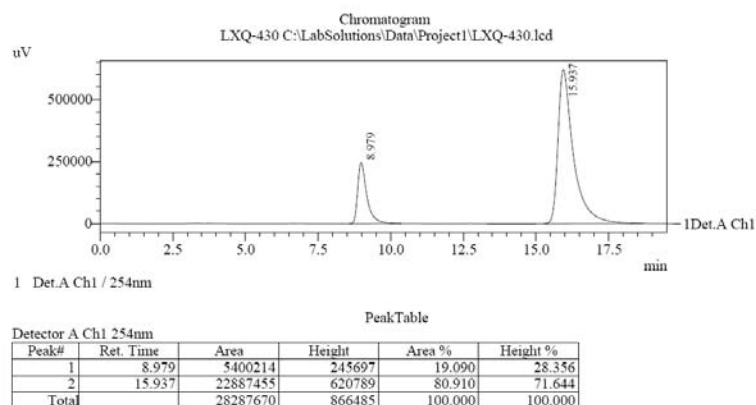


A yellow solid; Isolated in 43% yield after flash column chromatographic purification (hexane: ethyl acetate = 10: 1); ^1H NMR (300 MHz, CDCl_3) δ 6.92-6.95 (m, 1H), 7.27-7.31 (m, 5H), 7.35-7.38 (m, 2H), 7.50-7.62 (m, 6H), 7.79-7.83 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 55.7, 121.0, 124.6, 124.9, 125.9, 126.0, 126.1, 126.2, 126.7, 127.1, 128.0, 128.3, 128.4, 128.8, 129.0, 130.1, 132.8, 133.4, 134.5, 134.9, 135.4, 141.0, 144.0; The enantiomers were analyzed by HPLC using an AD-H column at 254 nm (2-propanol: hexane = 10: 90), 1.0 mL/min; Major enantiomer: t_R = 16.0 min, minor enantiomer: t_R = 9.0 min. HRMS (EI) m/z calcd for $\text{C}_{22}\text{H}_{15}\text{O}_4\text{N}_2\text{F}_3$ $^{32}\text{S}_1$ $[\text{M}]^+ = 460.0705$, found = 460.0711.



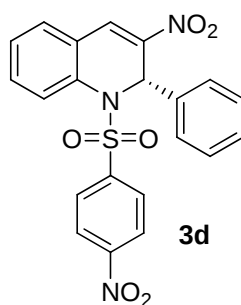
PeakTable					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.433	20063332	800073	51.077	64.712
2	18.204	19216990	436296	48.923	35.288
Total		39280322	1236369	100.000	100.000

Racemic **3c**

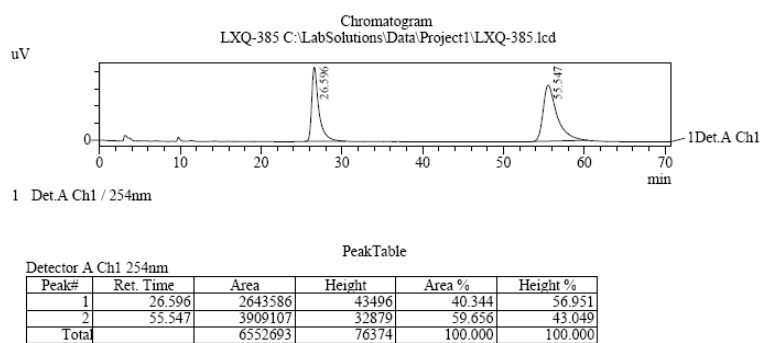


Enantiomeric enriched **3c**

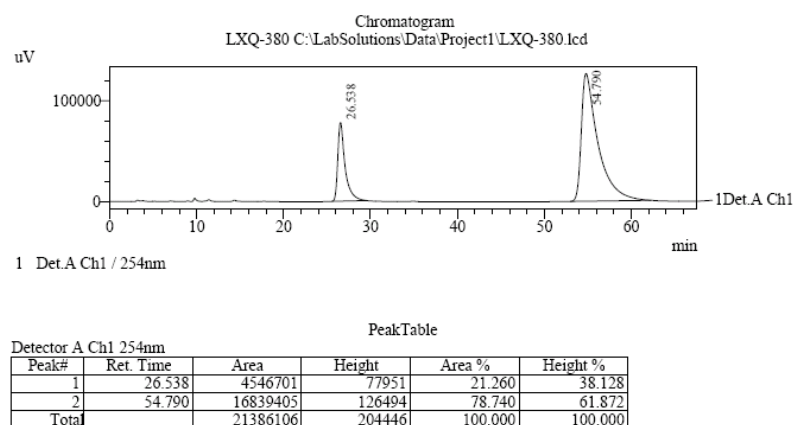
(S)-3-Nitro-1-(4-nitrophenylsulfonyl)-2-phenyl-1,2-dihydroquinoline **3d**



A yellow oil; Isolated in 79% yield after flash column chromatographic purification (hexane: ethyl acetate = 5: 1 to 3:1); ^1H NMR (300 MHz, CDCl_3) δ 6.91 (s, 1H), 7.21-7.27 (m, 5H), 7.34-7.37 (m, 2H), 7.51-7.60 (m, 4H), 7.76-7.79 (d, J = 7.9 Hz, 1H), 8.15-8.18 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 55.8, 124.1, 124.9, 126.7, 127.9, 128.2, 128.4, 128.9, 129.1, 130.2, 132.9, 133.1, 134.2, 143.0, 144.0, 150.4. The enantiomers were analyzed by HPLC using an IA -H column at 254 nm (2-propanol: hexane = 10: 90), 1.0 mL/min; Major enantiomer: t_R = 54.8 min, minor enantiomer: t_R = 26.5 min. HRMS (EI) m/z calcd for $\text{C}_{21}\text{H}_{15}\text{O}_6\text{N}_3^{32}\text{S}_1$ $[\text{M}]^+$ = 437.0682, found = 429.0680.

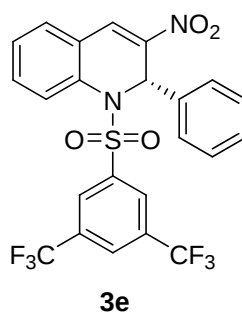


Racemic **3d**



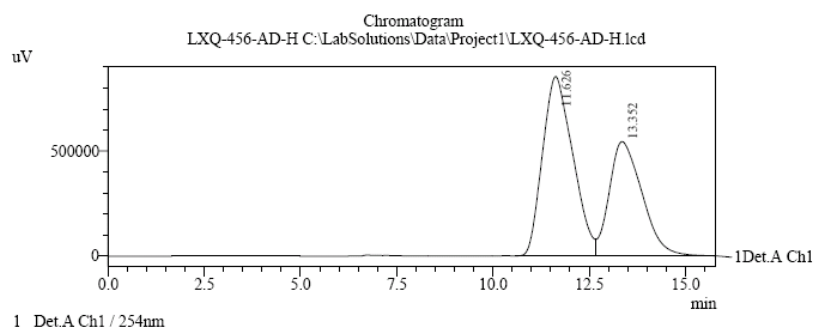
Enantiomeric enriched **3d**

(S)-1-(3,5-bis(trifluoromethyl)phenylsulfonyl)-3-nitro-2-phenyl-1,2-dihydroquinoline **3e**



A yellow solid, isolated in 95% yield; ^1H NMR (300 MHz, CDCl_3) δ 6.92 (s, 1H), 7.22-7.46 (m, 7H), 7.53-7.61 (m, 2H), 7.80-7.82 (d, $J = 1.3$ Hz, 2H), 8.05 (s, 1H); ^{13}C

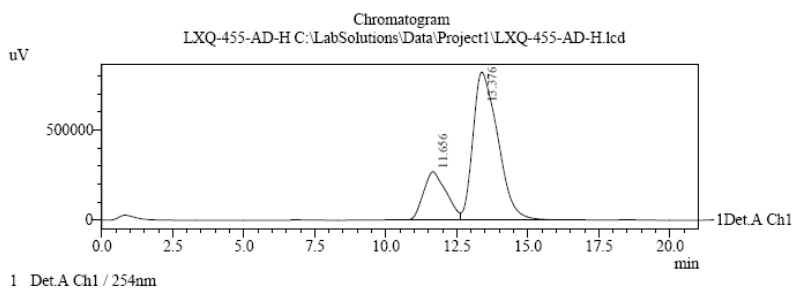
NMR (75 MHz, CDCl₃) δ 56.0, 123.7, 124.9, 126.6, 126.7, 126.8, 127.9, 128.4, 128.5, 128.9, 129.2, 130.2, 132.6, 132.9, 133.0, 133.9, 139.8, 144.0; The enantiomers were analyzed by HPLC using an AD-H column at 254 nm (2-propanol: hexane = 2: 98), 0.5 mL/min; Major enantiomer: t_R = 13.3 min, minor enantiomer: t_R = 11.6 min. HRMS (EI) m/z calcd for C₂₃H₁₄O₄N₂F₆ ³²S₁ [M]⁺ = 528.0578, found = 528.0572.



PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.626	46649141	853176	59.135	61.091
2	13.352	32236688	543385	40.865	38.909
Total		78885829	1396562	100.000	100.000

Racemic **3e**

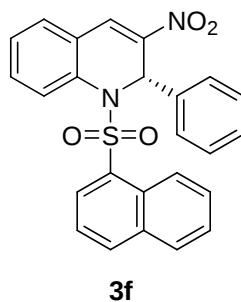


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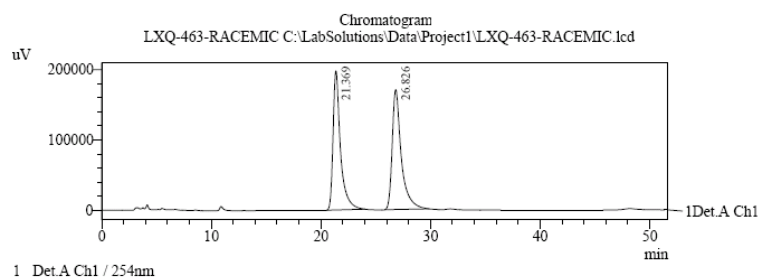
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.656	14742035	266876	22.831	24.550
2	13.376	49828082	820179	77.169	75.450
Total		64570118	1087056	100.000	100.000

Enantiomeric enriched **3e**

(S)-1-(Naphthalen-1-ylsulfonyl)-3-nitro-2-phenyl-1,2-dihydroquinoline **3f**



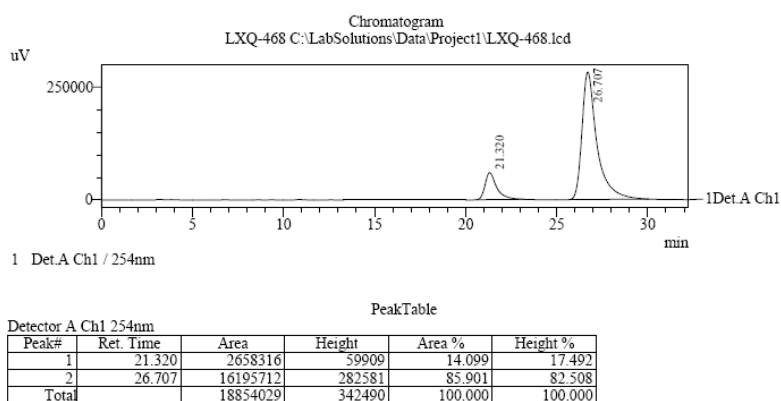
A yellow solid; Isolated in 95% yield after flash column chromatographic purification (hexane: ethyl acetate = 10: 1 to 5:1); ^1H NMR (300 MHz, CDCl_3) δ 7.04 (s, 1H), 7.23-7.31 (m, 7H), 7.33-7.42 (m, 2H), 7.50-7.67 (m, 3H), 7.78-7.80 (d, J = 8.5 Hz, 2H), 7.85-7.89 (m, 2H), 8.00-8.01 (d, J = 1.5 Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 55.6, 121.5, 125.1, 126.7, 127.6, 127.8, 127.8, 128.2, 128.3, 128.4, 128.7, 128.8, 129.1, 129.2, 129.3, 129.8, 131.7, 132.5, 134.0, 134.6, 134.9, 135.0, 143.9; The enantiomers were analyzed by HPLC using an AD-H column at 254 nm (2-propanol: hexane = 10: 90), 1.0 mL/min; Major enantiomer: t_R = 26.7 min, minor enantiomer: t_R = 21.3 min. HRMS (EI) m/z calcd for $\text{C}_{25}\text{H}_{18}\text{O}_4\text{N}_2^{32}\text{S}_1$ $[\text{M}]^+$ = 442.0987, found = 442.0986.



PeakTable

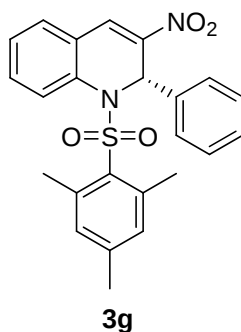
Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.369	9270913	197926	48.521	53.725
2	26.826	9835975	170476	51.479	46.275
Total		19106889	368402	100.000	100.000

Racemic **3f**



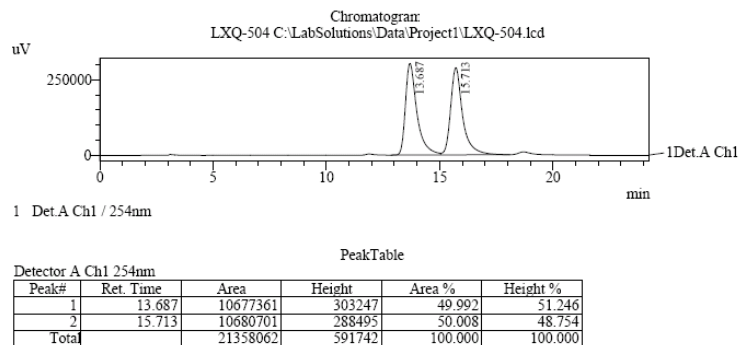
Enantiomeric enriched **3f**

(S)-1-(Mesitylsulfonyl)-3-nitro-2-phenyl-1,2-dihydroquinoline **3g**

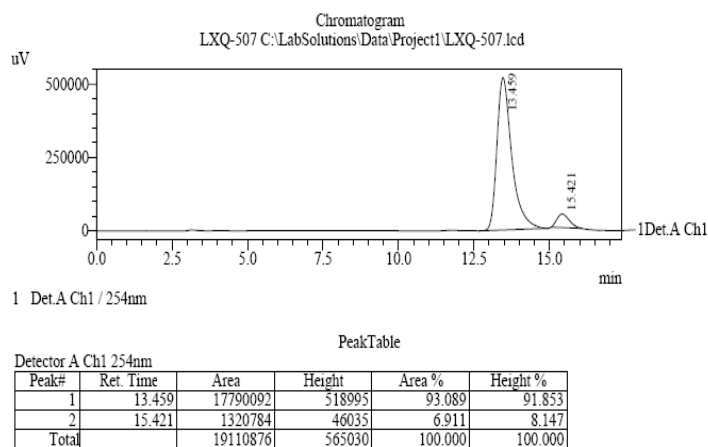


A yellow solid; Isolated in 80% yield after flash column chromatographic purification (hexane: ethyl acetate = 10: 1 to 5:1); ^1H NMR (300 MHz, CDCl_3) δ 2.32 (s, 3H), 2.46 (s, 6H), 6.68 (s, 1H), 6.94 (s, 2H), 7.19-7.30 (m, 7H), 7.40-7.43 (m, 2H), 7.53 (m, 1H), 7.92 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 20.9, 22.3, 54.4, 125.1, 126.7, 126.9, 128.6, 128.7, 129.0, 130.2, 132.1, 132.3, 132.5, 135.0, 135.3, 140.3, 143.6, 144.6; The enantiomers were analyzed by HPLC using an AD-H column at 254 nm (2-propanol: hexane = 5: 95), 1.0 mL/min; Major enantiomer: t_R = 13.5 min, minor enantiomer: t_R = 15.4 min. HRMS (ESI) m/z calcd for $\text{C}_{24}\text{H}_{22}\text{O}_4\text{N}_2^{23}\text{Na}_1^{32}\text{S}_1$

$$[M+Na]^+ = 457.1193, \text{ found} = 457.1173.$$

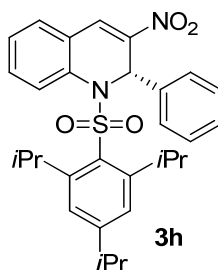


Racemic **3g**



Enantiomeric enriched **3g**

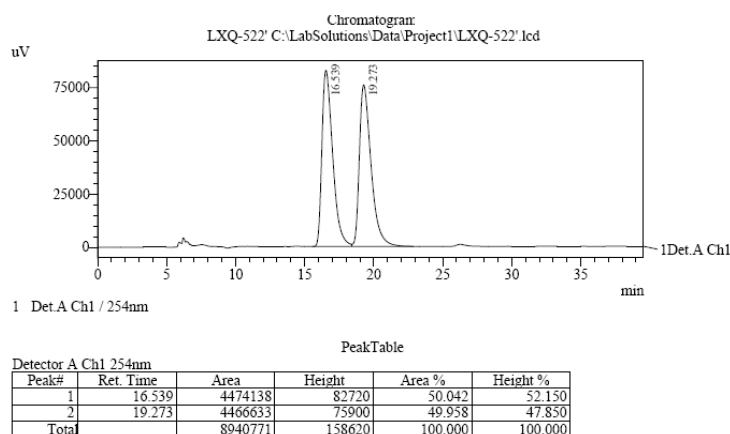
(S)-3-Nitro-2-phenyl-1-(2,4,6-triisopropylphenylsulfonyl)-1,2-dihydroquinoline **3h**



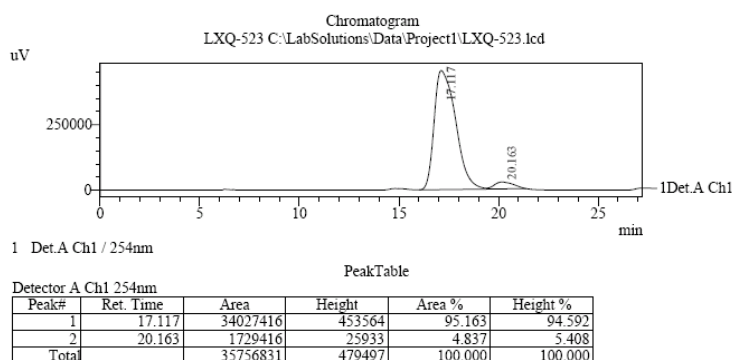
A yellow oil; Isolated in 81% yield after flash column chromatographic purification

(hexane: ethyl acetate = 10: 1 to 5:1); ^1H NMR (300 MHz, CDCl_3) δ 1.12-1.17 (t, J =

6.8 Hz, 12H), 1.27-1.29 (d, $J = 6.9$ Hz, 6H), 2.90-2.95 (m, 1H), 3.88-3.92 (m, 2H), 6.78 (s, 1H), 7.17-7.40 (m, 12H), 8.00 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 23.3, 23.4, 24.5, 24.8, 54.2, 124.1, 125.2, 126.5, 126.6, 126.8, 128.6, 128.7, 129.3, 130.4, 132.2, 135.1, 135.7, 145.2, 151.8, 154.2; The enantiomers were analyzed by HPLC using an AD-H column at 254 nm (2-propanol: hexane = 5: 95), 1.0 mL/min; Major enantiomer: $t_R = 17.1$ min, minor enantiomer: $t_R = 20.3$ min. HRMS (ESI) m/z calcd for $\text{C}_{30}\text{H}_{34}\text{O}_4\text{N}_2^{23}\text{Na}_1^{32}\text{S}_1$ $[\text{M}+\text{Na}]^+ = 541.2132$, found = 541.2157.

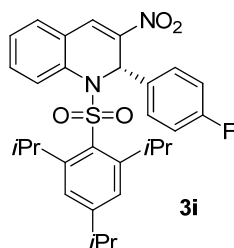


Racemic **3h**

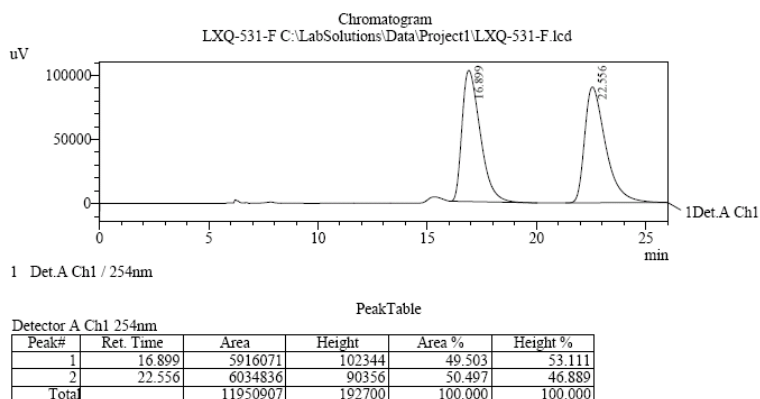


Enantiomeric enriched **3h**

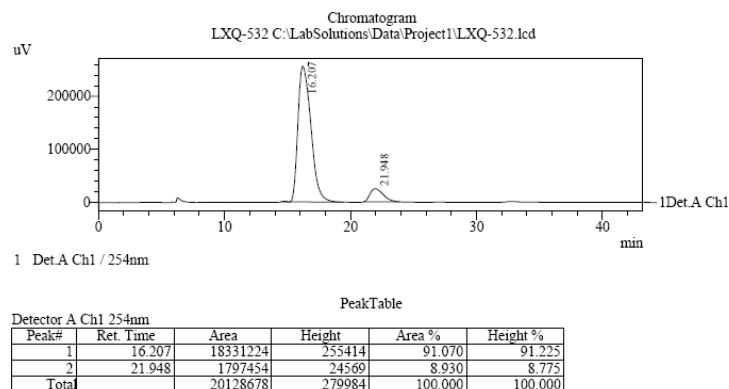
(S)-2-(4-Fluorophenyl)-3-nitro-1-(2,4,6-triisopropylphenylsulfonyl)-1,2-dihydroquinoline 3i



A yellow oil; Isolated in 77% yield after flash column chromatographic purification (hexane: ethyl acetate = 10: 1 to 5:1); ^1H NMR (300 MHz, CDCl_3) δ 1.12-1.14 (m, 12H), 1.27-1.29 (d, J = 6.9 Hz, 6H), 2.90-2.95 (m, 1H), 3.88-3.92 (m, 2H), 6.75 (s, 1H), 6.90-6.93 (m, 2H), 7.15-7.17 (m, 2H), 7.30 (s, 2H), 7.39-7.41 (m, 3H), 8.00 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 23.3, 23.4, 30.0, 34.1, 53.6, 115.5, 115.8, 124.2, 124.9, 126.4, 126.7, 128.6, 128.7, 129.4, 130.4, 130.8, 131.6, 132.4, 135.0, 145.0, 151.8, 154.3; The enantiomers were analyzed by HPLC using an AD-H column at 254 nm (2-propanol: hexane = 3: 97), 0.5 mL/min; Major enantiomer: t_R = 16.2 min, minor enantiomer: t_R = 21.9 min. HRMS (ESI) m/z calcd for $\text{C}_{30}\text{H}_{33}\text{O}_4\text{N}_2^{35}\text{F}_1^{23}\text{Na}_1^{32}\text{S}_1$ $[\text{M}+\text{Na}]^+ = 559.2037$, found = 559.2018.

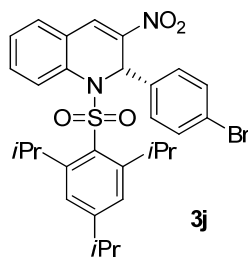


Racemic **3i**

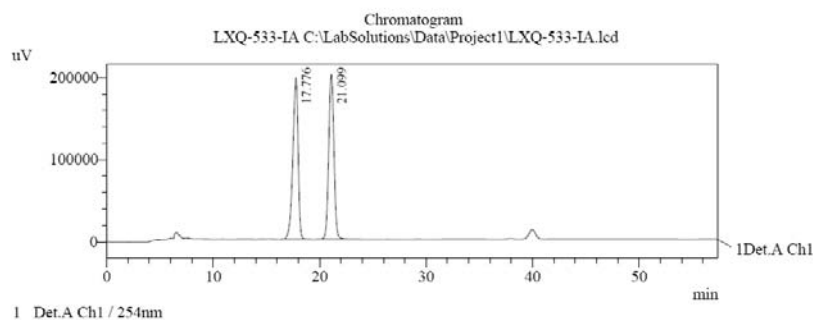
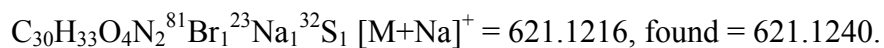


Enantiomeric enriched **3i**

(S)-2-(4-Bromophenyl)-3-nitro-1-(2,4,6-triisopropylphenylsulfonyl)-1,2-dihydroquinoline **3j**



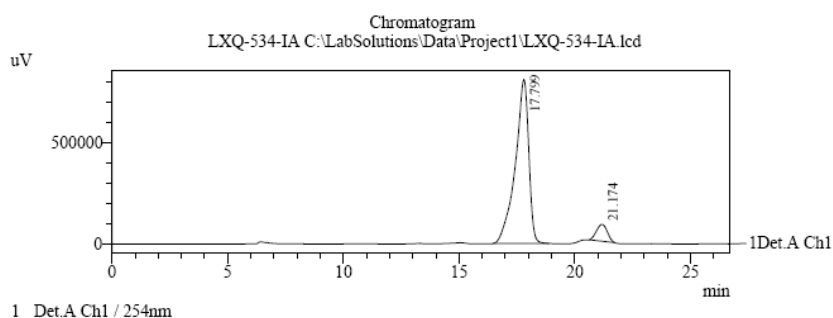
A yellow solid; Isolated in 91% yield after flash column chromatographic purification (hexane: ethyl acetate = 10: 1 to 5:1); ^1H NMR (300MHz, CDCl_3) δ 1.12-1.14 (m, 12H), 1.27-1.29 (d, $J = 6.9$ Hz, 6H), 2.90-2.95 (m, 1H), 3.85 (m, 2H), 6.74 (s, 1H), 7.08-7.10 (d, $J = 8.5$ Hz, 2H), 7.17 (s, 2H), 7.30-7.42 (m, 6H), 8.00 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 23.3, 23.4, 24.6, 24.8, 30.1, 34.1, 53.7, 122.9, 124.2, 124.8, 126.4, 126.7, 128.5, 129.6, 130.5, 130.7, 131.9, 132.5, 134.9, 135.0, 144.6, 151.8, 154.4; The enantiomers were analyzed by HPLC using an AD-H column at 254 nm (2-propanol: hexane = 3: 97), 0.5 mL/min; Major enantiomer: $t_R = 17.8$ min, minor enantiomer: $t_R = 22.2$ min; HRMS (ESI) m/z calcd for $\text{C}_{30}\text{H}_{33}\text{O}_4\text{N}_2^{79}\text{Br}_1^{23}\text{Na}_1^{32}\text{S}_1$ $[\text{M}+\text{Na}]^+ = 619.1237$, found = 619.1254; calcd for



PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.776	6761286	196042	49.662	49.434
2	21.099	6853212	200533	50.338	50.566
Total		13614498	396574	100.000	100.000

Racemic **3j**

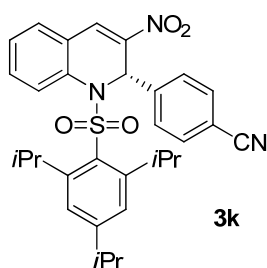


PeakTable

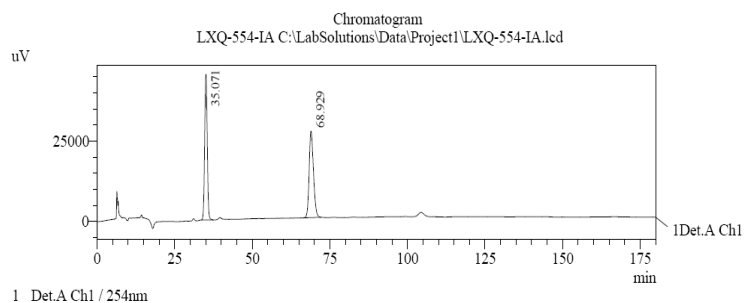
Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.799	32868643	811058	92.469	90.726
2	21.174	2677104	82905	7.531	9.274
Total		35545748	893963	100.000	100.000

Enantiomeric enriched **3j**

(S)-4-(3-Nitro-1-(2,4,6-triisopropylphenylsulfonyl)-1,2-dihydroquinolin-2-yl)benzonitrile **3k**



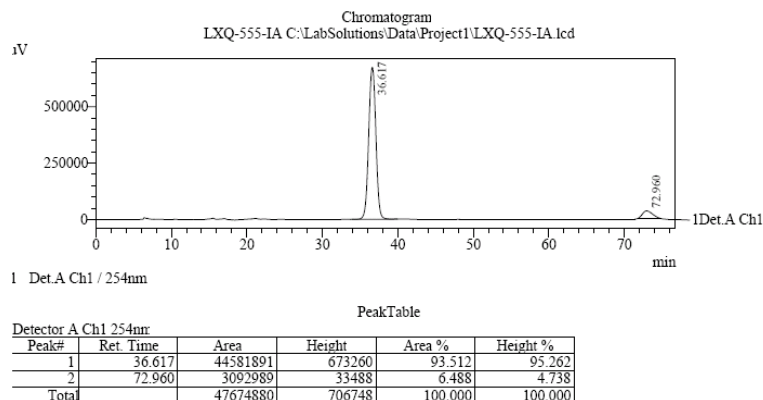
A yellow oil; Isolated in 92% yield after flash column chromatographic purification (hexane: ethyl acetate = 10: 1 to 5:1); ^1H NMR (300 MHz, CDCl_3) δ 1.11-1.17 (m, 12H), 1.26-1.28 (d, J = 6.9 Hz, 6H), 2.91 (m, 1H), 3.84 (m, 2H), 6.81 (s, 1H), 7.17 (s, 2H), 7.17-7.45 (m, 7H), 7.55-7.58 (d, J = 8.2 Hz, 2H), 8.08 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 23.3, 23.4, 24.6, 24.8, 30.2, 34.1, 53.8, 112.8, 118.0, 124.8, 126.2, 126.9, 127.6, 130.0, 130.5, 130.7, 132.5, 132.7, 134.9, 141.1, 143.9, 151.8, 154.6; The enantiomers were analyzed by HPLC using an IA -H column at 254 nm (2-propanol: hexane = 3: 97), 0.5 mL/min; Major enantiomer: t_R = 36.6 min, minor enantiomer: t_R = 73.0 min. HRMS (ESI) m/z calcd for $\text{C}_{31}\text{H}_{33}\text{O}_4\text{N}_3^{23}\text{Na}^{32}\text{S}_1$ $[\text{M}+\text{Na}]^+ = 566.2084$, found = 566.2085.



PeakTable

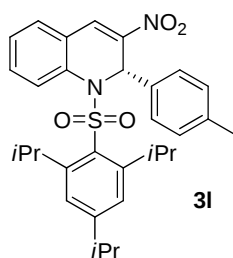
Peak#	Ret. Time	Area	Height	Area %	Height %
1	35.071	2607836	45186	50.214	62.707
2	68.929	2585653	26873	49.786	37.293
Total		5193489	72058	100.000	100.000

Racemic **3k**

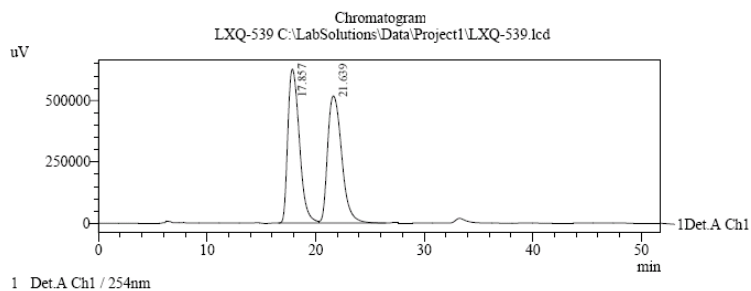


Enantiomeric enriched **3k**

(S)-3-Nitro-2-p-tolyl-1-(2,4,6-triisopropylphenylsulfonyl)-1,2-dihydroquinoline **3l**



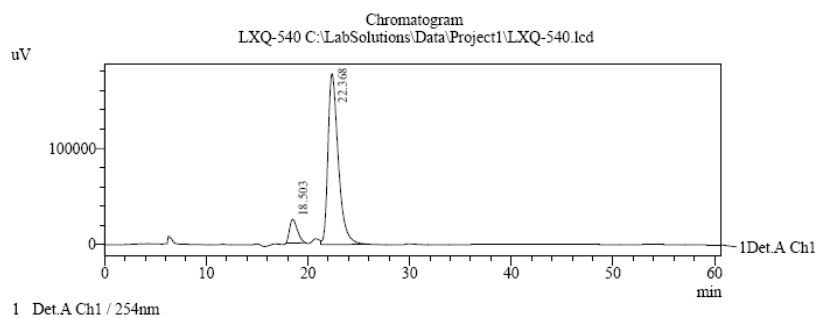
A yellow oil; Isolated in 83% yield after flash column chromatographic purification (hexane: ethyl acetate = 10: 1 to 5:1); ^1H NMR (300 MHz, CDCl_3) δ 1.12-1.17 (t, J = 7.2 Hz, 12H), 1.27-1.29 (d, J = 6.9 Hz, 6H), 2.28 (s, 3H), 2.90 (m, 2H), 3.90 (m, 2H), 6.74 (s, 1H), 7.05-7.06 (m, 4H), 7.17 (s, 2H), 7.17-7.41 (m, 5H), 8.00 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ = 21.0, 23.3, 23.4, 24.6, 24.8, 30.0, 34.1, 124.1, 125.2, 126.4, 126.5, 126.7, 129.2, 129.3, 130.3, 131.0, 132.2, 132.7, 135.1, 138.6, 145.3, 151.8, 154.1; The enantiomers were analyzed by HPLC using an AD-H column at 254 nm (2-propanol: hexane = 3: 97), 0.5 mL/min; Major enantiomer: t_R = 22.4 min, minor enantiomer: t_R = 18.5 min. HRMS (ESI) m/z calcd for $\text{C}_{31}\text{H}_{36}\text{O}_4\text{N}_2^{23}\text{Na}^{32}\text{S}_1$ $[\text{M}+\text{Na}]^+$ = 555.2288, found = 555.2305.



PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.857	46279769	626812	49.767	54.771
2	21.639	46712557	517602	50.233	45.229
Total		92992325	1144414	100.000	100.000

Racemic **3l**

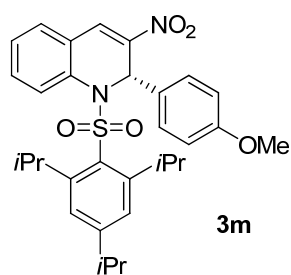


PeakTable

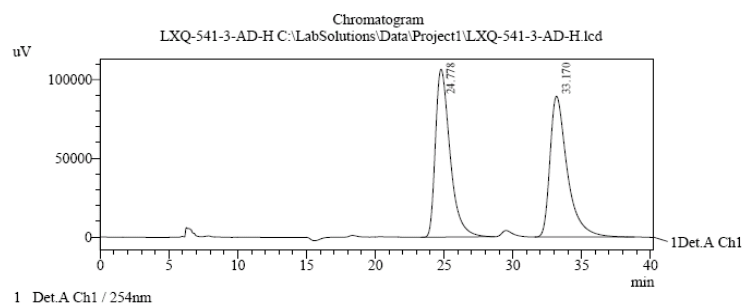
Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.503	1315525	24652	9.520	12.201
2	22.368	12502468	177389	90.480	87.799
Total		13817993	202041	100.000	100.000

Enantiomeric enriched **3l**

(S)-2-(4-Methoxyphenyl)-3-nitro-1-(2,4,6-triisopropylphenylsulfonyl)-1,2-dihydroquinoline **3m**

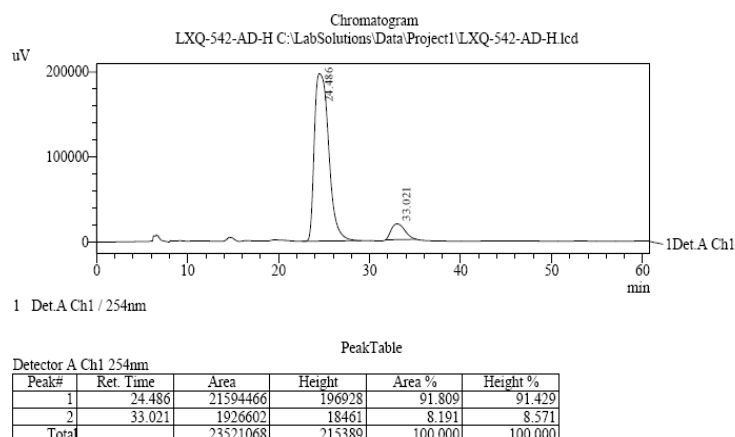


A yellow oil; Isolated in 75% yield after flash column chromatographic purification (hexane: ethyl acetate = 10: 1 to 5:1); ^1H NMR (300 MHz, CDCl_3) δ 1.12-1.17 (m, 12H), 1.27-1.29 (d, J = 6.9 Hz, 6H), 2.93 (m, 1H), 3.75 (s, 1H), 3.90 (m, 2H), 6.72-6.77 (m, 3H), 7.07-7.08 (d, J = 3.1 Hz, 2H), 7.12 (s, 2H), 7.30-7.49 (m, 3H), 8.00 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 23.3, 23.4, 24.6, 24.8, 29.6, 30.0, 53.8, 55.1, 114.0, 124.1, 125.1, 126.4, 126.5, 127.8, 128.2, 129.1, 130.3, 130.9, 132.2, 135.1, 145.4, 151.8, 154.1, 159.9; The enantiomers were analyzed by HPLC using an AD-H column at 254 nm (2-propanol: hexane = 3: 97), 0.5 mL/min; Major enantiomer: t_R = 24.5 min, minor enantiomer: t_R = 33.0 min. HRMS (ESI) m/z calcd for $\text{C}_{31}\text{H}_{36}\text{O}_5\text{N}_2^{23}\text{Na}_1^{32}\text{S}_1 [\text{M}+\text{Na}]^+ = 571.2237$, found = 571.2249.



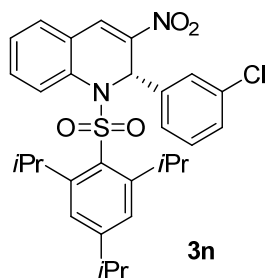
PeakTable					
Detector A Ch1 254nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.778	7886743	106634	50.135	54.391
2	33.170	7844231	89417	49.865	45.609
Total		15730974	196051	100.000	100.000

Racemic **3m**

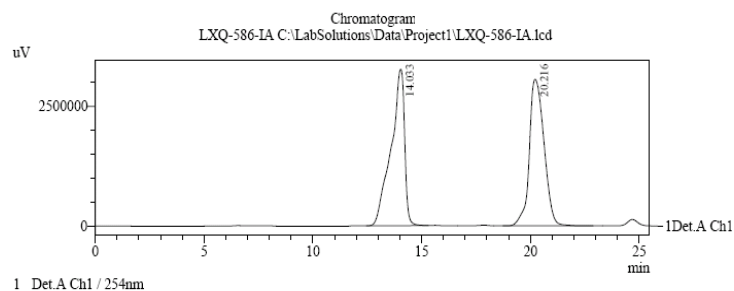
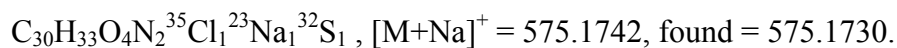


Enantiomeric enriched **3m**

(S)-2-(3-Chlorophenyl)-3-nitro-1-(2,4,6-triisopropylphenylsulfonyl)-1,2-dihydroquinoline **3n**



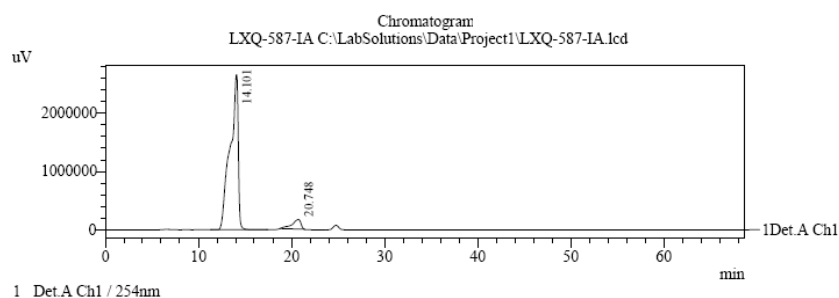
A yellow oil; Isolated in 90% yield after flash column chromatographic purification (hexane: ethyl acetate = 10: 1 to 5:1); ^1H NMR (300 MHz, CDCl_3) δ 1.12-1.17 (m, 12H), 1.27-1.29 (d, $J = 6.9$ Hz, 6H), 2.90-2.95 (m, 1H), 3.88-3.92 (m, 2H), 6.76 (s, 1H), 7.14-7.29 (m, 10H), 7.40-7.41 (d, $J = 3.6$ Hz, 2H), 8.03 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 23.4, 23.4, 24.5, 24.8, 30.1, 34.1, 53.7, 124.2, 124.9, 125.0, 126.6, 126.9, 127.1, 129.0, 129.7, 129.9, 130.6, 132.5, 134.6, 134.8, 137.7, 144.5, 151.9, 154.4. The enantiomers were analyzed by HPLC using an IA-H column at 254 nm (2-propanol: hexane = 3: 97), 0.5 mL/min; Major enantiomer: $t_R = 14.1$ min, minor enantiomer: $t_R = 20.7$ min. HRMS (ESI) m/z calcd for



PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.033	141991642	3264924	49.569	51.609
2	20.216	144463551	3061387	50.431	48.391
Total		286455192	6326311	100.000	100.000

Racemic **3n**

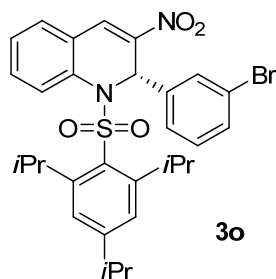


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.101	162117193	2664193	93.585	94.147
2	20.748	11112339	165634	6.415	5.853
Total		173229532	2829827	100.000	100.000

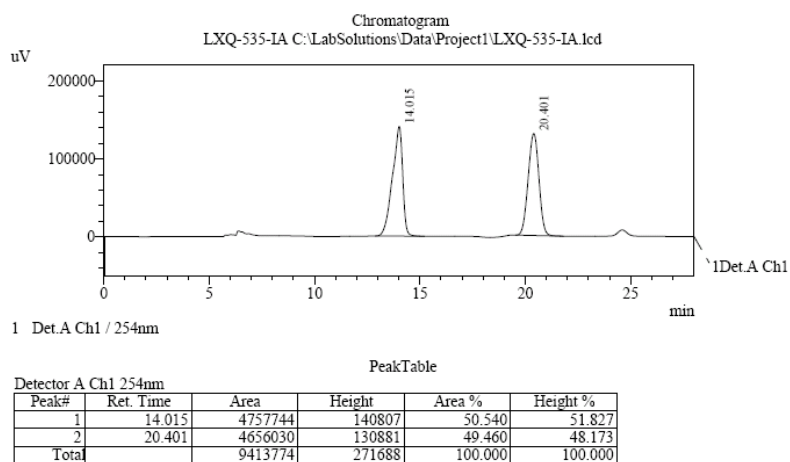
Enantiomeric enriched **3n**

(S)-2-(3-Bromophenyl)-3-nitro-1-(2,4,6-triisopropylphenylsulfonyl)-1,2-dihydroquinoline **3o**

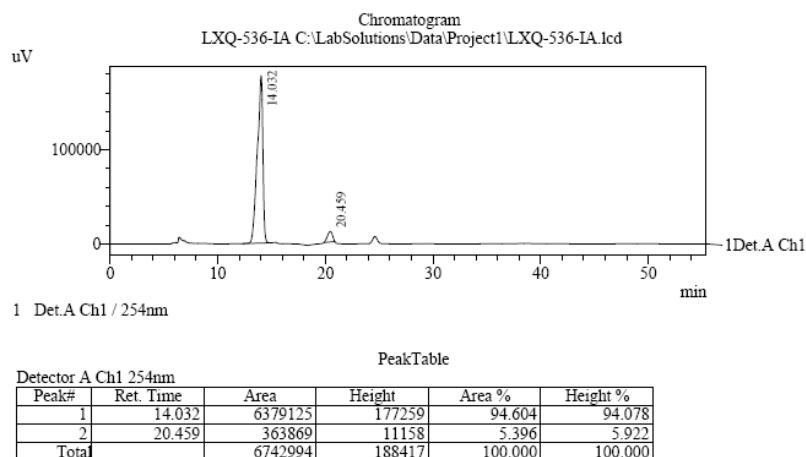


A yellow solid; Isolated in 86% yield after flash column chromatographic

purification (hexane: ethyl acetate = 10: 1 to 5:1); ^1H NMR (300 MHz, CDCl_3) δ 1.12-1.15 (m, 12H), 1.27-1.29 (d, $J = 6.9$ Hz, 6H), 2.91-2.96 (m, 1H), 3.85 (m, 2H), 6.74 (s, 1H), 7.11-7.13 (m, 2H), 7.19 (s, 2H), 7.33-7.42 (m, 3H), 7.48-7.51 (d, $J = 7.2$ Hz, 1H), 8.03 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 23.3, 23.4, 24.5, 25.8, 53.6, 122.7, 124.2, 125.1, 125.3, 126.6, 126.9, 129.8, 130.0, 130.2, 131.9, 132.5, 134.8, 138.0, 144.5, 151.9, 154.5; The enantiomers were analyzed by HPLC using an IA-H column at 254 nm (2-propanol: hexane = 3 : 97), 0.5 mL/min; Major enantiomer: $t_R = 14.0$ min, minor enantiomer: $t_R = 20.5$ min. HRMS (ESI) m/z calcd for $\text{C}_{30}\text{H}_{33}\text{O}_4\text{N}_2^{79}\text{Br}_1^{23}\text{Na}_1^{32}\text{S}_1$ and $\text{C}_{30}\text{H}_{33}\text{O}_4\text{N}_2^{81}\text{Br}_1^{23}\text{Na}_1^{32}\text{S}_1$, $[\text{M}+\text{Na}]^+ = 619.1237$ and 621.1216, found = 619.1260 and 621.1248.

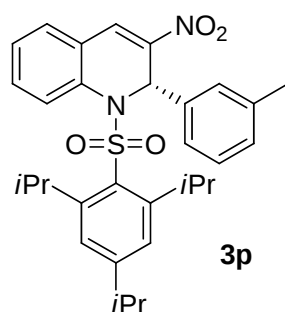


Racemic **3o**



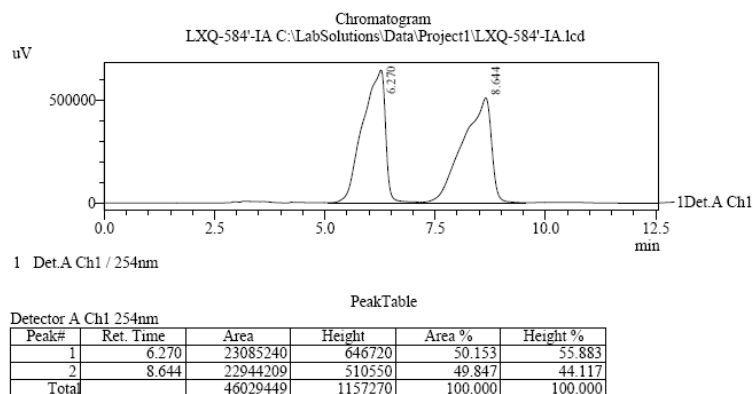
Enantiomeric enriched **3o**

(S)-3-Nitro-2-m-tolyl-1-(2,4,6-triisopropylphenylsulfonyl)-1,2-dihydroquinoline **3p**

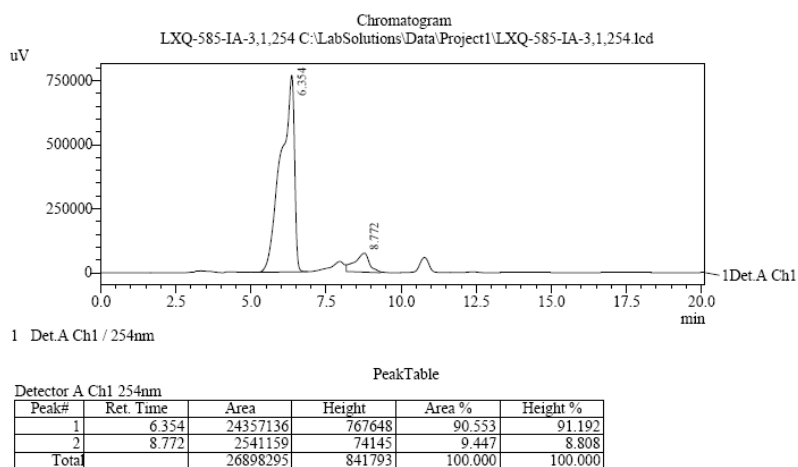


A yellow oil; Isolated in 83% yield after flash column chromatographic purification (hexane: ethyl acetate = 10: 1 to 5:1); ^1H NMR (300 MHz, CDCl_3) δ 1.12-1.17 (m, 12H), 1.27-1.29 (d, J = 6.9 Hz, 6H), 2.27 (s, 3H), 2.91-2.95 (m, 1H), 3.88-3.90 (m, 2H), 6.75 (s, 1H), 6.98 (m, 2H), 7.07-7.11 (m, 2H), 7.18 (s, 2H), 7.30 (m, 1H), 7.37-7.40 (m, 2H), 7.46 (m, 1H), 8.00 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 21.3, 23.3, 23.4, 24.5, 24.9, 29.6, 30.0, 34.1, 54.2, 123.7, 124.1, 125.3, 126.6, 127.6, 128.5, 129.3, 129.5, 130.4, 130.9, 132.2, 135.1, 135.5, 138.4, 145.3, 151.8, 154.2; The enantiomers were analyzed by HPLC using an IA-H column at 254 nm (2-propanol:

hexane = 3: 97), 1.0 mL/min; Major enantiomer: $t_R = 6.4$ min, minor enantiomer: $t_R = 8.8$ min. HRMS (ESI) m/z calcd for $C_{31}H_{36}O_4N_2^{23}Na_1^{32}S_1$ $[M+Na]^+ = 555.2288$, found = 555.2304.

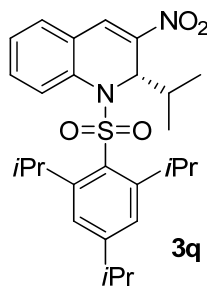


Racemic **3p**

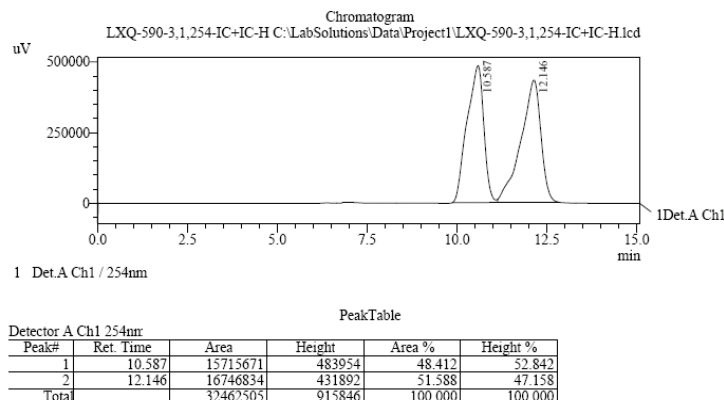


Enantiomeric enriched **3p**

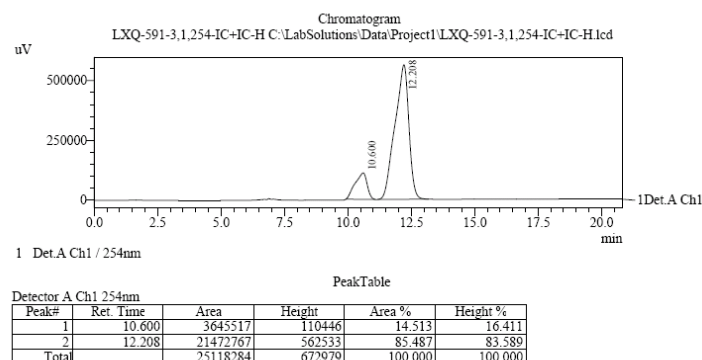
(S)-2-Isopropyl-3-nitro-1-(2,4,6-triisopropylphenylsulfonyl)-1,2-dihydroquinoline **3q**



A yellow oil; Isolated in 86% yield after flash column chromatographic purification (hexane: ethyl acetate = 10: 1 to 5:1); ^1H NMR (300 MHz, CDCl_3) δ 0.87-0.89 (d, J = 6.7 Hz, 3H), 1.03-1.05 (d, J = 6.6 Hz, 3H), 1.11-1.17 (m, 12H), 1.24-1.26 (d, J = 6.9 Hz, 6H), 2.84-2.94 (m, 1H), 3.72-3.81 (m, 2H), 5.63-5.67 (dd, J = 10.0 Hz, 4.11 Hz, 1H), 7.12 (s, 2H), 7.30-7.35 (m, 1H), 7.40-7.48 (m, 2H), 7.53-7.56 (m, 1H), 7.68 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 21.2, 23.1, 23.4, 24.6, 25.0, 30.2, 34.1, 40.5, 50.6, 123.9, 125.6, 126.7, 127.3, 127.8, 130.2, 131.3, 131.8, 134.6, 147.3, 151.6, 153.9; The enantiomers were analyzed by HPLC using two combined IC-H column at 254 nm (2-propanol: hexane = 3: 97), 1.0 mL/min; Major enantiomer: t_R = 12.2 min, minor enantiomer: t_R = 10.6 min. HRMS (ESI) m/z calcd for $\text{C}_{27}\text{H}_{36}\text{O}_4\text{N}_2^{23}\text{Na}_1^{32}\text{S}_1$ $[\text{M}+\text{Na}]^+$ = 507.2408, found = 507.2428.

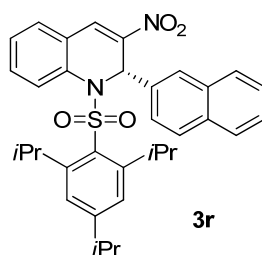


Racemic **3q**

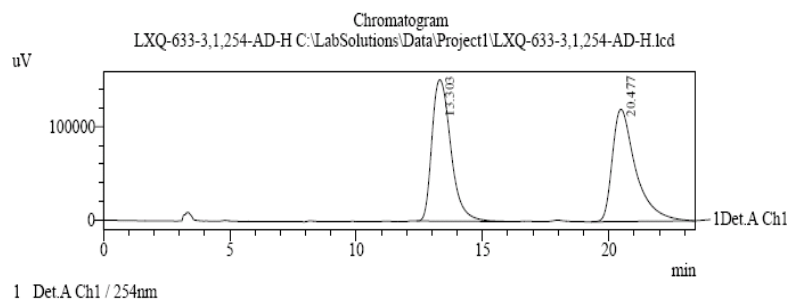


Enantiomeric enriched **3q**

(S)-2-(Naphthalen-2-yl)-3-nitro-1-(2,4,6-triisopropylphenylsulfonyl)-1,2-dihydroquinoline **3r**



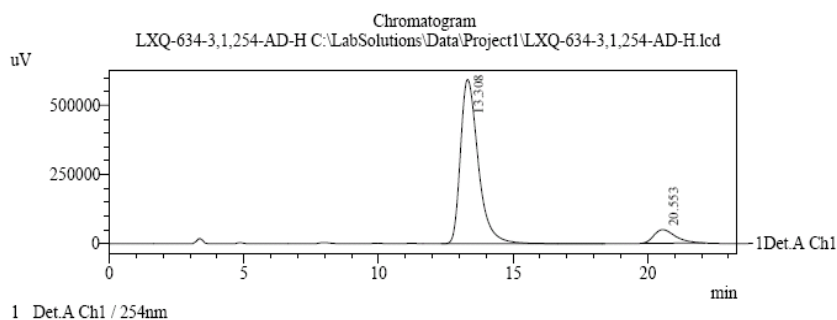
A yellow oil; Isolated in 75% yield after flash column chromatographic purification (hexane: ethyl acetate = 8:1); ^1H NMR (300 MHz, CDCl_3) δ 1.12-1.18 (m, 12H), 1.28-1.47 (d, J = 6.9 Hz, 6H), 2.91-2.96 (m, 1H), 3.92 (m, 2H), 6.97 (s, 1H), 7.19 (s, 2H), 7.18-7.52 (m, 8H), 7.68-7.78 (m, 3H), 8.09 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 23.4, 23.5, 24.7, 25.0, 30.2, 34.2, 54.4, 124.3, 124.7, 125.3, 126.0, 126.3, 126.5, 126.7, 126.8, 127.6, 128.1, 128.9, 129.7, 130.5, 131.1, 132.3, 132.9, 133.0, 133.3, 135.1, 145.1, 151.9, 154.3; The enantiomers were analyzed by HPLC using two combined IC-H column at 254 nm (2-propanol: hexane = 3: 97), 1.0 mL/min; Major enantiomer: t_R = 13.3 min, minor enantiomer: t_R = 20.6 min. HRMS (ESI) m/z calcd for $\text{C}_{34}\text{H}_{36}\text{O}_4\text{N}_2^{23}\text{Na}^{32}\text{S}_1$ $[\text{M}+\text{Na}]^+$ = 591.2288, found = 591.2310.



PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.303	7878424	151201	50.509	55.751
2	20.477	7719637	120005	49.491	44.249
Total		15598061	271206	100.000	100.000

Racemic **3r**

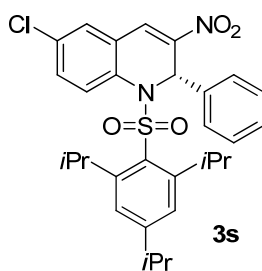


PeakTable

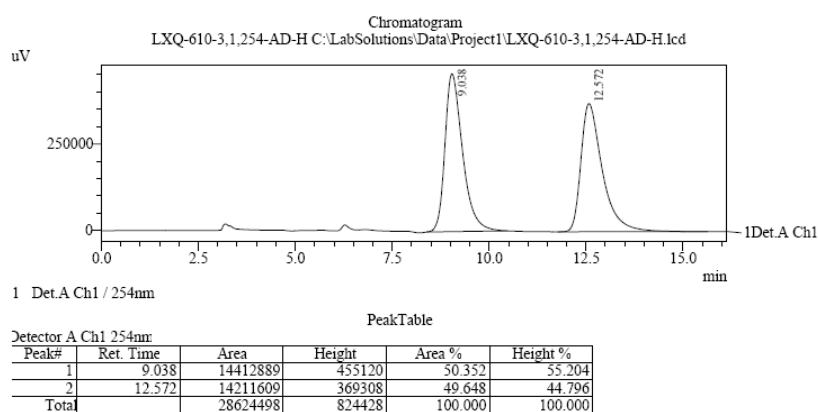
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.308	27296714	592496	90.959	92.397
2	20.553	2713123	48752	9.041	7.603
Total		30009837	641249	100.000	100.000

Enantiomeric enriched **3r**

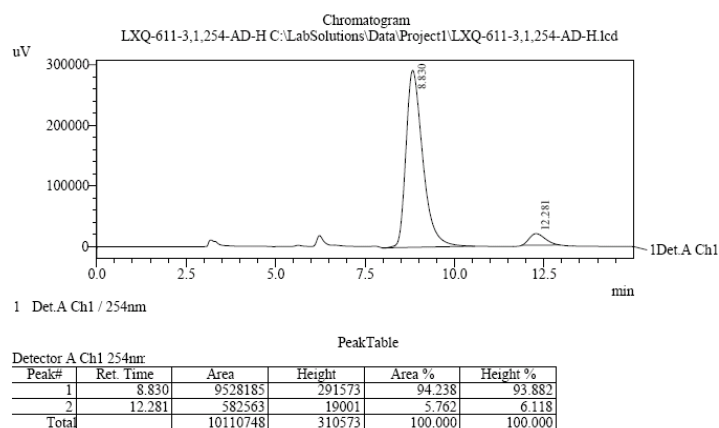
(S)-6-Chloro-3-nitro-2-phenyl-1-(2,4,6-triisopropylphenylsulfonyl)-1,2-dihydroquinoline **3s**



A yellow oil; Isolated in 78% yield after flash column chromatographic purification (hexane: ethyl acetate = 10: 1 to 5:1); ^1H NMR (300 MHz, CDCl_3) δ 1.12-1.13 (m, 12H), 1.24-1.25 (m, 6H), 2.87-2.92 (m, 1H), 3.81-3.87 (m, 2H), 6.70 (s, 1H), 7.11-7.15 (m, 2H), 7.22-7.26 (m, 3H), 7.31-7.33 (m, 2H), 7.42 (s, 1H), 7.88 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 23.3, 23.4, 24.5, 24.8, 30.1, 34.1, 124.2, 126.5, 126.7, 127.6, 128.0, 128.76, 128.8, 128.9, 129.0, 129.6, 130.4, 131.8, 132.1, 133.5, 135.3, 146.1, 151.9, 154.5; The enantiomers were analyzed by HPLC using two combined IC-H columns at 254 nm (2-propanol: hexane = 3: 97), 1.0 mL/min; Major enantiomer: t_R = 8.8 min, minor enantiomer: t_R = 12.2 min; HRMS (ESI) m/z calcd for $\text{C}_{30}\text{H}_{33}\text{O}_4\text{N}_2^{35}\text{Cl}_1^{23}\text{Na}_1^{32}\text{S}_1$ $[\text{M}+\text{Na}]^+ = 575.1742$, found = 575.1760.



Racemic **3s**



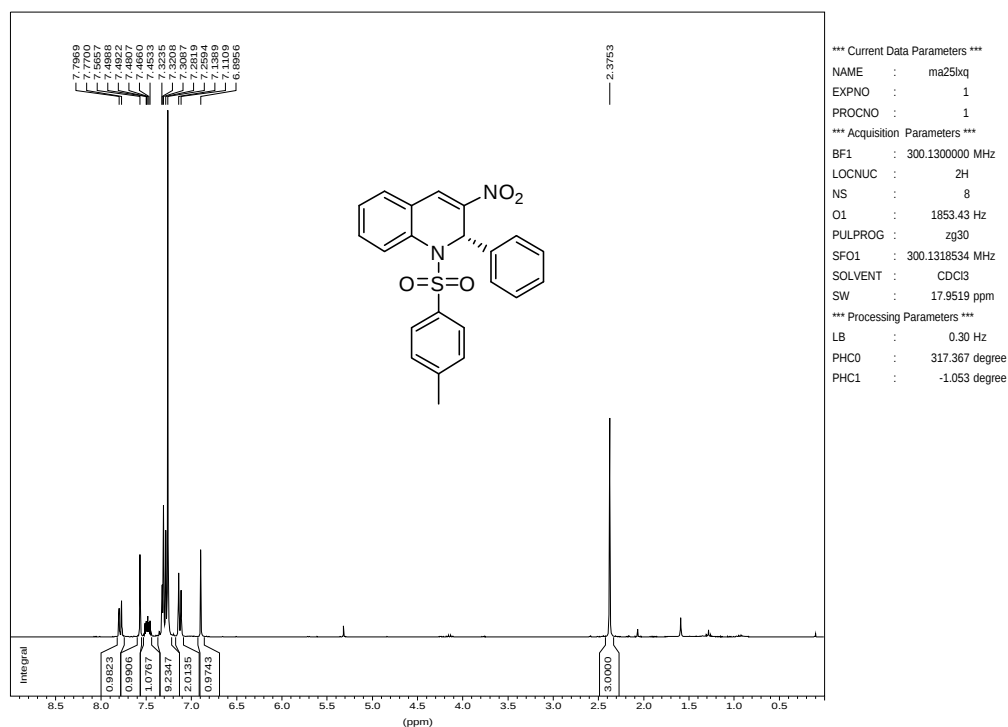
Enantiomeric enriched **3s**

References:

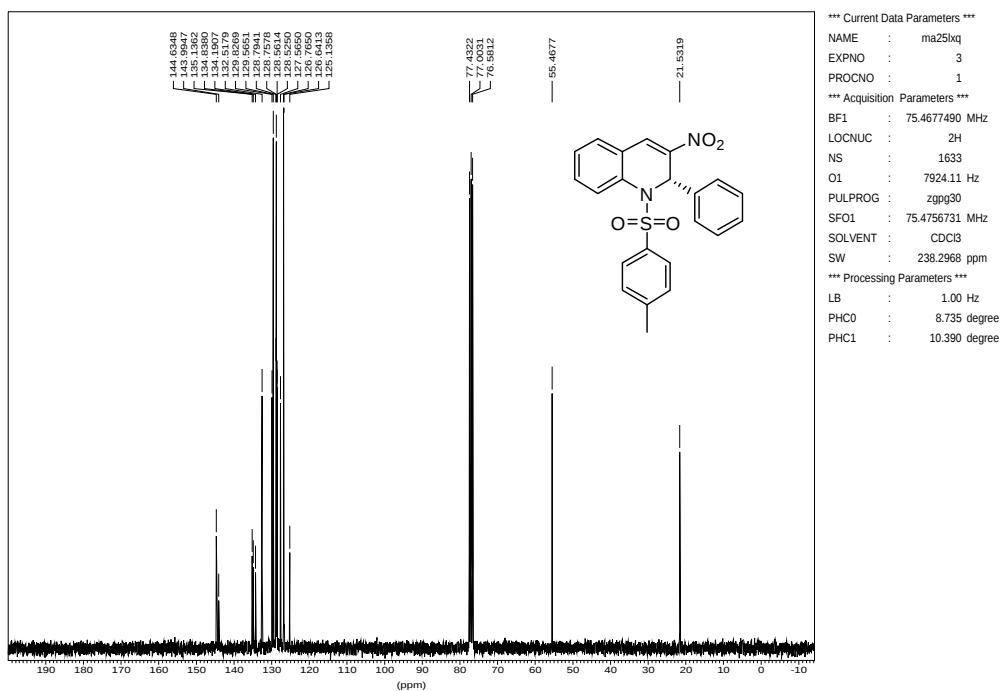
1. Fonseca, M. H.; Eibler, E.; Zabel, M.; Konig, B. *Tetrahedron: Asymmetry* **2003**, *14*, 1989.
2. Bassas, O.; Huuskonen, J.; Rissanen, K.; Koskinen, A. M. P. *Eur. J. Org. Chem.* **2009**, *9*, 1340.
3. Wang, Y.-F.; Zhang, W.; Luo, S.-P.; Li, B.-L.; Xia, A.-B.; Zhong, A.-G.; Xu, D.-Q. *Chem. Asian J.* **2009**, *4*, 1834.

F. NMR Spectra of Products

(S)-3-Nitro-2-phenyl-1-tosyl-1,2-dihydroquinoline 3a

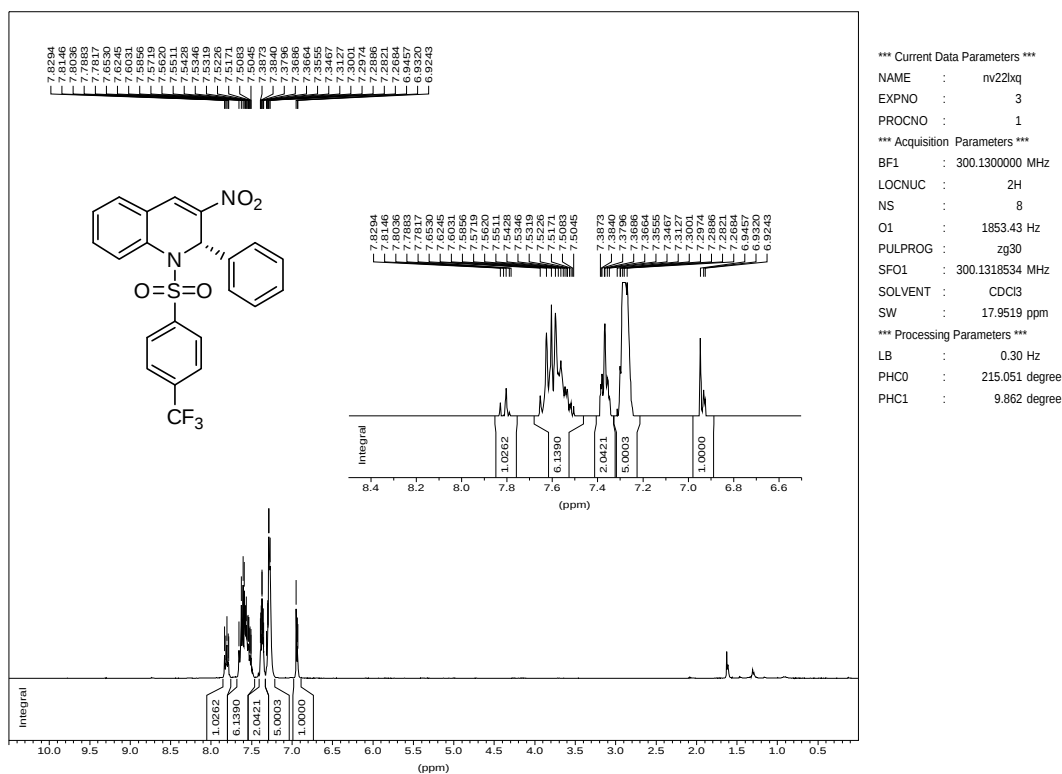


13C Standard AC300-270-C

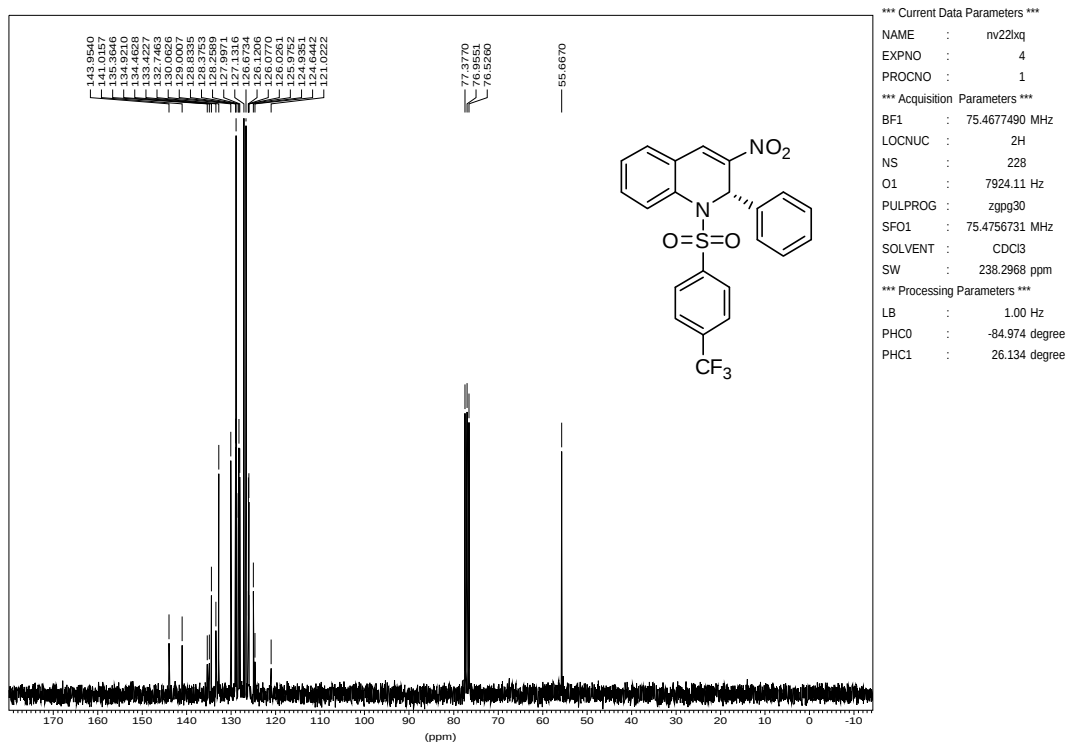


(S)-3-Nitro-2-phenyl-1-(4-(trifluoromethyl)phenylsulfonyl)-1,2-dihydroquinoline 3c

¹H normal range AC300-687

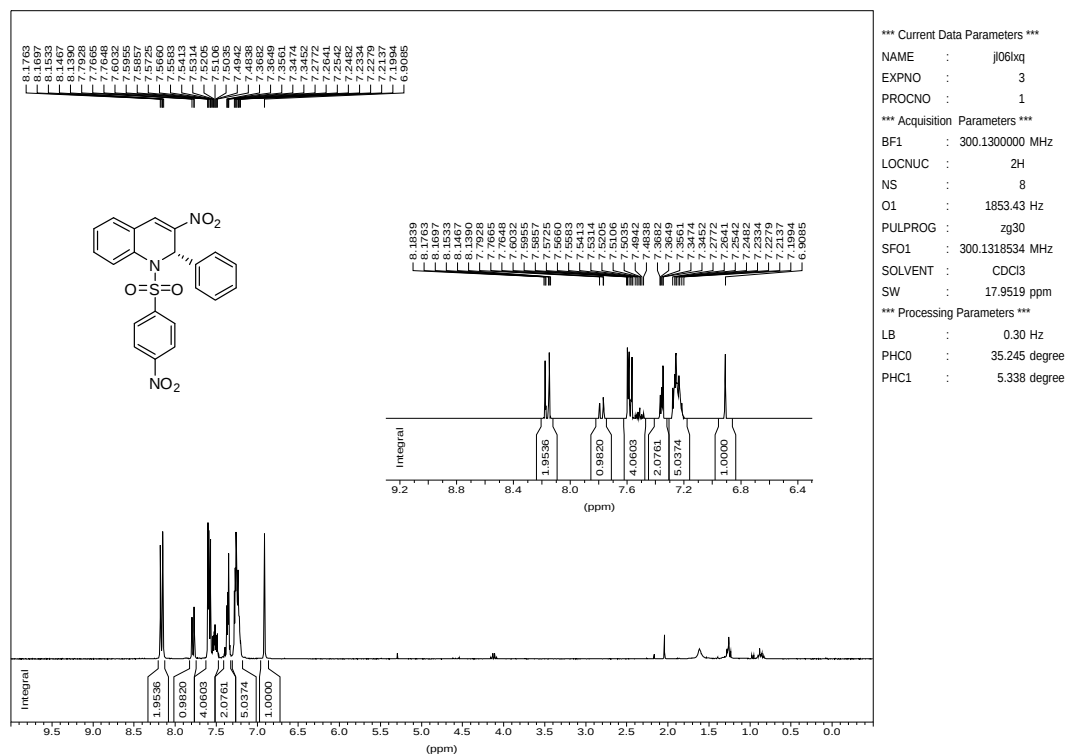


¹³C Standard AC300-687-C

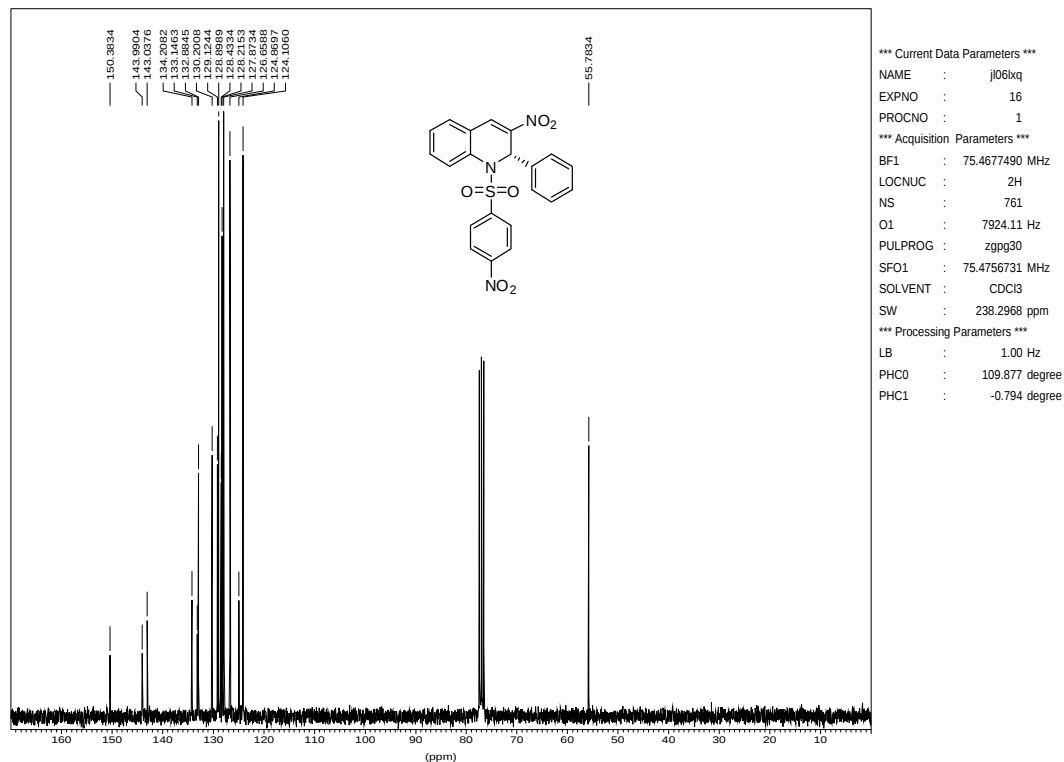


(S)-3-Nitro-1-(4-nitrophenylsulfonyl)-2-phenyl-1,2-dihydroquinoline 3d

¹H normal range AC300-553



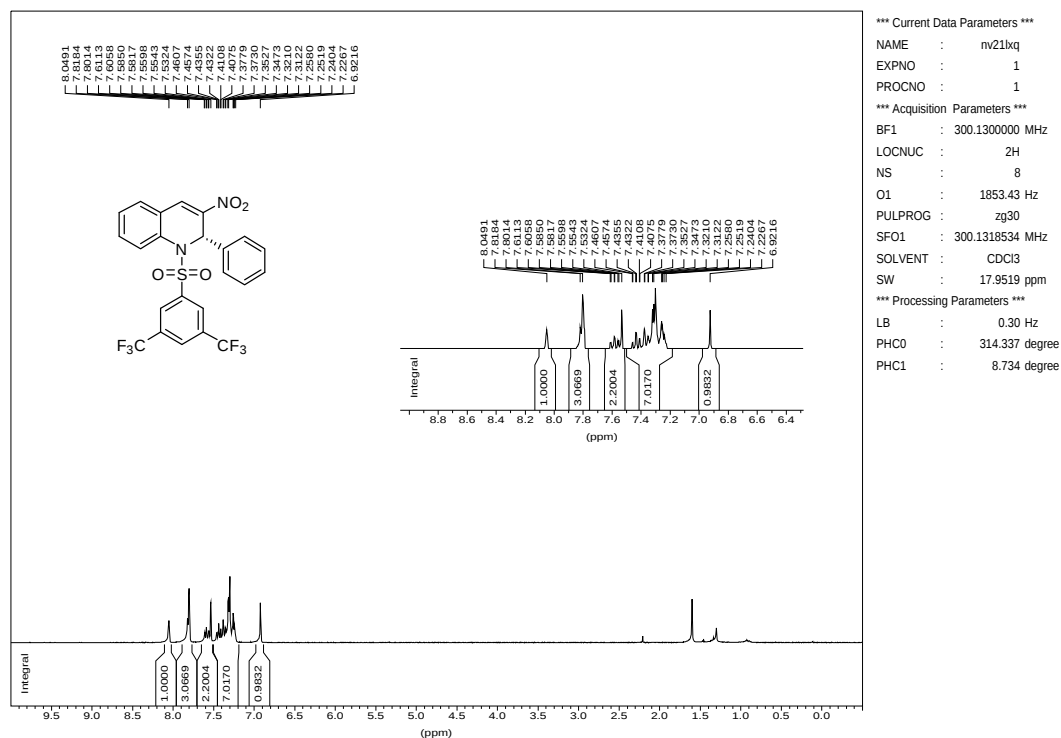
¹³C Standard AC300-553-C



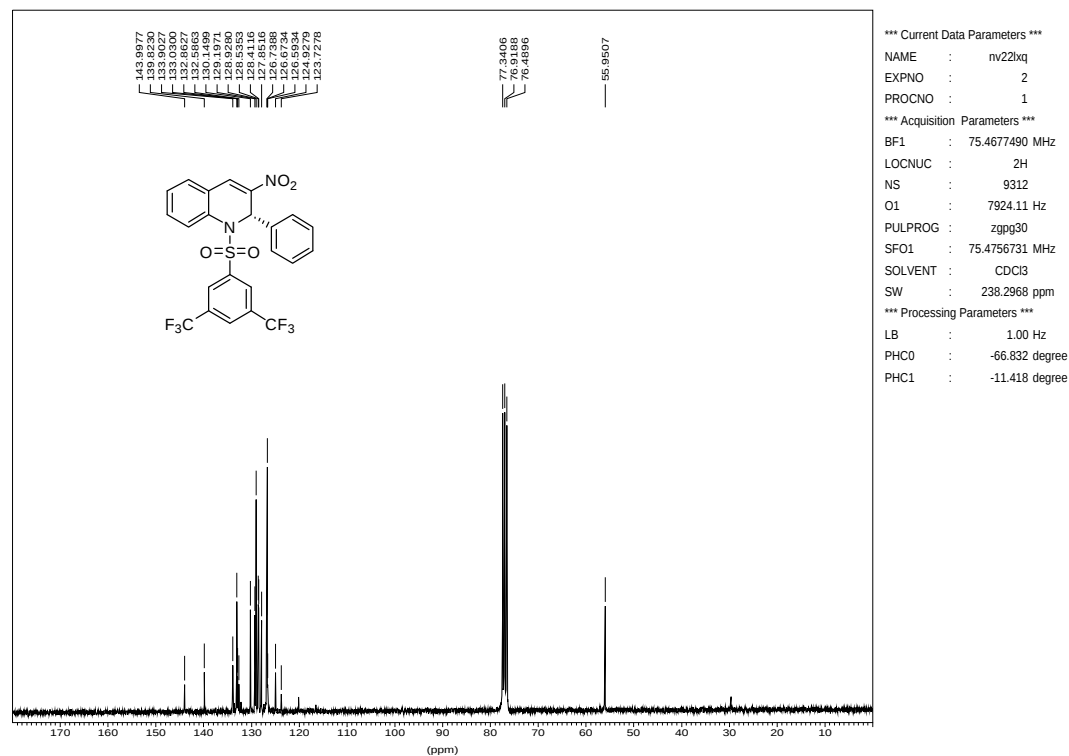
(S)-1-(3,5-Bis(trifluoromethyl)phenylsulfonyl)-3-nitro-2-phenyl-1,2-dihydroquinoline

3e

¹H normal range AC300-679

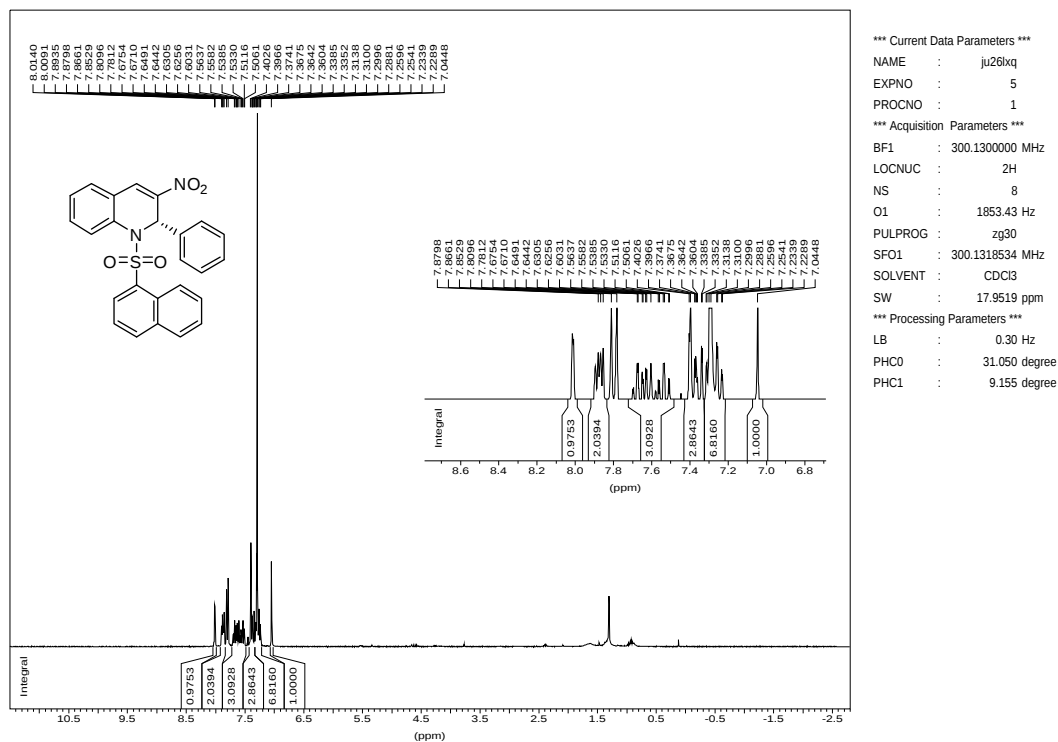


¹³C Standard AC300-679

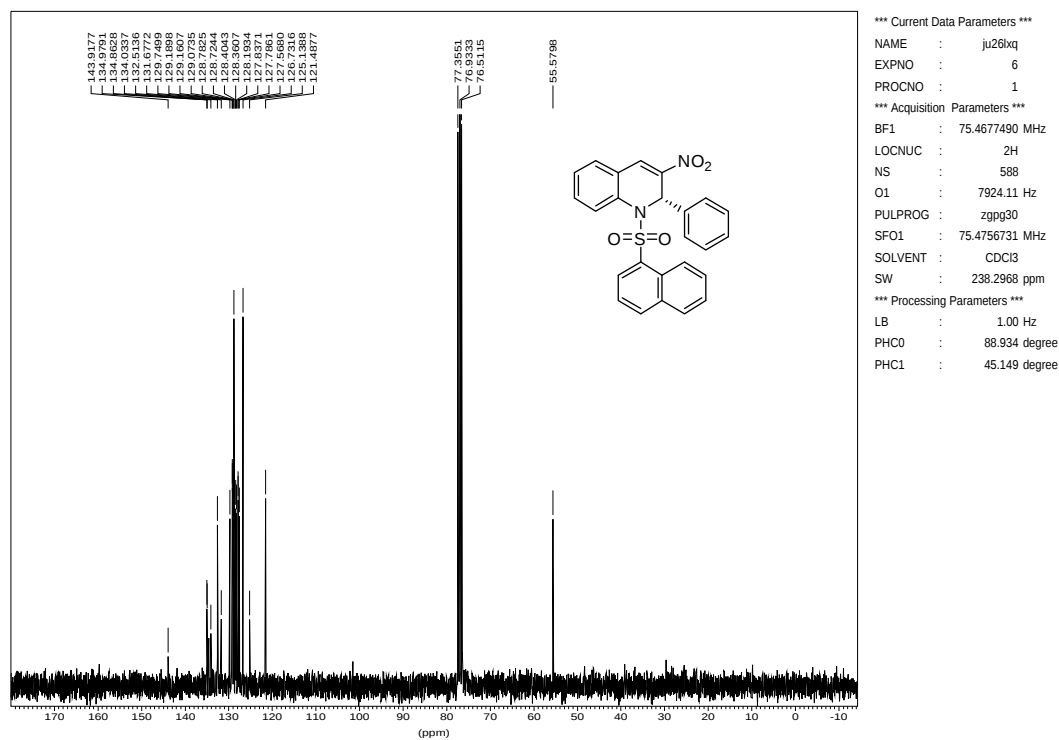


(S)-1-(Naphthalen-1-ylsulfonyl)-3-nitro-2-phenyl-1,2-dihydroquinoline 3f

¹H normal range AC300-463



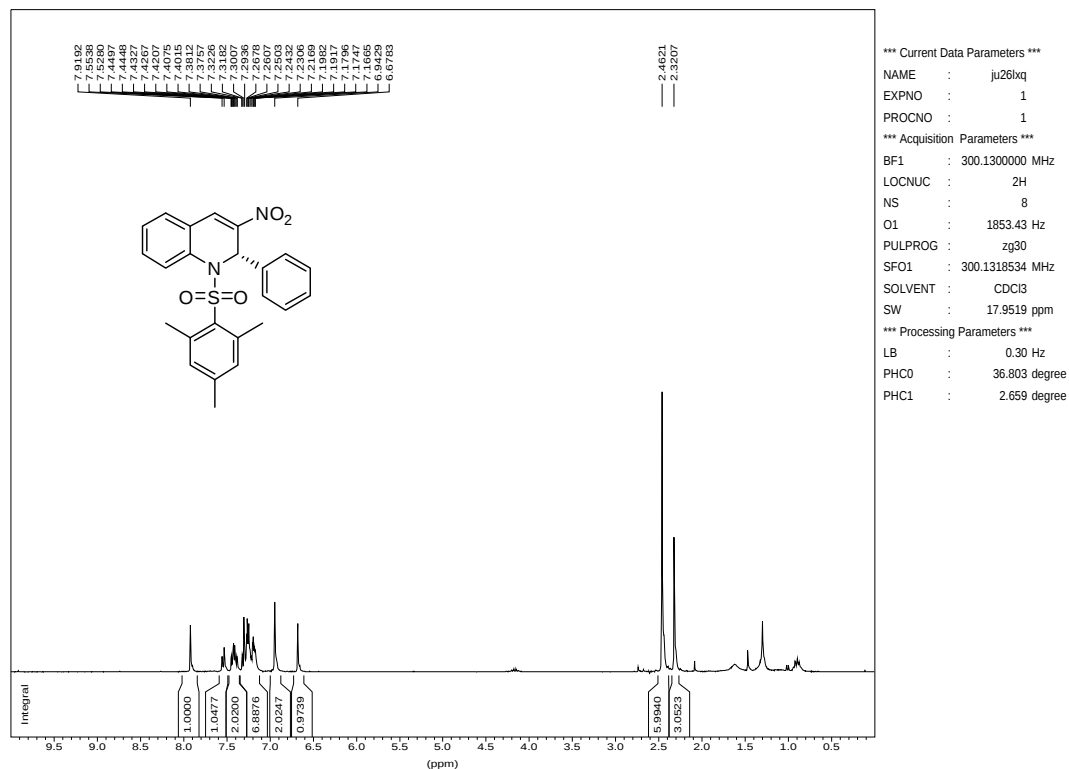
¹³C Standard AC300-463-C



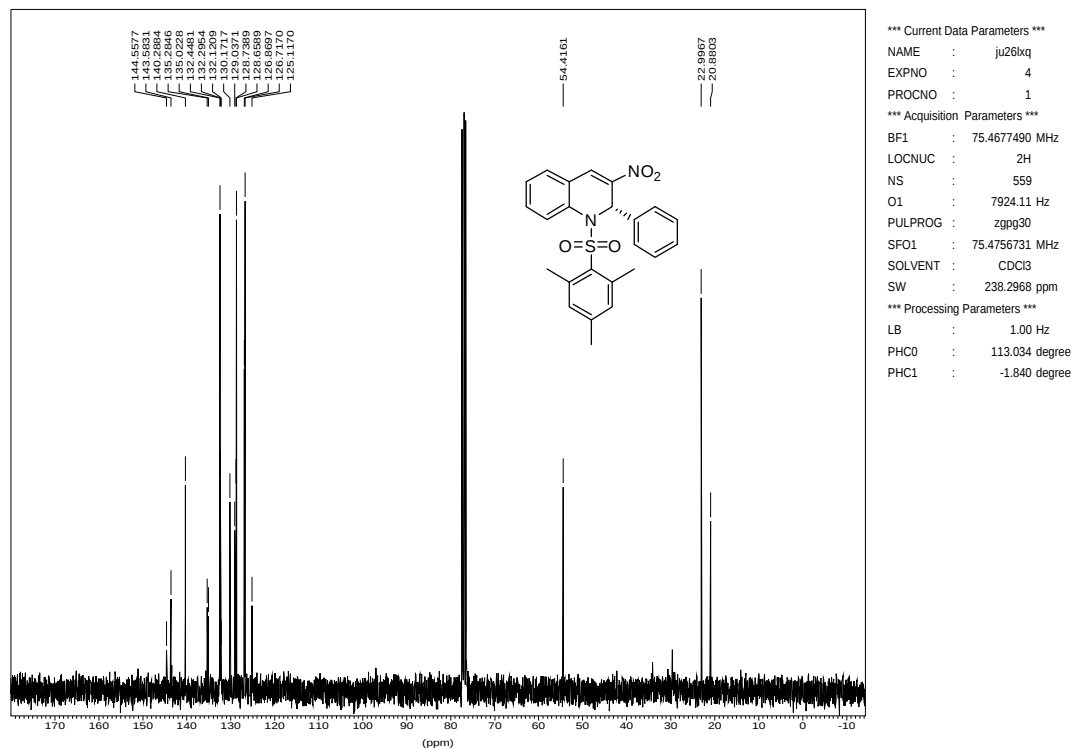
(S)-1-(Mesitylsulfonyl)-3-nitro-2-phenyl-1,2-dihydroquinoline 3g

¹H normal range AC300

464

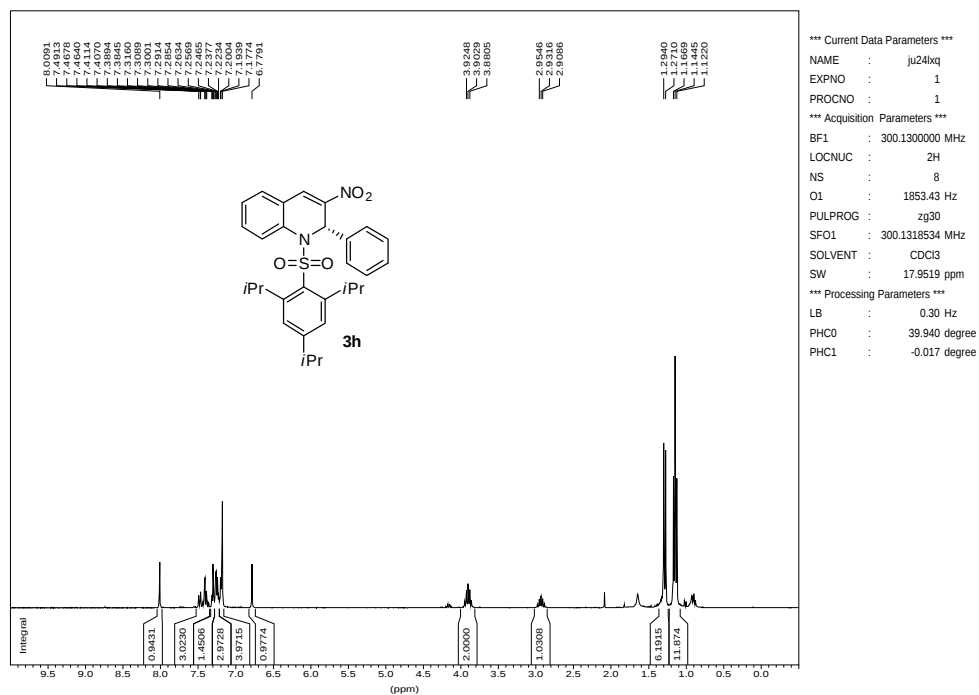


¹³C Standard AC300-464-C

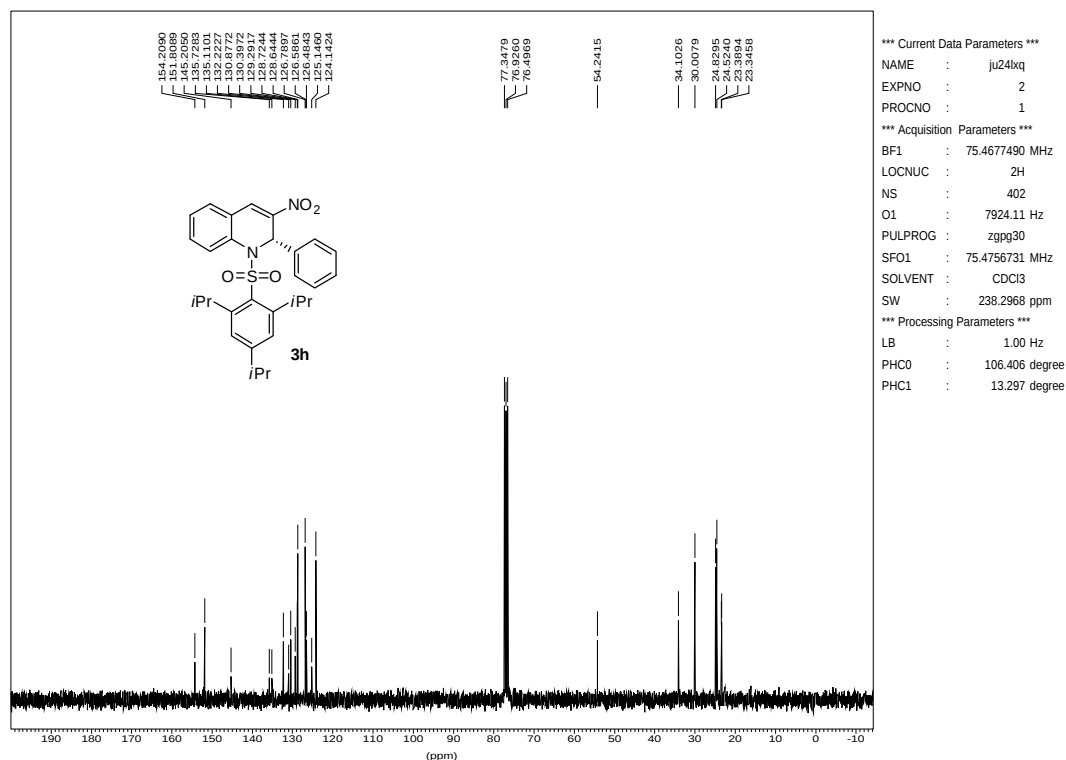


(S)-3-Nitro-2-phenyl-1-(2,4,6-triisopropylphenylsulfonyl)-1,2-dihydroquinoline 3h

¹H normal range AC300-522



¹³C Standard AC300-522C



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*** Current Data Parameters ***
NAME       : ju24bq
EXPNO      : 3
PROCNO     : 1

*** Acquisition Parameters ***
BF1        : 300.1300000 MHz
LOCNUC     : 2H
NS         : 8
O1         : 1853.43 Hz
PULPROG    : zg30
SOLVENT    : 300.1318534 MHz
SOLVENT    : CDCl3
SW         : 17.9519 ppm

*** Processing Parameters ***
LB         : 0.30 Hz
PHC0       : 38.243 degree
PHC1       : -0.018 degree
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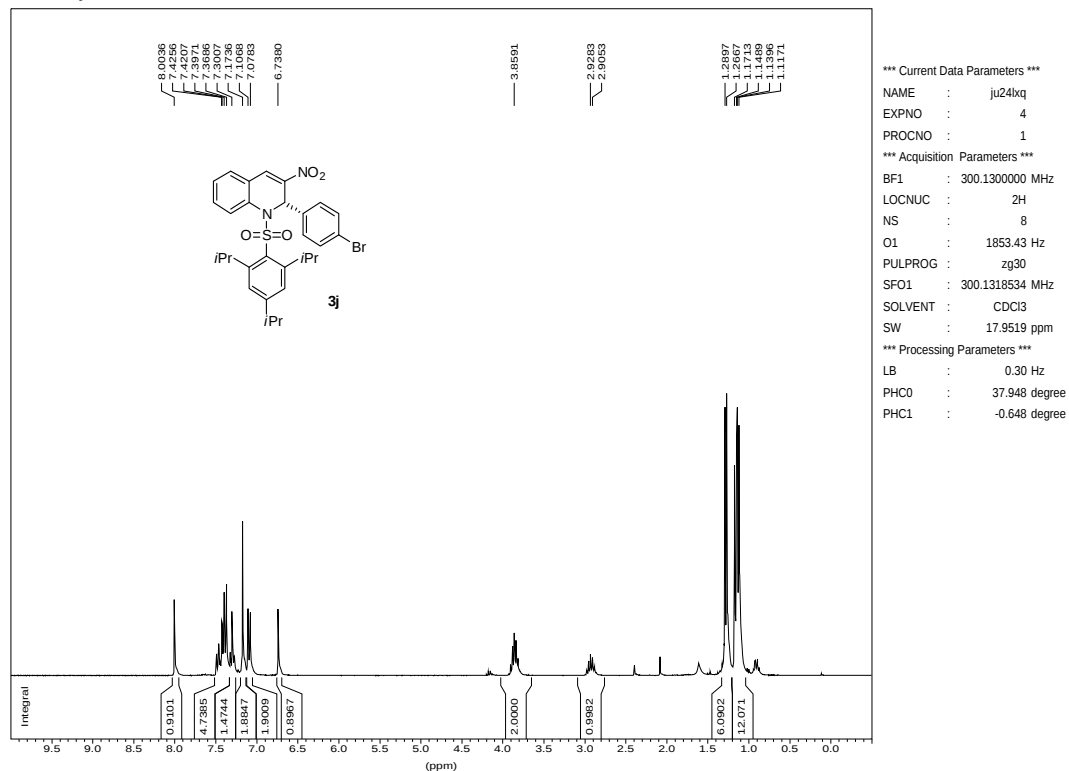
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*** Current Data Parameters ***
NAME       :   ju24hq
EXPNO      :       7
PROCNO     :       1

*** Acquisition Parameters ***
BF1        : 75.4677490 MHz
LOCNUC     :    2H
NS         :    903
O1         : 7924.11 Hz
PULPROG    : zgpg30
SF1        : 75.4756731 MHz
SOLVENT    :  CDCI3
SW         : 238.2968 ppm

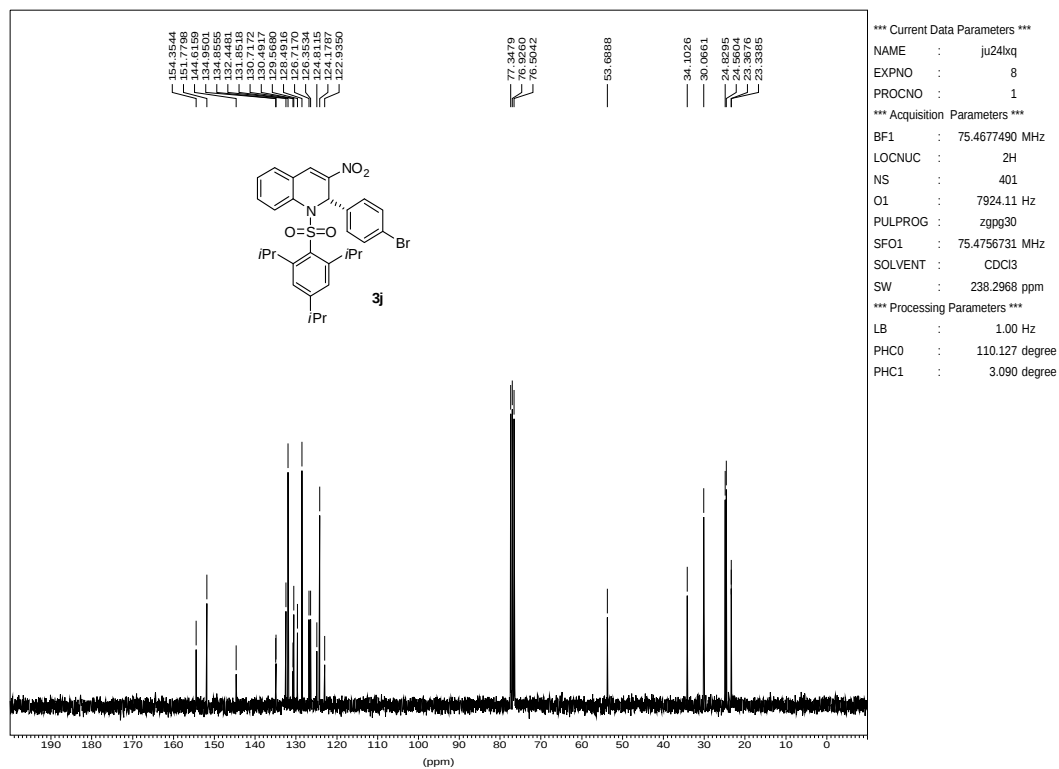
*** Processing Parameters ***
LB         :    1.00 Hz
PHC0       : 118.450 degree
PHC1       : -11.633 degree
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(S)-2-(4-Bromophenyl)-3-nitro-1-(2,4,6-triisopropylphenylsulfonyl)-1,2-dihydroquino
line 3j

¹H normal range AC300-533

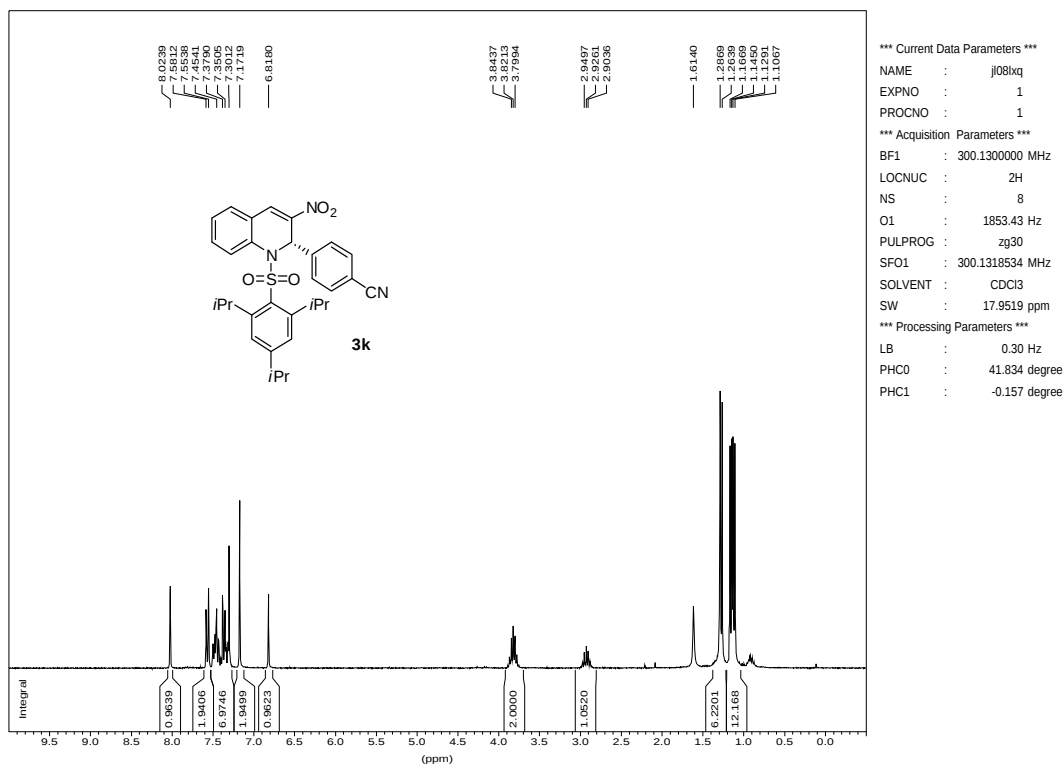


¹³C Standard AC300-533-C

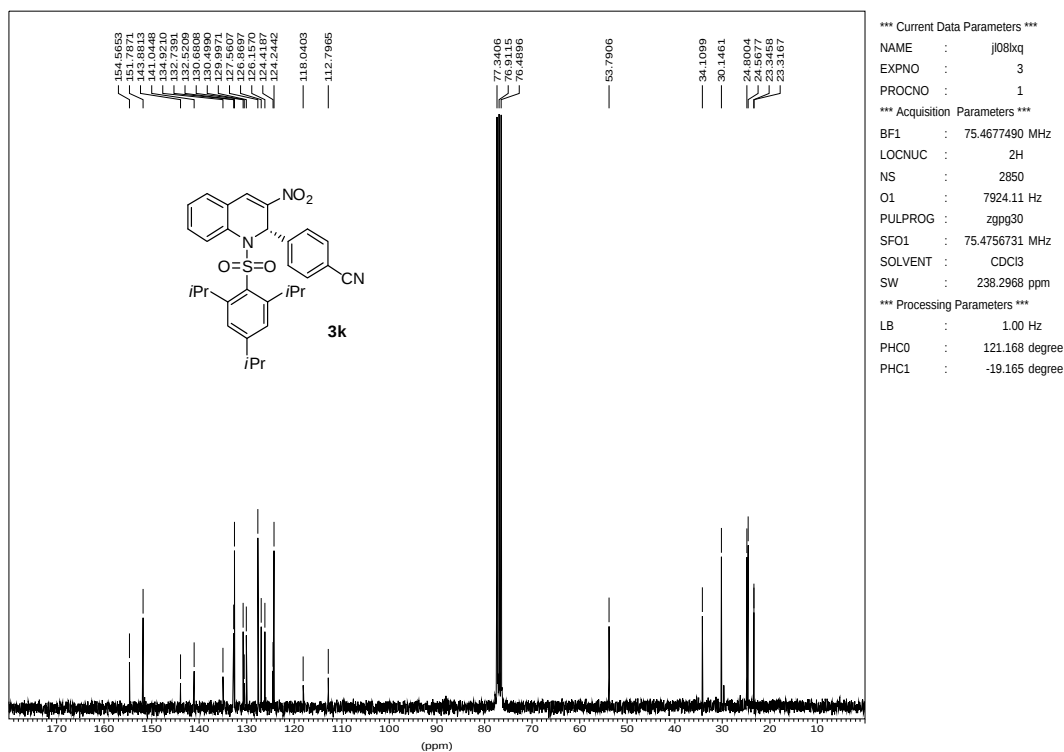


(S)-4-(3-Nitro-1-(2,4,6-triisopropylphenylsulfonyl)-1,2-dihydroquinolin-2-yl)benzonitrile **3k**

1H normal range AC300-554

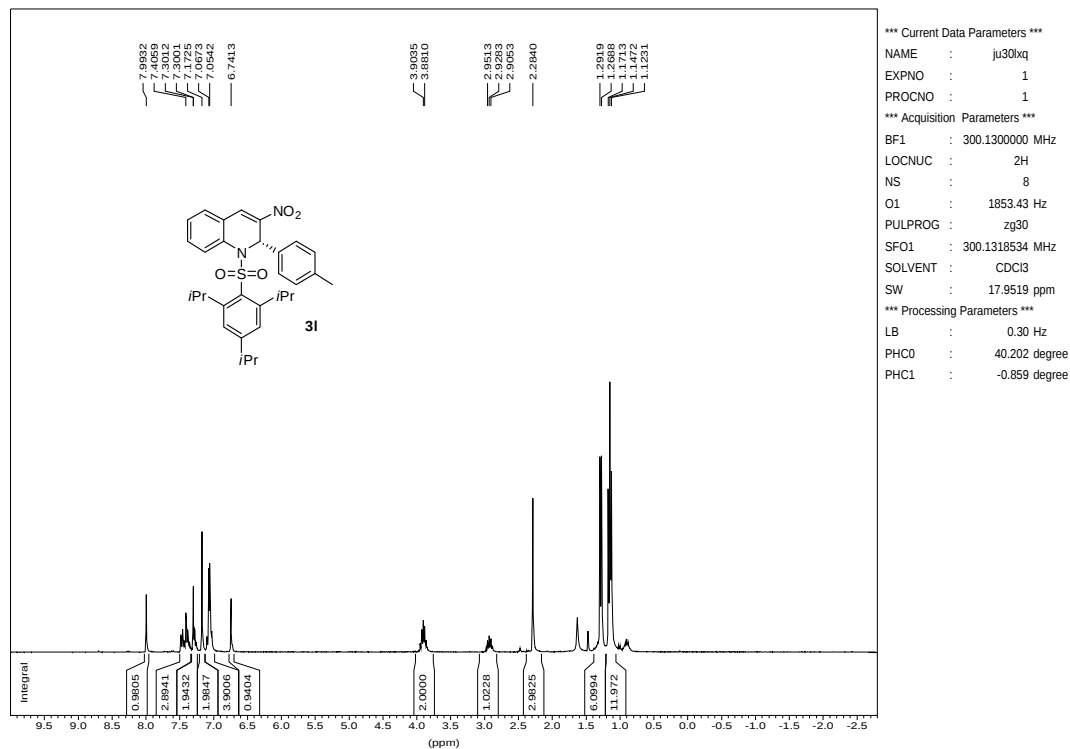


13C Standard AC300-554-C

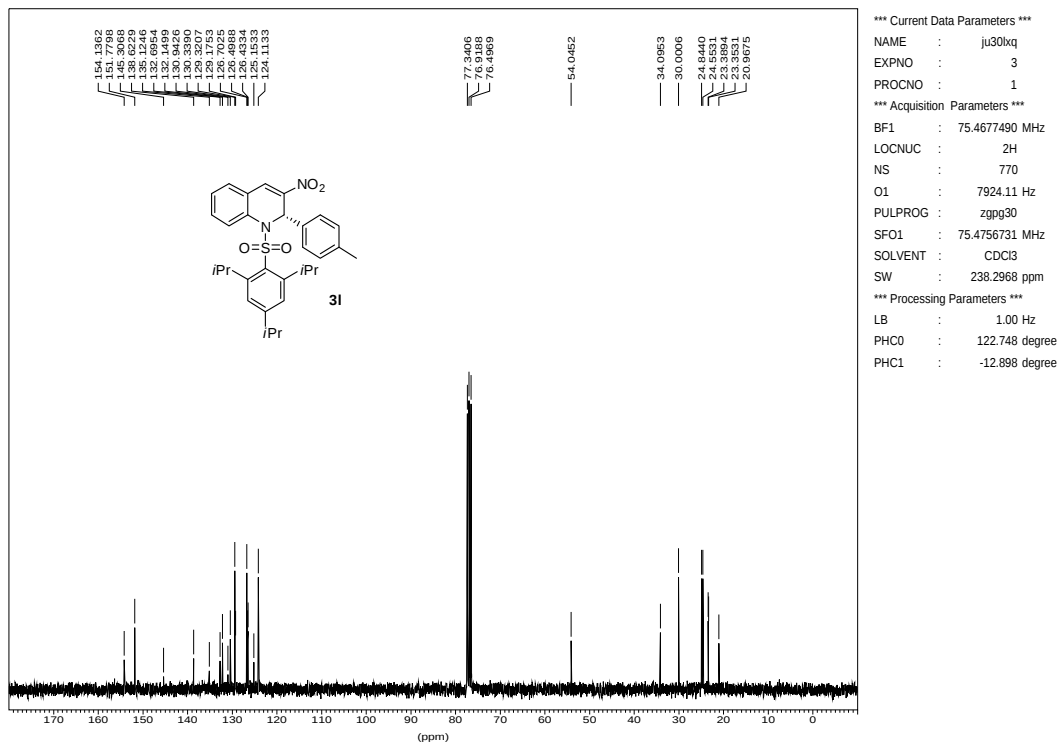


(S)-3-Nitro-2-p-tolyl-1-(2,4,6-triisopropylphenylsulfonyl)-1,2-dihydroquinoline 3I

¹H normal range AC300-539

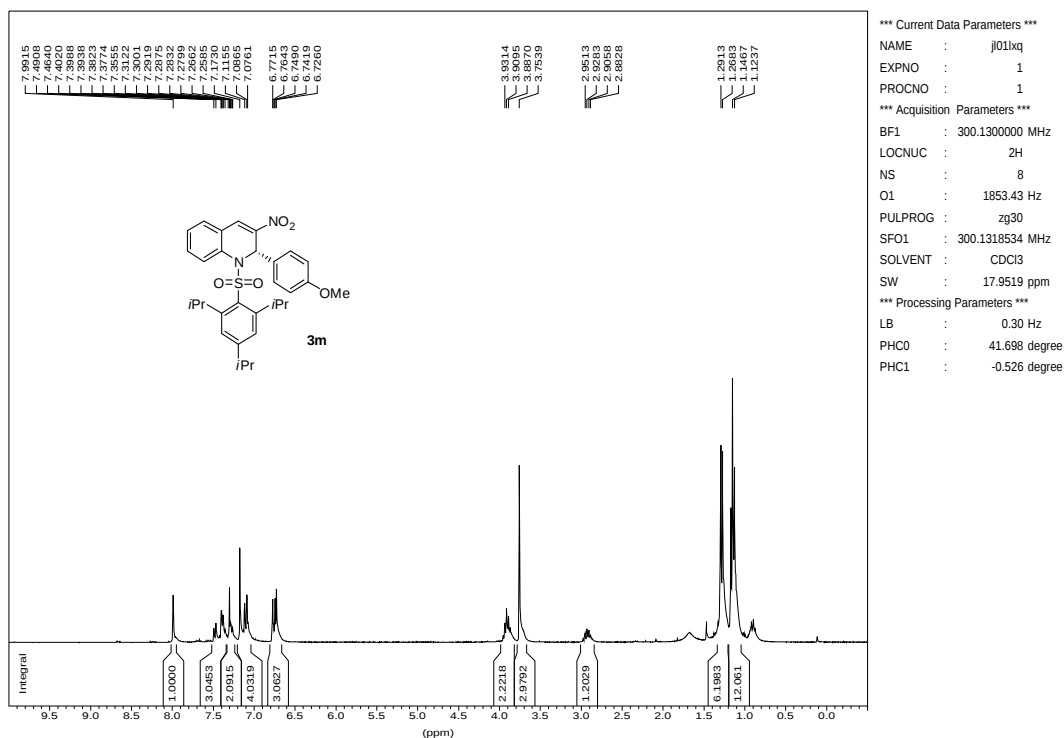


¹³C Standard AC300-539-C

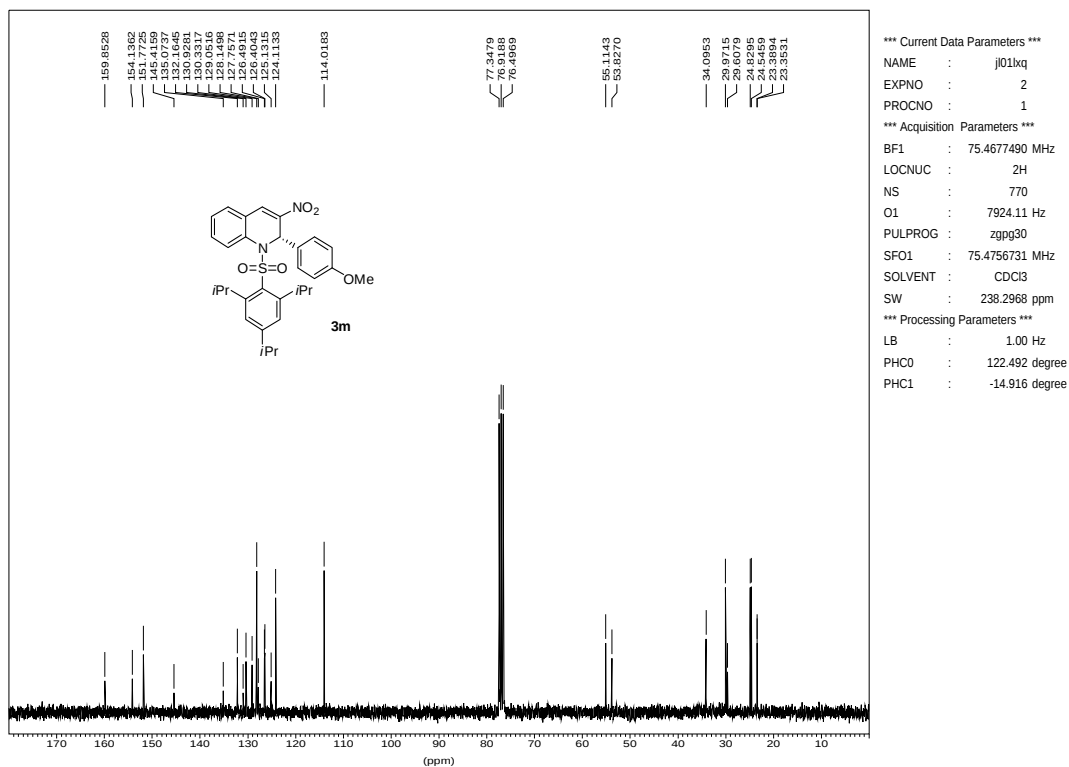


(S)-2-(4-Methoxyphenyl)-3-nitro-1-(2,4,6-triisopropylphenylsulfonyl)-1,2-dihydroquinoline 3m

¹H normal range AC300-541+542

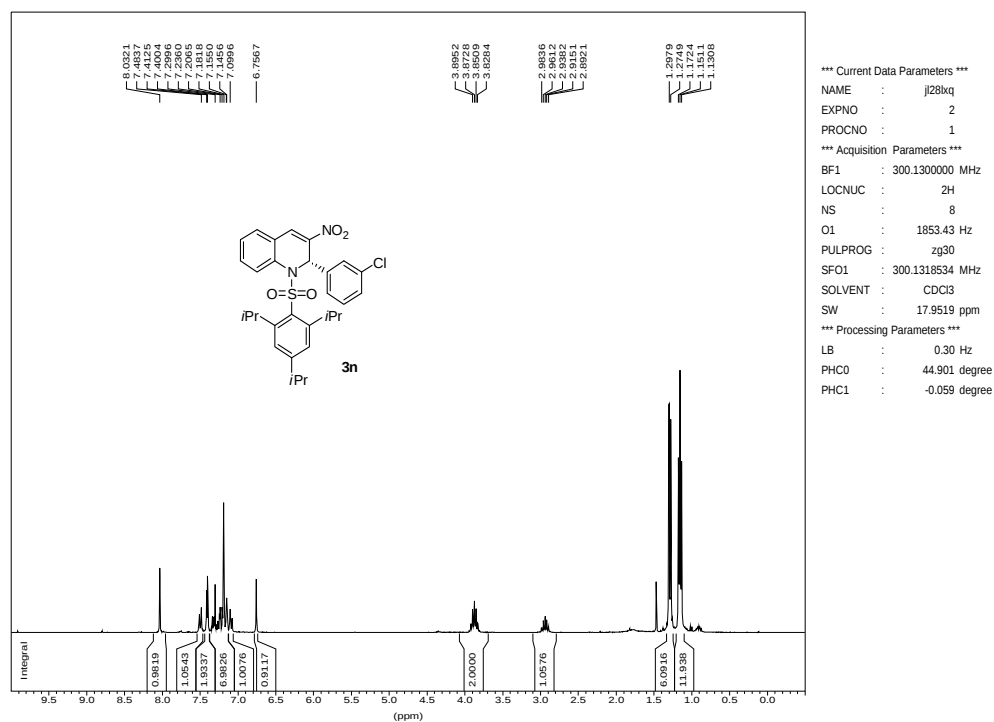


¹³C Standard AC300-541+542

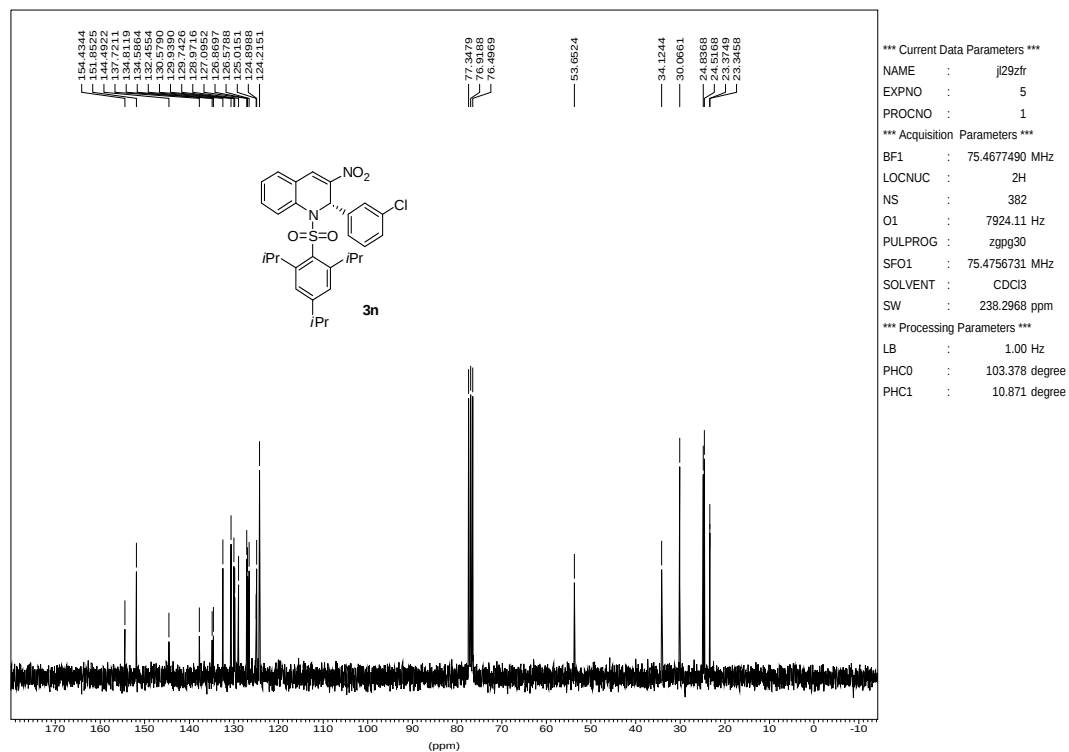


(S)-2-(3-Chlorophenyl)-3-nitro-1-(2,4,6-triisopropylphenylsulfonyl)-1,2-dihydroquino
line 3n

1H normal range AC300-586

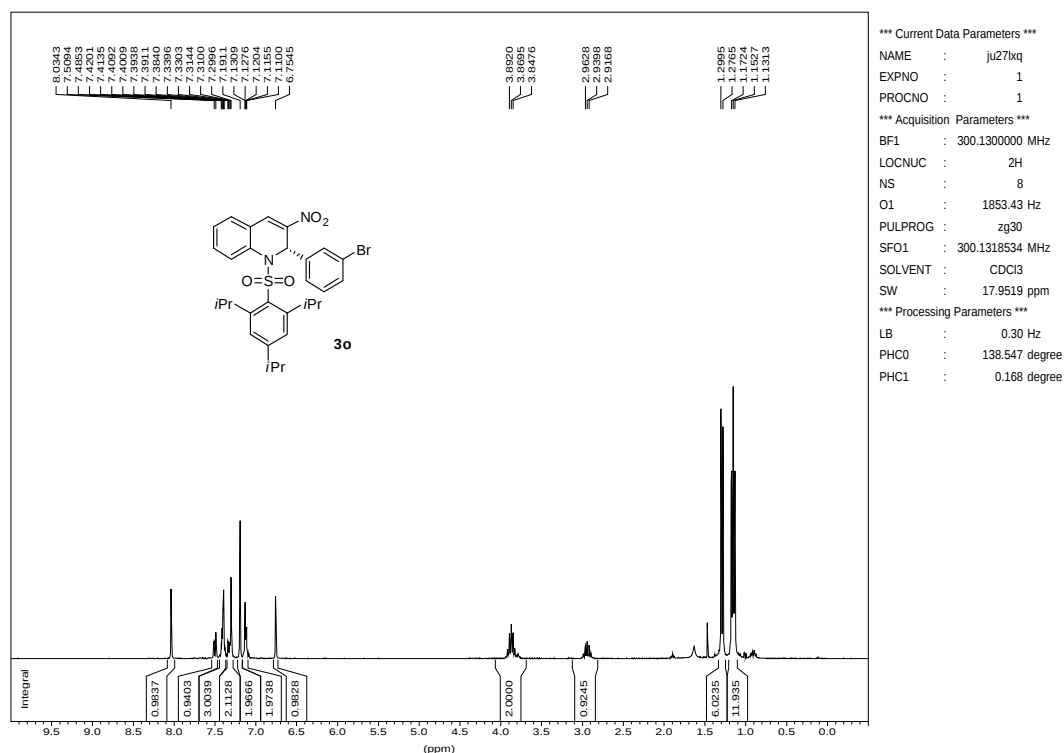


13C Standard AC300
lxq-586

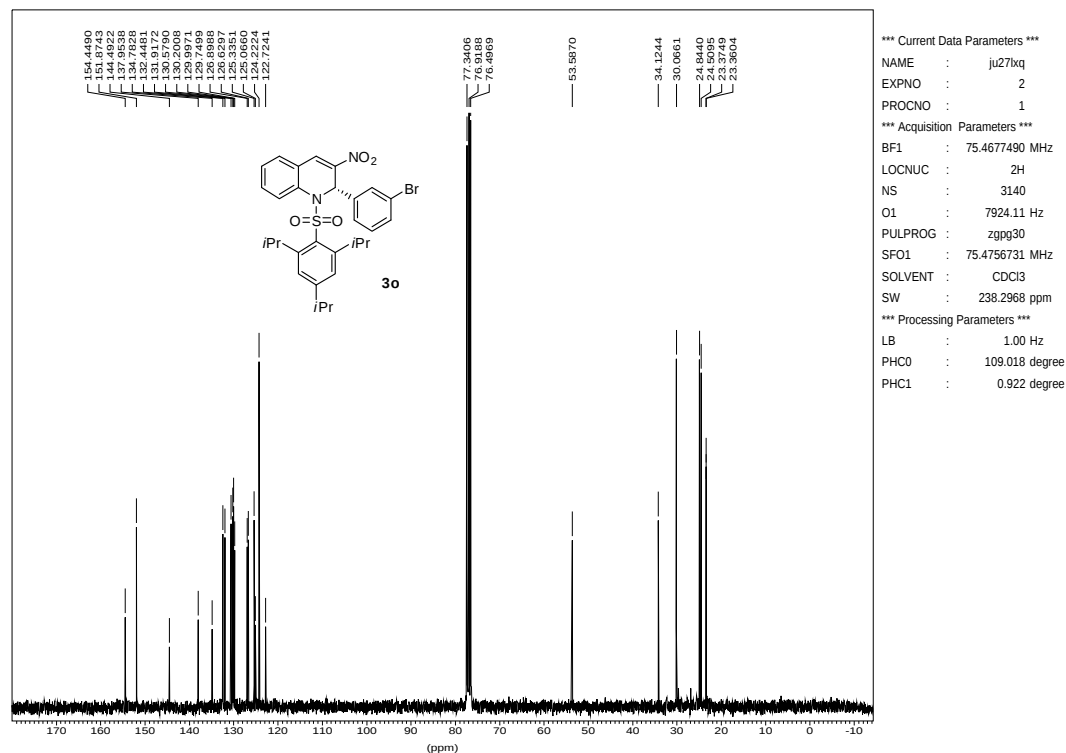


(S)-2-(3-Bromophenyl)-3-nitro-1-(2,4,6-triisopropylphenylsulfonyl)-1,2-dihydroquino
line **3o**

1H normal range AC300-535+536

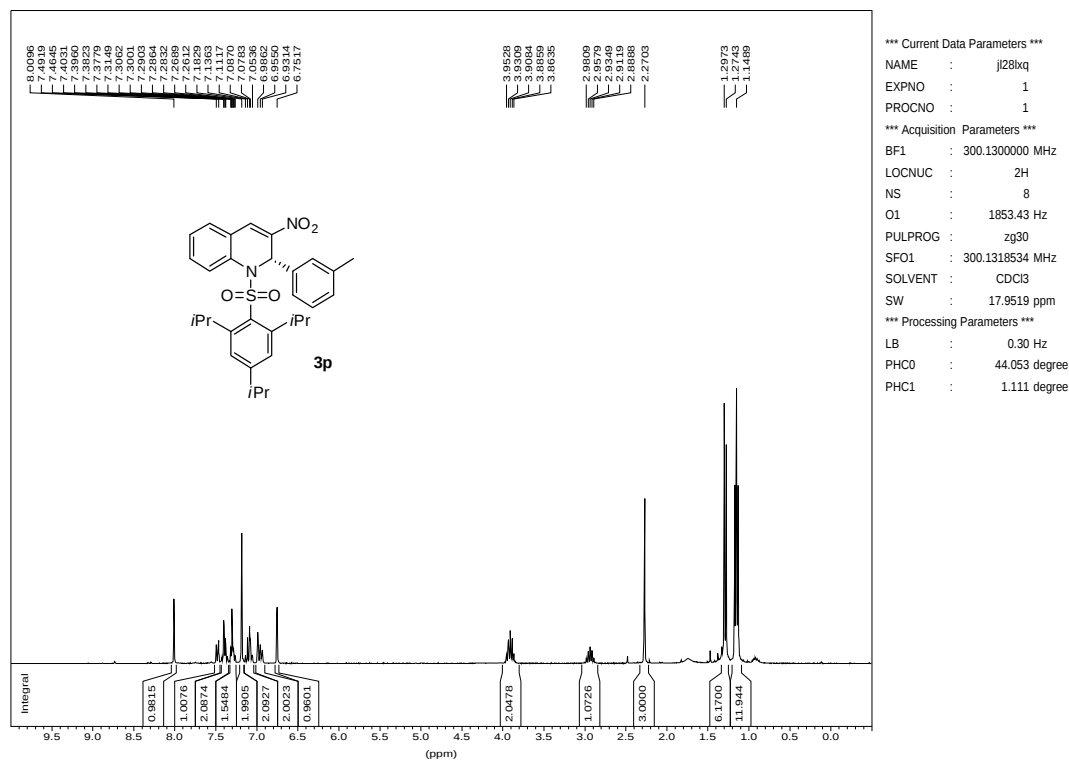


13C Standard AC300-535+536C

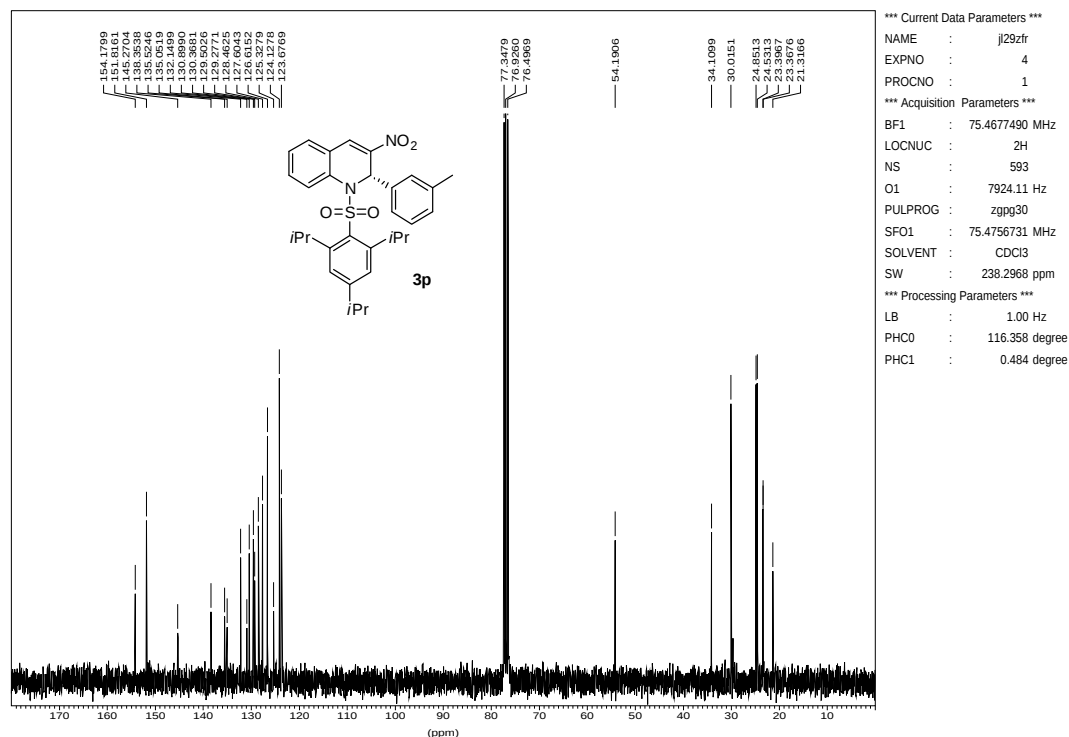


(S)-3-Nitro-2-m-tolyl-1-(2,4,6-triisopropylphenylsulfonyl)-1,2-dihydroquinoline 3p

¹H normal range AC300-584

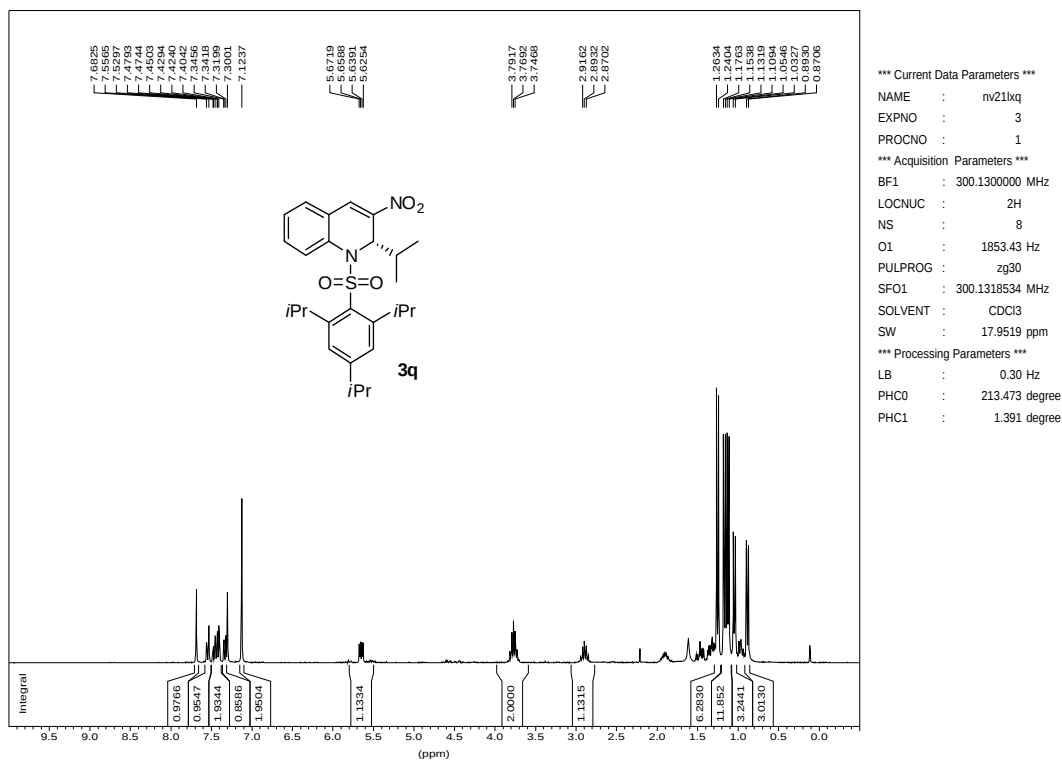


¹³C Standard AC300
lxq-584

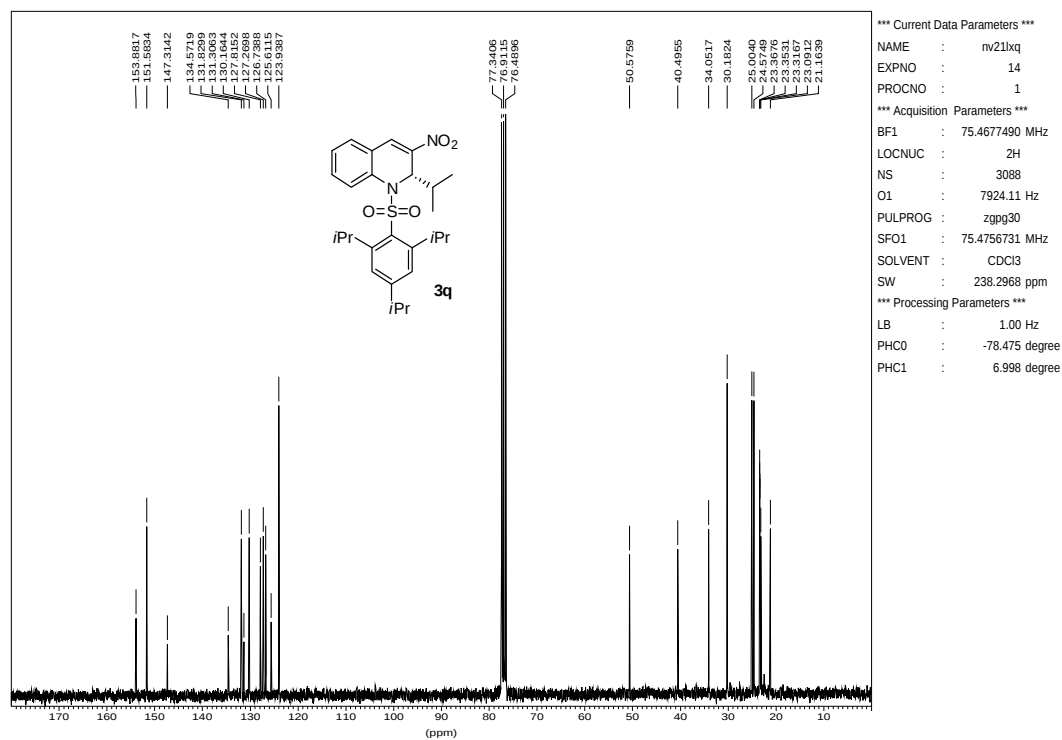


(S)-2-Isopropyl-3-nitro-1-(2,4,6-triisopropylphenylsulfonyl)-1,2-dihydroquinoline 3q

¹H normal range AC300-681

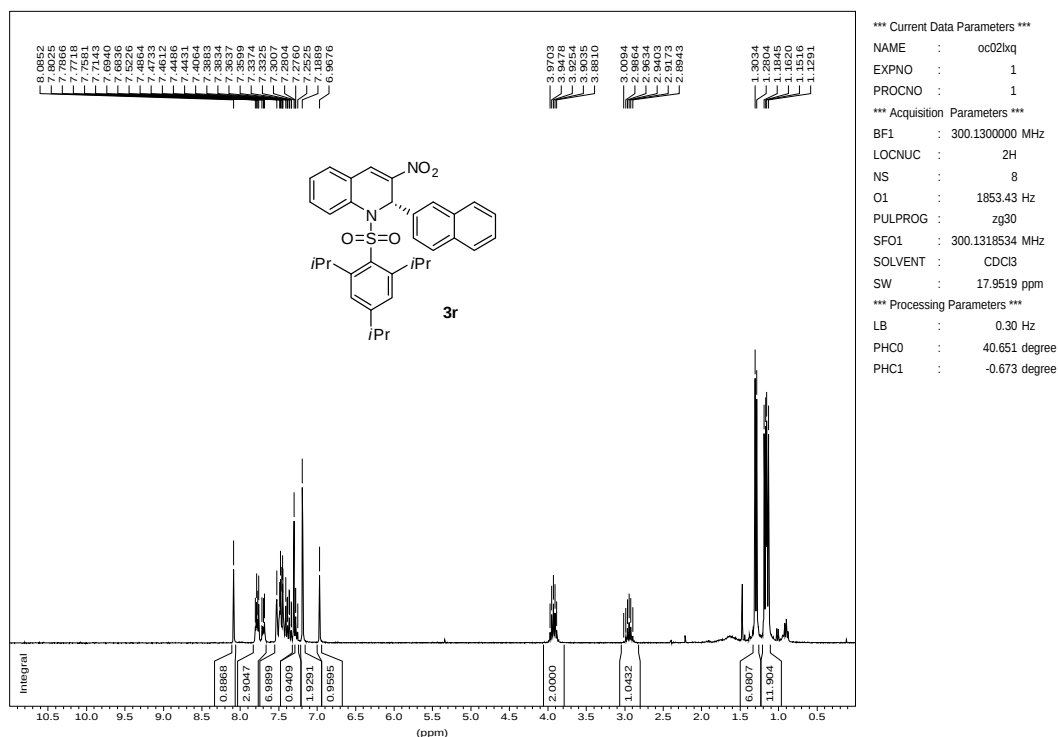


¹³C Standard AC300-681-C

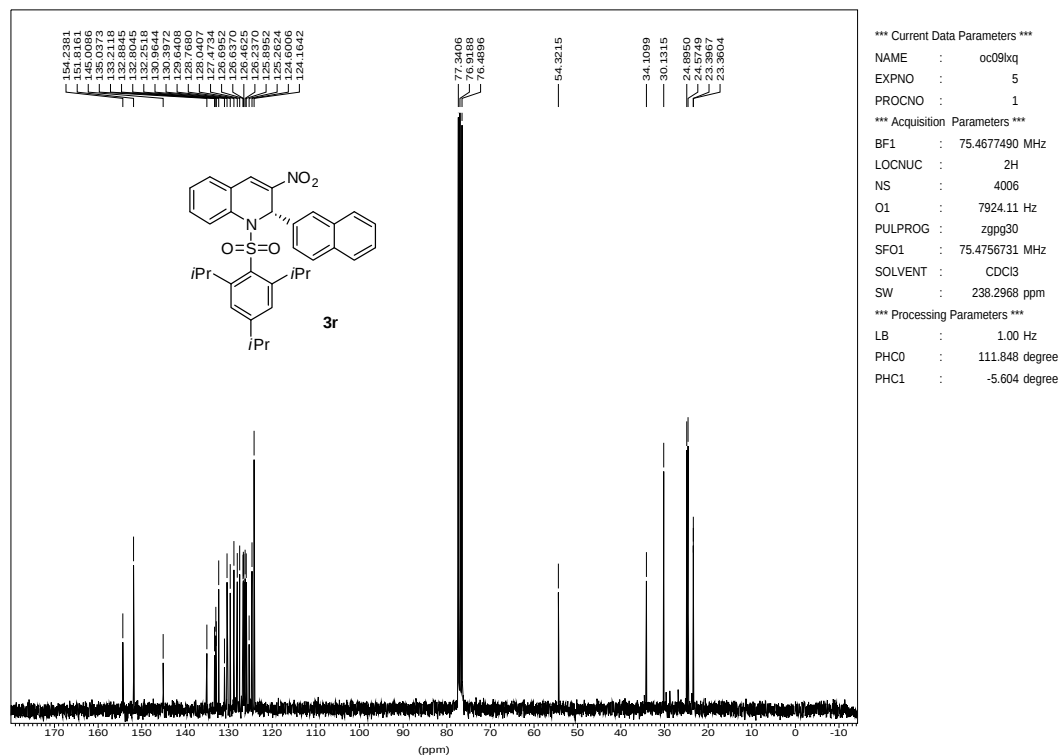


(S)-2-(Naphthalen-2-yl)-3-nitro-1-(2,4,6-triisopropylphenylsulfonyl)-1,2-dihydroquinoline 3r

¹H normal range AC300-633

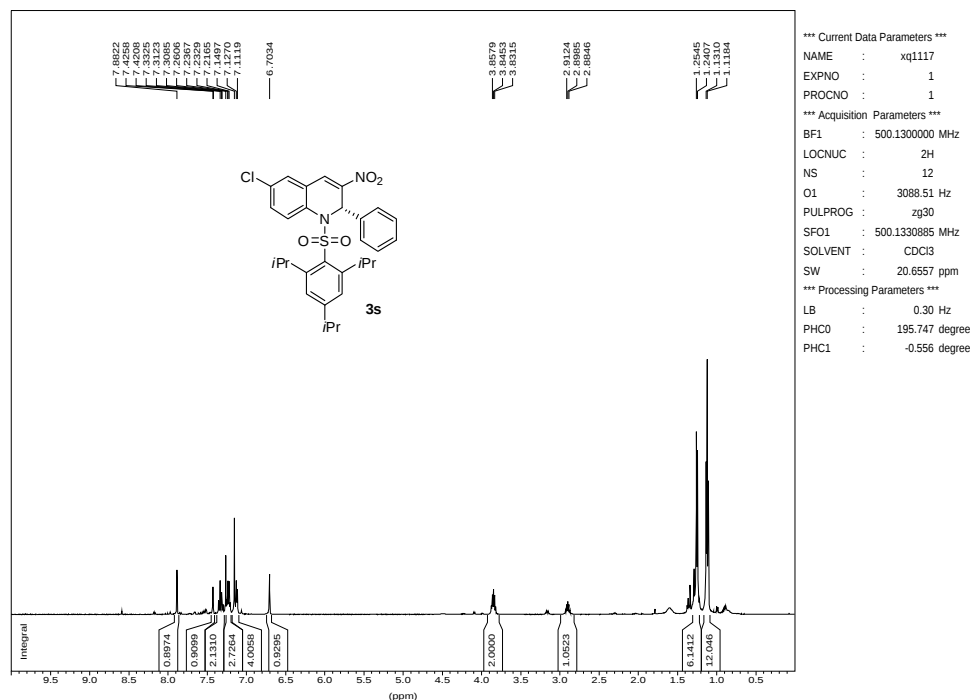


¹³C Standard AC300-633-C



(S)-6-Chloro-3-nitro-2-phenyl-1-(2,4,6-triisopropylphenylsulfonyl)-1,2-dihydroquinoline 3s

¹H AMX500 611



¹³C Standard AC300-611-C

