Supporting Information

Catalytic Enantioselective Oxysulfenylation of *o*-Vinylanildes

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1. General comments:

All reactions were carried out in dry reaction tube under nitrogen atmosphere. All the *o*-vinylanilines were synthesized from corresponding anilines and phenylacetylene derivatives employing literature procedure.[1] All electrophilic aryl/benzyl sulfenylating reagents were synthesized from either *N*-chlorosuccinamide or saccharine with corresponding thiols employing literature procedure.[2,3] Chiral Lewis-Bases were synthesized from literature protocol[3] and employing Chiral (S)-BINAM or (R)-BINOL is used as a model substrate.[4] Solvents such as 1,2-Dichloroethane (DCE), Chlorobenzene, Tetrahydrofuran (THF) and Toluene were purchased from Avra chemicals and dried over either CaH_2 or Na metal followed by stored with 4Å molecular sieves under argon atmosphere.

Column chromatography was performed using Rankem Silicagel (100-200 mesh) and ethylacetate-hexane with various percentage of polarity used depending on the nature of the substrate, unless otherwise specified.

2. Analytical Methods:

NMR data were recorded on Bruker DPX 400 AVC 500 MHz spectrometers. ^{1}H, ^{13}C spectra were referenced to signals of deuteron solvents and residual protonated solvents, respectively. Infrared spectra were recorded on a Thermo Nicolet iS10 FT spectrometer. HRMS were recorded by electron spry ionization (ESI) method on a Q-TOF Micro with lock spray source. An enantiomeric ratio was determined by HPLC analysis by using chiral columns in comparison with authentic racemic materials.

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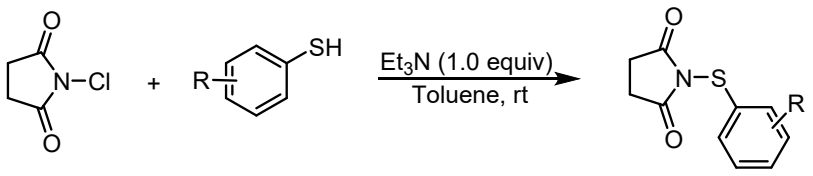
[1] Arienti, A.; Bigi, F.; Maggi, R.; Marzi, E.; Moggi, P.; Rastelli, M.; Sartori, G.; Tarantola, F. *Tetrahedron*, **1997**, *53*, 3795.

[2] Jyoti, S.; Roy, S.; Mukherjee, S. *Org. Biomol. Chem*. **2017**, *15*, 6921–6925.

[3] Denmark, S. E.; Rossi, S.; Webster, M. P.; Wang, H. *J. Am. Chem. Soc*. **2014**, *136*, 13016-13028.

[4] Denmark, S. E.; Chi, H. M.; *J. Am. Chem. Soc*. **2014**, *136*, 3655−3663.

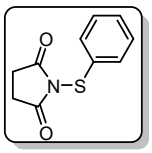
3. General procedure for synthesis of *N*-(thioaryl)succinimide:



An oven dried round bottomed flask was charged 1.01 gm (7.53 mmol) of *N*-chlorosuccinimide and 15 mL of dry toluene and the reaction was stir at room temperature for 10 minutes. Subsequently, 0.77mL (7.53 mmol) of thiol was added to the reaction mixture via syringe and the reaction was allowed to stir at room temperature for 30 min. Later, 1.05 mL (7.53 mmol) of triethylamine in dry toluene was added to the reaction mixture drop wise and further stirred at room temperature for additional 12 h. After completion of the reaction (monitored by TLC) it was quenched by addition of 10 mL saturated aq. $NaHCO_3$ solution, and compound was extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4 and was concentrated to afford the crude product. The pure compound was obtained by column chromatography, afforded the pure compound with high yield.[2]

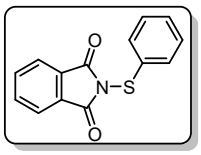
4. Properties of isolated thiolating reagents

1-(Phenylthio)pyrrolidine-2,5-dione (2a):



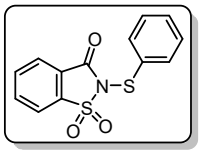
Yield: 81% (1.31 g); White solid. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.60 (d, J = 5.3 Hz, 2H), 7.34 (m, 3H), 2.80 (s, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 176.5 (2C), 134.0, 132.4 (2C), 130.0, 129.4 (2C), 28.7 (2C). HRMS: calcd. for $C_{10}H_9NO_2S$+H: 208.0426; found: 208.0421.

2-(Phenylthio)isoindoline-1,3-dione (2b):



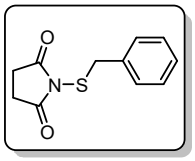
Yield: 78% (551 mg); White solid. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.92-7.85 (m, 2H), 7.77-7.63 (m, 2H), 7.59 (d, J = 5.7 Hz, 2H), 7.30 (m, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 167.8 (2C), 134.8 (2C), 134.4, 132.1 (2C), 131.6 (2C), 129.4 (2C), 124.1(2C), 123.7. HRMS: calcd. for $C_{14}H_9NO_2S$+H: 256.0426; found: 256.0422.

2-(Phenylthio)benzo[d]isothiazol-3(2*H*)-one 1,1-dioxide (2c):



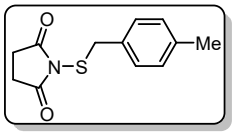
Yield: 72% (577 mg); White solid. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.09 (d, J = 7.4 Hz, 1H), 7.96-7.81 (m, 5H), 7.38-7.36 (m, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 159.5, 138.2, 135.6, 134.5, 133.2, 133.0 (2C), 130.6, 129.4 (2C), 127.2, 125.9, 121.7. HRMS: calcd. for $C_{13}H_9NO_3S_2$+H: 292.0096; found: 292.0092.

1-(Benzylthio)pyrrolidine-2,5-dione (2d):



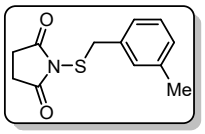
Yield: 79% (651 mg); White solid. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.78-7.27 (m, 5H), 4.09 (s, 2H), 2.62 (s, 4H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 176.6 (2C), 134.0, 129.7 (2C), 128.7 (2C), 128.1, 41.0, 28.4 (2C). HRMS: calcd. for $C_{11}H_{11}NO_2S$+H: 222.0583; found: 222.0577.

1-((4-Methylbenzyl)thio)pyrrolidine-2,5-dione (2e):



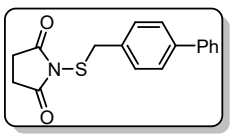
Yield: 74% (361 mg); White solid. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.14 (d, J = 7.3 Hz, 2H), 7.09 (d, J = 7.0 Hz, 2H), 4.05 (s, 2H), 2.63 (s, 4H), 2.30 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): 176.7 (2C), 138.0, 130.7, 129.6 (2C), 129.4 (2C), 40.8, 28.5 (2C), 21.2. HRMS: calcd. for $C_{12}H_{13}NO_2S$+H: 236.0739; found: 236.0732.

1-((3-Methylbenzyl)thio)pyrrolidine-2,5-dione (2f):



Yield: 77% (396 mg); White solid. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.18-7.13 (m, 1H), 7.09-7.02 (m, 2H), 4.05 (s, 2H), 2.63 (s, 4H), 2.31 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): 176.7 (2C), 138.5, 133.7, 130.5, 128.9, 128.5, 126.7, 41.0, 28.5 (2C), 21.3. HRMS: calcd. for $C_{12}H_{13}NO_2S$+H: 236.0739; found: 236.0733.

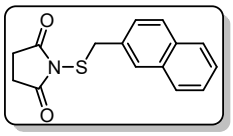
1-(([1,1'-Biphenyl]-4-ylmethyl)thio)pyrrolidine-2,5-dione (2g):



Yield: 68% (368 mg); White solid. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.45-7.42 (m, 2H), 7.38-7.34 (m, 3H), 4.15 (s, 2H), 2.64 (s, 4H). $^{13}C\{^{1}H\}$ NMR (100 MHz,

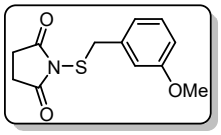
$CDCl_3$, 24 °C): 176.7 (2C), 132.8, 131.8, 130.2 (2C), 129.8, 128.9 (2C), 127.6, 127.3 (2C), 127.1 (2C), 40.8, 28.5 (2C). HRMS: calcd. for $C_{17}H_{15}NO_2S$+H: 298.0896; found: 298.0889.

1-((Naphthalen-2-ylmethyl)thio)pyrrolidine-2,5-dione (2h):



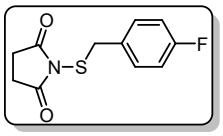
Yield: 63% (379 mg); White solid. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.81-7.79 (m, 2H), 7.76-7.74 (m, 1H), 7.57 (s, 1H), 7.50-7.46 (m, 3H), 4.25 (s, 2H), 2.52 (s, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): 176.6 (2C), 133.1, 132.9, 131.3, 128.8, 128.5, 127.9, 127.5, 127.3, 126.6, 126.4, 41.4, 28.4 (2C). HRMS: calcd. for $C_{15}H_{13}NO_2S$+H: 272.0739; found: 272.0729.

1-((3-Methoxybenzyl)thio)pyrrolidine-2,5-dione (2i):



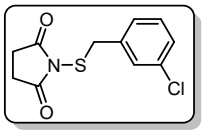
Yield: 76% (376 mg); White solid. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.18 (t, J = 7.9 Hz, 1H), 6.82-6.79 (m, 3H), 4.06 (s, 2H), 3.78 (s, 3H), 2.63 (s, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 176.6 (2C), 159.8, 135.4, 129.6, 122.0, 114.9, 114.0, 55.4, 41.1, 28.5 (2C). HRMS: calcd. for $C_{12}H_{13}NO_3S$+H: 252.0688; found: 252.0685.

1-((4-Fluorobenzyl)thio)pyrrolidine-2,5-dione (2j):



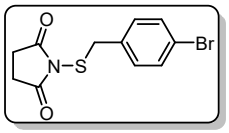
Yield: 62% (301 mg); White solid. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.27-7.26 (m, 2H), 7.01-6.97 (m, 2H), 4.08 (s, 2H), 2.67 (s, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 176.6 (2C), 162.5 (d, J = 248.0 Hz), 131.4 (d, J = 8.1 Hz, 2C), 129.7 (d, J = 3.1 Hz), 115.8 (d, J = 21.6 Hz, 2C), 40.3, 28.5 (2C). HRMS: calcd. for $C_{11}H_{10}FNO_2S$+H: 240.0489; found: 240.0476.

1-((3-Chlorobenzyl)thio)pyrrolidine-2,5-dione (2k):



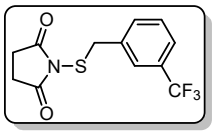
Yield: 71% (326 mg); White solid. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.25-7.20 (m, 4H), 4.05 (s, 2H), 2.69 (s, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 176.5 (2C), 136.2, 134.3, 130.1, 129.6, 128.3, 127.8, 40.5, 28.5 (2C). HRMS: calcd. for $C_{11}H_{10}ClNO_2S$+H: 256.0193; found: 256.0188.

1-((4-Bromobenzyl)thio)pyrrolidine-2,5-dione (2l):



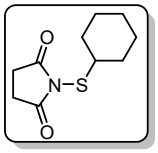
Yield: 68% (329 mg); White solid. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.41 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 4.04 (s, 2H), 2.66 (s, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 176.5 (2C), 133.1, 131.9 (2C), 131.3 (2C), 122.4, 40.5, 28.5 (2C). HRMS: calcd. for $C_{11}H_{10}BrNO_2S$+H: 299.9688; found: 299.9676.

1-((3-(Trifluoromethyl)benzyl)thio)pyrrolidine-2,5-dione (2m):



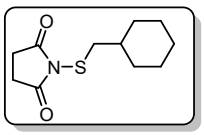
Yield: 58% (298 mg); White solid. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.51-7.53 (m, 2H), 7.45 (t, J = 7.6 Hz, 1H), 7.38 (s, 1H), 4.11 (s, 2H), 2.65 (s, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): 176.4 (2C), 135.5, 133.2, 130.8 (q, J = 32.5), 129.5, 126.9 (q, J = 3.6 Hz), 124.9 (q, J = 3.8 Hz), 123.9 (q, J = 274.4 Hz), 40.6, 28.4 (2C). HRMS: calcd. for $C_{12}H_{10}F_3NO_2S$+H: 290.0457; found: 290.0454.

1-(Cyclohexylthio)pyrrolidine-2,5-dione (2n):



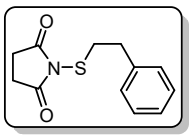
Yield: 64% (694 mg); White solid. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 3.19-3.17 (m, 1H), 2.83 (s, 4H), 1.83-1.76 (m, 4H), 1.65-1.60 (m, 1H), 1.34-1.21 (m, 5H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): 177.5 (2C), 48.5, 31.0 (2C), 28.6 (2C), 25.5 (3C). HRMS: calcd. for $C_{10}H_{15}NO_2S$+H: 214.0896; found: 214.0910.

1-((Cyclohexylmethyl)thio)pyrrolidine-2,5-dione (2o):



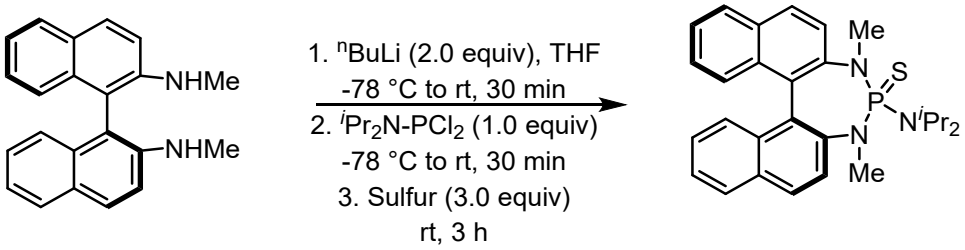
Yield: 66% (341 mg); White solid. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 2.80 (s, 4H), 2.71 (d, J = 6.4 Hz, 2H), 1.89-1.86 (m, 2H), 1.68-1.61 (m, 3H), 1.36 (m, 1H), 1.22-1.10 (m, 3H), 0.97-0.91 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): 177.2 (2C), 45.0, 36.7, 32.4 (2C), 28.7 (2C), 26.2, 25.9 (2C). HRMS: calcd. for $C_{11}H_{17}NO_2S$+H: 228.1052; found: 228.1050.

1-(Phenethylthio)pyrrolidine-2,5-dione (2p):



Yield: 77% (378 mg); White solid. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.30-7.26 (m, 2H), 7.21-7.19 (m, 3H), 3.18 (t, J = 7.2 Hz, 2H), 2.95 (t, J = 7.2 Hz, 2H), 2.63 (s, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): 177.1 (2C), 139.1, 128.8 (2C), 128.5 (2C), 126.7, 37.6, 35.4, 28.6 (2C). HRMS: calcd. for $C_{12}H_{13}NO_2S$+H: 236.0739; found: 236.0737.

5. General procedure for synthesis of chiral Lewis-Base:

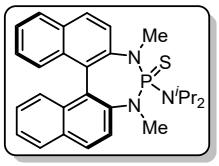


According to literature procedure,[4] an oven dried shlenck tube (S)-*N,N″*-dimethyl-1,1'-binaphthyl-2,2'-diamine (400 mg, 1.28 mmol, 1.0 equiv) and dry THF (0.15 M) was taken under argon atmosphere and the reaction was stir at -78 °C. After 20 min intervals 1.6 M ^{n}BuLi (1.6 mL, 2.56 mmol, 2.0 equiv) was drop-wise added to the reaction mixture via syringe over 10 min and further stir the reaction mixture at -78 °C for 45 min. The reaction mixture was removed from the cooling bath and stirred at room temperature for 30 min. A solution of diisopropylaminodichlorophosphine (388 mg, 1.92 mmol, 1.5 equiv) in THF (35-mL) was added slowly to the reaction mixture at -78 °C over 10 min. The reaction was removed from the cooling bath and stirred at room temperature for 2 h. Sulfur (124 mg, 3.84 mmol, 3.0 equiv) was added in one portion at room temperature and further stirred the reaction mixture at room temperature for 3 h. The reaction was filtered through a Celite pad to remove excess of sulfur from reaction medium and washed with DCM in thrice. Solvent were removed under reduced pressure and the crude mixture was purified column chromatography (SiO2, 100-200 mesh size) using hexanes/ ethylacetate (98:2) as a eluent and gave a pale yellow solid (656 mg) which still showed impurities by ^{1}H-NMR. The solid was further purified by recrystallization method by dissolving in CH_2Cl_2 (0.5 mL) and

pentane (10 mL) further it was stored at 0 °C for 18 h whereupon colorless needles were formed. These were filtered and washed with ice-cold pentane (2 ×10 mL). The crystals was dried in vacuo and gave pure (S)-4-(diisopropylamino)-3,5-dimethyl-4,5-dihydro-3H-dinaptho[2,1-d:1',2'-f][1,3,2]diazaphosphepine-4-sulfide) with 68% yield.

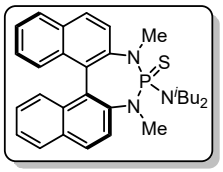
6. Properties of isolated chiral Lewis-Bases

(11bS)-4-(Diisopropylamino)-3,5-dimethyl-3,5-dihydrodinaphtho[2,1-d:1',2'-f][1,3,2]diazaphosphepine 4-sulfide (LB1):



Specific optical rotation: $[\alpha]_D^{25}$ 329.8 (c, 0.5, $CHCl_3$). Yield: 68% (411 mg); White solid. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.96 (d, J = 8.7 Hz, 1H), 7.91-7.83 (m, 3H), 7.68-7.62 (m, 2H), 7.40 (t, J = 7.3 Hz, 1H), 7.32 (t, J = 7.3 Hz, 1H), 7.28-1.19 (m, 2H), 7.08 (m, 1H), 6.96 (d, J = 8.6 Hz, 1H), 3.43 (d, J = 8.7 Hz, 2H), 3.26 (d, J = 11.6 Hz, 3H), 3.10 (d, J = 13.3 Hz, 3H), 1.41-1.26 (m, 12H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): 143.8 (d, J = 4.3 Hz), 142.4, 132.8, 132.4, 131.4, 130.7, 129.2, 128.4, 128.3 (d, J = 5.5 Hz), 128.1, 127.8, 127.7, 127.5, 127.4, 126.0, 125.7, 125.0, 124.8, 122.9, 122.6, 47.7, 36.9 (d, J = 11.0 Hz), 36.4 (d, J = 5.3 Hz), 34.2, 24.8 (2C), 22.4 (2C). ^{31}P NMR (202 MHz, $CDCl_3$, 24 °C): δ 81.3. HRMS: calcd. for $C_{28}H_{32}N_3PS$+H: 474.2127; found: 474.2132.

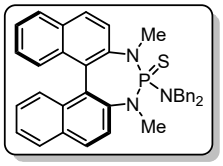
(11bS)-4-(Diisobutylamino)-3,5-dimethyl-3,5-dihydrodinaphtho[2,1-d:1',2'-f][1,3,2]diazaphosphepine 4-sulfide (LB2):



Specific optical rotation: $[\alpha]_D^{25}$ 1093.7 (c, 0.2, $CHCl_3$). Yield: 57% (186 mg); White solid. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.98 (d, J = 8.8 Hz, 1H), 7.89 (m, 3H), 7.66 (d, J = 8.8 Hz, 1H), 7.42 (t, J = 7.2 Hz, 1H), 7.34 (t, J = 7.3 Hz, 1H), 7.24 (m, 2H), 7.12 (t, J = 7.8 Hz, 1H), 7.01 (d, J = 8.5 Hz, 1H), 3.18 (d, J = 11.0 Hz, 3H), 3,05 (m, 2H), 3.00 (d, J =12.9 Hz, 3H), 2.79 (td, J = 13.5, 6.0 Hz, 2H), 1.89 (m, 2H), 0.85 (m, 12H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): 143.7, 142.4, 132.7, 132.5, 131.5, 131.3, 129.5, 129.3, 128.6, 128.5, 128.3, 127.9, 127.5, 127.3, 126.2, 125.9, 125.3, 124.8, 124.4, 122.5, 55.0 (2C), 38.2 (d, J = 9.8 Hz), 35.5 (d, J = 5.0 Hz), 27.4

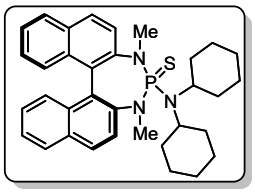
(2C), 20.9 (d, J = 5.9 Hz, 4C). ^{31}P NMR (202 MHz, $CDCl_3$, 24 °C): δ 91.2. HRMS: calcd. for $C_{30}H_{36}N_3PS$+H: 502.2440; found: 502.2448.

(11bS)-4-(Dibenzylamino)-3,5-dimethyl-3,5-dihydrodinaphtho[2,1-d:1',2'-f][1,3,2]diazaphosphepine 4-sulfide (LB3):



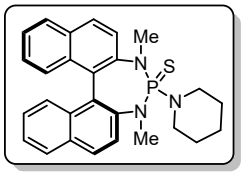
Specific optical rotation: $[\alpha]_D^{25}$ 155.2 (c, 0.5, $CHCl_3$). Yield: 47% (170 mg); White solid. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.99 (t, J = 8.7 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.79 (d, J = 8.1 Hz, 1H), 7.66 (d, J = 8.8 Hz, 1H), 7.58 (d, J = 8.7 Hz, 1H), 7.40-7.28 (m, 8H), 7.25-7.17 (m, 4H), 7.12 (t, J = 7.9 Hz, 1H), 7.03 (d, J = 8.5 Hz, 1H), 6.76 (d, J = 8.7 Hz, 1H), 4.29 (t, J = 14.5 Hz, 2H), 4.17 (t, J = 14.0 Hz, 2H), 3.14 (d, J = 11.1 Hz, 3H), 2.78 (d, J = 12.7 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 143.09, 143.05, 141.9, 137.4, 133.3, 132.5, 131.5, 131.4, 130.3, 130.0, 129.7, 128.99 (2C), 128.90, 128.4 (4C), 128.3, 128.0 (2C), 127.5 (2C), 127.3, 126.2, 127.1, 126.0, 125.5, 125.0, 124.6, 124.3, 122.7, 49.2 (2C), 38.8 (d, J = 10.1 Hz), 35.9 (d, J = 5.8 Hz). ^{31}P NMR (202 MHz, $CDCl_3$, 24 °C): δ 88.4. HRMS: calcd. for $C_{36}H_{32}N_3PS$+H: 570.2127; found: 570.2136.

(11bS)-4-(Dicyclohexylamino)-3,5-dimethyl-3,5-dihydrodinaphtho[2,1-d:1',2'-f][1,3,2]diazaphosphepine 4-sulfide (LB4):



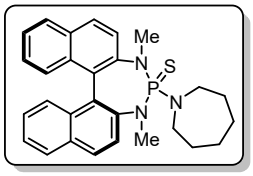
Specific optical rotation: $[\alpha]_D^{25}$ 295.3 (c, 0.5, $CHCl_3$). Yield: 48% (139 mg); White solid. ^{1}H NMR (500 MHz, $CDCl_3$, 24 °C): δ 7.09-7.75 (m, 4H), 7.59 (dd, J = 8.9 Hz, 0.9 Hz, 1H), 7.52 (d, J = 9.0 Hz, 1H), 7.31 (m, 1H), 7.24 (m, 1H), 7.14-7.10 (m, 2H), 6.99 (m, 1H), 6.85 (d, J = 8.5 Hz, 1H), 3.18 (d, J = 11.7 Hz, 3H), 3.05 (d, J = 13.3 Hz, 3H), 2.95-2.92 (m, 2H), 1.66-1.47 (m, 10H), 0.99-0.76 (m, 10H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 24 °C): δ 143.8, 143.7, 142.5, 132.8, 132.4, 131.4, 130.6, 129.8, 129.4, 129.1, 128.6, 128.3, 128.2, 127.8, 127.5, 126.0, 125.7, 124.9, 124.7, 122.4, 57.4 (2C), 36.8 (d, J = 11.0 Hz), 36.7 (d, J = 5.4 Hz), 34.2, 31.7, 25.4 (4C), 24.0 (d, J = 19.4 Hz, 2C), 22.7 (2C). ^{31}P NMR (202 MHz, $CDCl_3$, 24 °C): δ 85.0. HRMS: calcd. for $C_{34}H_{40}N_3PS$+H: 554.2753; found: 554.2761.

4-(Piperidin-1-yl)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine 4-sulfide (LB5):



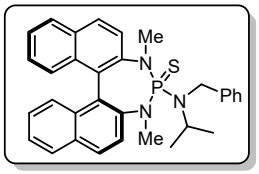
Specific optical rotation: $[\alpha]_D^{25}$ 379.3 (c, 0.5, $CHCl_3$). Yield: 48% (139 mg); White solid. ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.97 (d, J = 8.8 Hz, 1H), 7.93-7.85 (m, 3H), 7.64-7.61 (m, 2H), 7.43-7.40 (m, 1H), 7.35 (t, J = 7.5 Hz, 1H), 7.28-7.21 (m, 2H), 7.15-7.11 (m, 1H), 7.05 (d, J = 8.5 Hz, 1H), 3.20-3.13 (m, 2H), 3.15 (d, J = 11.8 Hz, 3H), 3.04-2.98 (m, 2H), 2.95 (d, J = 12.7 Hz,3H), 1.55-1.50 (m, 2H), 1.47-1.39 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 143.5, 143.4, 142.0, 132.7, 132.5, 131.4, 131.2, 129.6, 129.0, 128.2, 128.0, 127.5, 127.4, 126.2, 126.0, 125.5, 125.3, 124.9, 123.2, 122.4, 47.4 (2C), 37.4 (d, J = 9.3 Hz), 35.4 (d, J = 5.5 Hz), 26.8 (d, J = 4.7 Hz, 2C), 24.8. ^{31}P NMR (202 MHz, $CDCl_3$, 24 °C): δ 87.2. HRMS: calcd. for $C_{27}H_{28}N_3PS$+H: 458.1814; found: 458.1822.

(11bS)-4-(Azepan-1-yl)-3,5-dimethyl-3,5-dihydrodinaphtho[2,1-d:1',2'-f][1,3,2]diazaphosphepine 4-sulfide (LB6):



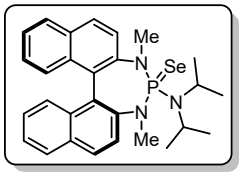
Specific optical rotation: $[\alpha]_D^{25}$ 1486.4 (c, 0.1, $CHCl_3$). Yield: 55% (164 mg); White solid. ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.94 (d, *J* = 8.8 Hz, 1H), 7.92 (d, *J* = 8.8 Hz, 1H), 7.87 (t, *J* = 8.0 Hz, 2H), 7.64-7.60 (m, 2H), 7.40 (t, *J* = 7.1 Hz, 1H), 7.36-7.32 (t, *J* = 7.3 Hz, 1H), 7.24-7.19 (m, 2H), 7.14-7.10 (m, 1H), 7.04 (d, *J* = 8.5 Hz, 1H), 3.28-3.26 (m, 2H), 3.21 (d, *J* = 11.5 Hz, 3H), 3.10-2.95 (m, 2H), 2.91 (d, *J* = 12.9 Hz, 3H), 1.66-1.62 (m, 8H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 143.6, 142.2, 132.7, 132.5, 131.4, 131.1, 129.6, 128.8, 128.6, 128.3, 128.1, 128.0, 127.4, 126.2, 125.9, 125.2, 124.9, 124.3, 123.1, 122.4, 49.4 (2C), 37.3 (d, *J* = 9.5 Hz), 34.5 (d, *J* = 5.9 Hz), 30.6 (d, *J* = 3.9 Hz, 2C), 27.0 (2C). ^{31}P NMR (202 MHz, $CDCl_3$, 24 °C): δ 88.3. HRMS: calcd. for $C_{28}H_{30}N_3PS$+H: 472.1970; found: 472.1974.

(11bS)-4-(Benzyl(isopropyl)amino)-3,5-dimethyl-3,5-dihydrodinaphtho[2,1-d:1',2'-f][1,3,2]diazaphosphepine 4-sulfide (LB7):



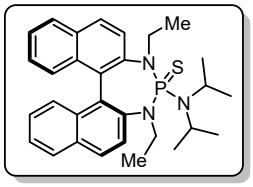
Specific optical rotation: $[\alpha]_D^{25}$ 259.4 (c, 0.5, $CHCl_3$). Yield: 58% (193 mg); White solid. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.00 (d, J = 8.7 Hz, 1H), 7.85 (t, *J* = 9.2 Hz, 2H), 7.79 (d, *J* = 8.8 Hz, 1H), 7.67 (d, *J* = 8.7 Hz, 1H), 7.47 (d, *J* = 8.1 Hz, 3H), 7.41-7.29 (m, 4H), 7.24-7.11 (m, 3H), 7.14-7.10 (m, 1H), 7.02 (d, 1H, *J* = 8.4 Hz), 4.76 (t, *J* = 14.5 Hz, 1H), 4.30 (t, *J* = 14.3 Hz, 1H), 3.87-3.85(m, 1H), 3.33 (d, *J* = 11.2 Hz, 3H), 3.01 (d, *J* = 13.2 Hz, 3H), 1.02 (d, *J* = 6.4 Hz, 3H), 0.97 (d, *J* = 6.5 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 143.8, 143.7, 142.3, 141.6, 141.5, 132.7, 132.5, 131.5, 131.1, 129.6, 128.7, 128.5, 128.3 (2C), 128.2 (2C), 127.9, 127.6, 127.5, 127.0, 126.1, 125.9, 125.3, 125.0, 123.3, 122.7, 48.8, 47.5 (d, *J* = 5.0 Hz), 38.1 (d, *J* = 10.5 Hz), 35.9 (d, *J* = 5.7 Hz), 24.0, 22.3. ^{31}P NMR (202 MHz, $CDCl_3$, 24 °C): δ 90.0. HRMS: calcd. for $C_{32}H_{32}N_3PS$+H: 522.2127; found: 522.2134.

(11bS)-4-(Diisopropylamino)-3,5-dimethyl-3,5-dihydrodinaphtho[2,1-d:1',2'-f][1,3,2]diazaphosphepine 4-selenide (LB8):



Specific optical rotation: $[\alpha]_D^{25}$ –252.8 (c, 0.5, $CHCl_3$). Yield: 64% (211 mg); White solid. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.97 (d, *J* = 8.8 Hz, 1H), 7.89 (t, *J* = 9.3 Hz, 2H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.69-7.63 (m, 2H), 7.42-7.39 (m, 1H), 7.33 (t, *J* =7.4 Hz, 1H), 7.27-7.25 (m, 1H), 7.23-7.20 (m, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.95 (d, *J* = 8.5 Hz, 1H), 3.66-3.54 (m, 1H), 3.31 (d, *J* = 12.5 Hz, 3H), 3.06 (d, *J* = 13.7 Hz, 3H), 1.37 (m, 12H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): 143.5, 143.4, 142.3, 132.8, 132.4, 131.5, 130.8, 129.1, 128.4, 128.37, 128.31, 127.9, 127.8, 127.5, 126.1, 125.7, 125.1, 124.9, 123.1, 122.9, 48.4 (2C), 37.7 (d, *J* = 12.6 Hz), 36.8 (d, *J* = 6.2 Hz), 24.9 (2C), 22.8 (2C). ^{31}P NMR (202 MHz, $CDCl_3$, 24 °C): δ 79.9. HRMS: calcd. for $C_{28}H_{32}N_3PSe$+H: 522.1571; found: 522.1576.

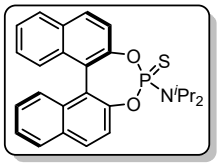
(11bS)-4-(Diisopropylamino)-3,5-diethyl-3,5-dihydrodinaphtho[2,1-d:1',2'-f][1,3,2]diazaphosphepine 4-sulfide (LB9):



Specific optical rotation: $[\alpha]_D^{25}$ –418.1 (c, 0.5, $CHCl_3$). Yield: 46% (136 mg); White solid. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.99 (d, J = 8.9 Hz, 1H), 7.92-7.85 (m,

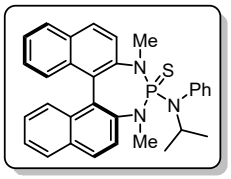
3H), 7.76 (d, J = 8.8 Hz, 1H), 7.65(d, J = 8.9 Hz, 1H), 7.45-7.41 (m, 1H), 7.36-7.32 (m, 1H), 7.24-7.20 (m, 2H), 7.11-7.08 (m, 1H), 6.94 (d, J = 8.5 Hz,1H), 4.35-4.29 (m, 1H), 3.66-3.55 (m, 3H), 3.53-3.40 (m, 2H), 1.43-1.27 (m, 12H), 0.79 (t, J = 7.1 Hz, 3H), 0.44 (t, J = 6.9 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 140.5, 138.9, 132.8, 132.5, 131.6, 131.0, 128.9, 128.2, 128.0, 127.8, 127.3, 127.0, 126.2, 125.7, 125.3, 125.0, 124.4, 124.0, 123.7, 122.9, 48.3 (2C), 44.0 (d, J = 13.7 Hz), 40.0 (d, J = 6.3 Hz), 24.9 (2C), 13.8 (d, J = 3.9 Hz, 2C), 13.4 (d, J = 9.0 Hz, 2C). ^{31}P NMR (202 MHz, $CDCl_3$, 24 °C): δ 88.4. HRMS: calcd. for $C_{30}H_{36}N_3PS$+H: 502.2440; found: 502.2449.

4-(Diisopropylamino)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine 4-sulfide (LB10):



Specific optical rotation: $[\alpha]_D^{25}$ –384.0 (c, 0.5, $CHCl_3$). Yield: 86% (268 mg); White solid. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.03 (d, J = 8.8 Hz, 1H), 7.97-7.91 (m, 3H), 7.61 (d, J = 8.8 Hz, 1H), 7.48-7.40 (m, 4H), 7.32-7.22 (m, 3H), 3.75 (2H, m), 1.35 (d, J = 6.7 Hz, 6H), 0.95 (d, J = 6.7 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 148.8, 148.6, 146.4, 146.3, 142.0, 132.7, 132.0, 131.3, 130.8, 130.3, 128.6, 128.4, 127.3, 127.2, 126.6, 126.4, 125.6, 125.5, 122.3, 121.4, 48.0 (d, J = 5.0 Hz, 2C), 22.5 (2C), 22.1 (2C). ^{31}P NMR (202 MHz, $CDCl_3$, 24 °C): δ 83.0. HRMS: calcd. for $C_{26}H_{26}NO_2PS$+H: 448.1494; found: 448.1498.

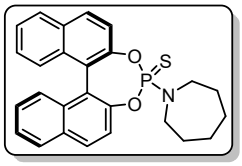
(11bS)-4-(Isopropyl(phenyl)amino)-3,5-dimethyl-3,5-dihydrodinaphtho[2,1-d:1',2'-f][1,3,2]diazaphosphepine 4-sulfide (LB11):



Specific optical rotation: $[\alpha]_D^{25}$ 237.5 (c, 0.5, $CHCl_3$). Yield: 64% (149 mg); White solid. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.98 (d, J = 8.8 Hz, 1H), 7.85 (d, J = 8.1 Hz, 1H), 7.76 (d, J = 8.3 Hz, 1H), 7.67 (d, J = 8.7 Hz, 1H), 7.42 (d, J = 8.7 Hz, 1H), 7.35-7.31 (m, 2H), 7.24-7.22 (m, 2H), 7.14-7.06 (m, 4H), 7.01 (d, J = 7.4 Hz, 2H), 6.97 (d, J = 8.2 Hz), 6.53 (d, J = 8.7 Hz, 1H), 4.44-4.37(m, 1H), 3.24 (d, J = 13.1 Hz, 3H), 3.17 (d, J = 11.2 Hz, 3H), 1.30 (d, J = 6.0 Hz, 3H), 0.93 (d, J = 6.3 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 143.6, 142.0, 139.6, 132.5, 132.2, 131.5 (2C), 130.5, 129.7, 129.4, 128.8 (2C), 128.2, 128.1, 127.7, 127.5, 127.4, 127.1, 126.8,

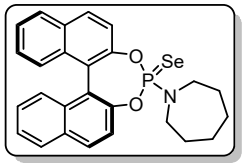
125.8 124.9 (2C), 123.7, 122.4, 121.8, 113.5, 51.3 (d, J = 6.3 Hz), 36.7 (d, J = 10.1 Hz), 35.5 (d, J = 5.6 Hz), 24.2, 21.9. ^{31}P NMR (202 MHz, $CDCl_3$, 24 °C): δ 84.3. HRMS: calcd. for $C_{31}H_{30}N_3PS$+H: 508.1970; found: 508.1978.

4-(Azepan-1-yl)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine 4-sulfide (LB12):



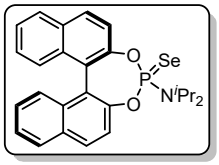
Specific optical rotation: $[\alpha]_D^{25}$ –406.2 (c, 0.5, $CHCl_3$). Yield: 85% (265 mg); White solid. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.03 (d, J = 8.8 Hz, 1H), 7.95 (m, 3H), 7.60 (d, J = 8.8 Hz, 1H), 7.46 (m, 4H), 7.31 (m, 2H), 7.25 (m, 1H), 3.29 (m, 2H), 3.10 (m, 2H), 1.60 (m, 8H).^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 149.3, 149.2, 147.0, 132.5, 131.9, 131.4, 130.9, 130.7, 128.6, 128.5, 127.4, 127.2, 126.7, 126.5, 125.7, 125.6, 122.9, 122.1, 121.8, 121.1, 49.6 (d, J = 3.4 Hz, 2C), 29.8 (d, J = 3.8 Hz, 2C), 26.7 (2C). ^{31}P NMR (202 MHz, $CDCl_3$, 24 °C): δ 83.4. HRMS: calcd. for $C_{26}H_{24}NO_2PS$+H: 446.1338; found: 474.1345.

(11bS)-4-(Azepan-1-yl)-3,5-dimethyl-3,5-dihydrodinaphtho[2,1-d:1',2'-f][1,3,2]diazaphosphepine 4-selenide (LB13):



Specific optical rotation: $[\alpha]_D^{25}$ 317.6 (c, 0.5, $CHCl_3$). Yield: 62% (206 mg); White solid. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.03 (d, J = 8.8 Hz, 2H), 7.97-7.92 (m, 3H), 7.62 (d, J = 8.8 Hz, 1H), 7.49-7.42 (m, 4H), 7.33-7.30 (m, 2H), 7.27-7.23 (m, 1H), 3.35-3.30 (m, 2H), 3.15-3.10 (m, 2H), 1.62-1.65 (m, 8H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 149.3, 149.1, 147.1, 147.0, 132.5, 132.0, 131.4, 130.8, 130.7, 128.6, 128.5, 127.4, 127.1, 126.7, 126.5, 125.7, 125.6, 122.4, 122.1, 121.1, 49.9 (d, J = 3.4 Hz, 2C), 29.7 (d, J = 3.9 Hz, 2C), 26.6 (2C). ^{31}P NMR (202 MHz, $CDCl_3$, 24 °C): δ 90.5. HRMS: calcd. for $C_{26}H_{24}NO_2PSe$+H: 494.0782; found: 494.0788.

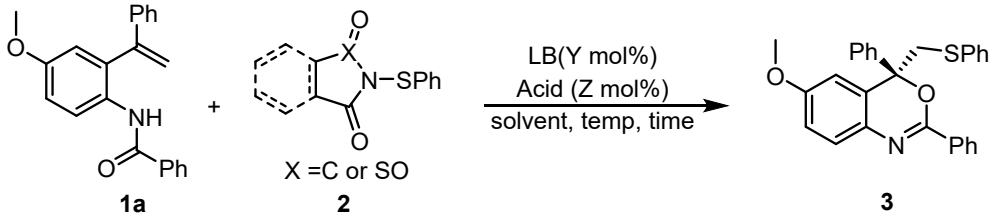
4-(Diisopropylamino)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine 4-selenide (LB14):



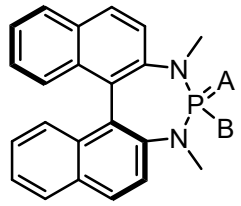
Specific optical rotation: $[\alpha]_D^{25}$ –401.1 (c, 0.5, $CHCl_3$). Yield: 63% (218 mg); White solid. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.04 (d, J = 8.8 Hz, 1H), 7.97-7.91 (m, 3H), 7.64 (d, J = 8.7 Hz, 1H), 7.48-7.39 (m, 4H), 7.31-7.22 (m, 3H), 3.88 (m, 2H), 1.36 (d, J = 6.6 Hz, 6H), 0.90 (d, J = 6.7 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 148.5, 148.4, 146.2, 146.1, 132.7, 132.6, 132.0, 131.4, 130.7, 130.3, 128.6, 128.4, 127.3, 127.1, 126.7, 126.5, 125.6, 122.7, 122.3, 121.4, 48.3 (d, J = 5.7 Hz, 2C), 22.4 (2C), 21.7 (2C). ^{31}P NMR (202 MHz, $CDCl_3$, 24 °C): δ 84.9. HRMS: calcd. for $C_{26}H_{26}NO_2PSe$+H: 496.0939; found: 496.0947.

7. Chiral Lewis base mediated oxysulfenylation: Optimization

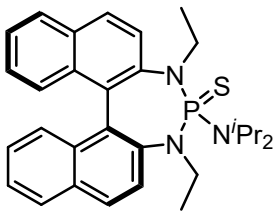
Table. 1 Enantioselective synthesis of benzoxazine from *o*-vinylanilide



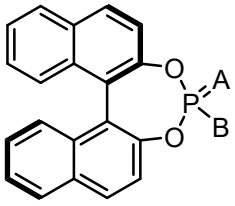
Chiral Lewis-bases:



A = S & B = N(^{i}Pr)$_2$; **LB1**
A = S & B = N(^{i}Bu)$_2$: **LB2**
A = S & B = N(^{i}Bn)$_2$: **LB3**
A = S & B = N(cy)$_2$: **LB4**
A = S & B = N(CH$_2$)$_5$: **LB5**
A = S & B = N(CH$_2$)$_6$: **LB6**
A = S & B = N(Bn)(^{i}pr): **LB7**
A = Se & B = N(^{i}Pr)$_2$; **LB8**
A = S & B = N(ph)(^{i}pr): **LB11**
A = Se & B = N(CH$_2$)$_6$: **LB13**

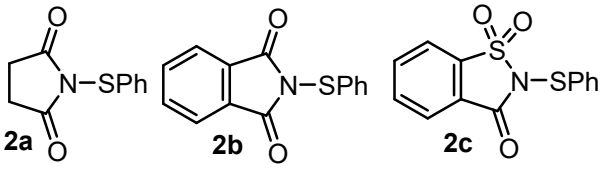


LB9



A = S & B = N(^{i}Pr)$_2$; **LB10**
A = S & B = N(Cycloheptyl); **LB12**
A = Se & B = N(^{i}Pr)$_2$; **LB14**

Sulfur sources:

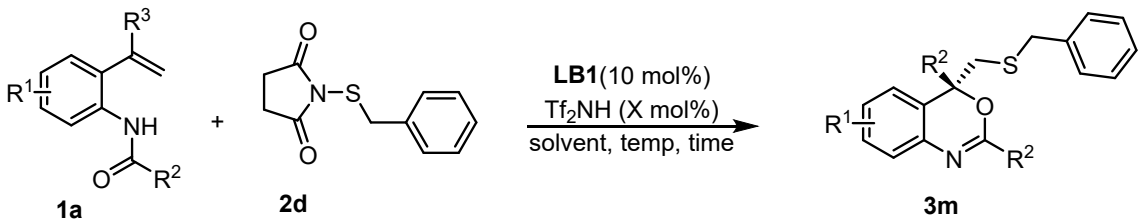


S. No.	Reagent "2"	LB(10 mol%)	Acid(eq)	Temp(°C)	Time(h)	Yield(%)[a]	er[b]
1	**2a** (1.2)	LB1	MsOH(1.0)	10	48	73	76:24
2	**2a** (1.2)	LB2	MsOH(1.0)	10	48	77	59:41
3	**2a** (1.2)	LB1	MsOH(1.0)	0	48	65	80:20
4	**2b** (1.2)	LB1	MsOH(1.0)	0	48	38	69:31

5	**2c** (1.2)	LB1	MsOH(1.0)	0	48	84	52:48
6	**2c** (1.2)	LB1	MsOH(0.5)	0	48	82	60:40
7	**2c** (1.2)	LB1	Tf_2NH(0.5)	0	36	86	79:21
8[c]	**2c** (1.2)	LB1	Tf_2NH(0.5)	0	36	83	84:16
9[d]	**2c** (1.2)	LB1	Tf_2NH(0.5)	0	36	80	81:19
10[e]	**2c** (1.2)	LB1	Tf_2NH(0.5)	0	36	43	81.5:19.5
11[c]	**2c (1.2)**	LB1	**Tf_2NH(0.3)**	**0**	**36**	**87**	**85:15**
12[c]	**2c** (1.2)	LB1	Tf_2NH(0.2)	0	36	71	84.5:15.5
13[c]	**2c** (1.2)	LB1	Tf_2NH(0.3)	-10	36	68	78:22
14[c]	**2c** (1.2)	LB3	Tf_2NH(0.3)	0	36	74	72:28
15[c]	**2c** (1.2)	LB4	Tf_2NH(0.3)	0	36	78	67:33
16[c]	**2c** (1.2)	LB5	Tf_2NH(0.3)	0	36	81	69.5:30.5
17[c]	**2c** (1.2)	LB6	Tf_2NH(0.3)	0	36	78	76:33
18[c]	**2c** (1.2)	LB7	Tf_2NH(0.3)	0	36	78	64:36
19[c]	**2c** (1.2)	LB8	Tf_2NH(0.3)	0	36	80	65:35
20[c]	**2c** (1.2)	LB9	Tf_2NH(0.3)	0	36	83	58:42
21[c]	**2c** (1.2)	LB10	Tf_2NH(0.3)	0	36	59	20.5:79.5
22[c]	**2c** (1.2)	LB11	Tf_2NH(0.3)	0	36	77	71:29
23[c]	**2c** (1.2)	LB12	Tf_2NH(0.3)	0	36	56	24.5:76.5
24[c]	**2c** (1.2)	LB13	Tf_2NH(0.3)	0	36	70	63:37
25[c]	**2c** (1.2)	LB14	Tf_2NH(0.3)	0	36	56	32:68

Reaction conditions: **1a** (1 equiv), **2** (x equiv), **LB1** (10 mol%), acid (y equiv), DCE (2 mL), 0 °C, time. [a] All are isolated yields. [b] Determined by HPLC using IG column. [c] Combination of solvents DCE:Ph-Cl (9:1) ratio was used. [d] Combination of solvents DCE:Toluene (9:1) ratio was used. [e] Chlorobenzene was used as the solvent.

Table. 2 Chiral Lewis base mediated oxysulfenylation of *o*-vinylanilide: Optimization

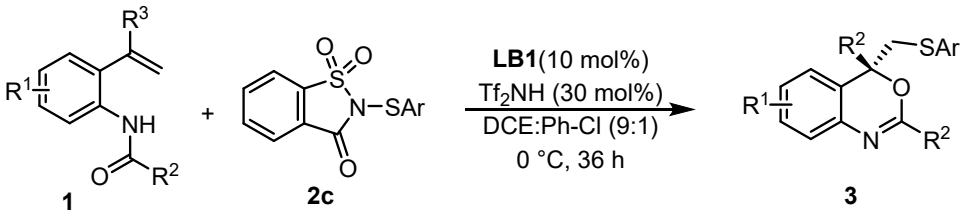


S. No.	Reagent "2"	LB(10 mol%)	Acid(equiv)	Temp(°C)	Yield(%)[a]	er[b]
1[c]	**2d** (1.2)	LB1	Tf_2NH(0.3)	0	34	91.5:8.5
2	**2d** (1.2)	LB1	Tf_2NH(1.0)	0	76	86.5:13.5
3	**2d** (1.2)	LB1	Tf_2NH(1.0)	-10	65	92:8
4	**2d** (1.2)	LB1	Tf_2NH(1.5)	-10	63	90.5:9.5
5	**2d** (1.2)	LB1	Tf_2NH(1.2)	-10	71	90:10
6	**2d** (2.0)	LB1	Tf_2NH(1.0)	-10	62	92:8
7	**2d** (1.2)	LB1	Tf_2NH(1.0)	10	80	89:11
8	**2d** (1.2)	LB1	Tf_2NH(0.8)	10	79	89.5:9.5
9	**2d** (1.2)	LB1	Tf_2NH(0.5)	10	50	89:90
10	**2d** (2.0)	LB1	Tf_2NH(0.5)	10	59	88:12
11	**2d (1.2)**	**LB1**	**Tf_2NH(0.8)**	**0**	**78**	**90.5:9.5**
12[c]	**2d** (1.2)	LB1	Tf_2NH(0.8)	0	61	90:10
13	**2d** (1.8)	LB1	Tf_2NH(0.8)	0	74	91:9

Reaction conditions: **1a** (1 equiv), **2d** (x equiv), **LB1** (10 mol%), Tf_2NH (y equiv), DCE (2 mL), temp, 48 h. [a] all are isolated yields. [b] determined by HPLC using IG column. [c] DCE:Ph-Cl was used as the solvent in (9:1) ratio.

8. General procedure for enantioselective synthesis of benzoxazine

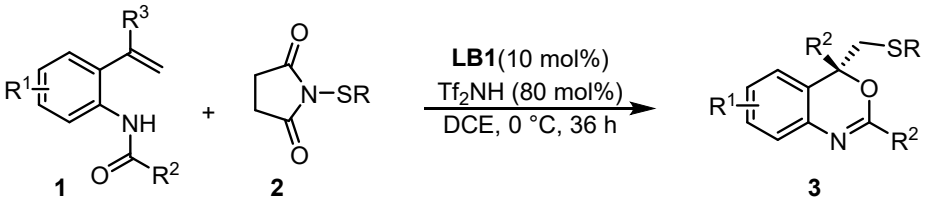
General procedure: A



In a dry schlenk tube 50 mg (0.15 mmol, 1.0 equiv) of *o*-vinylanilide, 38 mg (0.18 mmol, 1.2 equiv) of electrophilic thiolating reagent **2c** and chiral Lewis-Base **LB1** (7 mg, 10 mol%) was taken followed by (9:1) ratio of dry.1,2-dichloroethane: chlorobenzene (2mL) was added to the reaction mixture under argon atm. The reaction mixture was allowed to stir at 0 °C subsequently 30 mol% of bis(trifluoromethane)sulfonimide(Tf_2NH) in (0.5 mL) dry DCE was drop-wise added to the reaction

mixture over 5 min and further stirred at 0 °C for 48 h. After completion of the reaction (monitored by TLC) it was quenched by addition of 2 mL saturated aq. NH_4Cl solution, and compound was extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated to afford the crude product. The pure compound was obtained by column chromatography method using hexane/ethylacetate as an eluent.

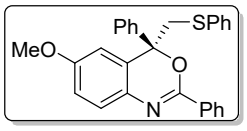
General procedure: B



In a dry schlenk tube 40 mg (0.12 mmol) of *o*-vinylanilide, 33 mg (0.14 mmol) of electrophilic thiolating reagent **2** and chiral Lewis-Base **LB1** (6 mg, 10 mol%) was taken followed by (2.0 mL) of dry 1,2-dichloroethane (DCE) was added to the reaction mixture under argon atm. The reaction mixture was allowed to stir at 0 °C subsequently 80 mol% of bis(trifluoromethane)sulfonimide(Tf_2NH) in (0.5 mL) dry DCE was drop-wise added to the reaction mixture over 5 min and further stirred at 0 °C for 48 h. After completion of the reaction (monitored by TLC) it was quenched by addition of 2 mL saturated aq. NH_4Cl solution, and compound was extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated to afford the crude product. The pure compound was obtained by column chromatography method using hexane/ethylacetate as an eluent.

9. Properties of isolated benzoxazines

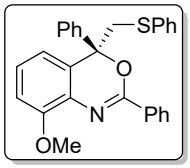
(*R*)-6-Methoxy-2,4-diphenyl-4-((phenylthio)methyl)-4*H*-benzo[d][1,3]oxazine (3a):



According to the general procedure **A**, the tittle compound **3a** was isolated in 87% yield (58 mg) as a colourless liquid using the mixture of ethyl acetate/hexanes (10:90) as an

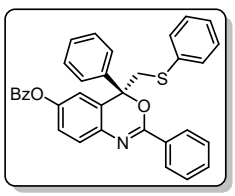
eluent for column chromatography. Enantiomeric ratio (85:15) was measured by HPLC (Chiralpak IG, 15% IPA/Hexanes, 1 mL/min, 254 nm), t_R = (major, 8.6 min.), t_R = (minor, 12.9 min.). Specific optical rotation: $[\alpha]_D^{25}$ –18.8 (c, 0.6, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.08 (d, J = 7.5 Hz, 2H), 7.46-7.36 (m, 5H), 7.31-7.23 (m, 6H), 7.18-7.09 (m, 3H), 6.88 (dd, J = 8.6, 2.5 Hz, 1H), 6.66 (s, 1H), 3.93 & 3,89 (ABq, J = 13.8 Hz, 2H), 3.91 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 158.2, 154.5, 141.9, 136.9, 133.3, 132.5, 131.1, 130.5 (2C), 128.9 (2C), 128.5 (2C), 128.4, 128.3 (2C), 128.2, 127.8 (2C), 126.8, 126.5, 126.2 (2C), 113.8, 111.3, 83.5, 55.6, 45.3. IR: 3059, 2932, 2836, 1580, 1486, 1316, 1267, 1077, 738, 699 cm^{-1}. HRMS: calcd. for $C_{28}H_{23}NO_2S$+H: 438.1527; found: 438.1533.

(*R*)-8-Methoxy-2,4-diphenyl-4-((phenylthio)methyl)-4*H*-benzo[d][1,3]oxazine (3b):



According to the general procedure **A**, the tittle compound **3b** was isolated in 81% yield (54 mg) as a colourless liquid using the mixture of ethyl acetate/hexanes (10:90) as an eluent for column chromatography. Enantiomeric ratio (75.5:24.5) was measured by HPLC (Chiralpak IG, 15% IPA/Hexanes, 0.4 mL/min, 254 nm), t_R = (major, 22.7 min.), t_R = (minor, 24.2 min.). Specific optical rotation: $[\alpha]_D^{25}$ –50.4 (c, 0.4, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.13 (d, J = 7.2 Hz, 2H), 7.46-7.42 (m, 1H), 7.39-7.35 (m, 4H), 7.31-7.25 (m, 5H), 7.16-7.08 (m, 5H), 6.91 (d, J = 8.2 Hz, 1H), 6.75 (d, J = 7.7 Hz, 1H), 3.95 (s, 3H), 3.92 & 3.88 (ABq, J = 14.0 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 155.8, 153.3, 141.9, 136.8, 132.3, 131.4, 130.4 (2C), 129.8, 129.0, 128.9 (2C), 128.4 (2C), 128.3, 128.2 (2C), 128.1 (2C), 126.9, 126.5, 126.2 (2C), 117.0, 111.5, 83.5, 56.3, 45.1. IR: 3057, 2932, 2837, 1622, 1577, 1479, 1312, 1266, 1076, 738, 699 cm^{-1}. HRMS: calcd. for $C_{28}H_{23}NO_2S$+H: 438.1527; found: 438.1537.

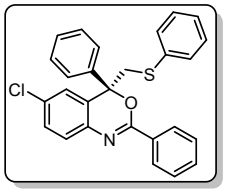
(*R*)-2,4-Diphenyl-4-((phenylthio)methyl)-4*H*-benzo[d][1,3]oxazin-6-yl benzoate (3c):



According to the general procedure **A**, the tittle compound **3c** was isolated in 89% yield (56 mg) as a yellow liquid using the mixture of ethyl acetate/hexanes (10:90) as an eluent for column chromatography. Enantiomeric ratio (30:70) was measured by

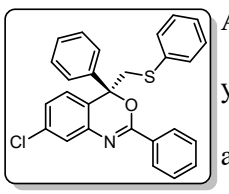
HPLC (Chiralpak IG, 99.9% MeOH/0.1% Diethylamine, 1 mL/min, 254 nm), t_R = (major, 9.5 min.), t_R = (minor, 7.2 min.). Specific optical rotation: $[\alpha]_D^{25}$ –66.7 (c, 0.4, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.18 (d, J = 7.6 Hz, 2H), 8.12 (d, J = 7.3 Hz, 2H), 7.63 (m, 1H), 7.63 (t, J = 7.4 Hz, 1H), 7.52-7.46 (m, 3H), 7.44-7.38 (m, 5H), 7.33-7.29 (m, 5H), 7.23-7.21 (m, 1H), 7.16 (t, J = 7.3 Hz, 2H), 7.10 (d, J = 7.1 Hz 1H), 7.01 (d, J = 2.3 Hz, 1H), 3.94 & 3.91 (ABq, J = 14.2 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 165.1, 156.1, 149.1, 141.5, 137.5, 136.6, 133.8, 132.2, 131.6, 130.7 (2C), 130.3 (2C), 129.5, 129.0 (2C), 128.8 (2C), 128.7 (2C), 128.6, 128.5, 128.3 (2C), 128.1 (2C), 128.0, 126.6, 126.2 (2C), 122.6, 118.4, 83.6, 45.3. IR: 3060, 2923, 2835, 1736, 1623, 1579, 1483, 1313, 1255, 1066, 737, 701 cm^{-1}. HRMS: calcd. for $C_{34}H_{25}NO_3S$+H: 528.1633; found: 528.1652.

(*R*)-6-Chloro-2,4-diphenyl-4-((phenylthio)methyl)-4*H*-benzo[d][1,3]oxazine (3d):



According to the general procedure **A**, the tittle compound **3d** was isolated in 74% yield (49 mg) as a colourless-foam using the mixture of ethyl acetate/hexanes (10:90) as an eluent for column chromatography. Enantiomeric ratio (80.5:19.5) was measured by HPLC (Chiralpak IG, 99.9% MeOH/0.1% Diethylamine, 1 mL/min, 254 nm), t_R = (major, 5.5 min.), t_R = (minor, 6.6 min.). Specific optical rotation: $[\alpha]_D^{25}$ –87.0 (c, 0.3, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.11 (d, J = 7.2 Hz, 2H), 7.50-7.47 (m, 1H), 7.42-7.38 (m, 4H), 7.34-7.29 (m, 7H), 7.20-7.17 (m, 2H), 7.15-7.12 (m, 1H), 7.07 (s, 1H), 3.91 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 156.5, 141.4, 138.3, 136.4, 132.0, 131.7, 131.6, 130.8 (2C), 129.5, 129.0 (2C), 128.7 (3C), 128.5, 128.4 (2C), 128.2 (2C), 126.9, 126.8, 126.1(2C), 125.1, 83.6, 45.4. IR: 3061, 2927, 2850, 1621, 1576, 1474, 1316, 1257, 1086, 739, 695 cm^{-1}. HRMS: calcd. for $C_{27}H_{20}NOSCl$+H: 442.1032; found: 442.1028.

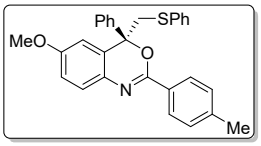
(*R*)-7-Chloro-2,4-diphenyl-4-((phenylthio)methyl)-4*H*-benzo[d][1,3]oxazine (3e):



According to the general procedure **A**, the tittle compound **3e** was isolated in 71% yield (47 mg) as a yellow liquid using the mixture of ethyl acetate/hexanes (10:90) as an eluent for column chromatography. Enantiomeric ratio (78:22) was measured by

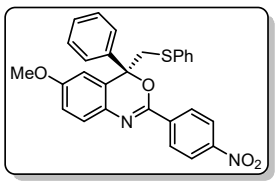
HPLC (Chiralpak IG, 99.9% MeOH/0.1% Diethylamine, 1 mL/min, 254 nm), t_R = (major, 5.6 min.), t_R = (minor, 6.7 min.). Specific optical rotation: $[\alpha]_D^{25}$ –66.2 (c, 0.4, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ8.09 (d, *J* = 7.8 Hz, 2H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.42-7.35 (m, 5H), 7.31-7.28 (m, 5H), 7.19-7.14 (m, 4H), 7.03 (d, *J* = 8.2 Hz, 1H), 3.90 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 157.2, 141.7, 141.1, 136.5, 134.9, 131.9, 131.8, 130.6 (2C), 129.0 (2C), 128.6 (3C), 128.4 (2C), 128.2 (2C), 126.7, 126.3, 126.1, 126.0 (2C), 125.6, 125.3, 83.8, 45.4. IR: 3060, 2925, 2853, 1624, 1574, 1471, 1319, 1257, 1084, 739, 694 cm^{-1}. HRMS: calcd. for $C_{27}H_{20}NOSCl$+H: 442.1032; found: 442.1038.

(*R*)-6-Methoxy-4-phenyl-4-((phenylthio)methyl)-2-(p-tolyl)-4*H*-benzo[d][1,3]oxazine (3f):



According to the general procedure **A**, the tittle compound **3f** was isolated in 86% yield (53 mg) as a colourless liquid using the mixture of ethyl acetate/hexanes (10:90) as an eluent for column chromatography. Enantiomeric ratio (80:20) was measured by HPLC (Chiralpak IG, 15% IPA/Hexanes, 1 mL/min, 254 nm), t_R = (major, 9.5 min.), t_R = (minor, 18.8 min.). Specific optical rotation: $[\alpha]_D^{25}$ –65.8 (c, 0.4, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.98 (d, *J* = 7.9 Hz, 2H), 7.39 (d, *J* = 6.9 Hz, 2H), 7.30-7.24 (m, 6H), 7.20-2.11(m, 6H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.67 (s, 1H), 3.92 & 3.87 (ABq, *J* = 13.8 Hz, 2H), 3.75 (3H, s), 2.38 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 158.0, 154.8, 141.8, 141.5, 136.9, 133.4, 130.4 (2C), 129.7, 129.0 (2C), 128.9 (2C), 128.5 (2C), 128.3, 128.2, 127.8 (2C), 126.6, 126.4, 126.2 (2C), 113.7, 111.2, 83.4, 55.6, 45.1, 21.7. IR: 3059, 2938, 2833, 1623, 1577, 1486, 1319, 1264, 1078, 738, 701 cm^{-1}. HRMS: calcd. for $C_{29}H_{25}NO_2S$+H: 452.1684; found: 452.1690.

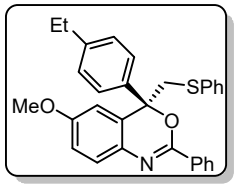
(*R*)-6-Methoxy-2-(4-nitrophenyl)-4-phenyl-4-((phenylthio)methyl)-4*H*-benzo[d][1,3]oxazine (3g):



According to the general procedure **A**, the tittle compound **3g** was isolated in 61% yield (39 mg) as a yellow solid using the mixture of ethyl acetate/hexanes (15:85) as an eluent for column chromatography. Enantiomeric ratio (84:16) was measured by HPLC (Chiralpak IG, 99.9% MeOH/0.1% Diethylamine, 1 mL/min, 254 nm), t_R = (major, 20.4 min.), t_R = (minor, 22.2 min.). Specific optical rotation: $[\alpha]_D^{25}$ –14.5 (c, 0.4, $CHCl_3$). ^{1}H NMR (400

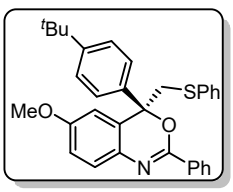
MHz, $CDCl_3$, 24 °C): δ 8.12-8.05 (m, 4H), 7.30-7.20 (m, 8H), 7.09-7.00 (m, 3H), 6.82 (dd, J = 8.6, 2.3 Hz, 1H), 6.56 (d, J = 2.2 Hz, 1H), 3.84 (s, 2H), 3.69 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 159.0, 152.3, 149.2, 141.6, 138.4, 136.5, 132.6, 130.5 (2C), 129.0 (2C), 128.6 (3C), 128.5 (2C), 128.2, 127.2, 126.7, 126.1 (2C), 123.4 (2C), 113.9, 111.5, 84.4, 55.6, 45.1. IR: 3060, 2932, 2838, 1627, 1590, 1486, 1344, 1269, 1078, 736, 698 cm^{-1}. HRMS: calcd. for $C_{28}H_{22}N_2O_4S$+H: 483.1378; found: 483.1366. HRMS: calcd. for $C_{29}H_{25}NO_3S$+H: 468.1633; found: 468.1639.

(*R*)-4-(4-Ethylphenyl)-6-methoxy-2-phenyl-4-((phenylthio)methyl)-4*H*-benzo[d][1,3]oxazine (3h):



According to the general procedure **A**, the tittle compound **3h** was isolated in 92% yield (63 mg) as a colourless liquid using the mixture of ethyl acetate/hexanes (10:90) as an eluent for column chromatography. Enantiomeric ratio (85:15) was measured by HPLC (Chiralpak IG, 99.9% MeOH/0.1% Diethylamine, 1 mL/min, 254 nm), t_R = (major, 7.2 min.), t_R = (minor, 5.9 min.). Specific optical rotation: $[\alpha]_D^{25}$ –77.8 (c, 0.4, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.10 (d, J = 7.7 Hz, 1H), 7.47-7.44 (m, 1H), 7.41-7.37 (m, 2H), 7.33-7.30 (m, 5H), 7.19-7.10 (m, 5H), 6.89 (dd, J = 8.5, 2.5 Hz, 1H), 6.68 (d, J = 2.5 Hz, 1H), 3.92 (s, 2H), 3.76 (s, 3H), 2.60 (q, J = 7.6 Hz, 2H), 1.19 (t, J = 7.6 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 158.1, 154.6, 144.4, 139.1, 136.9, 133.2, 132.5, 131.1, 130.4 (2C), 128.9 (2C), 128.4, 128.2 (2C), 128.0 (2C), 127.8 (2C), 126.7, 126.4, 126.2 (2C), 113.6, 111.2, 83.5, 55.6, 45.2, 28.5, 15.4. IR: 3055, 2932, 2839, 1622, 1578, 1488, 1318, 1266, 1072, 737, 699 cm^{-1}. HRMS: calcd. for $C_{30}H_{27}NO_2S$+H: 466.1841; found: 466.1837.

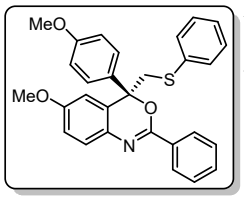
(*R*)-4-(4-(Tert-butyl)phenyl)-6-methoxy-2-phenyl-4-((phenylthio)methyl)-4*H*-benzo[d][1,3]oxazine (3i):



According to the general procedure **A**, the tittle compound **3i** was isolated in 87% yield (56 mg) colourless liquid using the mixture of ethyl acetate/hexanes (10:90) as an eluent for column chromatography. Enantiomeric ratio (87:13) was measured by

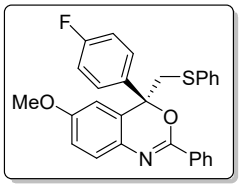
HPLC (Chiralpak IG, 99.9% MeOH/0.1% Diethylamine, 1 mL/min, 254 nm), t_R = (major, 6.6 min.), t_R = (minor, 5.5 min.). Specific optical rotation: $[\alpha]_D^{25}$ – 70.6 (c, 0.3, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.11 (d, J = 7.2 Hz, 2H), 7.48-7.44 (m, 1H), 7.40 (t, J = 7.6 Hz, 2H), 7.35-7.31 (m, 7H), 7.19-7.10 (m, 3H), 6.89 (d, J = 8.5 Hz, 1H), 6.70 (s, 1H), 3.93 (s, 2H), 3.77(s, 3H), 1.26 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 158.1, 154.6, 151.2, 138.8, 137.0, 133.3, 132.5, 131.1, 130.4 (2C), 128.9 (2C), 128.3, 128.2 (2C), 127.8 (2C), 126.7, 126.4, 125.8 (2C), 125.4 (2C), 113.5, 111.3, 83.5, 55.6, 45.3, 34.6, 31.3. IR: 3060, 2858, 2856, 1625, 1577, 1488, 1319, 1271, 1073, 740, 695 cm^{-1}. HRMS: calcd. for $C_{32}H_{31}NO_2S$+H: 494.2154; found: 494.2161.

(*R*)-6-Methoxy-4-(4-methoxyphenyl)-2-phenyl-4-((phenylthio)methyl)-4*H*-benzo[d][1,3]oxazine (3j):



According to the general procedure **A**, the tittle compound **3j** was isolated in 72% yield (47 mg) as a yellow liquid using the mixture of ethyl acetate/hexanes (15:85) as an eluent for column chromatography. Enantiomeric ratio (79:21) was measured by HPLC (Chiralpak IG, 15% IPA/Hexanes, 1 mL/min, 254 nm), t_R = (major, 11.6 min.), t_R = (minor, 17.4 min.). Specific optical rotation: $[\alpha]_D^{25}$ –102.5 (c, 0.3, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.09 (d, J = 7.6 Hz, 2H), 7.44 (t, J = 6.9 Hz, 1H), 7.40-7.37 (m, 2H), 7.34-7.30 (m, 5H), 7.17 (t, J = 7.4 Hz, 2H), 7.13-7.10 (m, 1H), 3.90 (s, 2H), 3.76 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 159.5, 158.2, 154.6, 136.9, 134.0, 133.3, 132.6, 132.1, 131.1, 130.8, 130.4 (2C), 128.9 (2C), 128.5, 128.2 (2C), 127.8 (2C), 126.7, 126.4, 113.8 (2C), 113.7, 111.2, 83.3, 55.6, 55.3, 45.2. IR: 3054, 2962, 2938, 2838, 1626, 1592, 1492, 1264, 1031, 808, 739 cm^{-1}. HRMS: calcd. for $C_{29}H_{25}NO_3S$+H:468.1627; found: 468.1636.

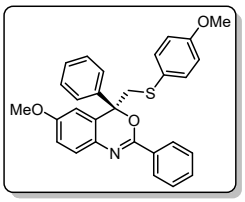
(*R*)-4-(4-Fluorophenyl)-6-methoxy-2-phenyl-4-((phenylthio)methyl)-4*H*-benzo[d][1,3]oxazine (3k):



According to the general procedure **A**, the tittle compound **3k** was isolated in 78% yield (51 mg) colourless liquid using the mixture of ethyl acetate/hexanes (10:90) as an eluent for column chromatography. Enantiomeric ratio (28:72) was measured by HPLC (Chiralpak IG, 0.8% IPA/Hexanes, 1 mL/min, 254 nm), t_R = (major, 40.3 min.), t_R =

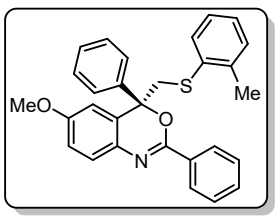
(minor, 33.5 min.). Specific optical rotation: $[\alpha]_D^{25}$ –55.9 (c, 0.5, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.08 (d, J = 7.6 Hz, 2H), 7.48-7.44 (m, 1H), 7.41-7.37 (m, 4H), 7.33-7.29 (m, 3H), 7.20-7.11 (m, 3H), 6.97 (t, J = 8.4 Hz, 2H), 6.90 (d, J = 8.6 Hz, 1H), 6.66 (s, 1H), 3.93 & 3.87 (ABq, J = 13.8 Hz, 2H), 3.77 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 162.2 (d, J = 248.5 Hz), 158.2, 154.4, 137.6 (d, J = 3.2 Hz), 136.6, 133.1, 132.3, 131.3, 130.5 (2C), 129.0 (2C), 128.6, 128.3 (d, 2C, J = 3.8 Hz), 128.2, 128.1, 127.8 (2C), 126.8, 126.6, 115.4 (d, J = 21.7 Hz), 115.1, 113.8, 111.1, 83.0, 55.6, 45.2. ^{19}F NMR (470 MHz, $CDCl_3$, 24˚C): δ –116.80. IR: 3060, 2935, 2843, 1626, 1585, 1498, 1321, 1265, 1075, 736, 706 cm^{-1}. HRMS: calcd. for $C_{28}H_{22}FNO_2S$+H:456.1433; found: 456.1438.

(*R*)-6-Methoxy-4-(((4-methoxyphenyl)thio)methyl)-2,4-diphenyl-4*H*-benzo[d][1,3]oxazine (3l):



According to the general procedure **A**, the tittle compound **3l** was isolated in 67% yield (48 mg) as a pale-yellow liquid using the mixture of ethyl acetate/hexanes (10:90) as an eluent for column chromatography. Enantiomeric ratio (88.5:11.5) was measured by HPLC (Chiralpak IG, 15% IPA/Hexanes, 1 mL/min, 254 nm), t_R = (major, 9.9 min.), t_R = (minor, 15.0 min.). Specific optical rotation: $[\alpha]_D^{25}$ –67.3 (c, 0.5, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$, 24 °C): 8.09-8.06 (m, 2H), 7.47-7.43 (m, 1H), 7.41-7.37 (m, 4H), 7.31-7.23 (m, 6H), 6.88 (dd, J = 8.6, 2.6 Hz, 1H), 6.68 (dd, J = 8.7, 1.9 Hz, 1H), 6.63 (d, J = 2.6 Hz, 1H), 3.84 & 3.78 (ABq, J = 14.1 Hz, 2H), 3.76 (s, 3H), 3.71 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 159.1, 158.2, 154.5, 142.1, 134.1 (2C), 133.3, 132.6, 131.1, 128.5 (2C), 128.4, 128.3, 128.2 (2C), 127.8 (2C), 127.2, 126.7, 126.2 (2C), 114.5 (2C), 113.7, 111.3, 83.9, 55.6, 55.4, 47.3. IR: 3052, 2954, 2931, 2826, 1624, 1578, 1477, 1254, 1031, 802, 738 cm^{-1}. HRMS: calcd. for $C_{29}H_{25}NO_3S$+H:468.1627; found: 468.1634.

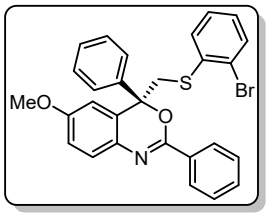
(*R*)-6-Methoxy-2,4-diphenyl-4-((o-tolylthio)methyl)-4*H*-benzo[d][1,3]oxazine (3m):



According to the general procedure **A**, the tittle compound **3m** was isolated in 71% yield (49 mg) as a pale-yellow liquid using the mixture of ethyl acetate/hexanes (10:90) as an eluent for column chromatography. Enantiomeric

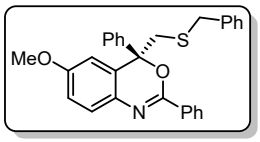
ratio (82.5:17.5) was measured by HPLC (Chiralpak IG, 100% MeOH, 0.5 mL/min, 254 nm), t_R = (major, 11.2 min.), t_R = (minor, 12.8 min.). Specific optical rotation: $[\alpha]_D^{25}$ –41.2 (c, 0.6, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.05 (d, J = 7.5 Hz, 2H), 7.39 (t, J = 7.2 Hz, 1H), 7.34-7.31 (m, 5H), 7.24-7.16 (m, 4H), 6.99-6.96 (m, 3H), 6.81 (dd, J = 5.9 Hz, 2.6 Hz, 1H), 6.58 (d, J = 2.7 Hz, 1H), 3.79 & 3.76 (ABq, J = 13.9 Hz, 2H), 3.67 (s, 3H), 2.18 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 158.3, 155.1, 141.8, 139.2, 136.0, 134.6, 132.2, 131.4, 130.9, 130.2, 128.6 (2C), 128.5, 128.3 (2C), 128.0, 127.7, 127.0, 126.8, 126.5, 126.3, 126.2 (2C), 113.9, 111.3, 84.3, 55.6, 45.1, 20.7. IR: 3004, 2927, 2891, 1628, 1454, 1269, 1227, 1169, 1086, 1034, 751, 720, 712 cm^{-1}. HRMS: calcd. for $C_{29}H_{25}NO_2S$+H: 452.1678; found: 452.1686.

(*R*)-4-(((2-Bromophenyl)thio)methyl)-6-methoxy-2,4-diphenyl-4*H*-benzo[d][1,3]oxazine (3n):



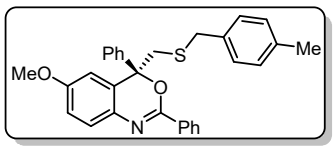
According to the general procedure **A**, the tittle compound **3n** was isolated in 58% yield (39 mg) as a pale-yellow liquid using the mixture of ethyl acetate/hexanes (10:90) as an eluent for column chromatography. Enantiomeric ratio (70:30) was measured by HPLC (Chiralpak IG, 100% MeOH, 1.0 mL/min, 254 nm), t_R = (major, 5.5 min.), t_R = (minor, 6.6 min.). Specific optical rotation: $[\alpha]_D^{25}$ –61.2 (c, 0.4, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.06 (d, J = 7.5 Hz, 2H), 7.41-7.37 (m, 2H), 7.34-7.30 (m, 5H), 7.24-7.17 (m, 4H), 7.01 (t, J = 7.5 Hz, 1H), 6.89 (t, J = 7.5 Hz, 1H), 6.81 (dd, J = 6.3 Hz, 2.0 Hz, 1H), 6.60 (d, J = 2.3 Hz, 1H), 3.85 & 3.80 (ABq, J = 13.8 Hz, 2H), 3.69 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 158.3, 141.6, 137.6, 137.3, 133.7, 133.3, 133.2, 133.1, 132.0, 131.8, 131.5, 128.7 (2C), 128.6, 128.3 (2C), 128.0, 127.9, 127.8, 126.8, 126.6, 126.2 (2C), 113.9, 111.3, 83.8, 55.6, 44.4. IR: 3006, 2982, 1711, 1644, 1538, 1527, 1399, 1262, 1069, 1016, 822, 752 cm^{-1}. HRMS: calcd. for $C_{28}H_{22}BrNO_2S$+H: 516.0627; found: 516.0638.

(*R*)-4-((Benzylthio)methyl)-6-methoxy-2,4-diphenyl-4*H*-benzo[d][1,3]oxazine (3o):



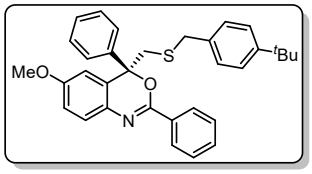
According to the general procedure **B**, the tittle compound **3o** was isolated in 74% yield (51 mg) as a colourless liquid using the mixture of ethyl acetate/hexanes (10:90) as an eluent for column chromatography. Enantiomeric ratio (92:8) was measured by HPLC (Chiralpak IG, 99.9% MeOH/0.1% Diethylamine, 0.6 mL/min, 254 nm), t_R = (major, 9.4 min.), t_R = (minor, 10.6 min.). Specific optical rotation: $[\alpha]_D^{25}$ –50.5 (c, 0.4, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.22 (d, J = 6.9 Hz, 2H), 7.46-7.44 (m, 3H), 7.35 (d, J = 6.7 Hz, 2H), 7.31-7.21 (m, 9H), 6.87 (d, J = 8.5 Hz, 1H), 6.60 (s, 1H), 3.76 (s, 3H), 3.62 & 3.57 (ABq, J = 13.5 Hz, 2H), 3.37 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 158.2, 154.6, 142.1, 138.0, 133.2, 132.7, 131.3, 129.6, 129.1 (2C), 128.8, 128.6 (2C), 128.4 (2C), 128.3, 127.9 (2C), 127.2, 126.6, 126.3 (2C), 115.4, 113.6, 111.4, 83.9, 55.6, 41.1, 37.9. IR: 3060, 2931, 2829, 1735, 1625, 1574, 1490, 1322, 1176, 1071, 781, 696 cm^{-1}. HRMS: calcd. for $C_{29}H_{25}NO_2S$+H: 452.1678; found: 452.1684.

(*R*)-6-Methoxy-4-(((4-methylbenzyl)thio)methyl)-2,4-diphenyl-4*H*-benzo[d][1,3]oxazine (3p):



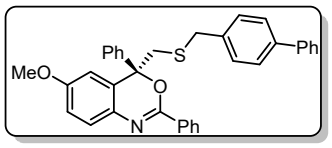
According to the general procedure **B**, the tittle compound **3p** was isolated in 72% yield (61 mg) as a colourless liquid using the mixture of ethyl acetate/hexanes (10:90) as an eluent for column chromatography. Enantiomeric ratio (87:13) was measured by HPLC (Chiralpak IG, 99.9% MeOH/0.1% Diethylamine, 0.6 mL/min, 254 nm), t_R = (major, 11.7 min.), t_R = (minor, 13.5 min.). Specific optical rotation: $[\alpha]_D^{25}$ –103.7 (c, 0.2, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.22 (d, J = 6.7 Hz, 2H), 7.48-7.44 (m, 3H), 7.35 (d, J = 6.8 Hz, 2H), 7.30-7.23 (m, 4H), 7.11-7.05 (m, 4H), 6.87 (d, J = 8.5 Hz, 1H), 6.59 (s, 1H), 3.76 (s, 3H), 3.58 & 3.53 (ABq, J = 13.3 Hz, 2H), 3.36 (s, 2H), 2.30 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 158.2, 154.6, 142.1, 136.8, 134.9, 133.3, 132.7, 131.2, 129.2 (2C), 129.0 (2C), 128.8, 128.4 (4C), 128.2, 127.9 (2C), 126.6, 126.3 (2C), 113.5, 111.4, 83.9, 55.6, 41.0, 37.6, 21.2. IR: 3043, 3006, 2979, 2869, 1712, 1512, 1471, 1359, 1275, 1115, 751, 683 cm^{-1}. HRMS: calcd. for $C_{30}H_{27}NO_2S$+H: 466.1835; found: 466.1841.

(*R*)-4-(((4-(Tert-butyl)benzyl)thio)methyl)-6-methoxy-2,4-diphenyl-4*H*-benzo[d][1,3]oxazine (3q):



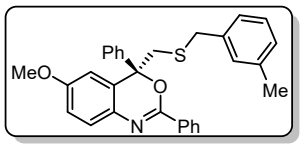
According to the general procedure **B**, the tittle compound **3q** was isolated in 71% yield (66 mg) as a colourless liquid using the mixture of ethyl acetate/hexanes (10:90) as an eluent for column chromatography. Enantiomeric ratio (86:14) was measured by HPLC (Chiralpak IG, 100% MeOH, 0.6 mL/min, 254 nm), t_R = (major, 10.5 min.), t_R = (minor, 16.2 min.). Specific optical rotation: $[\alpha]_D^{25}$ –64.6 (c, 0.3, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.23 (d, J = 6.7 Hz, 2H), 7.48-7.43 (m, 3H), 7.36 (d, J = 6.8 Hz, 2H), 7.31-7.24 (m, 6H), 7.14 (d, J = 7.8 Hz, 2H), 6.87 (d, J = 8.4 Hz, 1H), 6.61 (s, 1H), 3.76 (s, 3H), 3.60 & 3.55 (ABq, J = 13.2 Hz, 2H), 3.39 (s, 2H), 1.29 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 158.2, 154.6, 150.1, 142.1, 134.9, 133.3, 132.7, 131.2, 129.1, 128.8, 128.7 (2C), 128.4 (3C), 128.3, 127.9 (2C), 126.6, 126.3 (2C), 125.5 (2C), 113.5, 111.4, 83.9, 55.6, 41.2, 37.6, 34.6, 31.4. IR: 3066, 2959, 1739, 1626, 1491, 1321, 1223, 1029, 780, 695 cm^{-1}. HRMS: calcd. for $C_{33}H_{33}NO_2S$+H: 508.2304; found: 508.2320.

(*R*)-4-((([1,1'-Biphenyl]-4-ylmethyl)thio)methyl)-6-methoxy-2,4-diphenyl-4*H*-benzo[d][1,3]oxazine (3r):



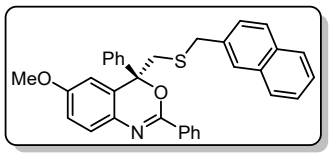
According to the general procedure **B**, the tittle compound **3r** was isolated in 72% yield (69mg) as a colourless liquid using the mixture of ethyl acetate/hexanes (10:90) as an eluent for column chromatography. Enantiomeric ratio (12.5:87.5) was measured by HPLC (Chiralpak IG, 100% MeOH, 0.6 mL/min, 254 nm), t_R = (major, 15.4 min.), t_R = (minor, 19.1 min.). Specific optical rotation: $[\alpha]_D^{25}$ –70.6 (c, 0.3, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.23 (d, J = 7.4 Hz, 2H), 7.60-7.52 (m, 3H), 7.50-7.40 (m, 7H), 7.37-7.23 (m, 8H), 6.87 (d, J = 7.8 Hz, 1H), 6.61 (s, 1H), 3.75 (s, 3H), 3.66 & 3.61 (ABq, J = 13.4 Hz, 2H), 3.41 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 158.2, 154.5, 142.1, 140.8, 140.0, 137.1, 133.3, 132.7, 131.3, 129.9, 129.5 (2C), 128.8 (2C), 128.4 (3C), 128.3, 127.9 (2C), 127.4, 127.3 (2C), 127.1 (2C), 126.6, 126.3 (2C), 126.1, 113.5, 111.5, 83.9, 55.6, 41.2, 37.6. IR: 3056, 2929, 2834, 1735, 1626, 1490, 1320, 1225, 780, 696 cm^{-1}. HRMS: calcd. for $C_{35}H_{29}NO_2S$+H: 528.1991; found: 528.2012.

(*R*)-6-Methoxy-4-(((3-methylbenzyl)thio)methyl)-2,4-diphenyl-4*H*-benzo[d][1,3]oxazine (3s):



According to the general procedure **B**, the tittle compound **3s** was isolated in 74% yield (62 mg) as a colourless liquid using the mixture of ethyl acetate/hexanes (10:90) as an eluent for column chromatography. Enantiomeric ratio (92:8) was measured by HPLC (Chiralpak IG, 99.9% MeOH/0.1% Diethylamine, 0.6 mL/min, 254 nm), t_R = (major, 11.1 min.), t_R = (minor, 14.4 min.). Specific optical rotation: $[\alpha]_D^{25}$ –64.8 (c, 0.3, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.22 (d, J = 6.3 Hz, 2H), 7.46-7.42 (m, 3H), 7.35 (d, J = 6.5 Hz, 2H), 7.31-2.24 (m, 4H), 7.14 (t, J = 7.2 Hz, 1H), 7.04-7.01 (m, 3H), 6.87 (d, J = 8.5 Hz, 1H), 6.60 (s, 1H), 3.76 (s, 3H), 3.59 & 3.53 (ABq, J = 13.3 Hz, 2H), 3.37 (s, 2H), 2.29 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 158.2, 154.6, 142.1, 138.2, 137.9, 133.3, 132.7, 131.5, 131.2, 129.8, 128.8, 128.4 (4C), 128.3, 127.9 (2C), 127.8, 126.6, 126.3 (2C), 126.1, 113.5, 111.5, 83.9, 55.6, 41.1, 37.9, 21.4. IR: 3007, 2920, 2885, 1624, 1450, 1262, 1223, 1169, 1085, 1032, 751, 720, 711 cm^{-1}. HRMS: calcd. for $C_{30}H_{27}NO_2S$+H: 466.1835; found: 466.1842.

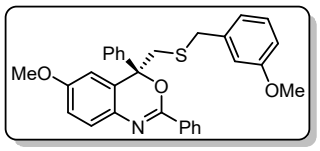
(*R*)-6-Methoxy-4-(((naphthalen-2-ylmethyl)thio)methyl)-2,4-diphenyl-4*H*-benzo[d][1,3]oxazine (3t):



According to the general procedure **B**, the tittle compound **3t** was isolated in 68% yield (62 mg) as a pale-yellow liquid using the mixture of ethyl acetate/hexanes (10:90) as an eluent for column chromatography. Enantiomeric ratio (93:7) was measured by HPLC (Chiralpak IG, 99.9% MeOH/0.1% Diethylamine, 1 mL/min, 254 nm), t_R = (major, 14.3 min.), t_R = (minor, 18.7 min.). Specific optical rotation: $[\alpha]_D^{25}$ –61.4 (c, 0.3, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.22 (d, J = 7.2 Hz, 2H), 7.80-7.73 (m, 3H), 7.60 (s, 1H), 7.48-7.38 (m, 6H), 7.34-7.29 (m, 3H), 7.25-7.23 (m, 3H), 6.87 (d, J = 8.6 Hz, 1H), 6.57 (s, 1H), 3.78 & 3.71 (ABq, J = 13.4 Hz, 2H), 3.73 (s, 3H), 3.37 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 158.2, 154.6, 142.1, 135.4, 133.3, 132.7, 132.6, 131.2, 128.7, 128.6, 128.5, 128.4 (4C), 128.3, 127.9 (2C), 127.7 (2C), 127.6, 127.2, 126.6, 126.3(3C), 125.9, 113.6, 111.4, 83.9, 55.6, 41.0, 38.1. IR: 3056,

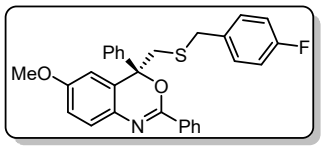
2925, 2837, 1735, 1626, 1491, 1321, 1261, 1149, 1070, 820, 741, 696 cm^{-1}. HRMS: calcd. for $C_{33}H_{27}NO_2S$+H: 502.1835; found: 502.1855.

(*R*)-6-Methoxy-4-(((3-methoxybenzyl)thio)methyl)-2,4-diphenyl-4*H*-benzo[d][1,3]oxazine (3u):



According to the general procedure **B**, the tittle compound **3u** was isolated in 64% yield (56 mg) as a pale-yellow liquid using the mixture of ethyl acetate/hexanes (15:85) as an eluent for column chromatography. Enantiomeric ratio (94.5:5.5) was measured by HPLC (Chiralpak IG, 99.9% MeOH/0.1% Diethylamine, 0.6 mL/min, 254 nm), t_R = (major, 11.7 min.), t_R = (minor, 14.3 min.). Specific optical rotation: $[\alpha]_D^{25}$ – 111.3 (c, 0.2, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.22 (d, J = 7.0 Hz, 2H), 7.49-7.43 (m, 3H), 7.35 (d, J = 7.1 Hz, 2H), 7.31-7.25 (m, 4H), 7.17 (d, J = 7.7 Hz, 1H), 6.88 (d, J = 8.6 Hz, 1H), 6.81-6.75 (m, 3H), 6.60 (s, 1H), 3.78 (s, 3H), 3.75 (s, 3H), 3.59 & 3.54 (ABq, J = 13.6 Hz, 2H), 3.37 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 159.8, 158.2, 154.6, 142.1, 139.6, 133.3, 132.7, 131.3, 129.5, 128.7, 128.4 (4C), 128.3, 127.9 (2C), 126.6, 126.3 (2C), 121.5, 114.3, 113.5, 113.1, 111.5, 83.9, 56.6, 56.3, 41.0, 37.9. IR: 3006, 2925, 1597, 1466, 1263, 1151, 1046, 750, 684 cm^{-1}. HRMS: calcd. for $C_{30}H_{27}NO_3S$+H: 482.1784; found: 482.1788.

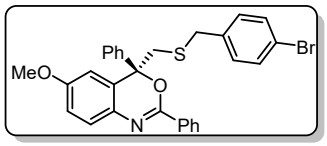
(*R*)-4-(((4-fluorobenzyl)thio)methyl)-6-methoxy-2,4-diphenyl-4*H*-benzo[d][1,3]oxazine (3v):



According to the general procedure **B**, the tittle compound **3v** was isolated in 54% yield (46 mg) as a pale-yellow liquid using the mixture of ethyl acetate/hexanes (10:90) as an eluent for column chromatography. Enantiomeric ratio (89.5:10.5) was measured by HPLC (Chiralpak IG, 99.9% MeOH/0.1% Diethylamine, 0.6 mL/min, 254 nm), t_R = (major, 10.1 min.), t_R = (minor, 11.2 min.). Specific optical rotation: $[\alpha]_D^{25}$ – 50.2 (c, 0.4, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.13 (d, J = 7.3Hz, 2H), 7.41-7.35 (m, 3H), 7.28 (d, J = 7.1Hz, 2H), 7.23-7.17 (m, 4H), 7.10-7.07 (m, 2H), 6.87-6.79 (m, 3H), 6.51 (s, 1H), 3.69 (s, 3H), 3.51 & 3.46 (ABq, J = 13.6 Hz, 2H), 3.28 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 161.9

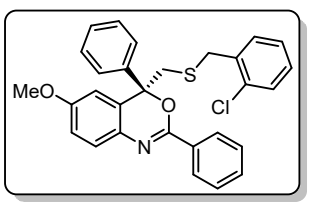
(d, *J* = 246.4 Hz), 158.2, 154.5, 142.07, 133.8, 133.7, 133.2, 132.6, 131.3, 130.6 (d, *J* = 8 Hz), 128.7, 128.5 (2C), 128.4 (2C), 128.3, 127.9 (2C), 126.7, 126.3 (2C), 115.4 (d, *J* = 21.4 Hz), 113.5, 111.5, 83.8, 55.6, 41.1, 37.1. ^{19}F NMR (470 MHz, $CDCl_3$, 24˚C): δ –118.62. IR: 3114, 3007, 2988, 1713, 1597, 1508, 1469, 1262, 1223, 1157, 1016, 831, 750, 685 cm^{-1}. HRMS: calcd. for $C_{29}H_{24}FNO_2S$+H: 470.1584; found: 470.1591.

(*R*)-4-(((4-Bromobenzyl)thio)methyl)-6-methoxy-2,4-diphenyl-4*H*-benzo[d][1,3]oxazine (3w):



According to the general procedure **B**, the tittle compound **3w** was isolated in 61% yield (59 mg) as a pale-yellow liquid using the mixture of ethyl acetate/hexanes (10:90) as an eluent for column chromatography. Enantiomeric ratio (90:10) was measured by HPLC (Chiralpak IG, 99.9% MeOH/0.1% Diethylamine, 0.6 mL/min, 254 nm), t_R = (major, 12.9 min.), t_R = (minor, 18.0 min.). Specific optical rotation: $[\alpha]_D^{25}$ –67.9 (c, 0.3, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.19 (d, *J* = 7.0 Hz, 2H), 7.51-7.43 (m, 3H), 7.35 (m, 4H), 7.31-7.25 (m, 4H), 7.07 (d, *J* = 7.8 Hz, 2H), 6.88 (d, *J* = 8.5 Hz, 1H), 6.58 (s, 1H), 3.78 (s, 3H), 3.56 & 3.51 (ABq, *J* = 3.7 Hz, 2H), 3.34 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 158.2,154.2, 142.0, 137.1, 133.2, 132.6, 131.7 (2C), 131.3, 130.7 (2C), 128.6, 128.5 (2C), 128.4 (2C), 128.3, 127.8 (2C), 126.7, 126.2 (2C), 121.0, 113.5, 111.5, 83.8, 55.6, 41.1, 37.2. IR: 3006, 2986, 1713, 1648, 1541, 1529, 1399, 1262, 1069, 1012, 817, 750 cm^{-1}. HRMS: calcd. for $C_{29}H_{24}BrNO_2S$+H: 530.0783; found: 530.0788.

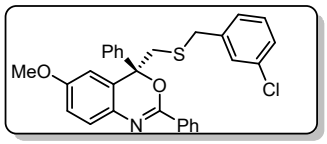
(*R*)-4-(((2-chlorobenzyl)thio)methyl)-6-methoxy-2,4-diphenyl-4*H*-benzo[d][1,3]oxazine (3x):



According to the general procedure **B**, the tittle compound **3x** was isolated in 61% yield (54 mg) as a pale-yellow liquid using the mixture of ethyl acetate/hexanes (10:90) as an eluent for column chromatography. Enantiomeric ratio (92:8) was measured by HPLC (Chiralpak IG, 100% MeOH, 1.0 mL/min, 254 nm), t_R = (major, 7.7 min.), t_R = (minor, 10.5 min.). Specific optical rotation: $[\alpha]_D^{25}$ –30.3 (c, 0.6, $CHCl_3$). ^{1}H NMR (400 MHz,

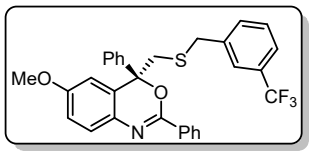
$CDCl_3$, 24 °C): δ 8.21 (d, J = 7.2 Hz, 2H), 7.48-7.42 (m, 3H), 7.37 (d, J = 7.1 Hz, 2H), 7.31-7.25 (m, 6H), 7.15-7.14 (m, 2H), 6.86 (d, J = 8.5 Hz, 1H), 6.63 (s, 1H), 3.81-3.73 (s, 5H), 3.47 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 158.2, 154.5, 142.0, 136.0, 134.1, 133.3, 132.6, 131.2, 130.8, 129.8, 128.7, 128.6 (2C), 128.5 (2C), 128.4, 128.3, 127.9 (2C), 126.9, 126.7, 126.3 (2C), 113.6, 111.3, 83.9, 55.6, 41.8, 35.6. IR: 3064, 3008, 2832, 1574, 1470, 1428, 1276, 1071, 874, 752, 688 cm^{-1}. HRMS: calcd. for $C_{29}H_{24}ClNO_2S$+H: 486.1289; found: 486.1294.

(*R*)-4-(((3-Chlorobenzyl)thio)methyl)-6-methoxy-2,4-diphenyl-4*H*-benzo[d][1,3]oxazine (3y):



According to the general procedure **B**, the tittle compound **3y** was isolated in 68% yield (60 mg) as a colourless liquid using the mixture of ethyl acetate/hexanes (10:90) as an eluent for column chromatography. Enantiomeric ratio (90.5:9.5) was measured by HPLC (Chiralpak IG, 99.9% MeOH/0.1% Diethylamine, 0.6 mL/min, 254 nm), t_R = (major, 11.1 min.), t_R = (minor, 16.1 min.). Specific optical rotation: $[\alpha]_D^{25}$ – 69.4 (c, 0.3, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.21 (d, J = 6.9 Hz, 2H), 7.49-7.43 (m, 3H), 7.36-7.22 (m, 7H), 7.18-7.14 (m, 2H), 7.08 (d, J = 5.0 Hz, 1H), 6.88 (d, J = 8.7 Hz, 1H), 6.60 (s, 1H), 3.77 (s, 3H), 3.58 & 3.52 (ABq, J = 13.6 Hz, 2H), 3.36 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 158.2, 154.5, 142.0, 140.1, 134.4, 133.2, 132.6, 131.3, 129.8, 129.1, 128.6, 128.5 (4C), 128.4, 127.8 (2C), 127.4, 127.2, 127.7, 126.2 (2C), 113.5, 111.4, 83.8, 55.6, 41.2, 37.3. IR: 3066, 3006, 2837, 1574, 1472, 1431, 1276, 1076, 874, 750, 687 cm^{-1}. HRMS: calcd. for $C_{29}H_{24}ClNO_2S$+H: 486.1289; found: 486.1291.

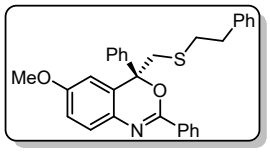
(*R*)-6-Methoxy-2,4-diphenyl-4-(((3-(trifluoromethyl)benzyl)thio)methyl)-4*H*-benzo[d][1,3]oxazine (3z):



According to the general procedure **B**, the tittle compound **3z** was isolated in 51% yield (48 mg) as a pale-yellow liquid using the mixture of ethyl acetate/hexanes (10:90) as an eluent for column chromatography. Enantiomeric ratio (89.5:10.5) was measured by HPLC (Chiralpak IG, 99.9% MeOH/0.1% Diethylamine, 0.6 mL/min,

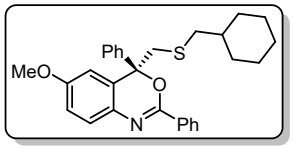
254 nm), t_R = (major, 8.2 min.), t_R = (minor, 9.9 min.). Specific optical rotation: $[\alpha]_D^{25}$ –71.1 (c, 0.3, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.21 (d, J = 7.0 Hz, 2H), 7.49-7.43 (m, 5H), 7.41-7.32 (m, 5H), 7.30-7.24 (m, 3H), 6.89 (d, J = 8.6 Hz, 1H), 6.60 (s, 1H), 3.78 (s, 3H), 3.66 & 3.59 (ABq, J = 13.5 Hz, 2H), 3.36 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 158.2, 154.4, 141.9, 139.1, 133.3, 132.6, 132.4, 131.3, 130.9 (q, J = 32.7 Hz), 129.1, 128.6, 128.54 (2C), 128.51 (2C) 128.4, 127.8 (2C), 126.7, 126.2 (2C), 125.8 (q, J = 3.5Hz), 124.1 (q, J = 272.3 Hz), 124.0, 113.5, 111.5, 83.9, 55.6, 41.2, 37.5. ^{19}F NMR (470 MHz, $CDCl_3$, 24˚C): δ –65.82. IR: 3056, 2933, 2840, 1736, 1626, 1491, 1328, 1161, 1123, 1071, 1031, 782, 735, 697 cm^{-1}. HRMS: calcd. for $C_{30}H_{24}F_3NO_2S$+H: 520.1552; found: 520.1570.

(*R*)-6-Methoxy-4-((phenethylthio)methyl)-2,4-diphenyl-4*H*-benzo[d][1,3]oxazine (3aa):



According to the general procedure **B**, the tittle compound **3aa** was isolated in 67% yield (67 mg) as a colourless liquid using the mixture of ethyl acetate/hexanes (10:90) as an eluent for column chromatography. Enantiomeric ratio (91.5:8.5) was measured by HPLC (Chiralpak IG, 99.9% MeOH/0.1% Diethylamine, 0.6 mL/min, 254 nm), t_R = (major, 11.6 min.), t_R = (minor, 14.0 min.). Specific optical rotation: $[\alpha]_D^{25}$ –62.7 (c, 0.4, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.21 (d, J = 7.0 Hz, 2H), 7.49-7.39 (m, 5H), 7.31-7.28 (m, 4H), 7.25-7.14 (m, 3H), 7.04 (d, J = 7.3 Hz, 2H), 6.88 (d, J = 8.5 Hz, 1H), 6.66 (s, 1H), 3.78 (s, 3H), 3.47 (s, 2H), 2.78-2.68 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 158.2, 154.5, 142.1, 140.4, 133.3, 132.7, 131.2, 128.8, 128.6, 128.56 (2C), 128.50 (3C), 128.4 (2C), 128.3, 127.8 (2C), 126.7, 126.4, 126.3 (2C), 113.5, 111.5, 83.9, 55.6, 42.5, 36.4, 35.6. IR: 3061, 2932, 2831, 1737, 1626, 1577, 1492, 1321, 1224, 1029, 782, 695 cm^{-1}. HRMS: calcd. for $C_{30}H_{27}NO_2S$+H: 466.1835; found: 466,1853.

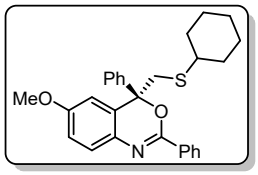
(*R*)-4-(((Cyclohexylmethyl)thio)methyl)-6-methoxy-2,4-diphenyl-4*H*-benzo[d][1,3]oxazine (3ab):



According to the general procedure **B**, the tittle compound **3ab** was isolated in 59% yield (49 mg) as a colourless liquid using the mixture of ethyl acetate/hexanes (10:90) as an eluent for column chromatography. Enantiomeric

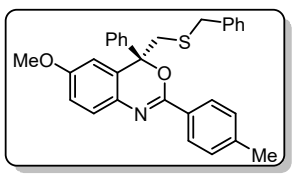
ratio (91.5:8.5) was measured by HPLC (Chiralpak IG, 99.9% MeOH/0.1% Diethylamine, 1 mL/min, 254 nm), t_R = (major, 11.2 min.), t_R = (minor, 17.2 min.). Specific optical rotation: $[\alpha]_D^{25}$ –81.6 (c, 0.3, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.22 (d, J = 7.1 Hz, 2H), 7.47-7.42 (m, 5H), 7.30-7.25 (m, 4H), 6.87 (d, J = 8.5 Hz, 1H), 6.67 (s, 1H), 3.79 (s, 3H), 3.45 (s, 2H), 2.33 (m, 2H), 1.70-1.60 (m, 5H), 1.41-1.25 (m, 1H), 1.09-1.01 (m, 3H), 0.88-.78 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 158.2, 154.6, 142.1, 133.3, 132.7, 131.2, 128.4 (2C), 128.3 (3C), 128.2, 127.9 (2C), 126.6, 126.4 (2C), 113.5, 111.5, 83.9, 55.6, 43.0, 42.0, 38.0, 32.8, 32.7, 26.4, 26.1 (2C). IR: 3060, 2923, 2849, 1742, 1626, 1577, 1491, 1321, 1224, 1070, 1033, 781, 695 cm^{-1}. HRMS: calcd. for $C_{29}H_{31}NO_2S$+H: 458.2148; found: 458.2167.

(*R*)-4-((Cyclohexylthio)methyl)-6-methoxy-2,4-diphenyl-4*H*-benzo[d][1,3]oxazine (3ac):



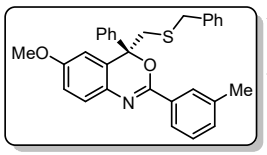
According to the general procedure **B**, the tittle compound **3ac** was isolated in 41% yield (33 mg) as a colourless liquid using the mixture of ethyl acetate/hexanes (10:90) as an eluent for column chromatography. Enantiomeric ratio (88:12) was measured by HPLC (Chiralpak IG, 99.9% MeOH/0.1% Diethylamine, 0.6 mL/min, 254 nm), t_R = (major, 10.7 min.), t_R = (minor, 15.9 min.). Specific optical rotation: $[\alpha]_D^{25}$ –124.7 (c, 0.2, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.22 (d, J = 7.2 Hz, 2H), 7.47-7.43 (m, 5H), 7.32-7.24 (m, 4H), 6.87 (d, J = 8.6 Hz, 1H), 6.66 (s, 1H), 3.79 (s, 3H), 3.50 &3.45 (ABq, J = 14.2 Hz, 2H), 2.50 (t, J = 10.3 Hz, 1H), 1.94-1.82 (m, 2H), 1.68-1.60 (m, 2H), 1.58-1.49 (m, 1H), 1.22-1.05 (m, 5H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 158.2, 154.7, 142.1, 133.2, 131.2, 131.1, 129.1, 128.4 (2C), 128.3 (2C), 128.2, 127.9 (2C), 127.8, 126.6, 126.4 (2C), 126.0, 113.5, 113.2, 111.5, 83.3, 55.6, 45.3, 40.0, 33.8, 25.8. IR: 3063, 2962, 2834, 1734, 1626, 1488, 1317, 1222, 1074, 829, 778, 736, 695 cm^{-1}. HRMS: calcd. for $C_{28}H_{29}NO_2S$+H: 444.1991; found: 444.2007.

(*R*)-4-((Benzylthio)methyl)-6-methoxy-4-phenyl-2-(p-tolyl)-4*H*-benzo[d][1,3]oxazine (3ad):



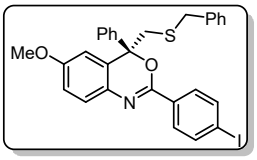
According to the general procedure **B**, the tittle compound **3ad** was isolated in 72% yield (58 mg) as a colourless liquid using the mixture of ethyl acetate/hexanes (10:90) as an eluent for column chromatography. Enantiomeric ratio (91:9) was measured by HPLC (Chiralpak IG, 10% IPA/Hexanes/0.1% Diethyamine, 1 mL/min, 254 nm), t_R = (major, 12.2 min.), t_R = (minor, 15.5 min.). Specific optical rotation: $[\alpha]_D^{25}$ –48.3 (c, 0.4, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.11 (d, J = 8.0 Hz, 2H), 7.35 (m, 2H), 7.24 (m, 11H), 6.86 (dd, J = 8.5, 2.5 Hz, 1H), 6.59 (d, J = 2.6 Hz, 1H), 3.76 (s, 3H), 3.63 & 3.57 (ABq, J = 13.3 Hz, 2H), 3.35 (s, 2H), 2.41 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 158.1, 154.8, 142.2, 141.8, 138.2, 133.5, 130.0, 129.3 (2C), 129.2 (2C), 128.9, 128.7 (2C), 128.5 (2C), 128.3, 128.0 (2C), 127.2, 126.6, 126.4 (2C), 113.6, 111.5, 83.8, 56.7, 41.1, 38.0, 21.8. IR: 3053, 2901, 2829, 1630, 1577, 1487, 1245, 1066, 780, 694 cm^{-1}. HRMS: calcd. for $C_{30}H_{27}NO_2S$+H: 466.1835; found: 466.1840.

(*R*)-4-((Benzylthio)methyl)-6-methoxy-4-phenyl-2-(m-tolyl)-4*H*-benzo[d][1,3]oxazine (3ae):



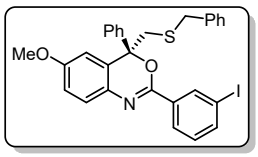
According to the general procedure **B**, the tittle compound **3ae** was isolated in 64% yield (61 mg) as a colourless liquid using the mixture of ethyl acetate/hexanes (10:90) as an eluent for column chromatography. Enantiomeric ratio (91:9) was measured by HPLC (Chiralpak IG, 99.9% MeOH/0.1% Diethylamine, 0.4 mL/min, 254 nm), t_R = (major, 10.8 min.), t_R = (minor, 12.8 min.). Specific optical rotation: $[\alpha]_D^{25}$ –109.1 (c, 0.2, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.94 (m, 2H), 7.21 (m, 13H), 6.79 (dd, J = 8.6, 1.8 Hz, 1H), 6.51 (d, J = 1.8 Hz, 1H), 3.68 (s, 3H), 3.55 & 3.49 (ABq, J = 13.5 Hz, 2H), 3.28 (s, 2H), 2.34 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 158.1, 154.8, 142.1, 138.1, 138.0, 133.3, 132.6, 132.1, 129.1 (2C), 128.8, 128.6 (2C), 128.4 (2C), 127.1, 126.6, 126.3 (2C), 125.1, 113.5, 111.4, 83.9, 77.4, 77.1, 76.8, 55.6, 41.0, 37.9, 21.5. IR: 3055, 2933, 2829, 1622, 1486, 1248, 833, 780, 735 cm^{-1}. HRMS: calcd. for $C_{30}H_{27}NO_2S$+H: 466.1835; found: 466.1843.

(*R*)-4-((Benzylthio)methyl)-2-(4-iodophenyl)-6-methoxy-4-phenyl-4*H*-benzo[d][1,3]oxazine (3af):



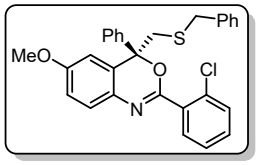
According to the general procedure **B**, the tittle compound **3af** was isolated in 66% yield (58 mg) as a pale-yellow liquid using the mixture of ethyl acetate/hexanes (10:90) as an eluent for column chromatography. Enantiomeric ratio (91:9) was measured by HPLC (Chiralpak IG, 12% IPA/Hexanes/0.1% Diethylamine, 1 mL/min, 254 nm), t_R = (major, 9.2 min.), t_R = (minor, 10.6 min.). Specific optical rotation: $[\alpha]_D^{25}$ –64.5 (c, 0.3, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.54 (d, J = 8.2 Hz, 2H), 7.71 (d, J = 8.3 Hz, 2H), 7.24-7.12 (m, 11H), 6.80 (dd, J = 8.5, 2.3 Hz, 1H), 6.50 (d, J = 1.4 Hz, 1H), 3.69 (s, 3H), 3.52 & 3.48 (ABq, J = 13.4 Hz, 2H), 3.27 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 158.4, 153.9, 141.8, 137.9, 137.6 (2C), 133.0, 132.2, 129.4 (2C), 129.1 (2C), 128.8, 128.6 (2C), 128.5 (2C), 128.4, 127.2, 126.7, 126.2 (2C), 113.6, 111.5, 98.3, 83.9, 55.6, 41.0, 37.8. IR: 3058, 2840, 1736, 1627, 1574, 1489, 1248, 984, 781, 738, 694 cm^{-1}. HRMS: calcd. for $C_{29}H_{24}INO_2S$+H: 578.0645; found: 578.0641.

(*R*)-4-((Benzylthio)methyl)-2-(3-iodophenyl)-6-methoxy-4-phenyl-4*H*-benzo[d][1,3]oxazine (3ag):



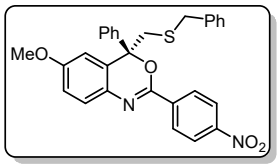
According to the general procedure **B**, the tittle compound **3ag** was isolated in 60% yield (53 mg) as a pale-yellow liquid using the mixture of ethyl acetate/hexanes (10:90) as an eluent for column chromatography. Enantiomeric ratio (91:9) was measured by HPLC (Chiralpak IG, 99.9% MeOH/0.1% Diethylamine, 0.6 mL/min, 254 nm), t_R = (major, 10.9 min.), t_R = (minor, 15.8 min.). Specific optical rotation: $[\alpha]_D^{25}$ –63.1 (c, 0.3, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.47(s, 1H), 8.08 (d, J = 7.8 Hz, 1H), 7.73 (d, J = 7.8 Hz, 1H), 7.25-7.08 (m, 12H), 6.81 (dd, J = 8.6, 2.6 Hz, 1H), 6.49 (d, J = 2.5 Hz, 1H), 3.69 (s, 3H), 3.54 & 3.48 (ABq, J = 13.4 Hz, 2H), 3.28 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 158.4, 153.0, 141.9, 140.0, 137.9, 136.6, 134.7, 132.9, 130.1, 129.1 (2C), 128.7, 128.6 (2C), 128.5 (2C), 128.4, 127.2, 127.0, 126.8, 126.3 (2C), 113.6, 111.5, 94.2, 84.1, 55.6, 40.9, 37.8. IR: 3008, 2963, 2852, 1589, 1557, 1486, 1262, 1054, 799, 752, 707, 679 cm^{-1}. HRMS: calcd. for $C_{29}H_{24}INO_2S$+H: 578.0645; found: 578.0650.

(*R*)-4-((Benzylthio)methyl)-2-(2-chlorophenyl)-6-methoxy-4-phenyl-4*H*-benzo[d][1,3]oxazine (3ah):



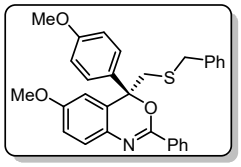
According to the general procedure **B**, the tittle compound **3ah** was isolated in 66% yield (53 mg) as colourless foam using the mixture of ethyl acetate/hexanes (10:90) as an eluent for column chromatography. Enantiomeric ratio (90.5:9.5) was measured by HPLC (Chiralpak IG, 100% MeOH, 0.8 mL/min, 254 nm), t_R = (major, 7.6 min.), t_R = (minor, 10.6 min.). Specific optical rotation: $[\alpha]_D^{25}$ –233.3 (c, 0.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.66 (d, 1H, J = 7.3 Hz), 7.36 (d, 1H, J = 7.7 Hz), 7.31-7.12 (m, 13H), 6.82 (dd, 1H, J = 8.6 Hz, 2.6 Hz), 6.46 (d, 1H, J = 2.5 Hz), 3.69 (s, 3H), 3.50 & 3.45 (ABq, 2H, J = 13.3 Hz), 3.32 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 158.5, 154.9, 142.2, 138.0, 133.0, 132.9, 132.8, 131.1, 131.0, 130.7, 129.1 (2C), 128.6 (2C), 128.5 (2C), 128.4, 127.9, 127.2, 126.9 (2C), 126.8, 126.7, 113.7, 111.8, 84.9, 55.6, 41.0, 37.8. IR: 3003, 2837, 1737, 1321, 1275, 1146, 1050, 988, 888, 756, 701, 654 cm^{-1}. HRMS: calcd. for $C_{29}H_{24}ClNO_2S$+H: 486.1289; found: 486.1297.

(*R*)-4-((Benzylthio)methyl)-6-methoxy-2-(4-nitrophenyl)-4-phenyl-4*H*-benzo[d][1,3]oxazine (3ai):



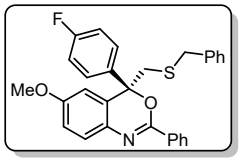
According to the general procedure **B**, the tittle compound **3ai** was isolated in 51% yield (33 mg) as a yellow liquid using the mixture of ethyl acetate/hexanes (15:85) as an eluent for column chromatography. Enantiomeric ratio (19:81) was measured by HPLC (Chiralpak IG, 99.9% MeOH/0.1% Diethylamine, 0.4 mL/min, 254 nm), t_R = (major, 21.1 min.), t_R = (minor, 22.9 min.). Specific optical rotation: $[\alpha]_D^{25}$ –70.3 (c, 0.3, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.31 (m, 4H), 7.25 (m, 11H), 6.90 (d, J = 8.8 Hz, 1H), 6.58 (d, J = 2.0 Hz, 1H), 3.79 (s, 3H), 3.59 & 3.55 (ABq, J = 13.3 Hz, 2H), 3.38 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 159.0, 152.5, 149.4, 141.7, 138.6, 137.8, 132.6, 129.0 (2C), 128.7, 128.6 (4C), 128.5, 128.4 (2C), 127.3, 127.2, 126.3, 125.4, 123.6, 122.0, 113.7, 111.7, 84.3, 55.7, 41.2, 37.8. IR: 2998, 2929, 2850, 1732, 1628, 1521, 1348, 1146, 1077, 853, 701, 686 cm^{-1}. HRMS: calcd. for $C_{29}H_{24}N_2O_4S$+H: 497.1529; found: 497.1524.

(*R*)-4-((Benzylthio)methyl)-6-methoxy-4-(4-methoxyphenyl)-2-phenyl-4*H*-benzo[d][1,3]oxazine (3aj):



According to the general procedure **B**, the tittle compound **3aj** was isolated in 69% yield (46 mg) as a yellow liquid using the mixture of ethyl acetate/hexanes (15:85) as an eluent for column chromatography. Enantiomeric ratio (90.5:9.5) was measured by HPLC (Chiralpak IG, 99.9% MeOH/0.1% Diethylamine, 0.6 mL/min, 254 nm), t_R = (major, 11.7 min.), t_R = (minor, 17.5 min.). Specific optical rotation: $[\alpha]_D^{25}$ –3.1 (c, 0.3, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.20 (d, J = 6.9 Hz, 2H), 7.48-7.42 (m, 3H), 7.31-7.21 (m, 8H), 6.88 (dd, J = 8.6, 2.5 Hz, 1H), 6.79 (d, J = 2.5Hz, 1H), 3.77 (s, 3H), 3.74 (s, 3H), 3.63 & 3.57 (ABq, J = 13.4 Hz, 2H), 3.34 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 159.4, 158.1, 154.6, 138.1, 134.2, 133.3, 132.8, 131.2, 129.1 (2C), 129.0, 128.6 (2C), 128.4 (2C), 127.9 (2C), 127.7 (2C), 127.2, 126.6, 113.7 (2C), 113.5, 111.4, 83.7, 55.6, 55.3, 41.0, 37.9. IR: 3408, 2998, 2926, 2847, 1671, 1607, 1514, 1416, 1251, 1179, 1035, 839, 706 cm^{-1}. HRMS: calcd. for $C_{30}H_{27}NO_3S$+H: 482.1784; found: 482.1786.

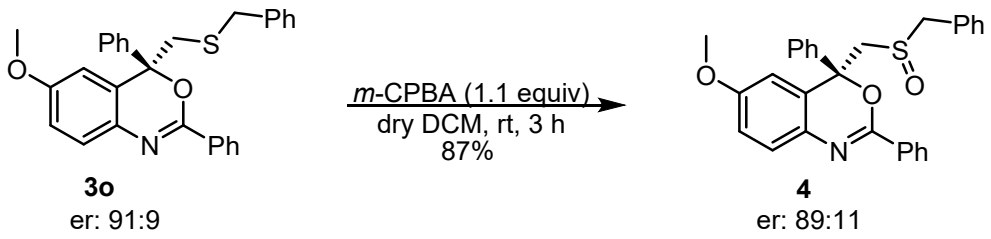
(*R*)-4-((Benzylthio)methyl)-4-(4-fluorophenyl)-6-methoxy-2-phenyl-4*H*-benzo[d][1,3]oxazine (3ak):



According to the general procedure **B**, the tittle compound **3ak** was isolated in 57% yield (31 mg) as a pale-yellow liquid using the mixture of ethyl acetate/hexanes (10:90) as an eluent for column chromatography. Enantiomeric ratio (87:13) was measured by HPLC (Chiralpak IG, 99.9% MeOH/0.1% Diethylamine, 1 mL/min, 254 nm), t_R = (major, 5.4 min.), t_R = (minor, 7.3 min.). Specific optical rotation: $[\alpha]_D^{25}$ –81.4 (c, 0.3, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.24 (d, J = 6.4 Hz, 2H), 7.52-7.45 (m, 4H), 7.32-7.21 (m, 7H), 6.98-6.94 (m, 2H), 6.90 (d, J = 8.4 Hz, 1H), 6.55 (s, 1H), 3.78 (s, 3H), 3.65 & 3.57 (ABq, J = 13.4 Hz, 2H), 3.37 & 3.33 (ABq, J = 14.5 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 162.1 (d, J = 2481.1 Hz), 158.2, 154.1, 137.9 (d, J = 9.0 Hz), 136.5, 128.5, 132.5, 131.4, 129.1 (2C), 128.7, 128.6 (2C), 128.5 (2C), 128.3, 128.2, 127.8 (2C), 127.2, 126.7, 115.3 (d, J = 21.4 Hz), 126.4, 113.6, 111.3, 83.3, 55.6, 40.9, 37.9. ^{19}F NMR (470 MHz, $CDCl_3$, 24°C): δ –116.81. IR: 3055, 2876, 1657, 1590, 1480, 1352, 1167, 1088, 816, 754 cm^{-1}. HRMS: calcd. for $C_{29}H_{24}FNO_2S$+H: 470.1584; found: 470.1589.

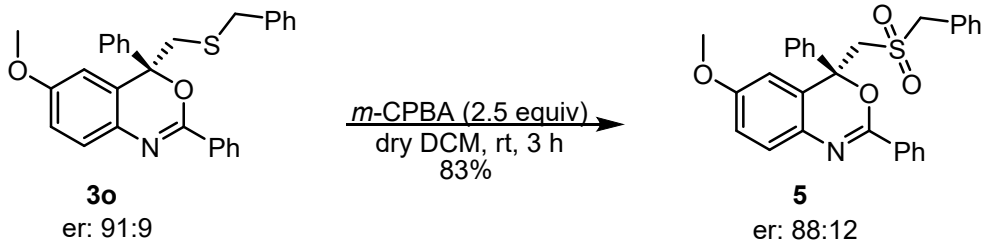
10. Synthetic application

10(a). Synthesis of (4*R*)-4-((Benzylsulfinyl)methyl)-6-methoxy-2,4-diphenyl-4*H*-benzo[d][1,3]oxazine (4)



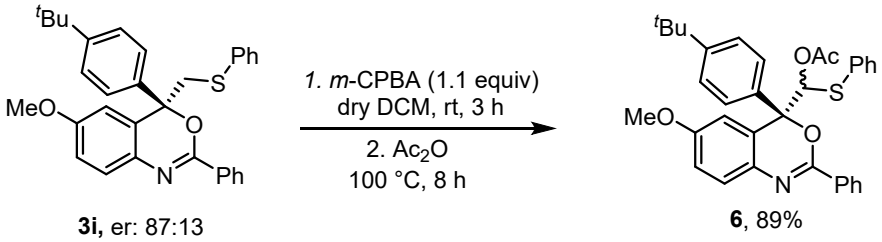
An oven dried reaction tube was charged compound **3o** (0.13 mmol), *m*-CPBA (0.34 mmol) and 2 mL of dry DCM under nitrogen atmosphere and stir at room temperature for 3 h. The reaction was monitored by TLC analysis, the crude reaction mixture was quenched with saturated $NaHCO_3$ (3 mL) solution and extracted with DCM (2 x 20 mL). The combined organic layer was concentrated in vacuo and purified by column chromatography and gave the compound **4** in 1:1 ratio of diastereomers in 87% yield (54 mg) as a white solid. Enantiomeric ratio (89:11) was measured by HPLC (Chiralpak IG, 70% ^{i}PrOH/Hexane, 1.0 mL/min, 254 nm), t_R = (major, 8.0 min.), t_R = (minor, 9.5 min.). Specific optical rotation: $[\alpha]_D^{25}$ –84.5 (c, 0.4, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.13 (d, J = 7.2 Hz, 2H), 8.06 (d, J = 7.3 Hz, 2H), 7.44-7.35 (m, 6H), 7.33-7.27 (m, 7H), 7.24-7.22 (m, 6H), 7.20-7.12 (m, 9H), 6.86 (dd, J = 8.6, 2.6 Hz, 1H), 6.82-6.80 (m, 2H), 6.33 (d, J = 2.5 Hz, 1H), 3.98 (m, 6H), 3.76 (s, 3H), 3.67 (s, 3H), 3.55-3.47 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 158.7, 158.6, 141.0, 140.6, 131.9, 131.7, 130.4 (2C), 130.2 (2C), 130.0, 129.9, 129.1 (2C), 128.9 (2), 128.8 (2C), 128.6 (2C), 128.5 (2C), 128.0, 127.9, 127.0, 126.9, 126.1 (2C), 125.6 (2C), 114.6, 114.0, 111.1, 111.0, 63.5, 63.1, 60.1, 59.9, 55.8, 55.6. IR: 3060, 2911, 1624, 1487, 1227, 1085, 991, 779, 695 cm^{-1}. HRMS: calcd. for $C_{29}H_{25}NO_3S$+H: 468.1627; found: 468.1636.

10(b). Synthesis of (*R*)-4-((Benzylsulfonyl)methyl)-6-methoxy-2,4-diphenyl-4*H*-benzo[d][1,3]oxazine (5):



In a dry reaction tube was charged compound **3o** (0.13 mmol), *m*-CPBA (0.33 mmol) and 2 mL of dry DCM under nitrogen atmosphere and stir at room temperature for 3 h. The reaction was monitored by TLC analysis, the crude reaction mixture was quenched with saturated $NaHCO_3$ (8 mL) solution and extracted with DCM (2 x 20 mL). The combined organic layer was concentrated in vacuo and purified by column chromatography and gave the compound **5** in 83% yield (53 mg) as a yellow liquid. Enantiomeric ratio (88:12) was measured by HPLC (Chiralpak IG, 10% MeCN/ 89.9% MeOH/0.1% Diethylamine, 0.6 mL/min, 254 nm), t_R = (major, 7.0 min.), t_R = (minor, 8.8 min.). Specific optical rotation: $[\alpha]_D^{25}$ –80.5 (c, 0.3, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.28 (d, J = 7.1 Hz, 2H), 7.53-7.47 (m, 3H), 7.38-7.27 (m, 11H), 6.92 (d, J = 6.8 Hz, 1H), 6.74 (d, J = 1.7 Hz, 1H), 4.18-4.05 (m, 3H), 3.98-3.95 (m, 1H), 3.81 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 158.5, 140.9, 131.8 (2C), 131.1, 130.8, 129.2, 129.1 (2C), 128.9, 128.8 (2C), 128.7 (2C), 128.0 (2C), 127.6, 127.5, 127.2, 126.8, 125.8 (2C), 119.1, 114.1, 111.4, 81.2, 62.3, 59.5, 55.7. IR: 2993, 2831, 1733, 1630, 1495, 1322, 1129, 783, 698 cm^{-1}. HRMS: calcd. for $C_{29}H_{25}NO_4S$+H: 484.1577; found: 484.1599.

10(c). Synthesis of (*R*)-4-(4-(Tert-butyl)phenyl)-6-methoxy-2-phenyl-4*H*-benzo[d][1,3]oxazin-4-yl)(phenylthio)methyl acetate (6):



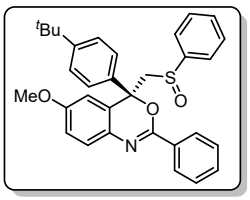
3i, er: 87:13

6, 89%

An oven dried reaction tube was charged with a compound **3i** (0.08 mmol) and *m*-CPBA (0.8 mmol) and added 1 mL of dry DCM under nitrogen atmosphere. The reaction was stir at room temperature for 3 h (monitored by TLC analysis), the crude reaction mixture was quenched with saturated $NaHCO_3$ (3 mL) solution and extracted with DCM (2 x 20 mL). The combined organic layer was concentrated in vacuo and purified by column chromatography and gave the corresponding sulfoxide in 1:0.8 ratio of diastereomers in 82% yield (34 mg) as a yellow liquid.

The sulfoxide compound was treated with (3.0 equiv) of acetic anhydride (Ac_2O) at 100 ºC for 8 h. The reaction was monitored by TLC analysis, the crude reaction mixture was quenched with saturated $NaHCO_3$ (8 mL) solution and extracted with DCM (3 x 10 mL). The combined organic layer was concentrated in vacuo and purified by column chromatography and gave the compound 7 in 1:0.7 ratio of diastereomers in 89% yield (24 mg) as a pale-yellow liquid.

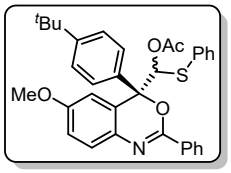
(*R*)-4-(4-(Tert-butyl)phenyl)-6-methoxy-2-phenyl-4-((phenylsulfinyl)methyl)-4*H*-benzo[d][1,3]oxazine:



Yield: 82%; White solid. Enantiomeric ratio (87:13) was measured by HPLC (Chiralpak IG, 100% MeOH, 1.0 mL/min, 254 nm), t_R = (major, 6.5 min.), t_R = (minor, 10.7 min.). Specific optical rotation: $[\alpha]_D^{25}$ –82.5 (c, 0.2, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.18 (dd, J = 8.3, 1.2 Hz, 1.5H), 8.02-8.00 (m, 1.8H), 7.52-7.48 (m, 3.4H), 7.42-7.38 (m, 3H), 7.37-7.33 (m, 7.4H), 7.30-7.27 (m, 2.3H), 7.25-7.22 (m, 3H), 7.19 (s, 1H), 7.15-7.13 (m, 2H), 6.93 (d, J = 2.6 Hz, 1H), 6.87 (dd, J = 8.6, 2.7 Hz, 1H), 6.80 (dd, J = 8.6, 2.7 Hz, 0.8H), 6.51 (d, J = 2.7 Hz, 0.8 H), 3.92-3.83 (m, 3.5H), 3.80 (s, 3H), 3.69 (s, 2.4H), 1.17 (s, 7.2H), 1.14 (s, 9H). ^{13}C{^{1}H}

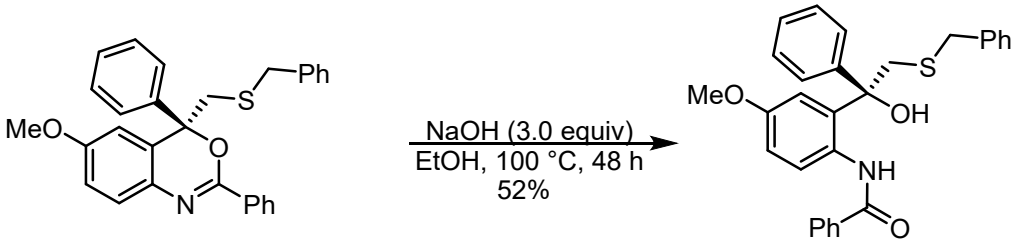
NMR (100 MHz, $CDCl_3$, 24 °C): δ 158.6, 158.4, 151.7, 145.6, 138.4, 137.9, 132.9, 132.2, 131.4, 131.3, 131.1 (2C), 129.5 (2C), 129.4 (2C), 128.5 (2C), 128.4 (2C), 127.9 (2C), 127.8 (2C), 127.2 (2C), 127.0, 125.9 (2C), 125.8 (2C), 125.7 (2), 125.3 (2C), 124.4 (2C), 124.2 (2C), 114.5, 113.9, 111.3, 111.2, 81.9, 81.8, 71.0, 70.7, 55.8, 55.6, 34.7, 34.6, 31.3, 31.2. IR: 3064, 2912, 1629, 1495, 1230, 1088, 991, 774, 696 cm^{-1}. HRMS: calcd. for $C_{32}H_{31}NO_3S$+H: 510.2097; found: 510.2108.

(*R*)-4-(4-(Tert-butyl)phenyl)-6-methoxy-2-phenyl-4*H*-benzo[d][1,3]oxazin-4-yl)(phenylthio)methyl acetate (6):



Yield: 89%; pale-yellow liqiud. Specific optical rotation: $[\alpha]_D^{25}$ –124.2 (c, 0.4, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.21-8.16 (m, 3.3H), 7.43-7.36 (m, 5.5H), 7.32-7.29 (m, 3.8H), 7.24-7.19 (m, 8.4H), 7.15-7.10 (m, 5.2H), 6.88 (d, J = 5.0 Hz, 1.7 H), 6.81-6.77 (m, 2.5H), 6.69 (d, J = 2.7 Hz), 3.70 (s, 2H), 3.64 (s, 3H), 1.81 (s, 3H), 1.75 (s, 2H), 1.18 (s, 6H), 1.17 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 169.3, 158.0, 153.9, 151.3, 137.1, 133.9 (2C), 133.7 (2C), 133.1, 133.0, 132.9 (2C), 132.5, 132.4, 131.3, 129.0, 128.5 (2C), 128.4 (2C), 128.3 (2C), 128.0 (2C), 126.8, 126.4 (2C), 126.3 (2C), 126.2, 125.3 (2C), 125.2 (2C), 114.3, 114.2, 111.9, 111.0, 87.3, 85.9, 85.6, 85.4, 55.7, 55.6, 34.6, 31.3, 20.9, 20.7. IR: 3032, 2756, 1718, 1621, 1464, 1307, 1212, 1065, 839, 761, 691 cm^{-1}. HRMS: calcd. for $C_{34}H_{33}NO_4S$+H: 552.2203; found: 552.2197.

10(d). Synthesis of (*R*)-*N*-(2-(2-(Benzylthio)-1-hydroxy-1-phenylethyl)-4-methoxyphenyl)benzamide (7):

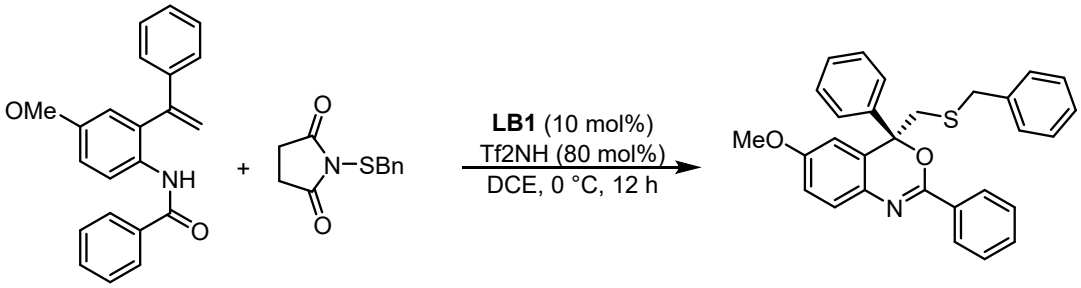


3o; er: 91:9 **7**; er: 88:12

The compound **3o** (0.16 mmol) and NaOH (0.49 mmol) was charged in a 25 mL round bottom flask subsequently 3 mL of ethanol was added to the reaction mixture. The reaction was reflux at 100 ºC for 48

h (monitored by TLC analysis), the crude reaction mixture was acetified with dil.HCl and extracted with DCM (2 x 10 mL). The combined organic layer was concentrated in vacuo and purified by column chromatography to afford the product **7** in 52% yield (29 mg) as a pale-yellow liquid. Enantiomeric ratio (88:12) was measured by HPLC (Chiralpak IG, 50% IPA/Hexane, 1.0 mL/min, 254 nm), t_R = (major, 38.8 min.), t_R = (minor, 20.6 min.). Specific optical rotation: $[\alpha]_D^{25}$ –81.5 (c, 0.5, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.39 (d, J = 8.9 Hz, 1H), 7.71 (s, 1H), 7.45-7.41 (m, 3H), 7.33-7.28 (m, 7H), 7.23-7.21 (m, 2H), 7.17-7.15 (m, 2H), 6.98 (dd, J = 9.0 Hz, 2.9 Hz), 6.91 (s, 1H), 6.75 (d, J = 2.9 Hz, 1H), 3.96 (s, 3H), 3.79 (s, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 165.0.156.3, 138.9, 137.5, 135.1, 134.2, 131.3, 130.6, 128.8 (2C), 128.7 (3C), 128.6, 128.5 (2C), 127.7, 127.6, 127.5, 126.8 (2C), 125.7 (2C), 123.1, 115.4, 114.2, 77.2, 55.5, 38.2. IR: 3058, 2961, 2816, 1722, 1607, 1479, 1278, 1074, 830, 749, 692 cm^{-1}. HRMS: calcd. for $C_{29}H_{27}NO_3S$+H: 470.1784; found: 470.1772.

10(e). Gram-Scale Synthesis:

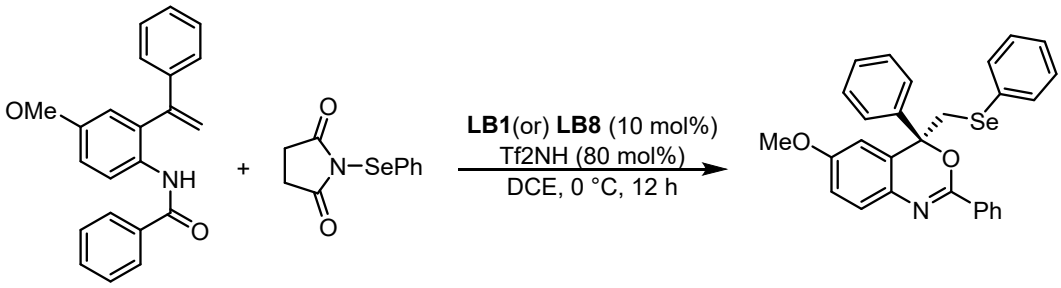


(1.51 mmol) (1.82 mmol) 477 mg

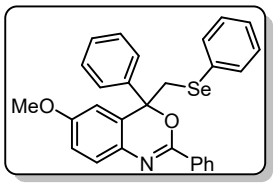
In a dry schlenk tube 500 mg (1.51 mmol) of *o*-vinylanilide, 403 mg (1.82 mmol) of electrophilic thiolating reagent **2** and chiral Lewis-Base **LB1** (74 mg, 10 mol%) was taken followed by (18.0 mL) of dry 1,2-dichloroethane (DCE) was added to the reaction mixture under argon atm. The reaction mixture was allowed to stir at 0 °C subsequently 80mol% of bis(trifluoromethane)sulfonimide(Tf_2NH) in (2.0 mL) dry DCE was drop-wise added to the reaction mixture over 10 min and further stirred at 0 °C for 48 h. After completion of the reaction (monitored by TLC) it was quenched by addition of 20 mL saturated aq. NH_4Cl solution, and compound was extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated to afford the crude product. The compound **3m** was isolated in 69%

yield (477 mg) as a pale-yellow liquid using the mixture of ethyl acetate/hexanes (10:90) as an eluent for column chromatography. Enantiomeric ratio (90.5:9.5) was measured by HPLC (Chiralpak IG, 100% MeOH, 0.6 mL/min, 254 nm), t_R = (major, 9.8 min.), t_R = (minor, 11.2 min.).

10(f). Chiral Lewis base mediated oxyselenation of *o*-vinylanilide:



6-Methoxy-2,4-diphenyl-4-((phenylselanyl)methyl)-4*H*-benzo[d][1,3]oxazine:

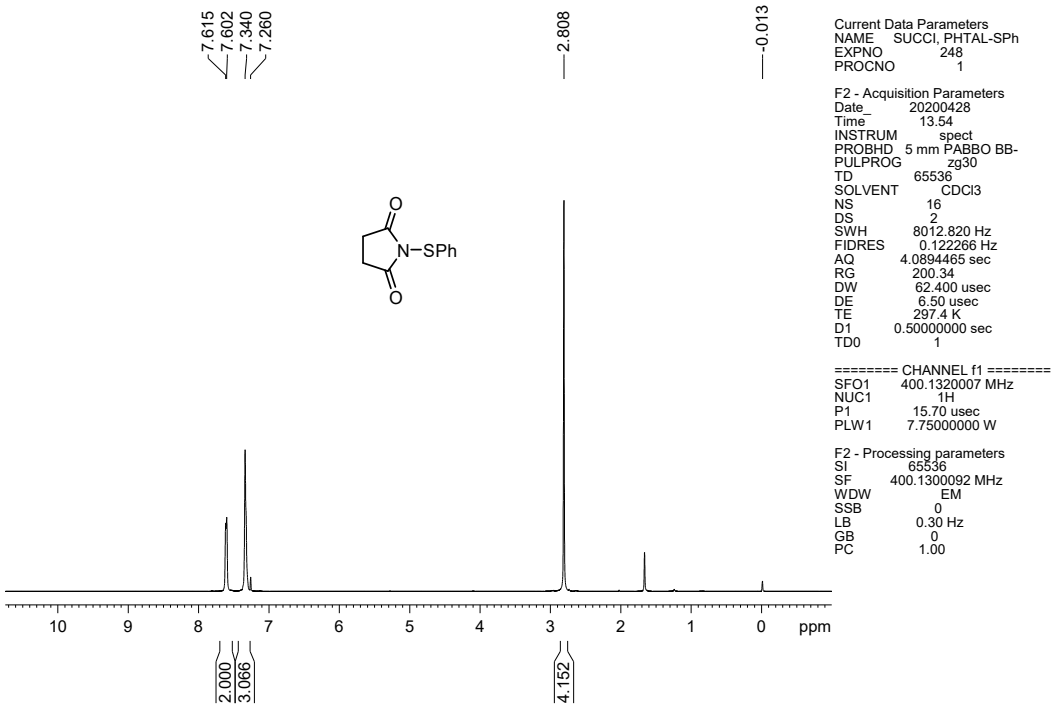


According to the general procedure **B**, the expected oxyselenation compound was isolated as a racemic with 95% yield (87 mg) in pale-yellow liquid using the mixture of ethyl acetate/hexanes (10:90) as an eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.05 (d, J = 7.3 Hz, 2H), 7.39-7.30 (m, 7H), 7.23 (d, J = 8.5 Hz, 1H), 7.21-7.15 (m, 3H), 7.08-7.03 (m, 3H), 6.79 (dd, J = 8.5 Hz, 2.6 Hz, 1H), 6.56 (d, J = 2.5 Hz, 1H), 3.82 & 3.79 (ABq, J = 13.2 Hz, 2H), 3.65 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 158.2, 154.6, 142.2, 133.5 (2C), 133.0, 132.4, 131.2, 131.0, 129.1 (2C), 128.7, 128.5 (2C), 128.3, 128.3 (2C), 127.9 (2C), 127.2, 126.7, 126.1 (2C), 113.7, 111.0, 83.5, 55.6, 39.3. IR: 3063, 2928, 1621, 1584, 1476, 1258, 1152, 1072, 748, 692 cm^{-1}. HRMS: calcd. for $C_{28}H_{23}NO_2S$+H: 486.0966; found: 486.0972.

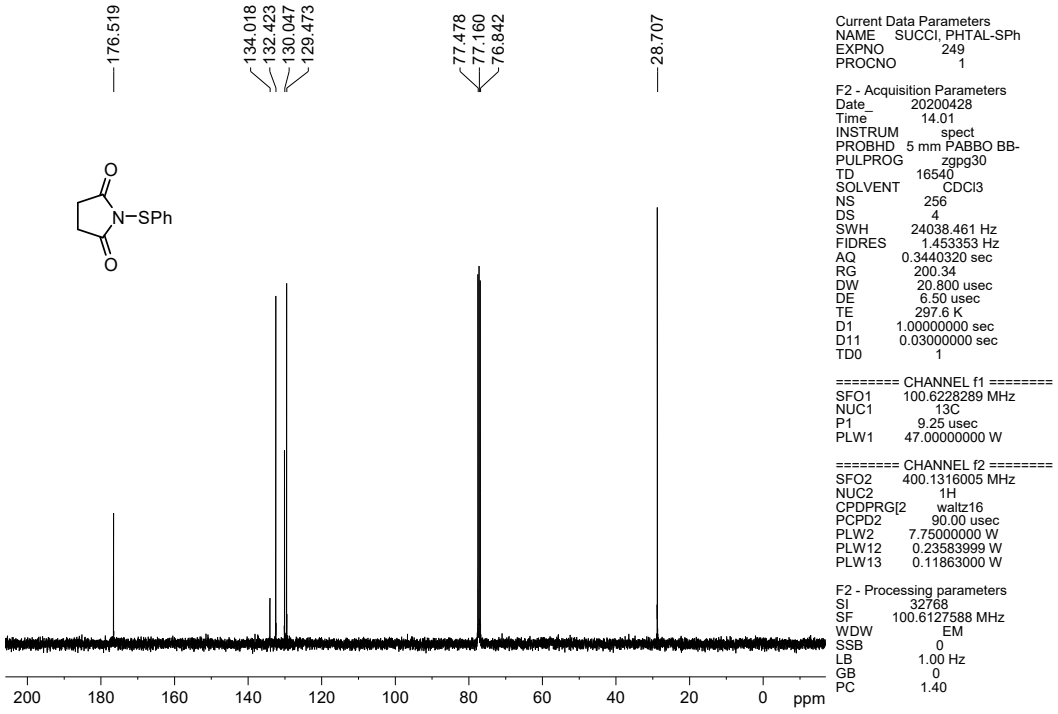
11. NMR spetra of electrophilic Sulfur reagents:

1-(Phenylthio)pyrrolidine-2,5-dione (2a)

^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):

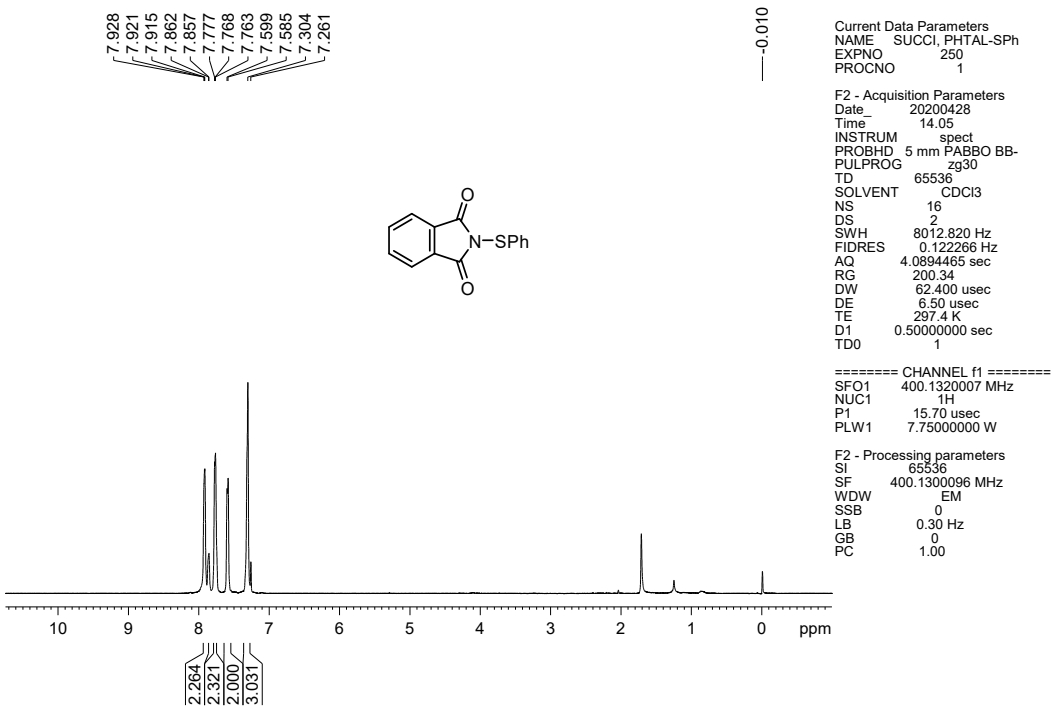


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24˚C):

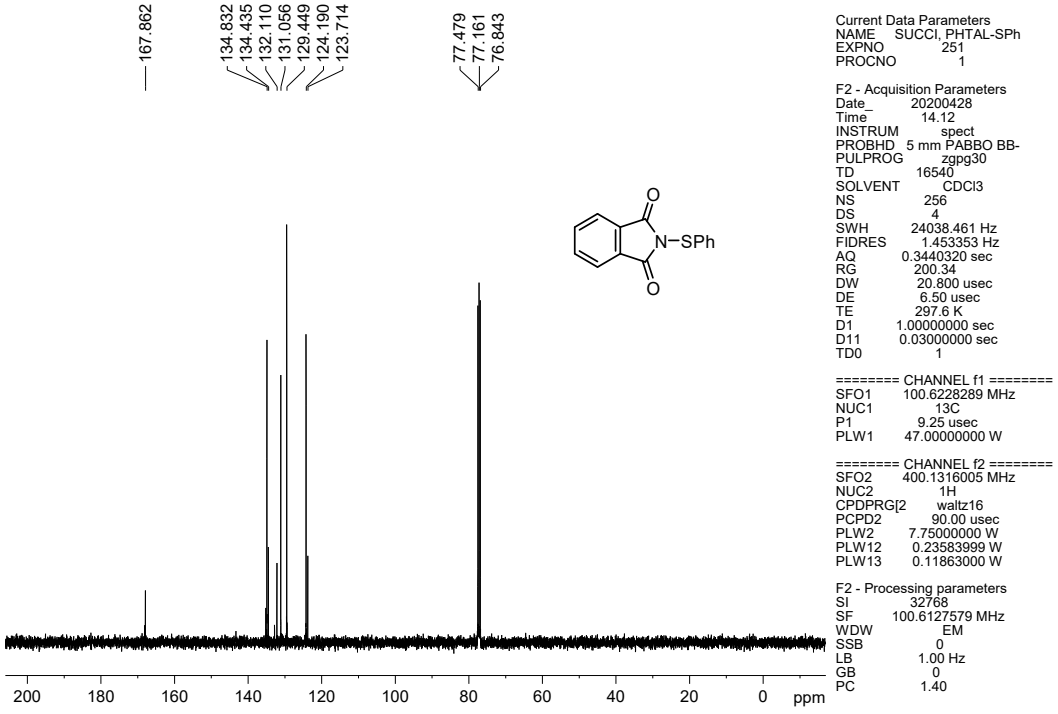


2-(Phenylthio)isoindoline-1,3-dione (2b)

^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):

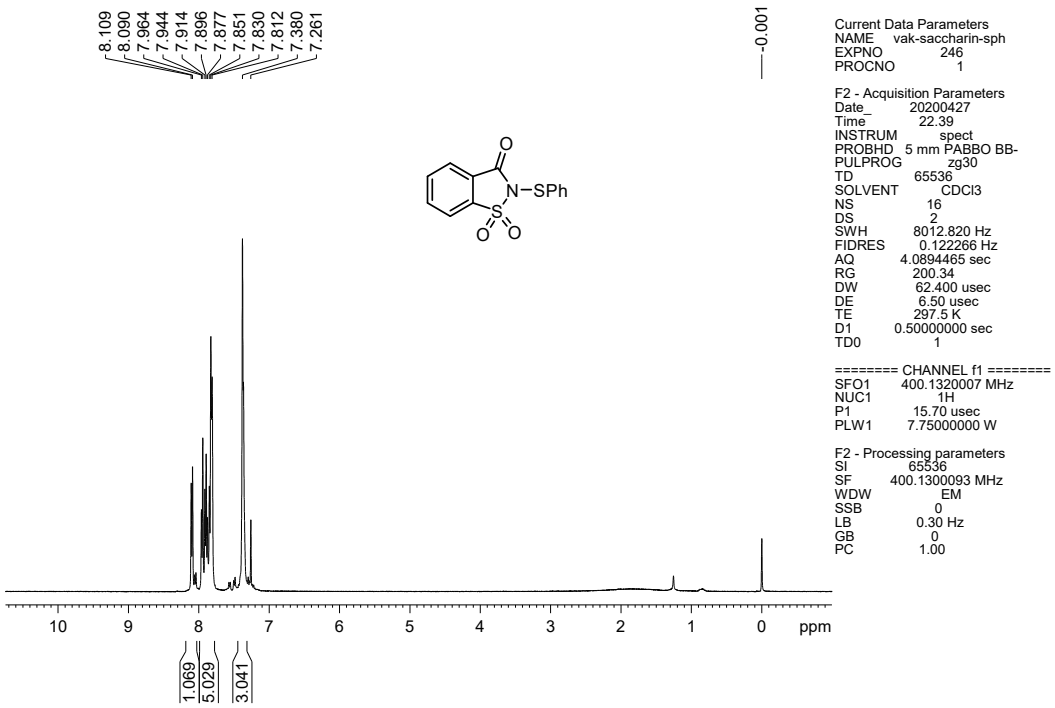


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24˚C):

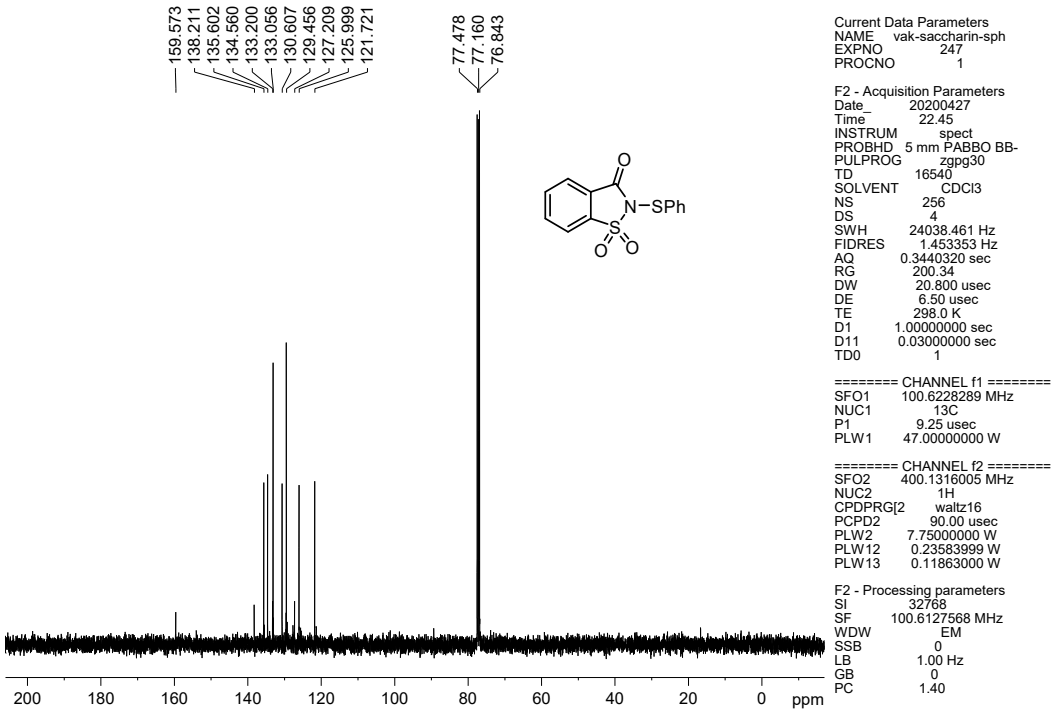


2-(Phenylthio)benzo[d]isothiazol-3(2*H*)-one 1,1-dioxide (2c)

^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):

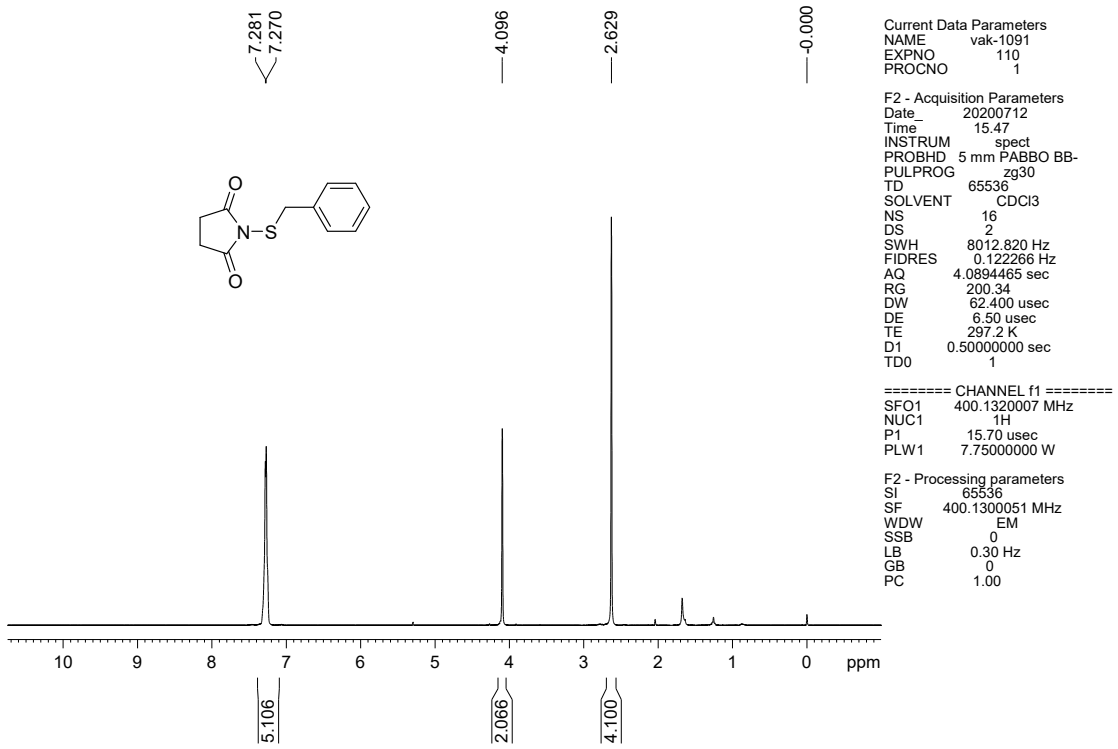


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24˚C):

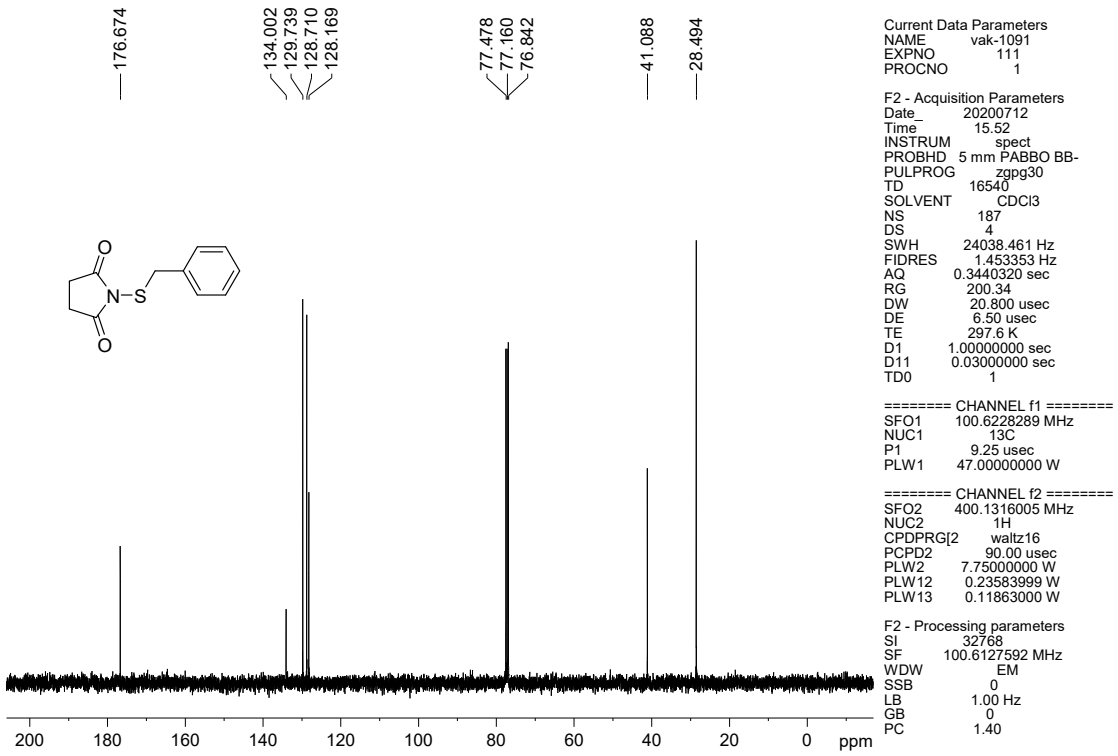


1-(Benzylthio)pyrrolidine-2,5-dione (2d)

^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):

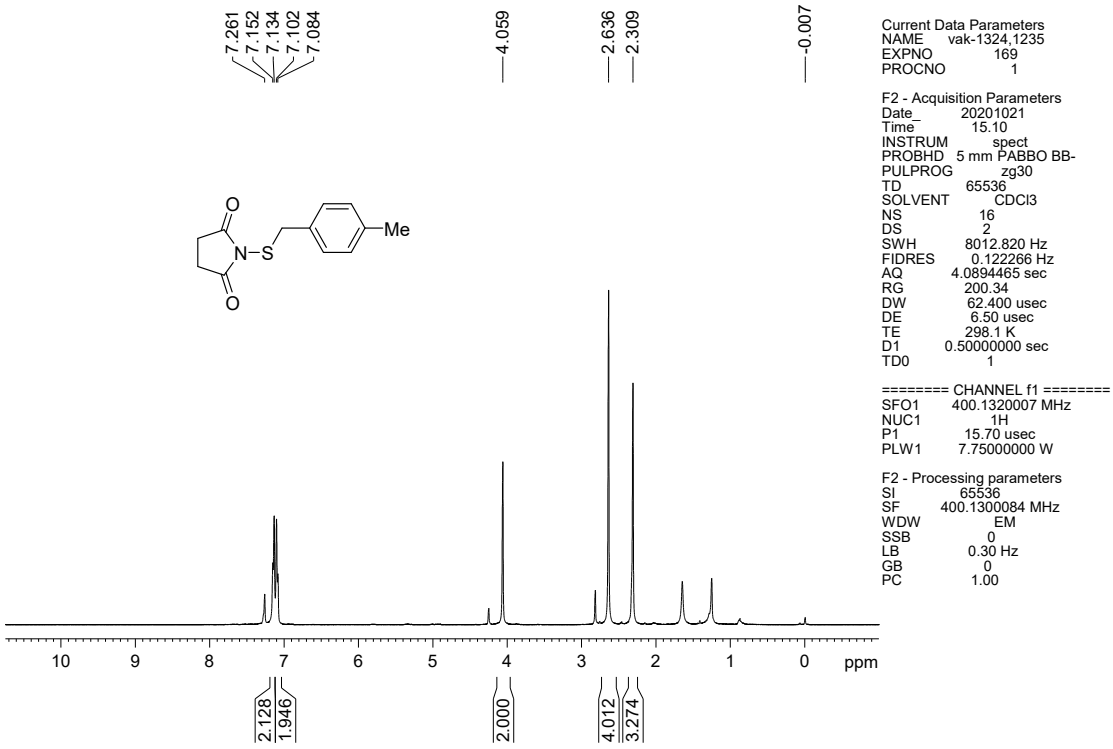


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24˚C):

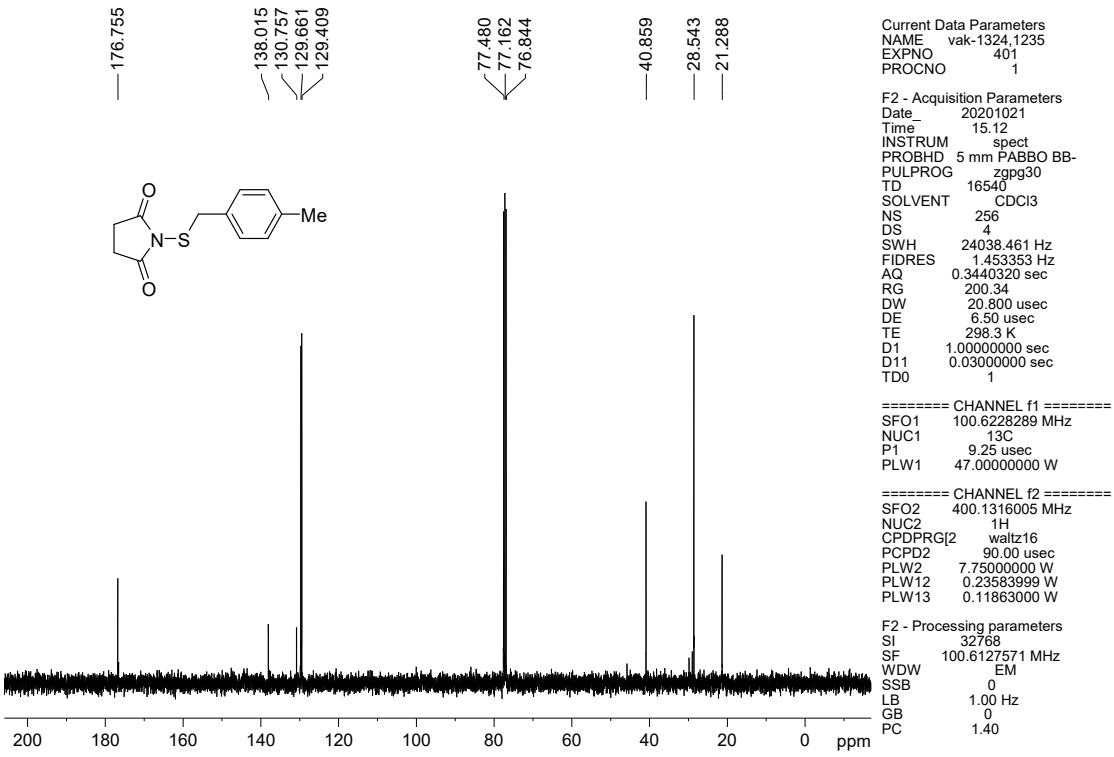


1-((4-Methylbenzyl)thio)pyrrolidine-2,5-dione (2e)

^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):

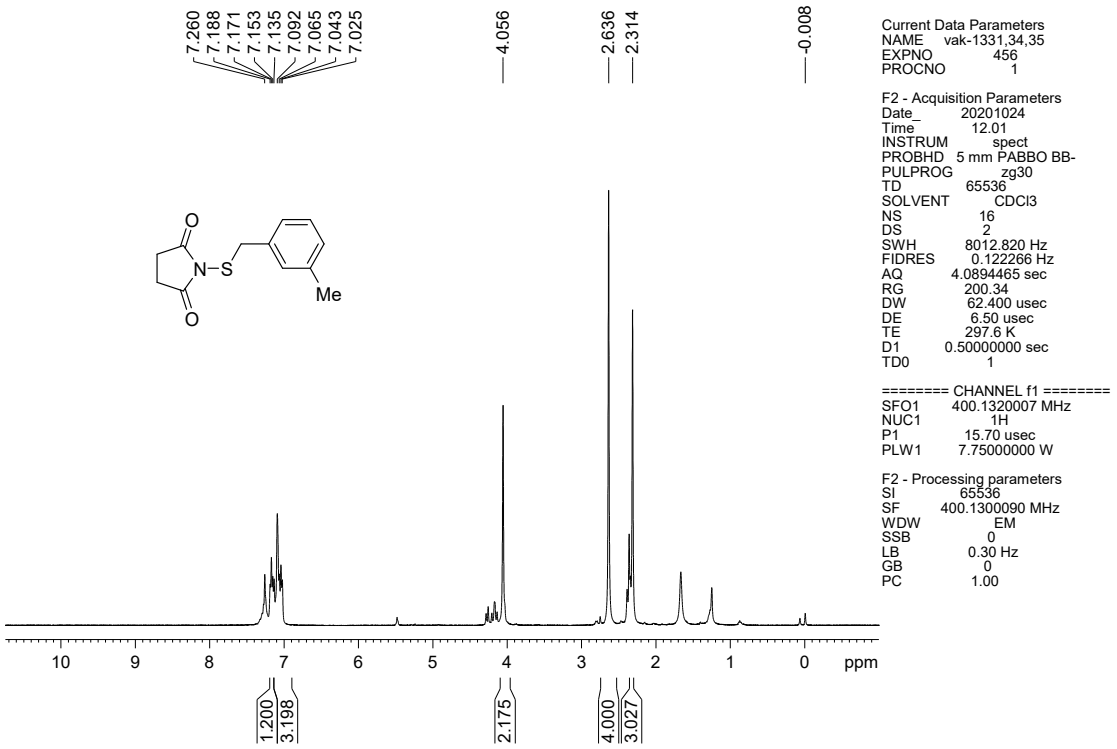


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24˚C):

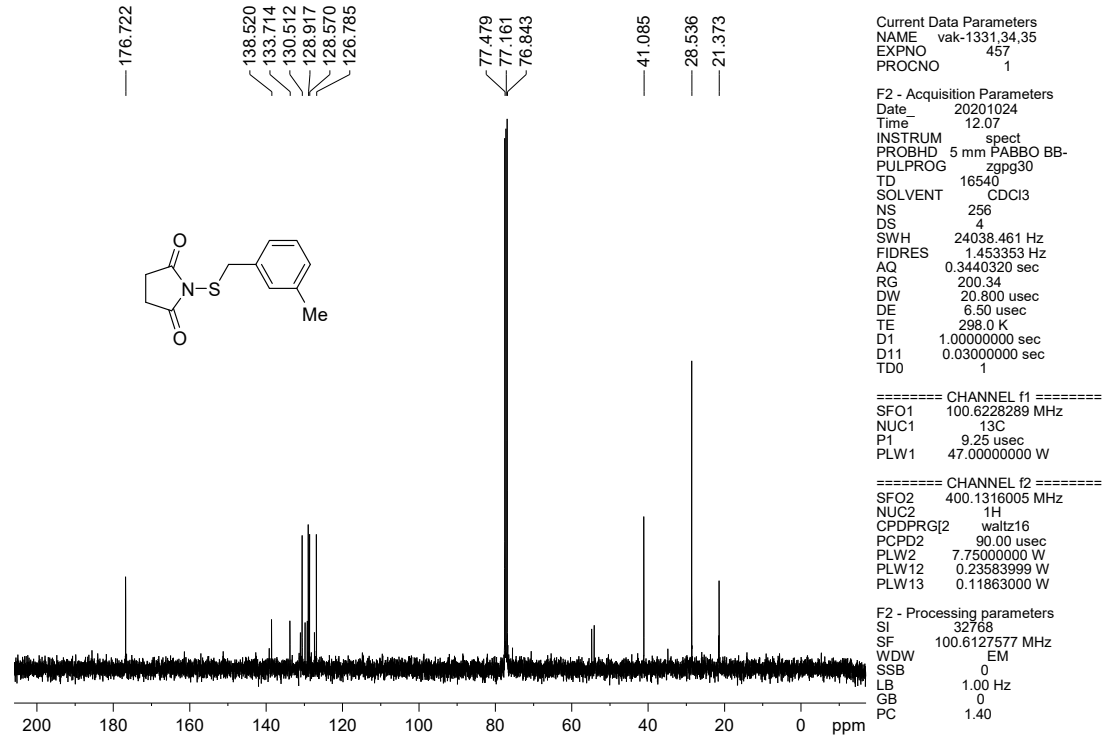


1-((3-Methylbenzyl)thio)pyrrolidine-2,5-dione (2f)

^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):

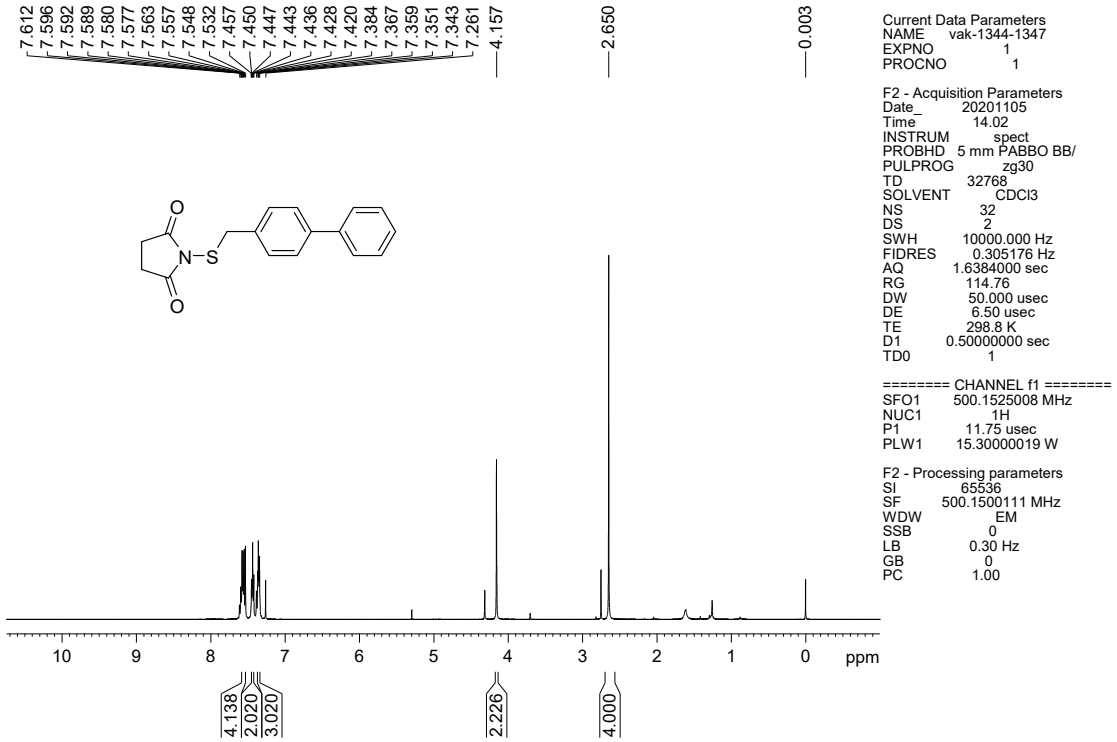


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24˚C):

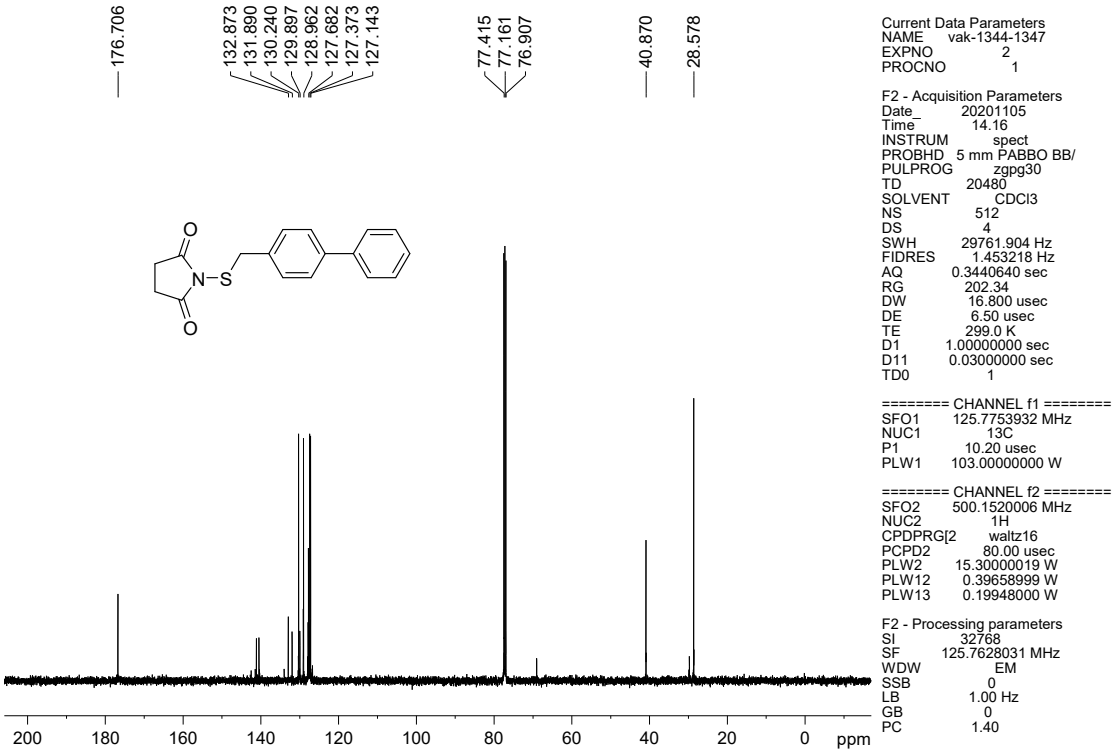


1-(([1,1'-Biphenyl]-4-ylmethyl)thio)pyrrolidine-2,5-dione (2g)

^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):

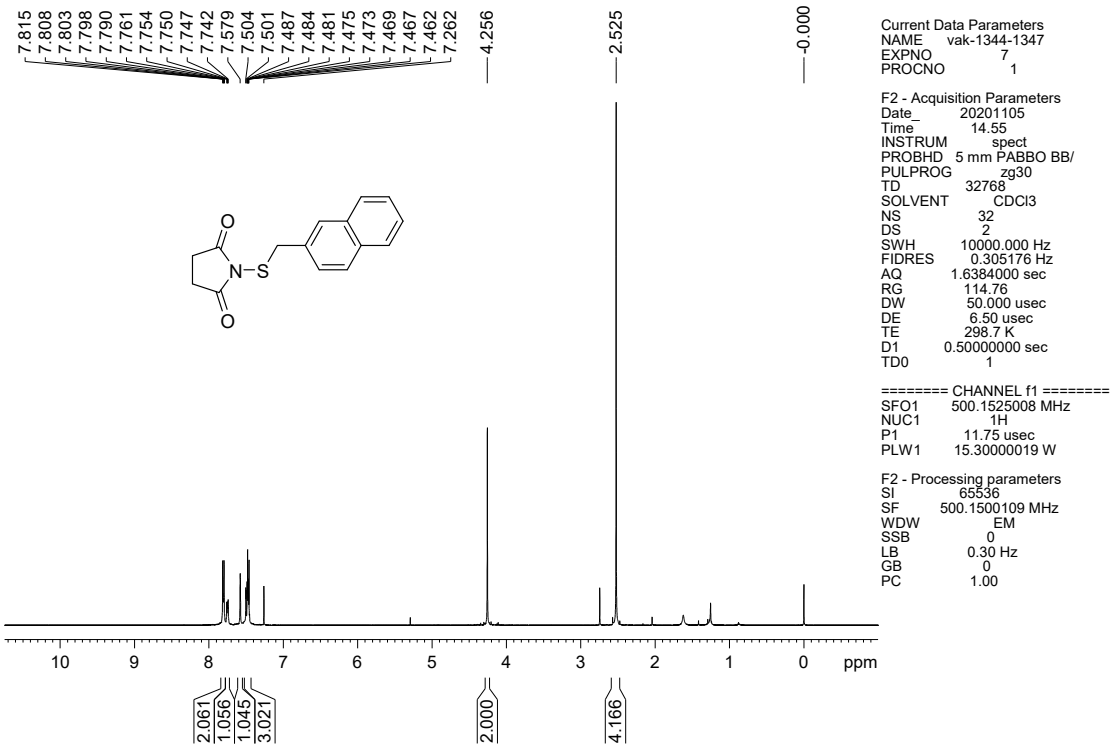


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24°C):

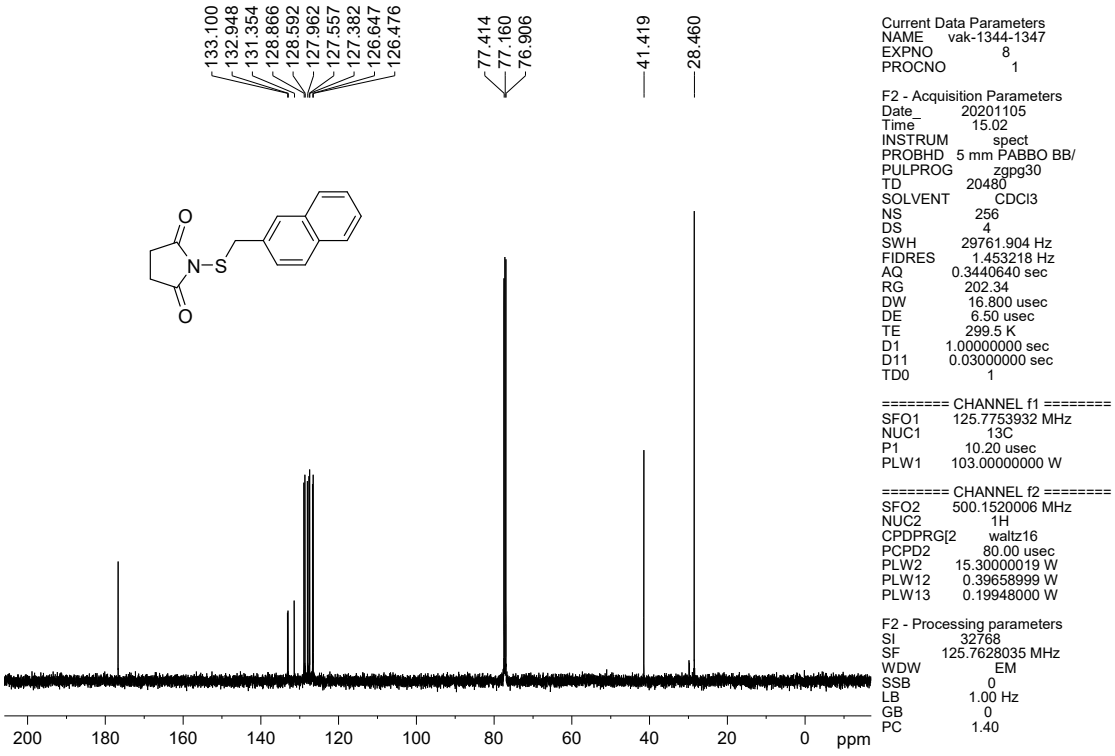


1-((Naphthalen-2-ylmethyl)thio)pyrrolidine-2,5-dione (2h)

^{1}H NMR (400 MHz, $CDCl_3$, 24°C):

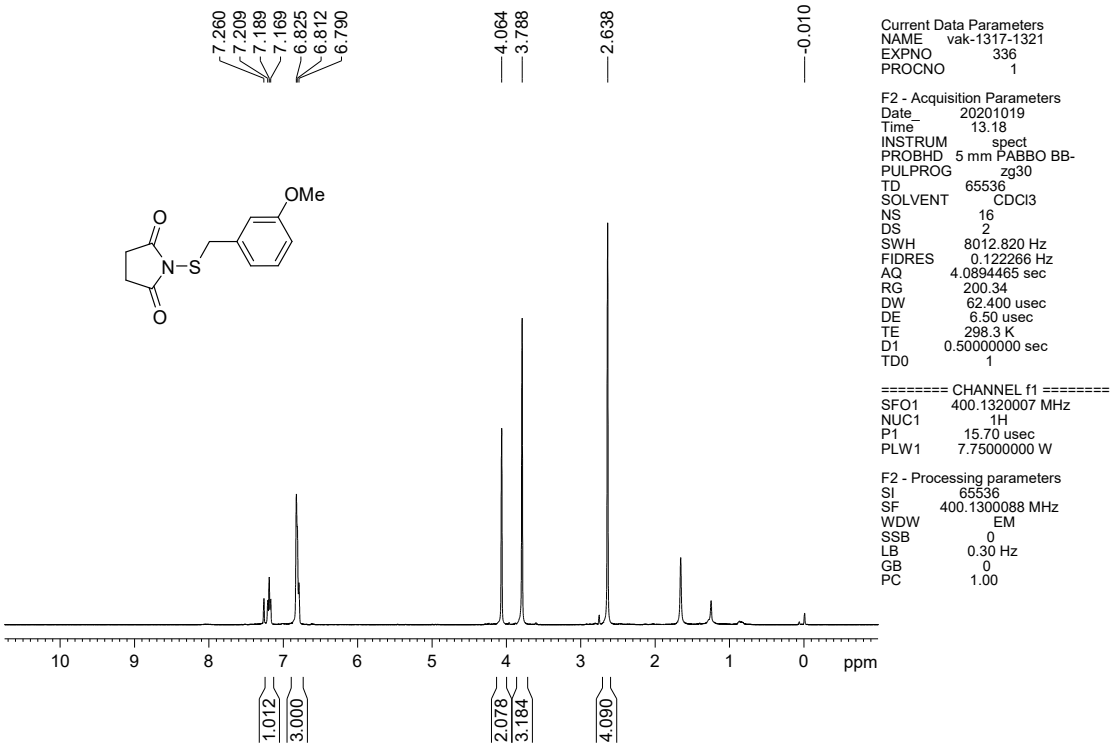


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24˚C):

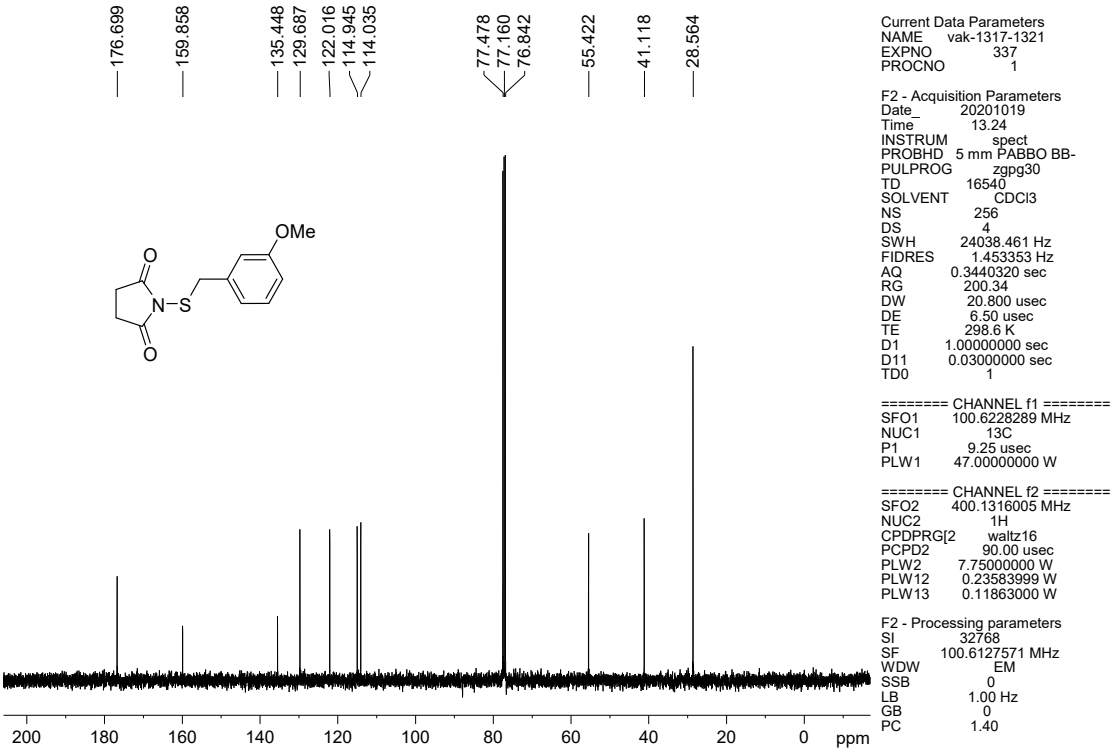


1-((3-Methoxybenzyl)thio)pyrrolidine-2,5-dione (2i)

^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):

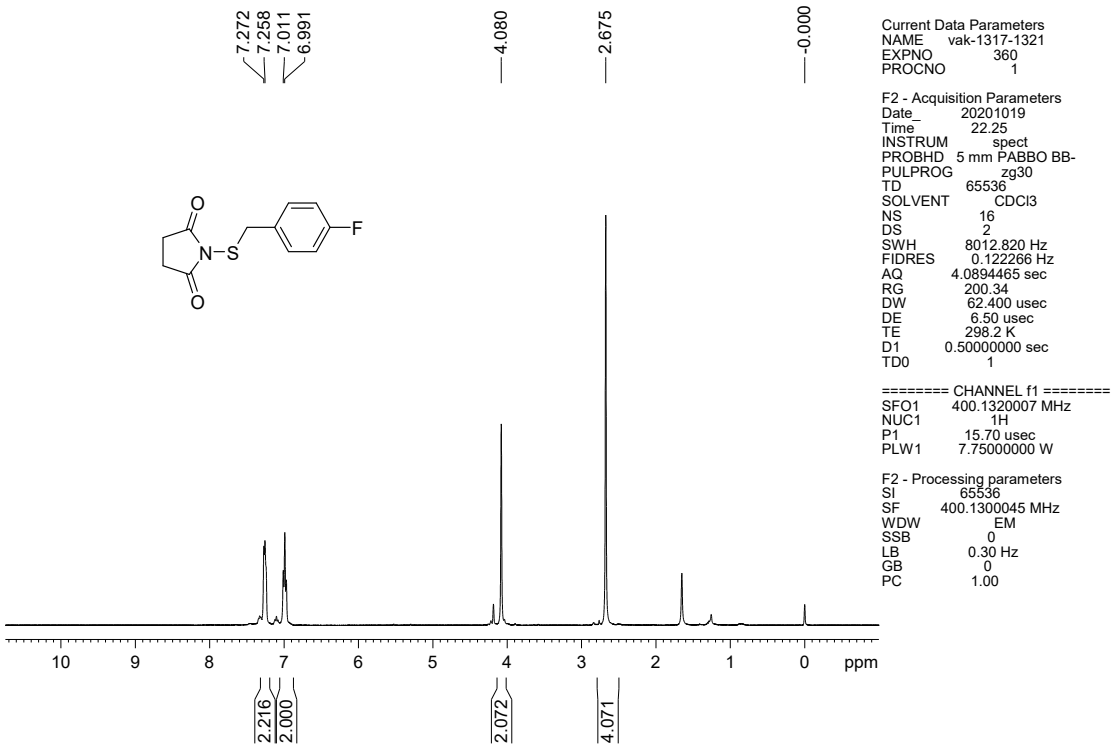


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24˚C):

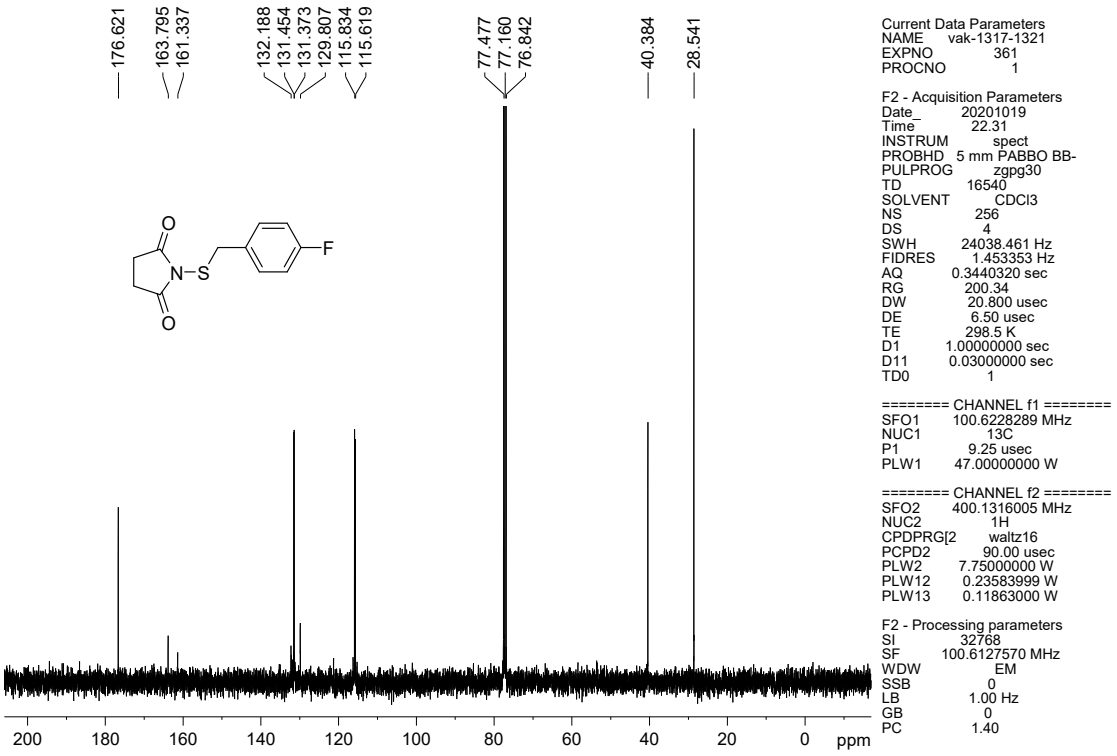


1-((4-Fluorobenzyl)thio)pyrrolidine-2,5-dione (2j)

^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):

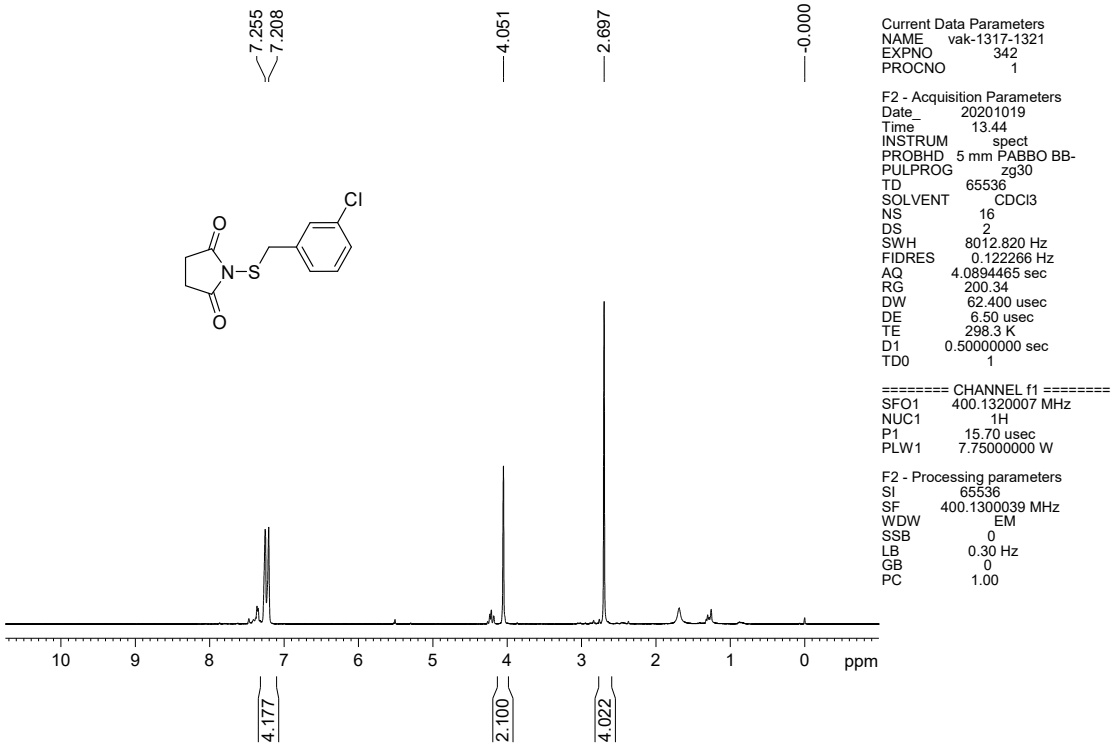


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24˚C):

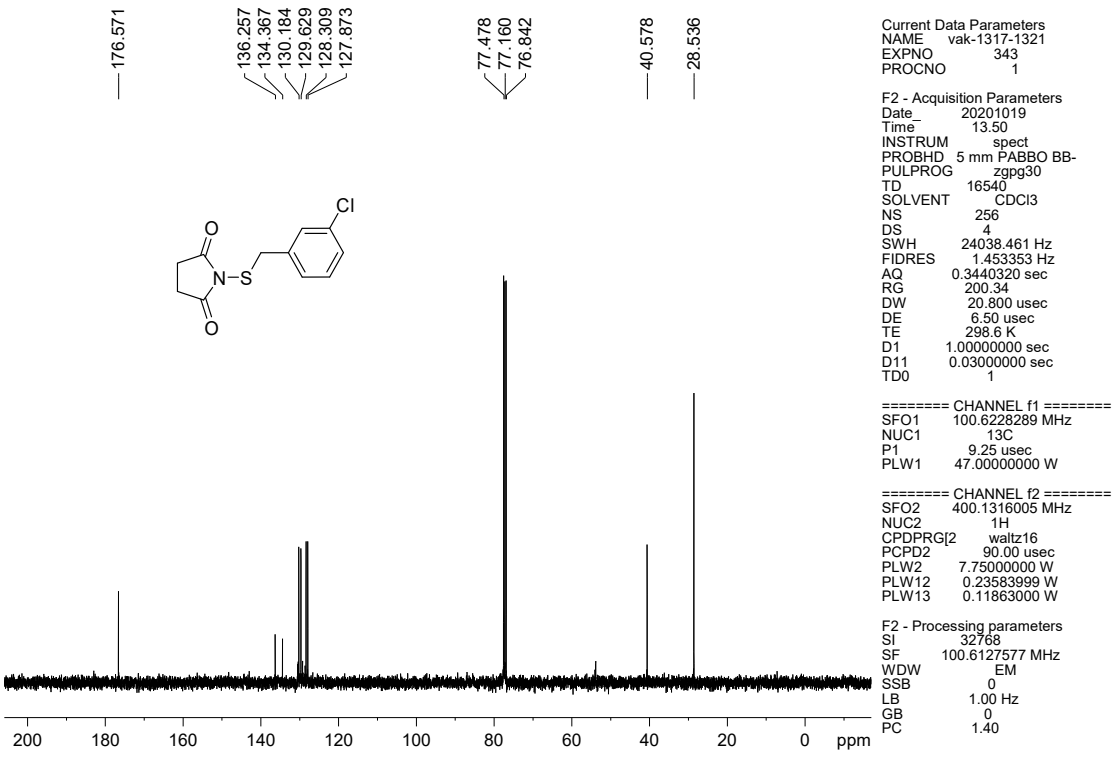


1-((3-Chlorobenzyl)thio)pyrrolidine-2,5-dione (2k)

^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):

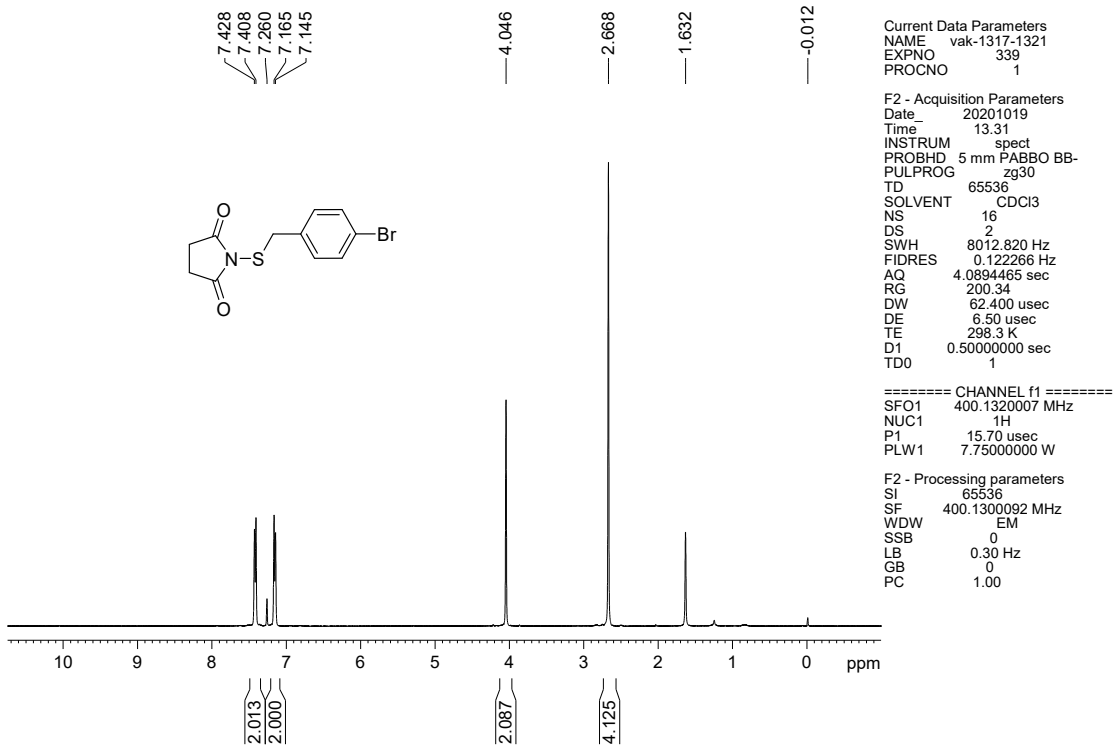


$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24˚C):

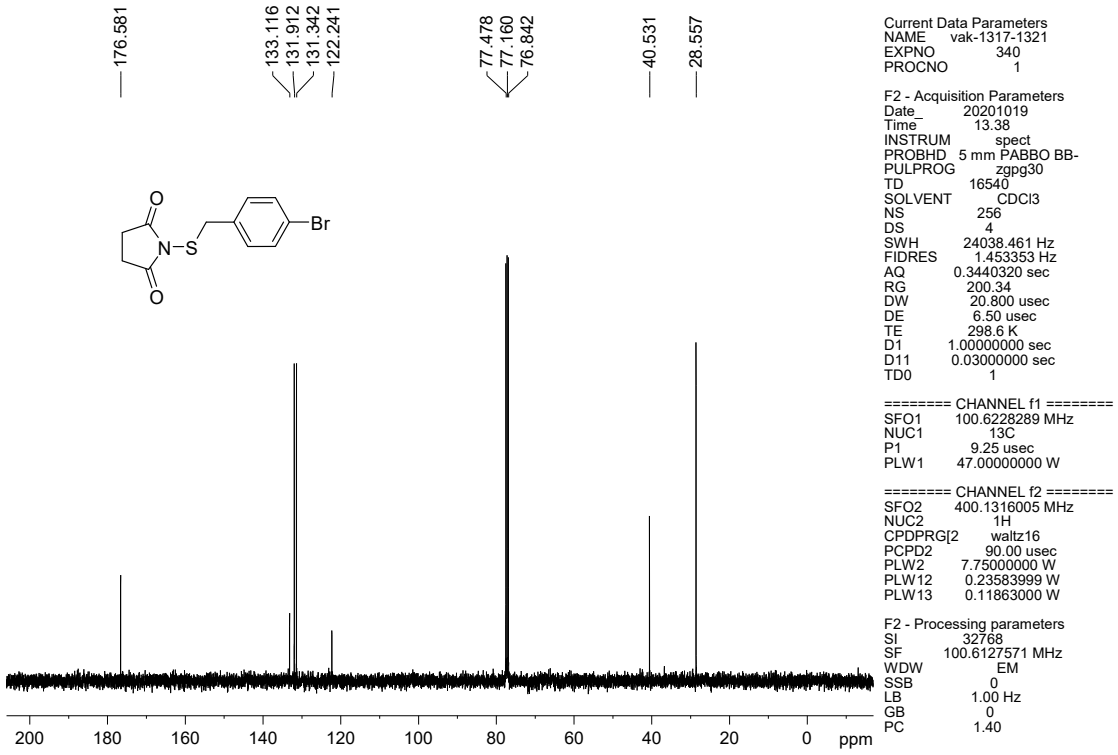


1-((4-Bromobenzyl)thio)pyrrolidine-2,5-dione (2l)

^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):

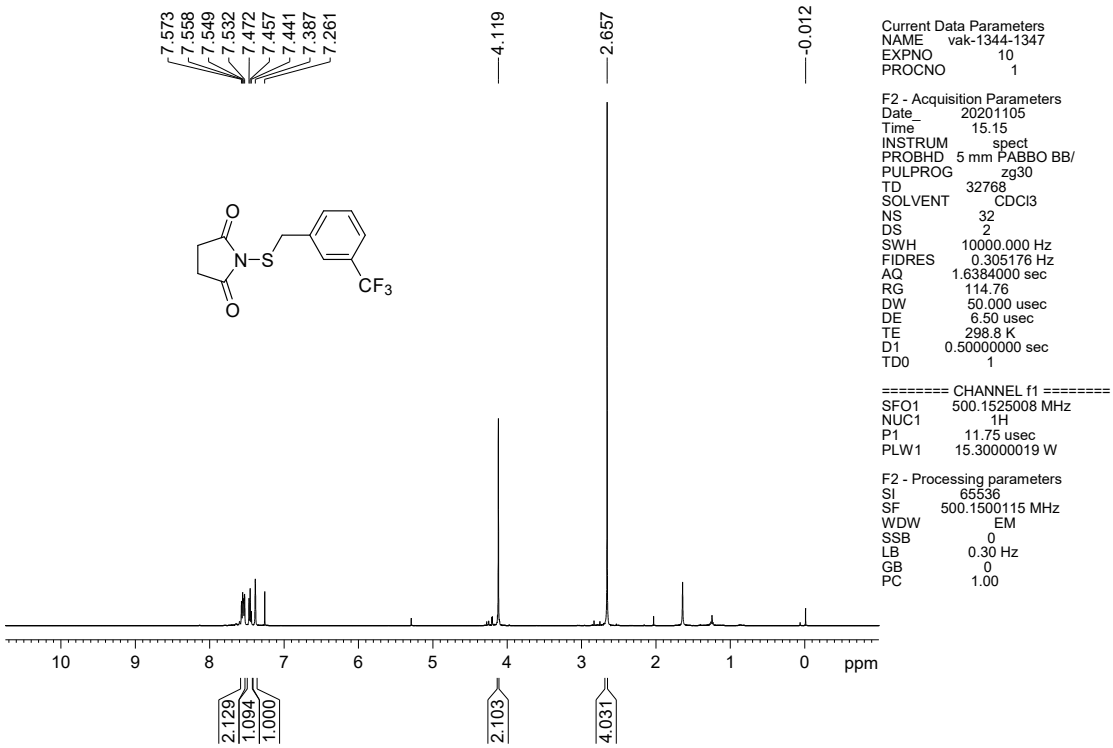


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24˚C):

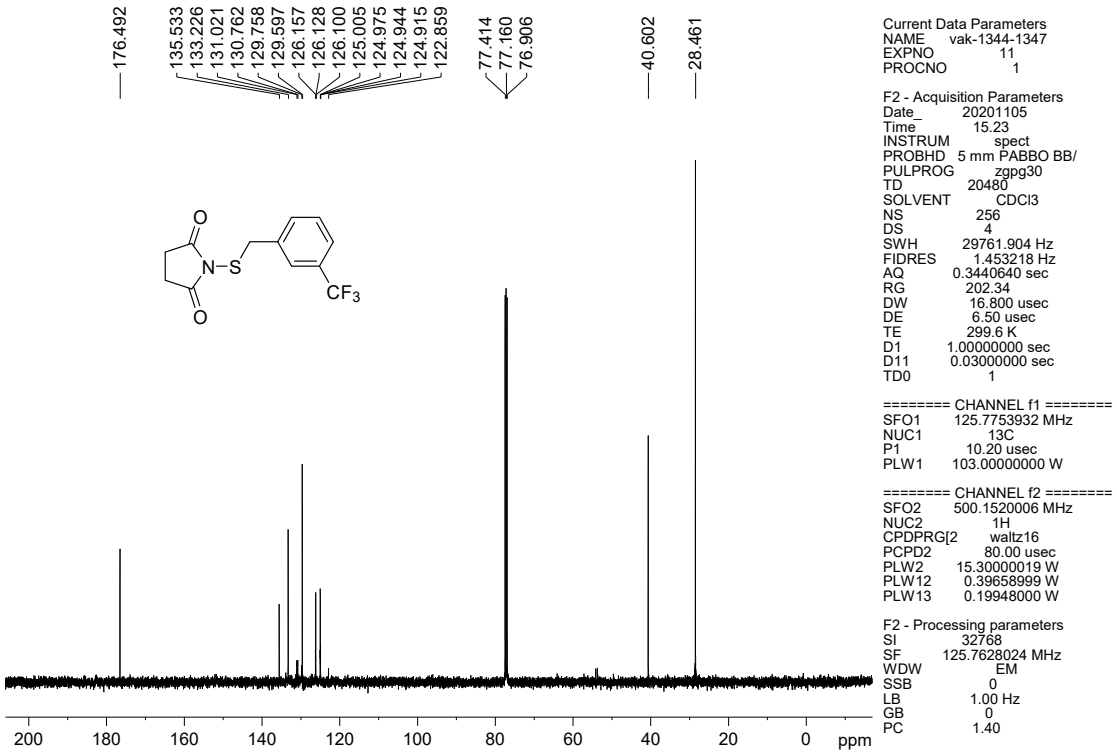


1-((3-(Trifluoromethyl)benzyl)thio)pyrrolidine-2,5-dione (2m)

^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):

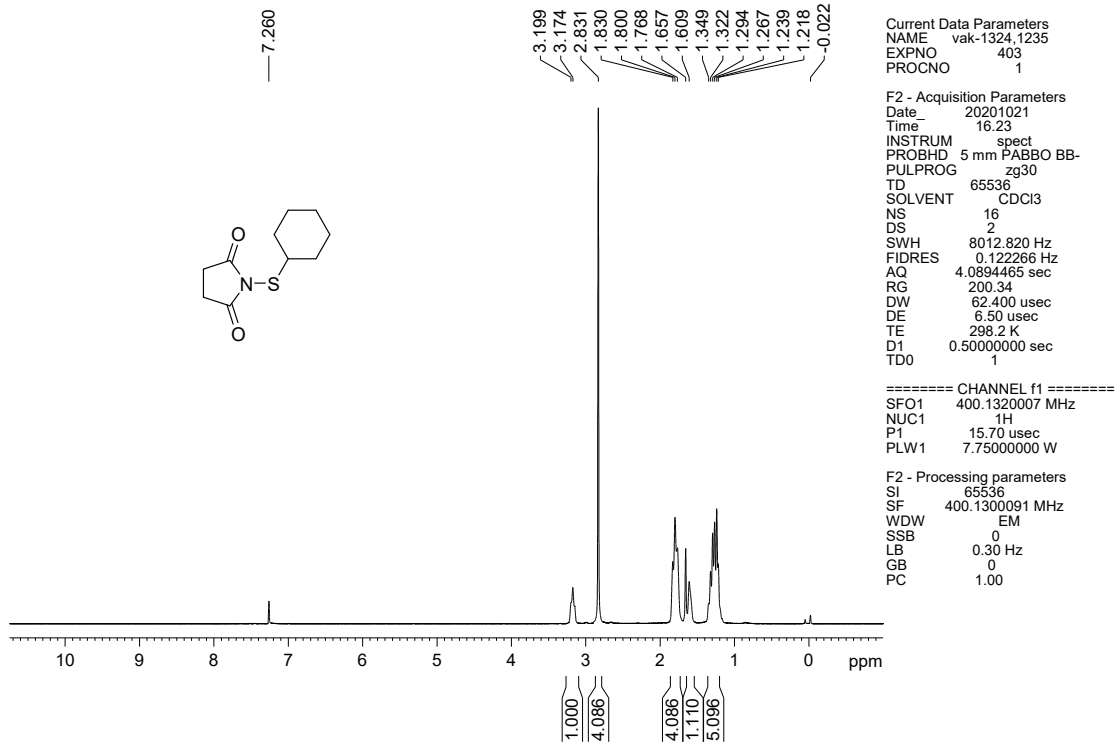


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24˚C):

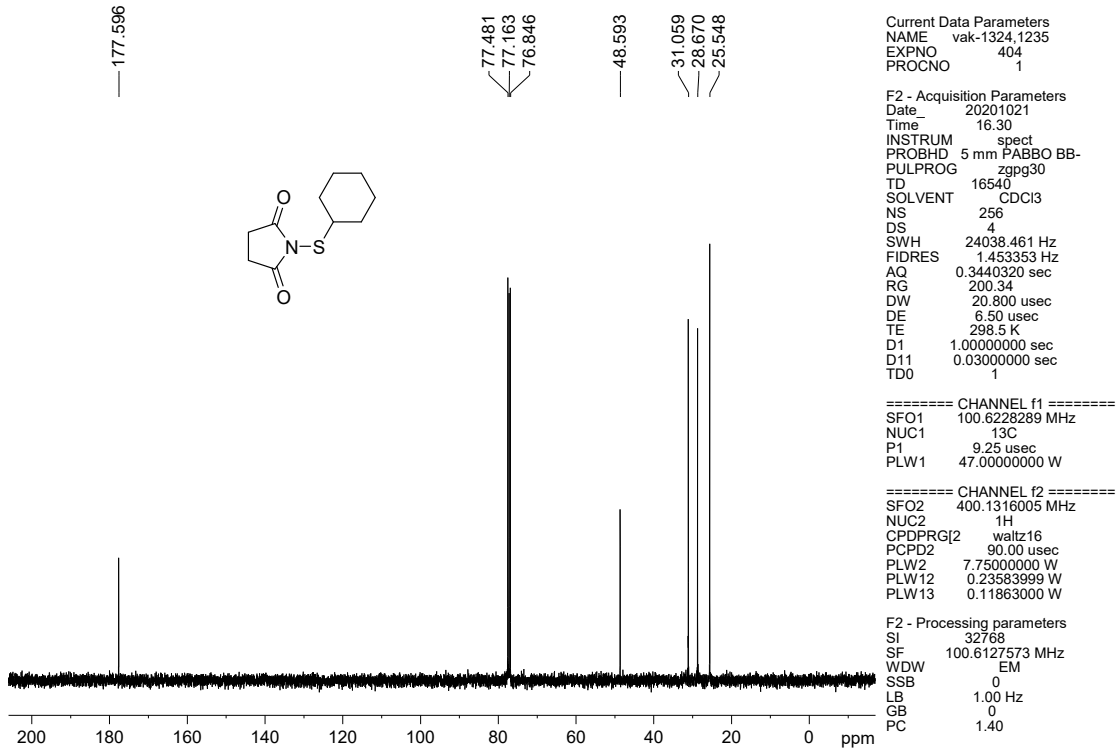


1-(Cyclohexylthio)pyrrolidine-2,5-dione (2n)

^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):

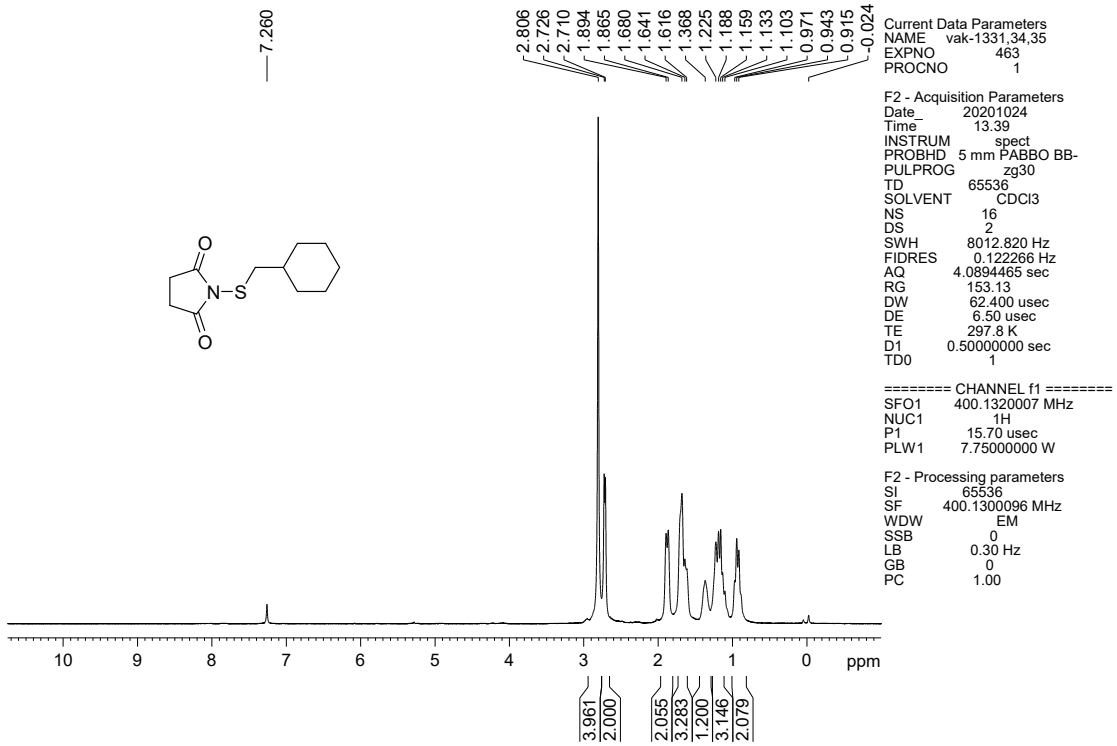


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24˚C):

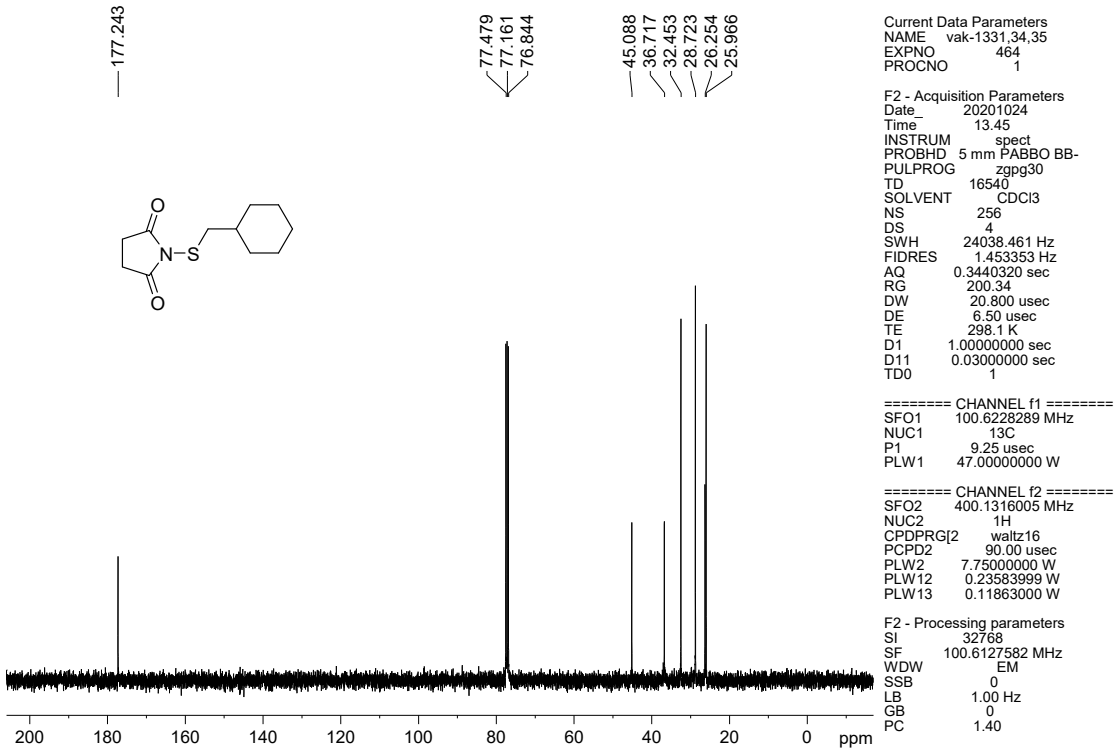


1-((Cyclohexylmethyl)thio)pyrrolidine-2,5-dione (2o)

^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):

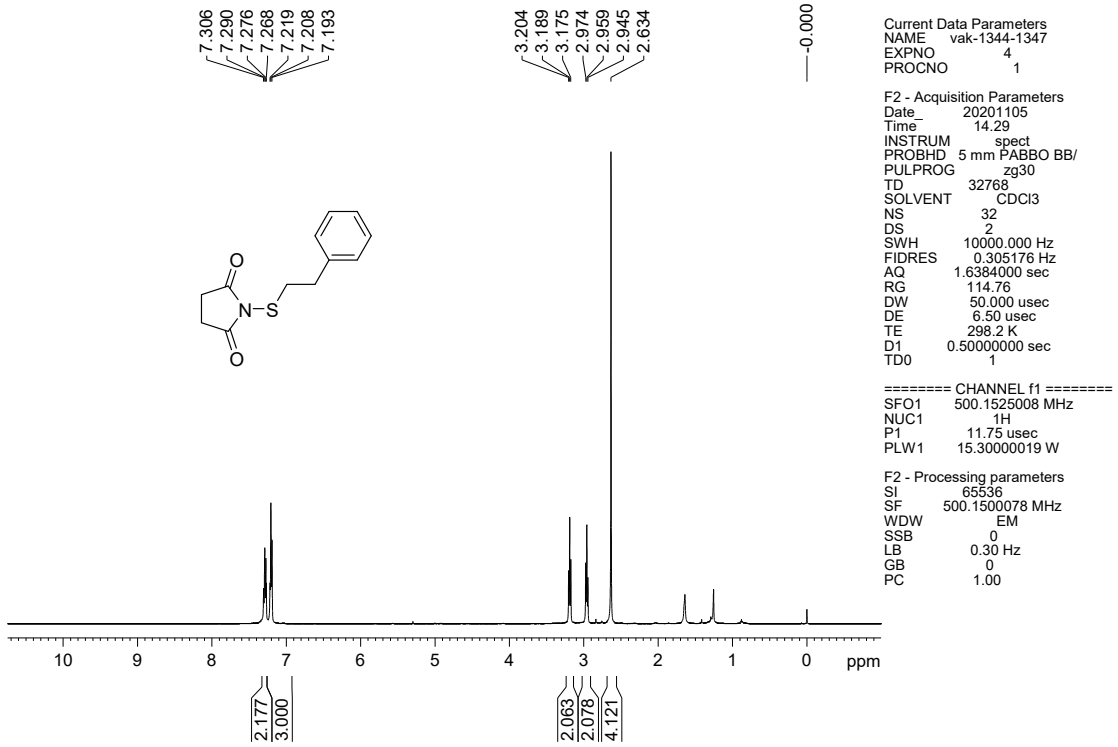


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24˚C):

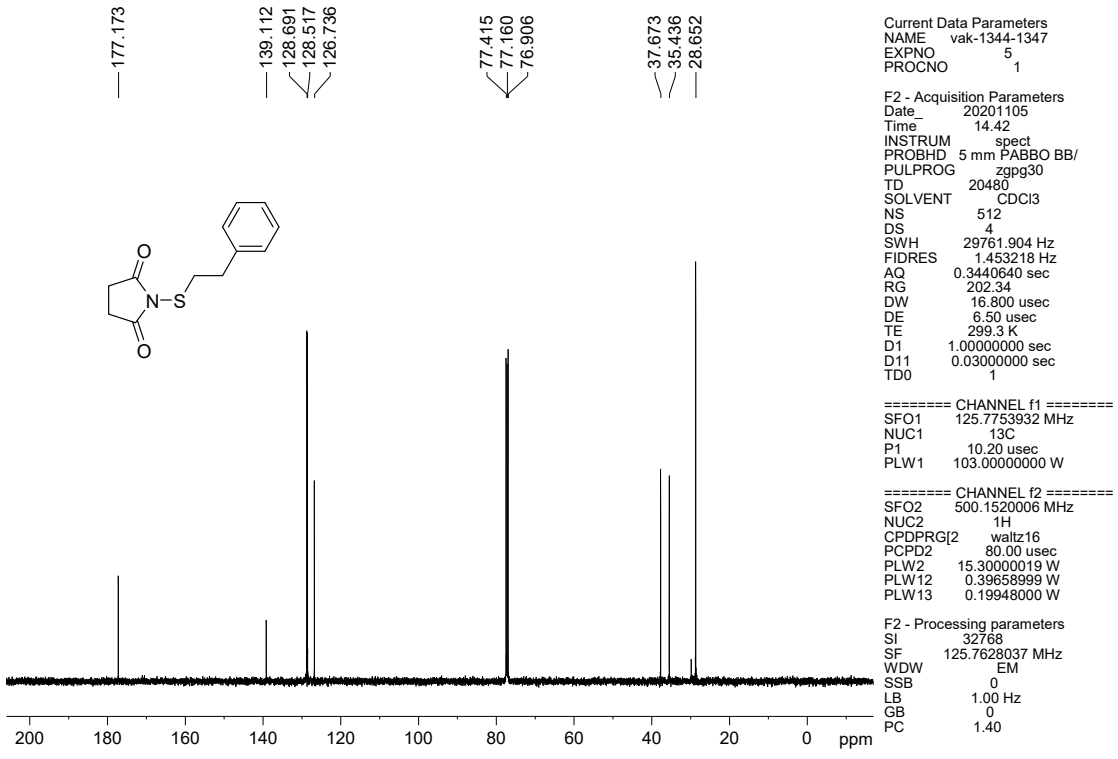


1-(Phenethylthio)pyrrolidine-2,5-dione (2p)

^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):



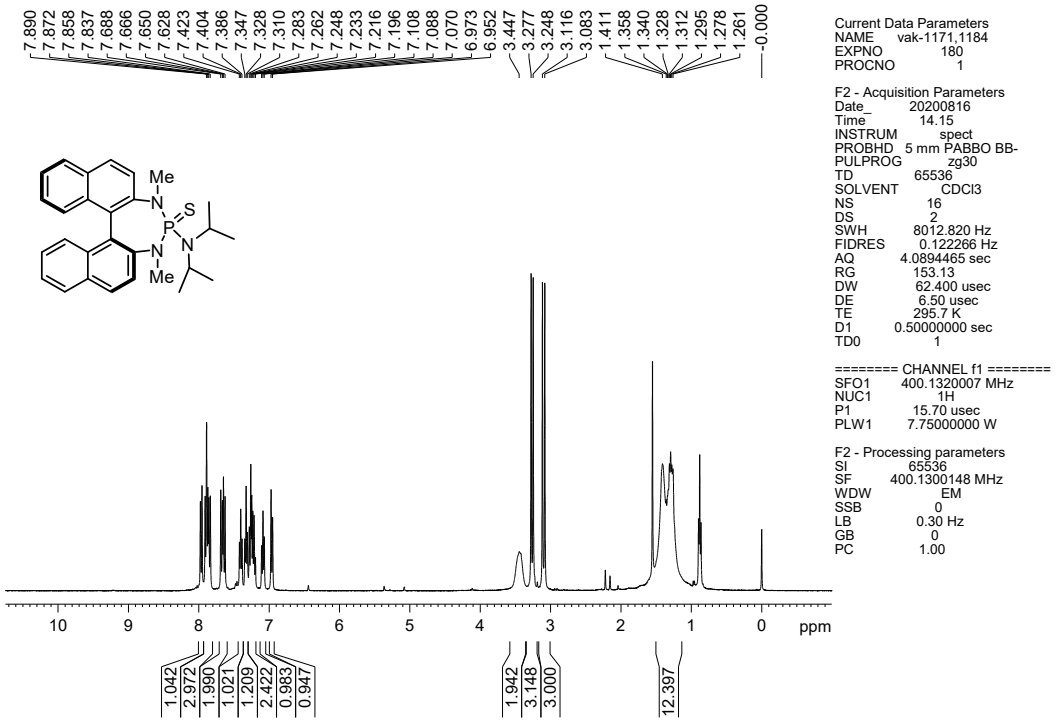
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24˚C):



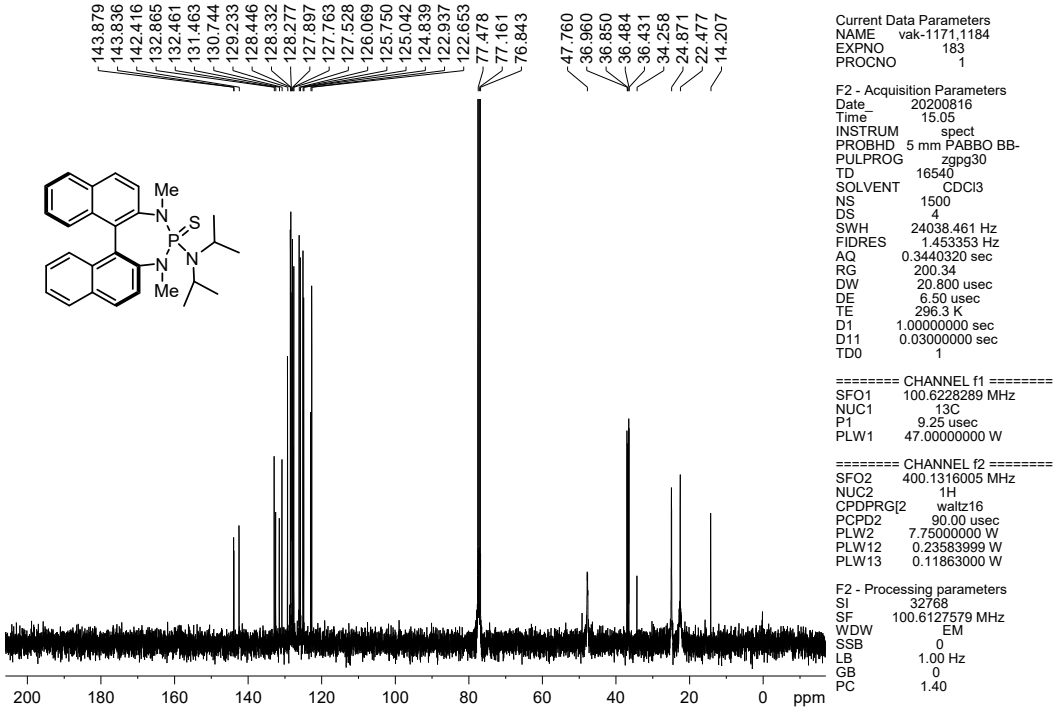
12. NMR spetra of Chiral Lewis-Bases:

(11bS)-4-(Diisopropylamino)-3,5-dimethyl-3,5-dihydrodinaphtho[2,1-d:1',2'-f][1,3,2]diazaphosphepine 4-sulfide (LB1)

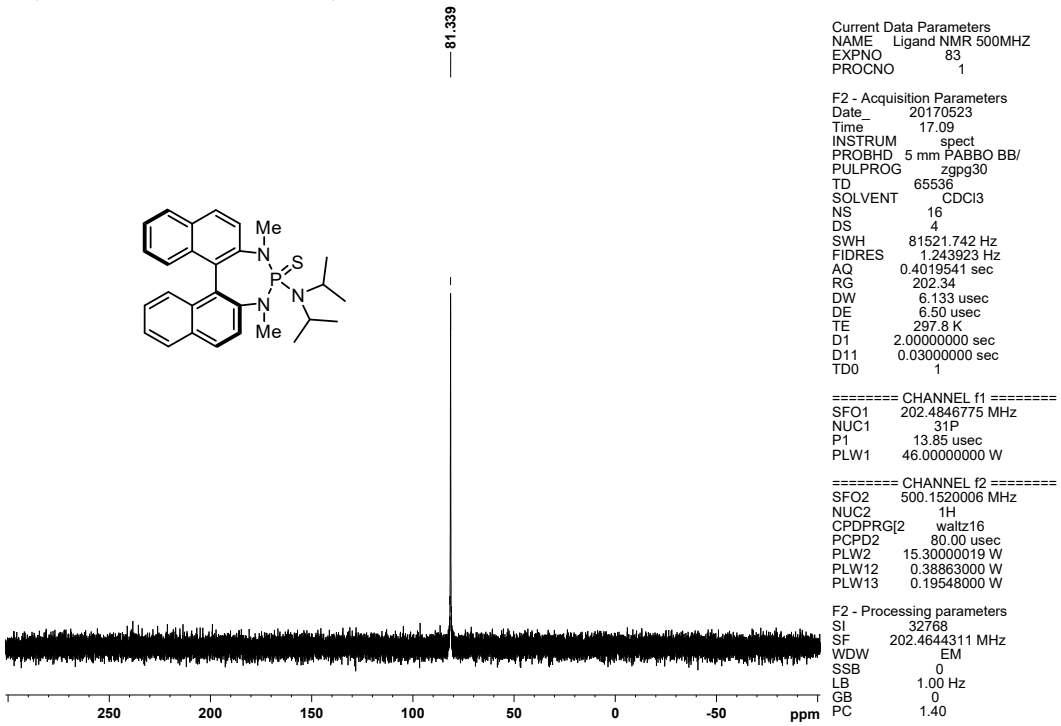
^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24˚C):

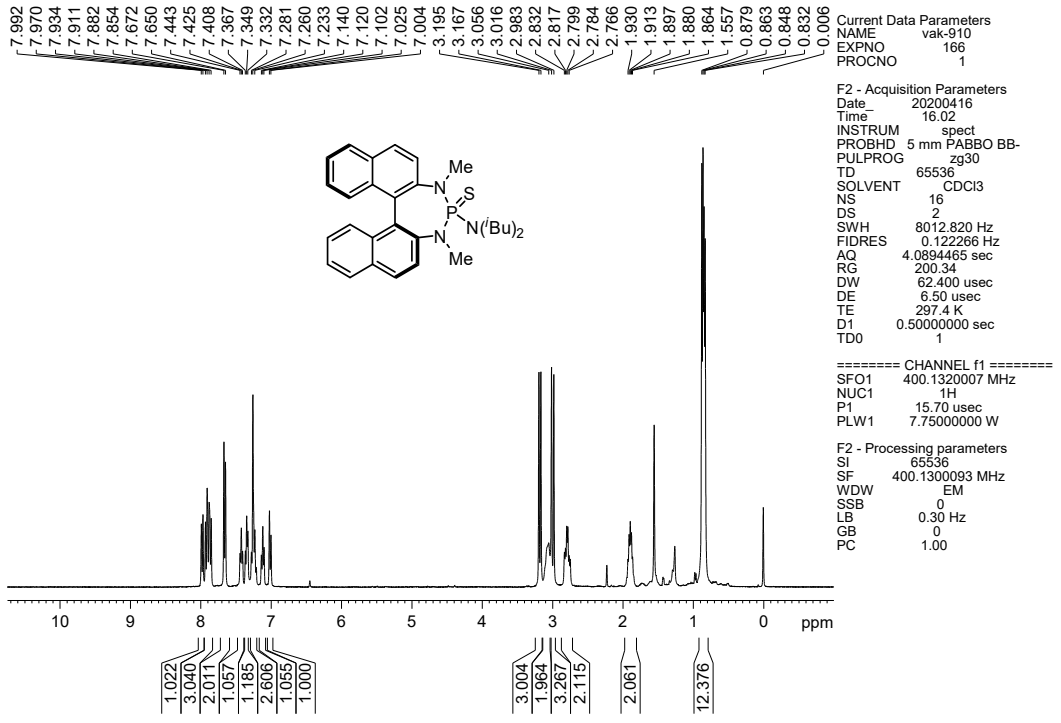


^{31}P NMR (202 MHz, $CDCl_3$, 24 °C):

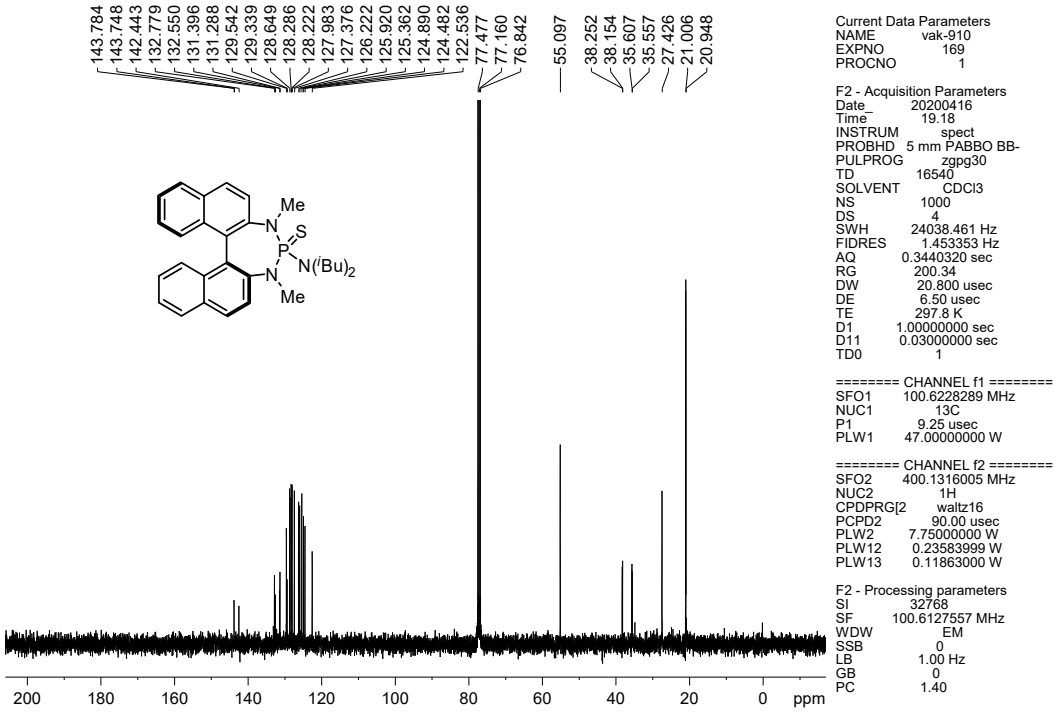


(11bS)-4-(Diisobutylamino)-3,5-dimethyl-3,5-dihydrodinaphtho[2,1-d:1',2'-f][1,3,2]diazaphosphepine 4-sulfide (LB2)

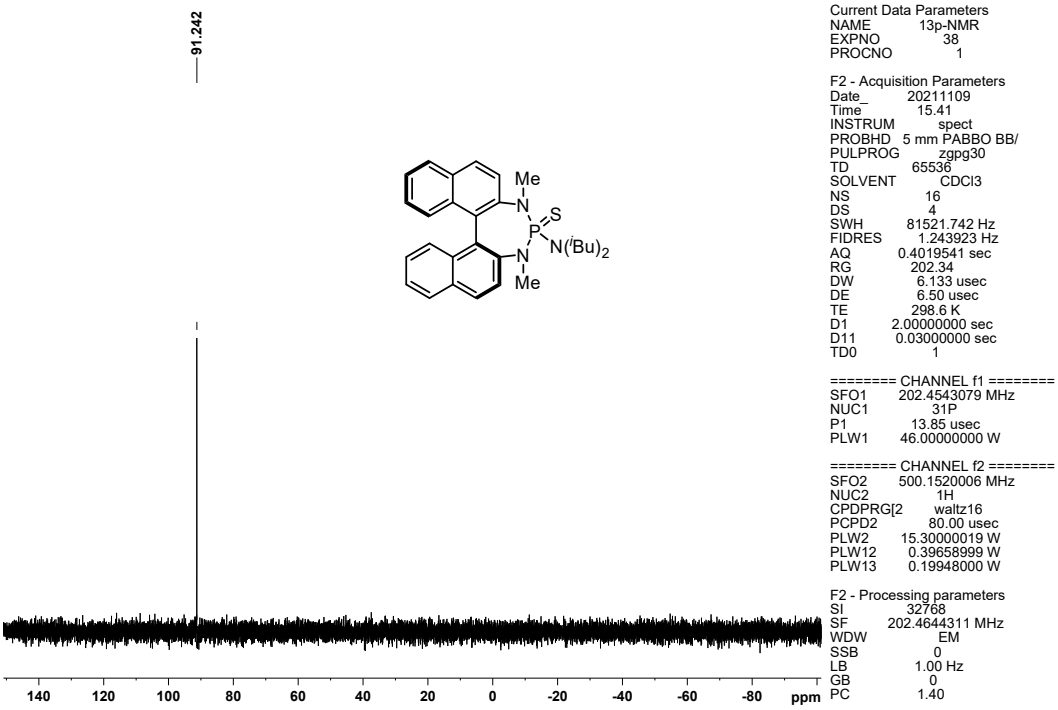
^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24˚C):

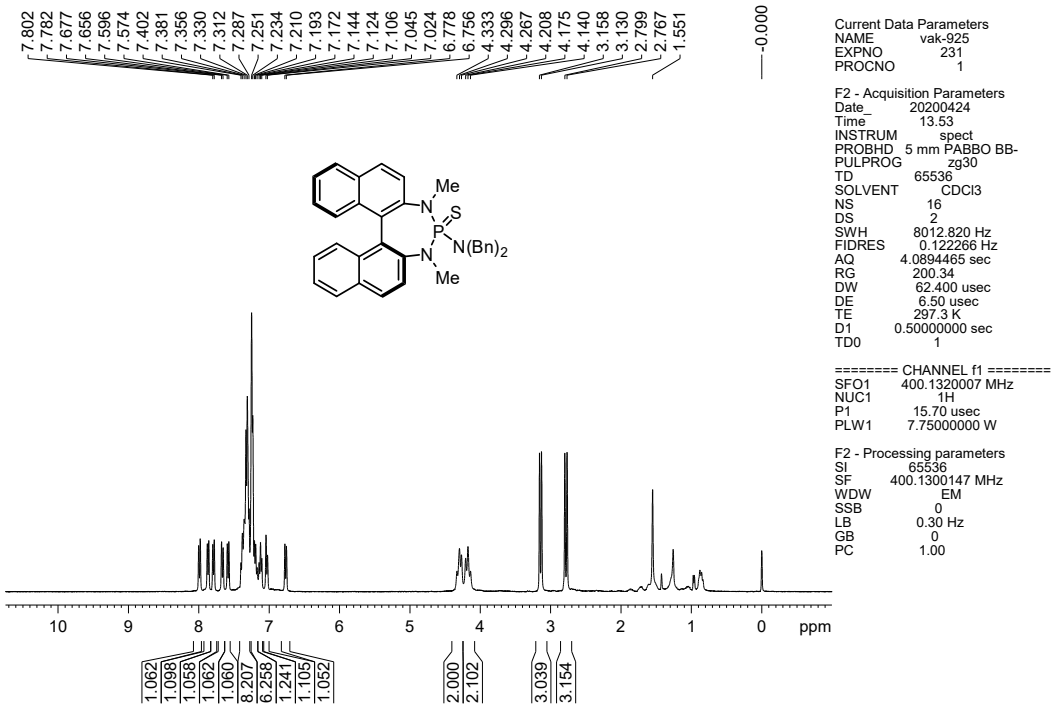


^{31}P NMR (202 MHz, $CDCl_3$, 24 °C):

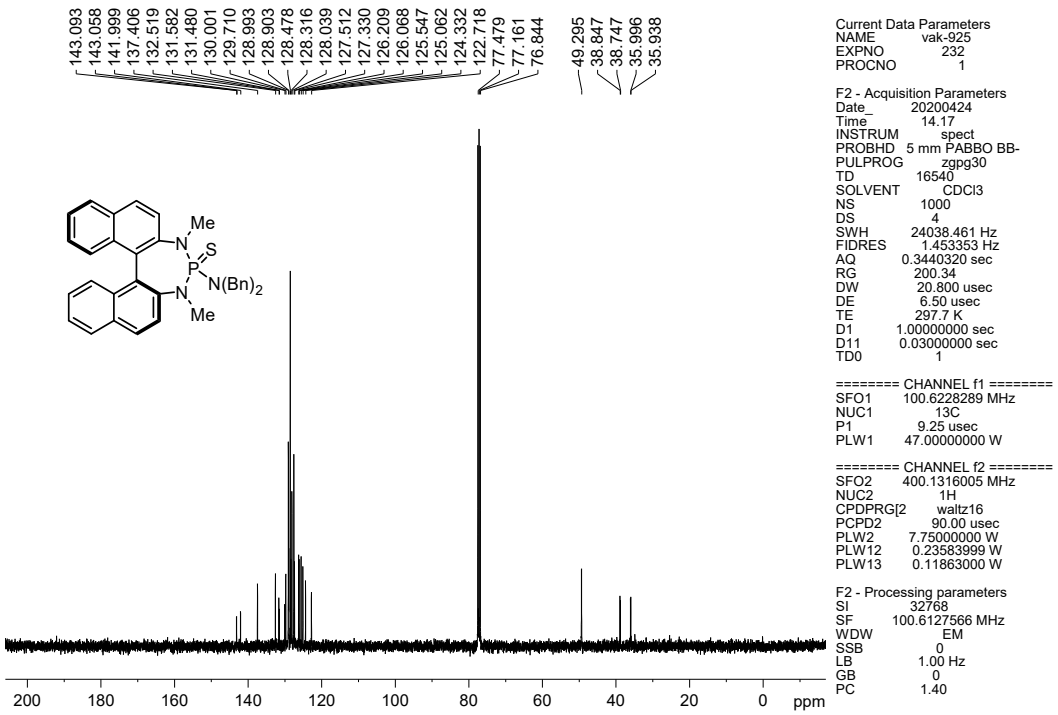


(11bS)-4-(Dibenzylamino)-3,5-dimethyl-3,5-dihydrodinaphtho[2,1-d:1',2'-f][1,3,2]diazaphosphepine 4-sulfide (LB3)

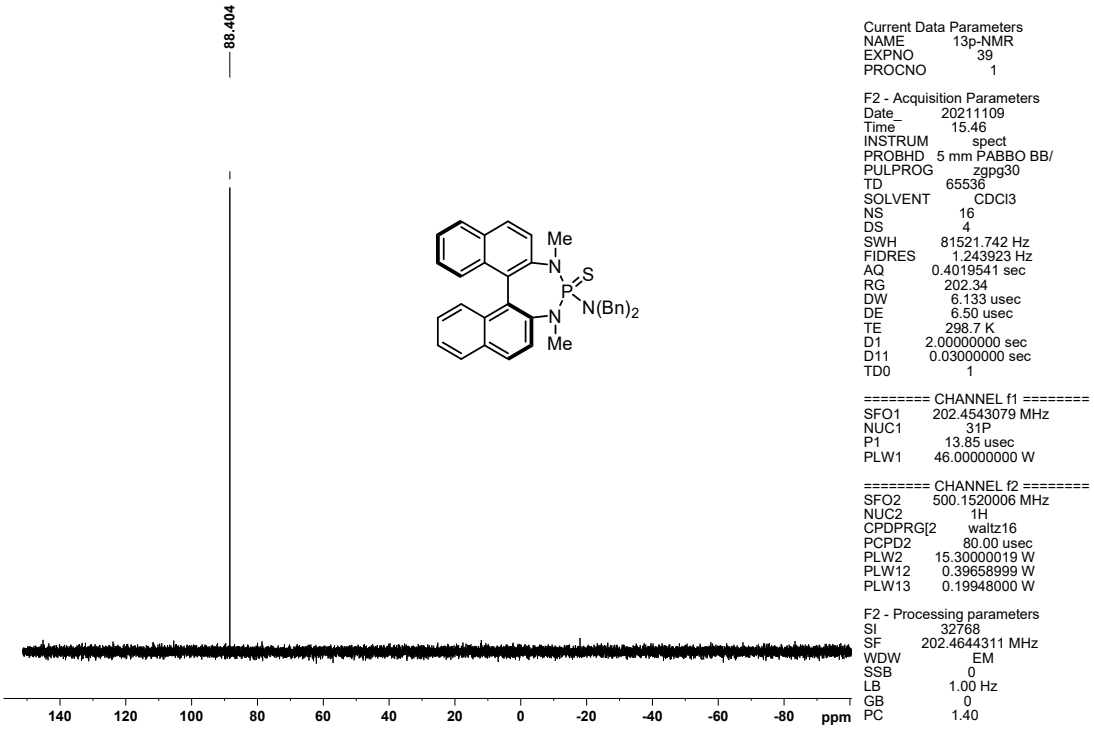
^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24˚C):

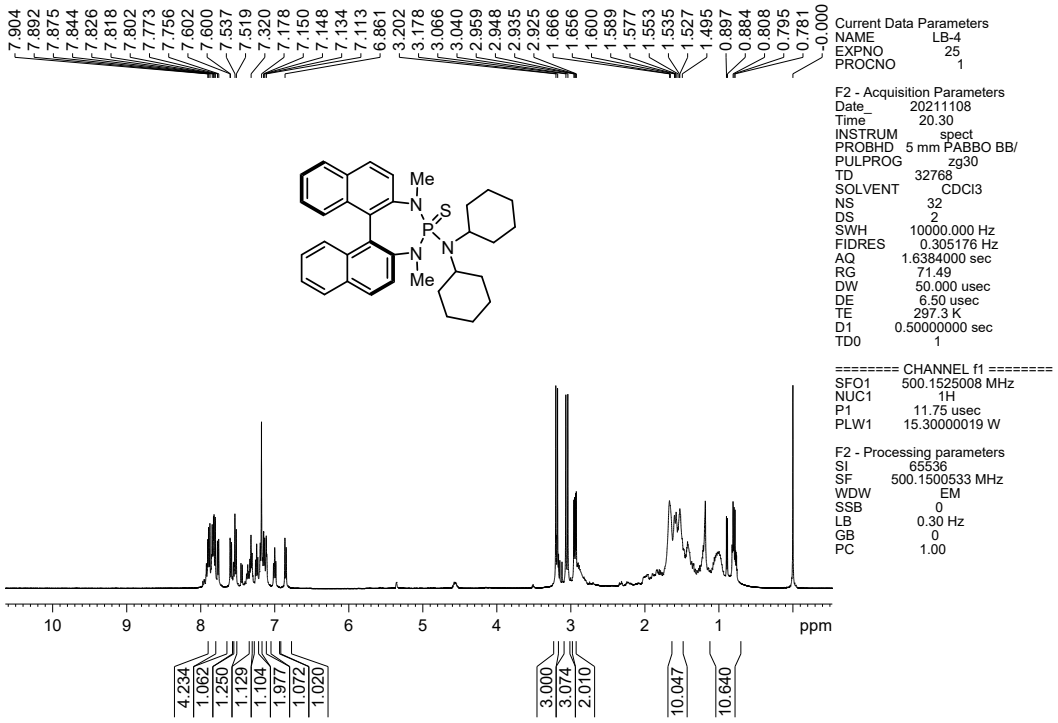


^{31}P NMR (202 MHz, $CDCl_3$, 24 °C):

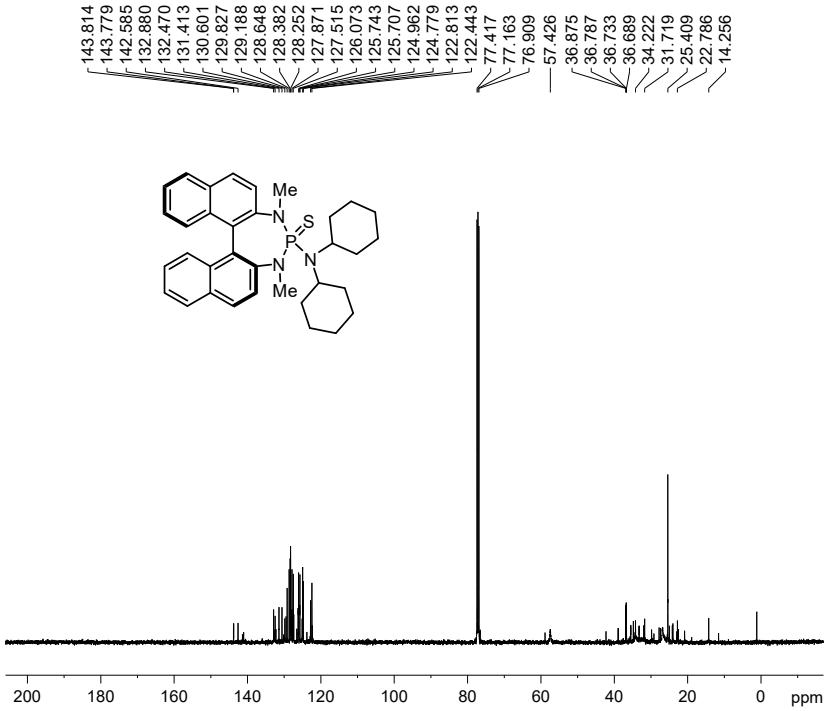


(11bS)-4-(Dicyclohexylamino)-3,5-dimethyl-3,5-dihydrodinaphtho[2,1-d:1',2'-f][1,3,2]diazaphosphepine 4-sulfide (LB4)

^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24˚C):



Current Data Parameters
NAME LB-4
EXPNO 26
PROCNO 1

F2 - Acquisition Parameters
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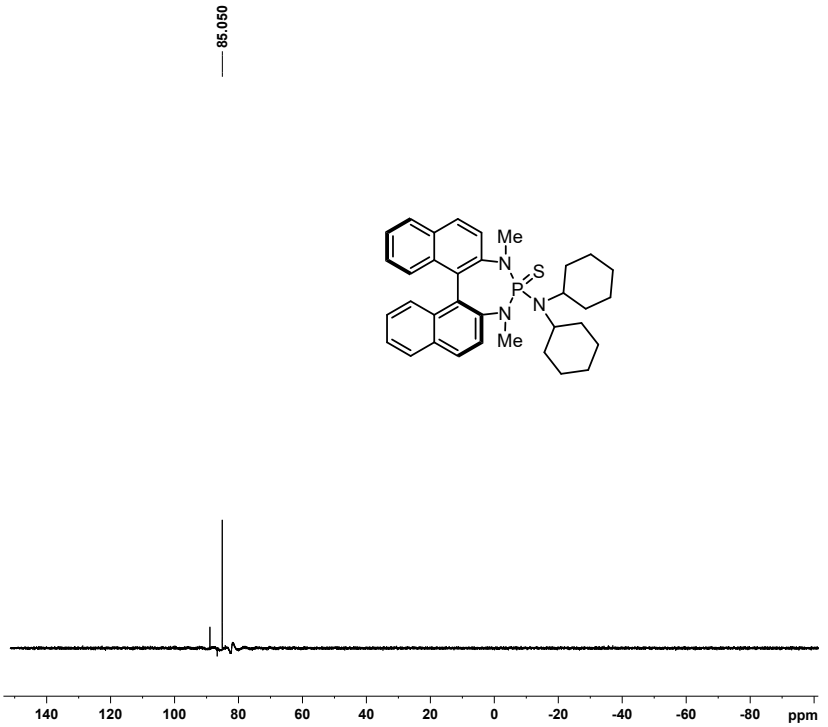
Time 21.18
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 20480
SOLVENT CDCl3
NS 2000
DS 4
SWH 29761.904 Hz
FIDRES 1.453218 Hz
AQ 0.3440640 sec
RG 202.34
DW 16.800 usec
DE 6.50 usec
TE 297.8 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 125.7753932 MHz
NUC1 13C
P1 10.20 usec
PLW1 103.00000000 W

======== CHANNEL f2 ========
SFO2 500.1520006 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 15.30000019 W
PLW12 0.39658999 W
PLW13 0.19948000 W

F2 - Processing parameters
SI 32768
SF 125.7628038 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

^{31}P NMR (202 MHz, $CDCl_3$, 24 °C):



Current Data Parameters
NAME 13p-NMR
EXPNO 29
PROCNO 1

F2 - Acquisition Parameters
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Time 14.58
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 16
DS 4
SWH 81521.742 Hz
FIDRES 1.243923 Hz
AQ 0.4019541 sec
RG 202.34
DW 6.133 usec
DE 6.50 usec
TE 298.5 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

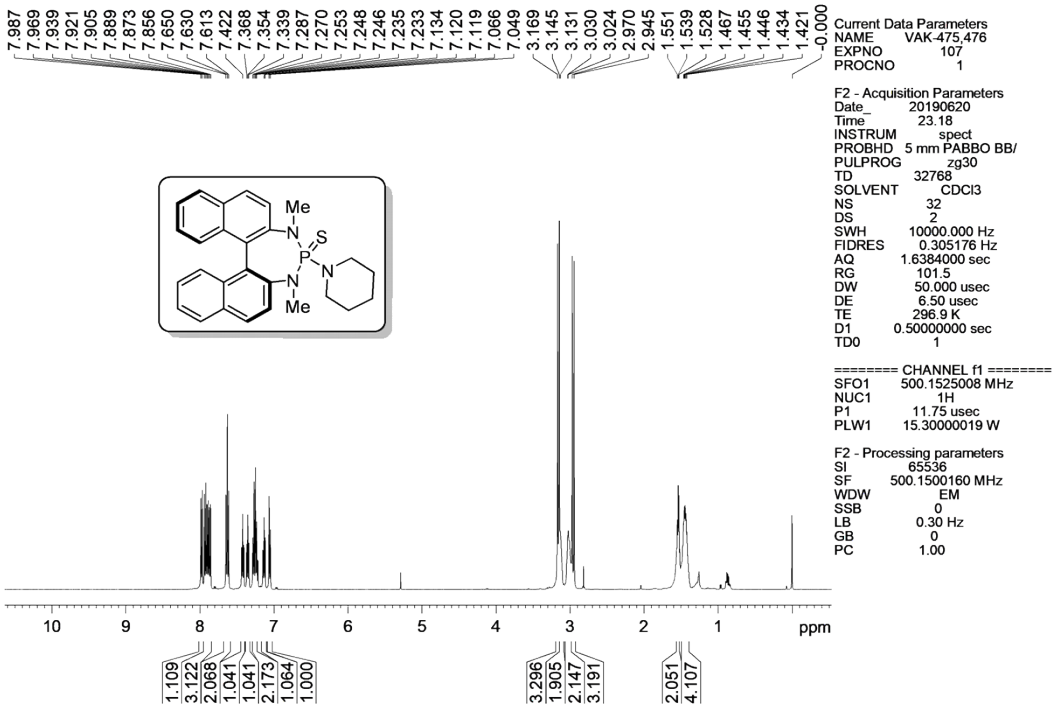
======== CHANNEL f1 ========
SFO1 202.4543079 MHz
NUC1 31P
P1 13.85 usec
PLW1 46.00000000 W

======== CHANNEL f2 ========
SFO2 500.1520006 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 15.30000019 W
PLW12 0.39658999 W
PLW13 0.19948000 W

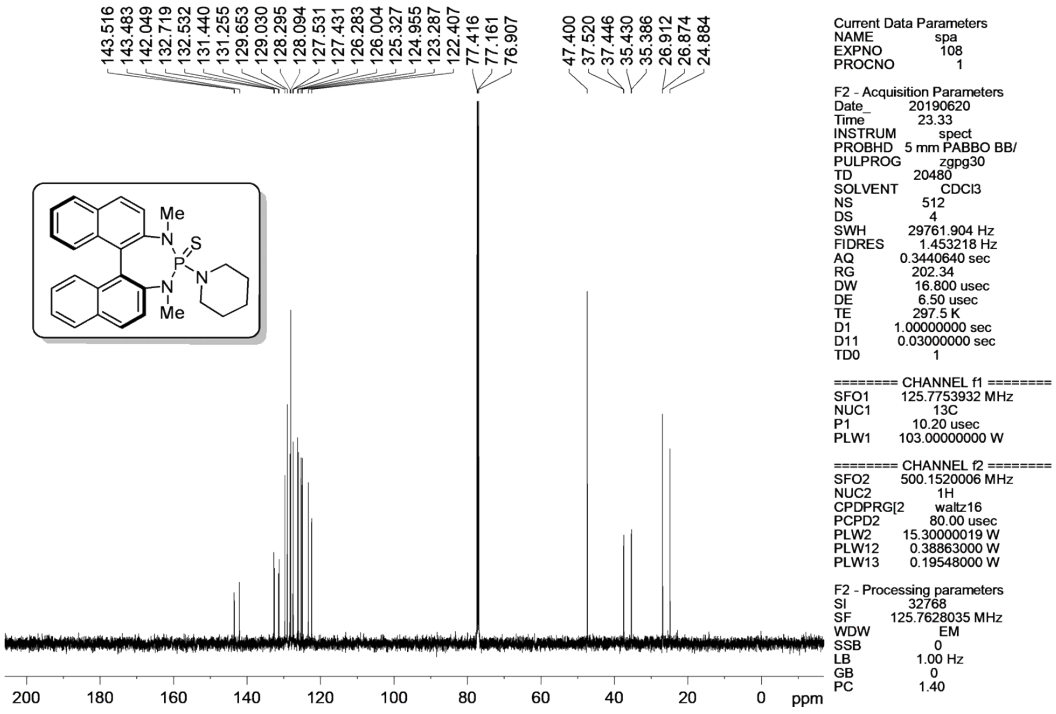
F2 - Processing parameters
SI 32768
SF 202.4644311 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

4-(Piperidin-1-yl)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine 4-sulfide (LB5)

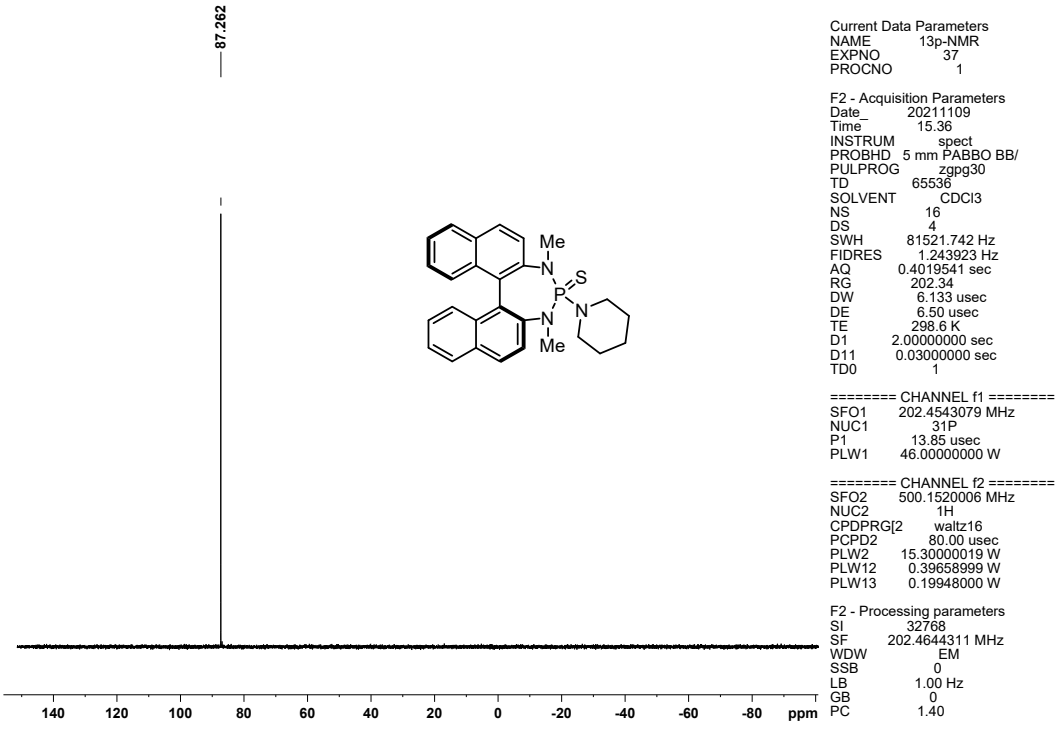
^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24˚C):

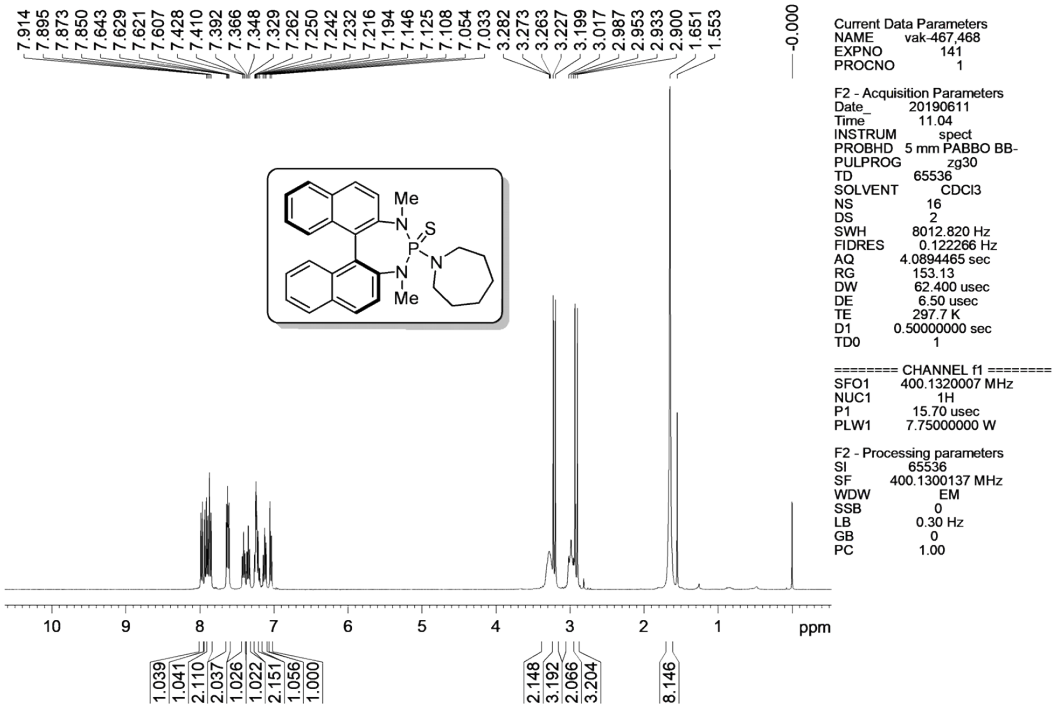


^{31}P NMR (202 MHz, $CDCl_3$, 24 °C):

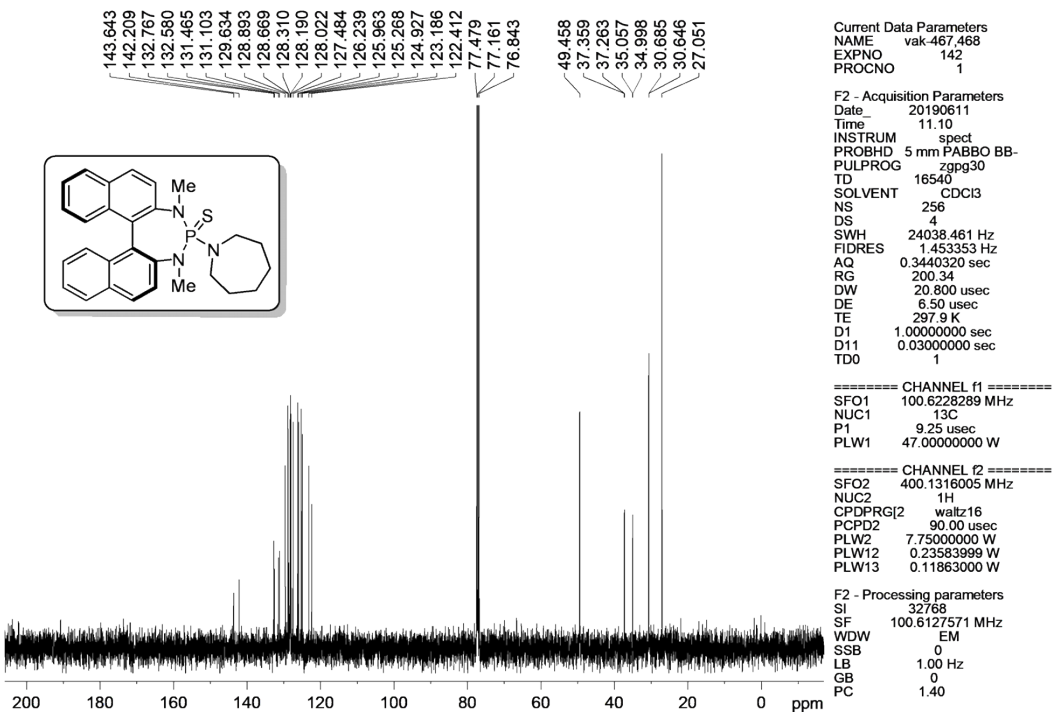


(11bS)-4-(Azepan-1-yl)-3,5-dimethyl-3,5-dihydrodinaphtho[2,1-d:1',2'-f][1,3,2]diazaphosphepine 4-sulfide (LB6)

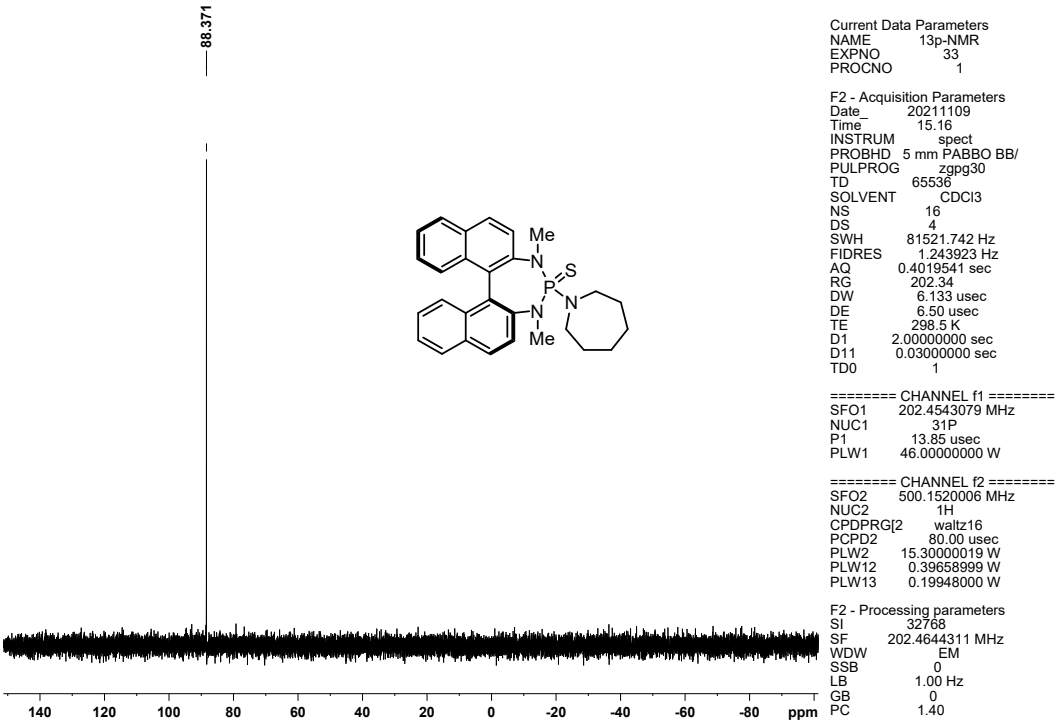
^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24˚C):

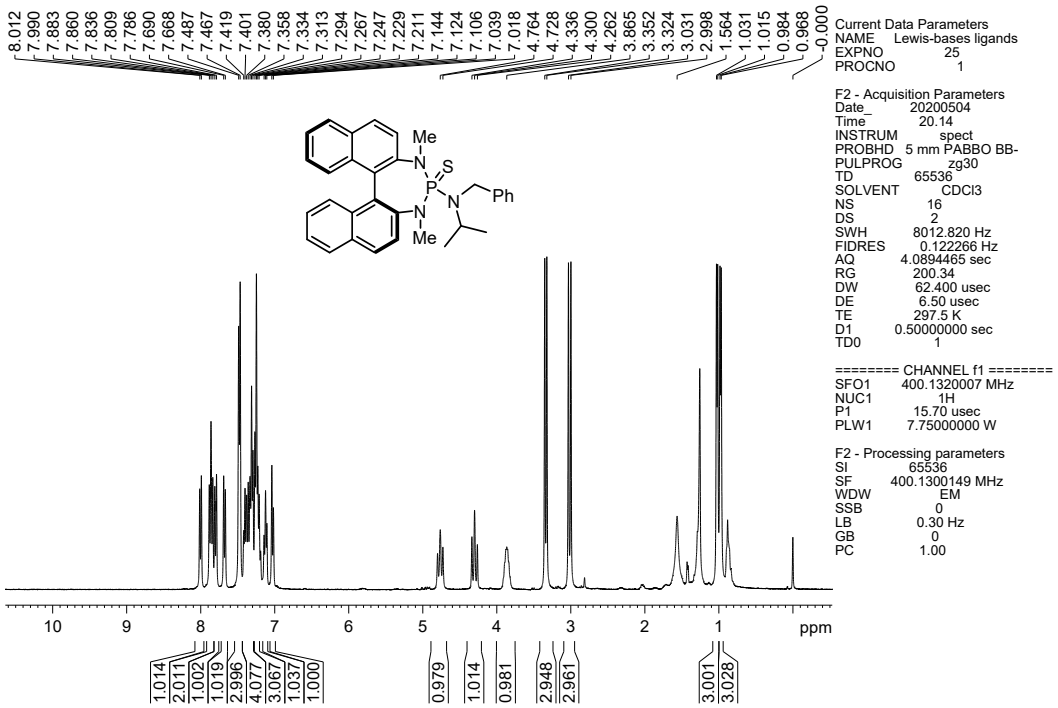


^{31}P NMR (202 MHz, $CDCl_3$, 24 °C):

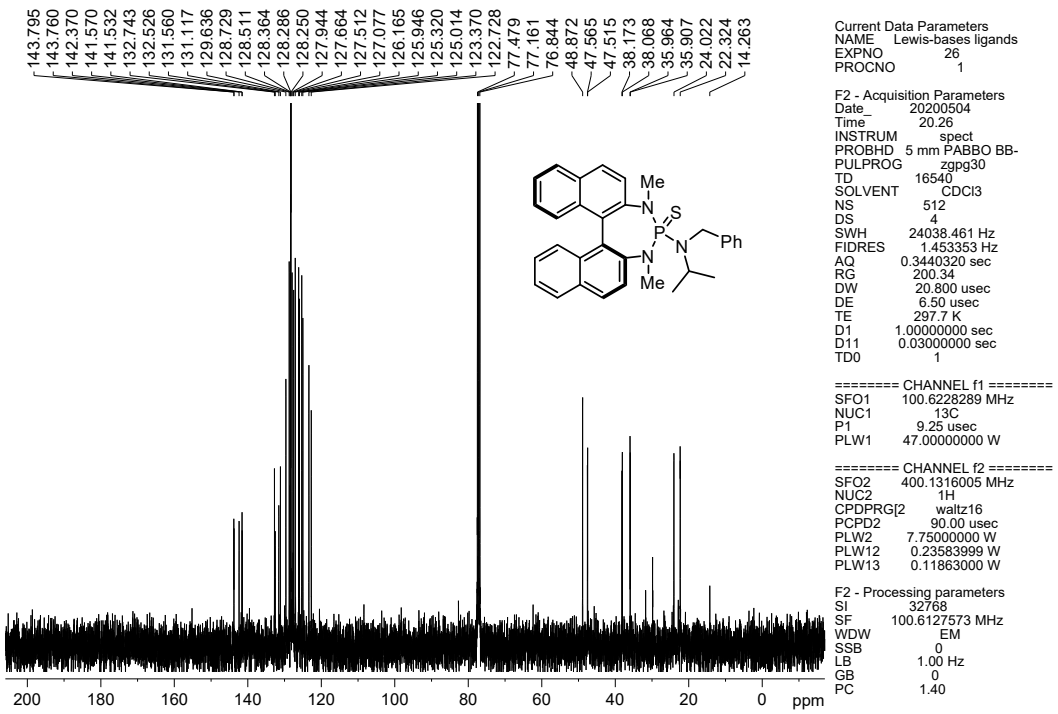


(11bS)-4-(Benzyl(isopropyl)amino)-3,5-dimethyl-3,5-dihydrodinaphtho[2,1-d:1',2'-f][1,3,2]diazaphosphepine 4-sulfide (LB7)

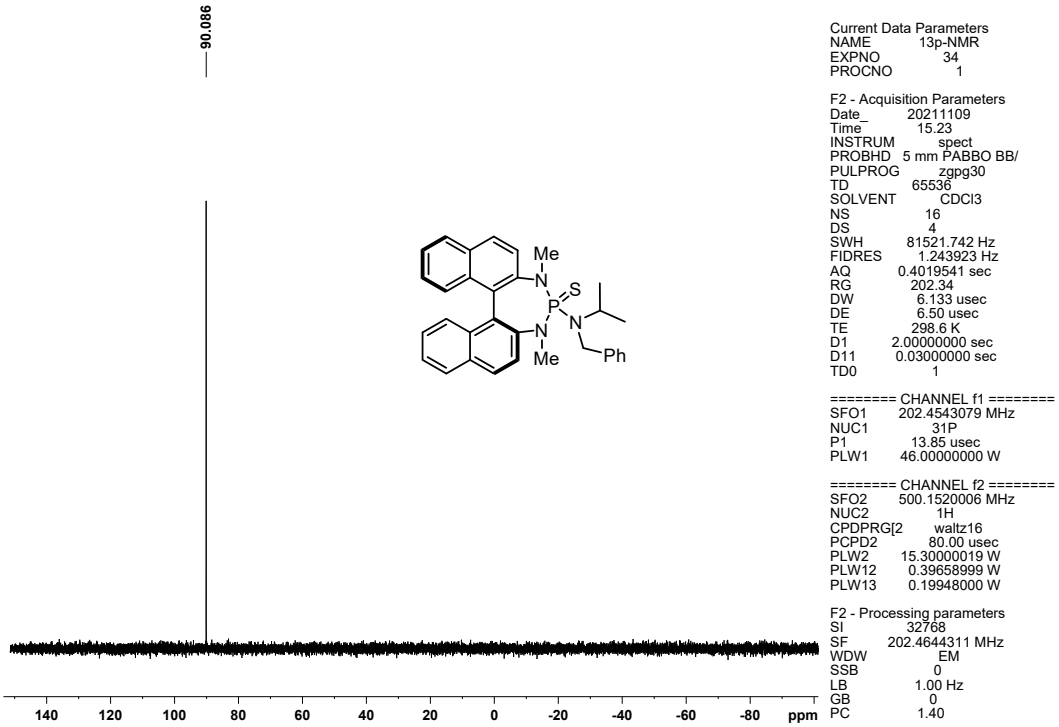
^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24˚C):

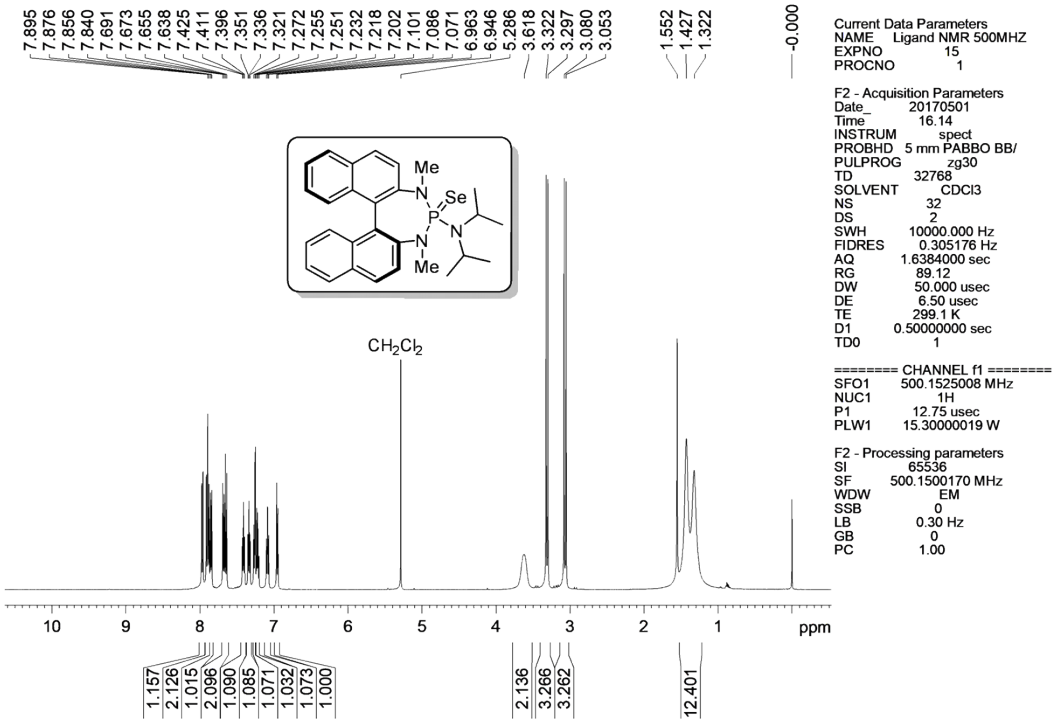


^{31}P NMR (202 MHz, $CDCl_3$, 24 °C):

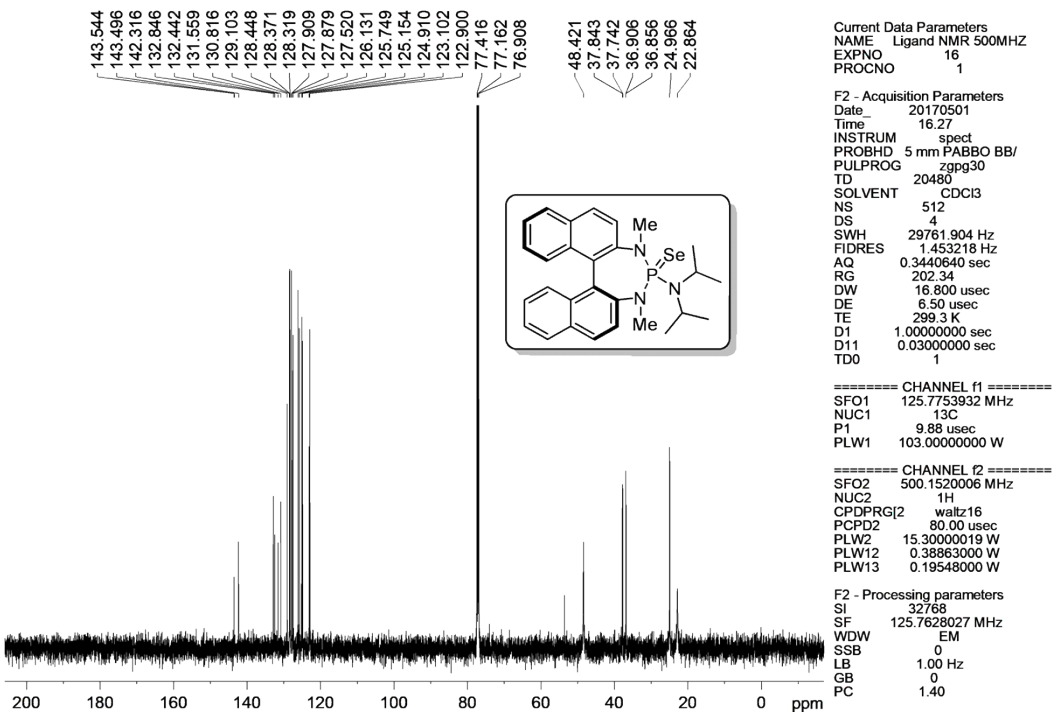


(11bS)-4-(Diisopropylamino)-3,5-dimethyl-3,5-dihydrodinaphtho[2,1-d:1',2'-f][1,3,2]diazaphosphepine 4-selenide (LB8)

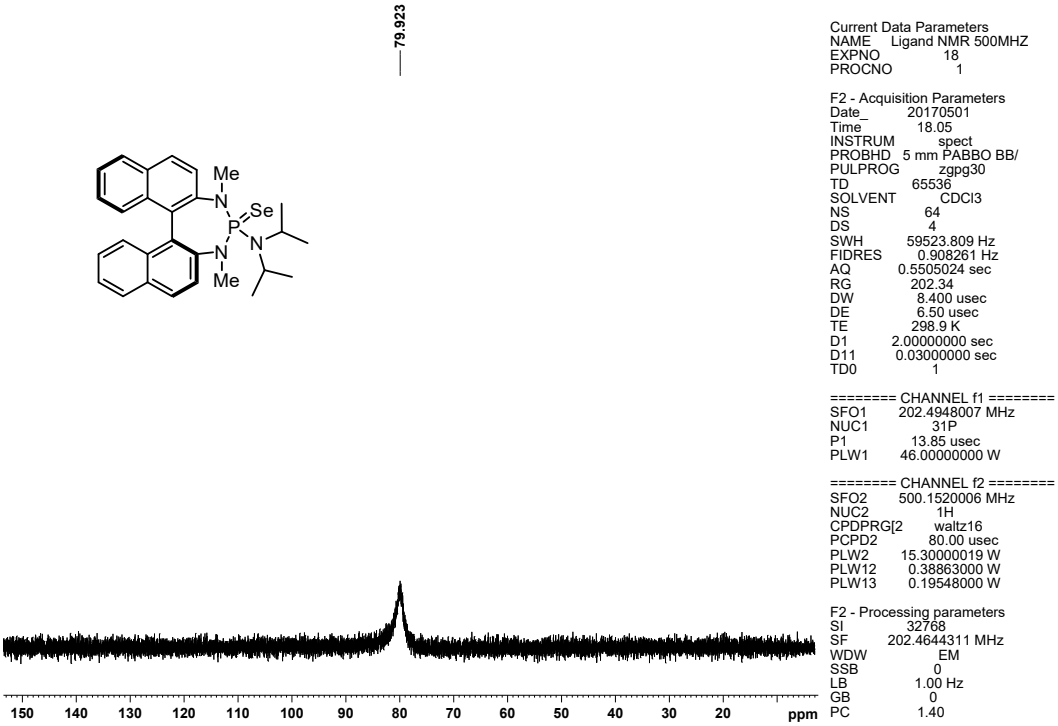
^{1}H NMR (400 MHz, $CDCl_3$, 24°C):



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24˚C):

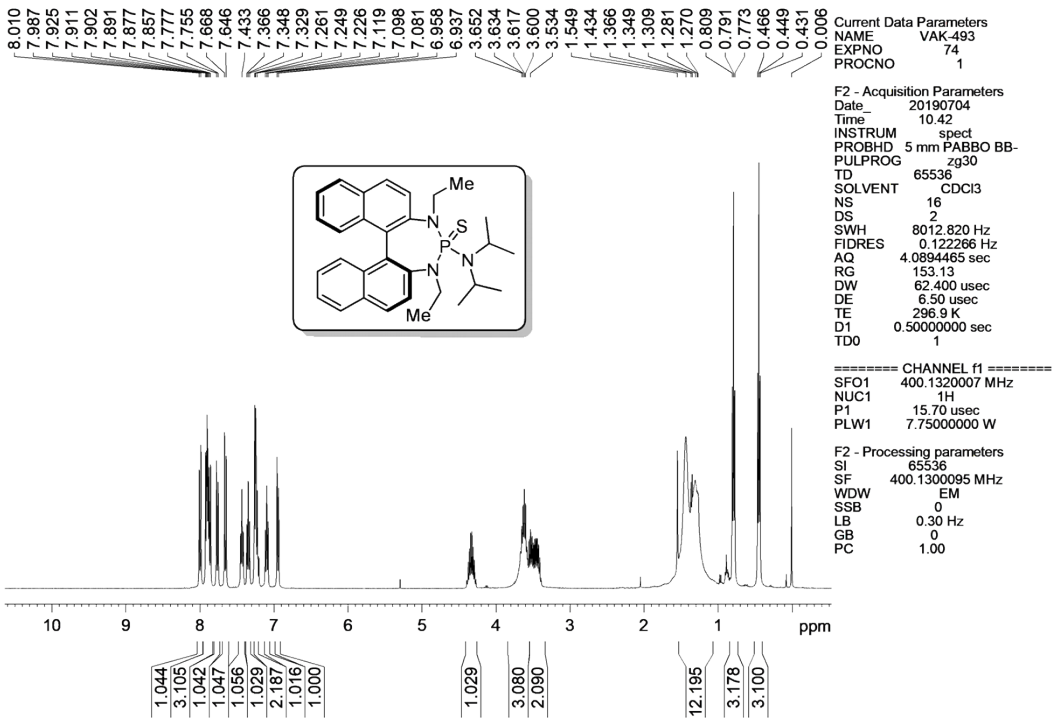


^{31}P NMR (202 MHz, $CDCl_3$, 24 °C):



(11bS)-4-(Diisopropylamino)-3,5-diethyl-3,5-dihydrodinaphtho[2,1-d:1',2'-f][1,3,2]diazaphosphepine 4-sulfide (LB9)

^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):



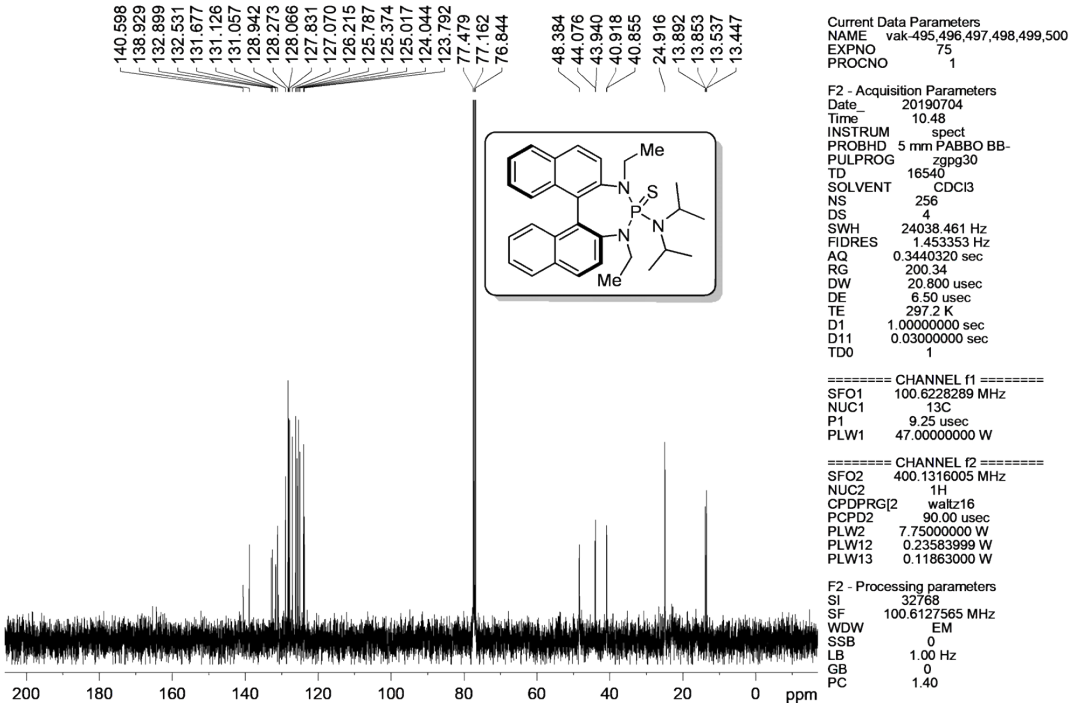
Current Data Parameters
NAME VAK-493
EXPNO 74
PROCNO 1

F2 - Acquisition Parameters
Date_ 20190704
Time 10.42
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894465 sec
RG 153.13
DW 62.400 usec
DE 6.50 usec
TE 296.9 K
D1 0.50000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 400.1320007 MHz
NUC1 1H
P1 15.70 usec
PLW1 7.75000000 W

F2 - Processing parameters
SI 65536
SF 400.1300095 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24˚C):



Current Data Parameters
NAME vak-495,496,497,498,499,500
EXPNO 75
PROCNO 1

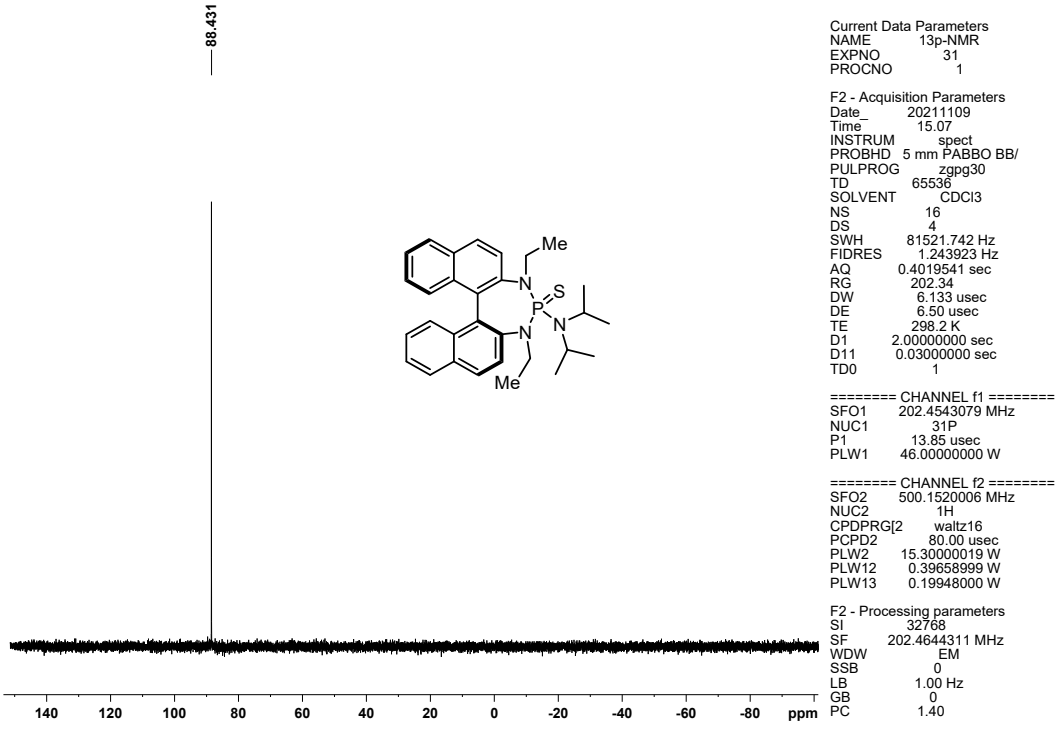
F2 - Acquisition Parameters
Date_ 20190704
Time 10.48
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 16540
SOLVENT CDCl3
NS 256
DS 4
SWH 24038.461 Hz
FIDRES 1.453353 Hz
AQ 0.3440320 sec
RG 200.34
DW 20.800 usec
DE 6.50 usec
TE 297.2 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 100.6228289 MHz
NUC1 13C
P1 9.25 usec
PLW1 47.00000000 W

======== CHANNEL f2 ========
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 7.75000000 W
PLW12 0.23583999 W
PLW13 0.11863000 W

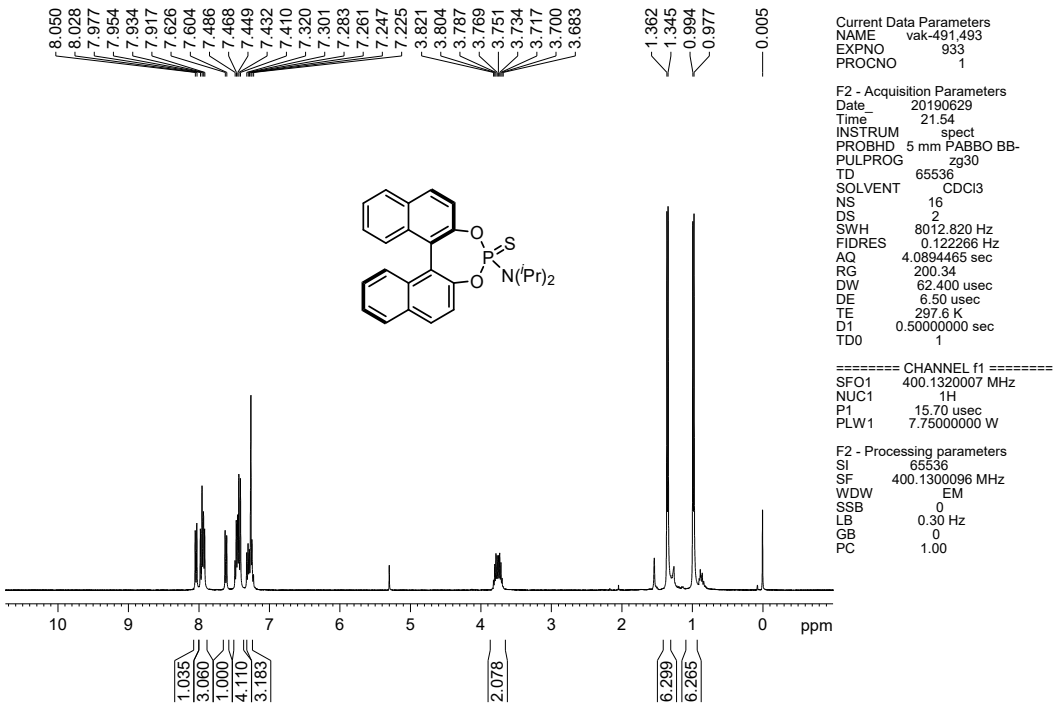
F2 - Processing parameters
SI 32768
SF 100.6127565 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

^{31}P NMR (202 MHz, $CDCl_3$, 24 °C):

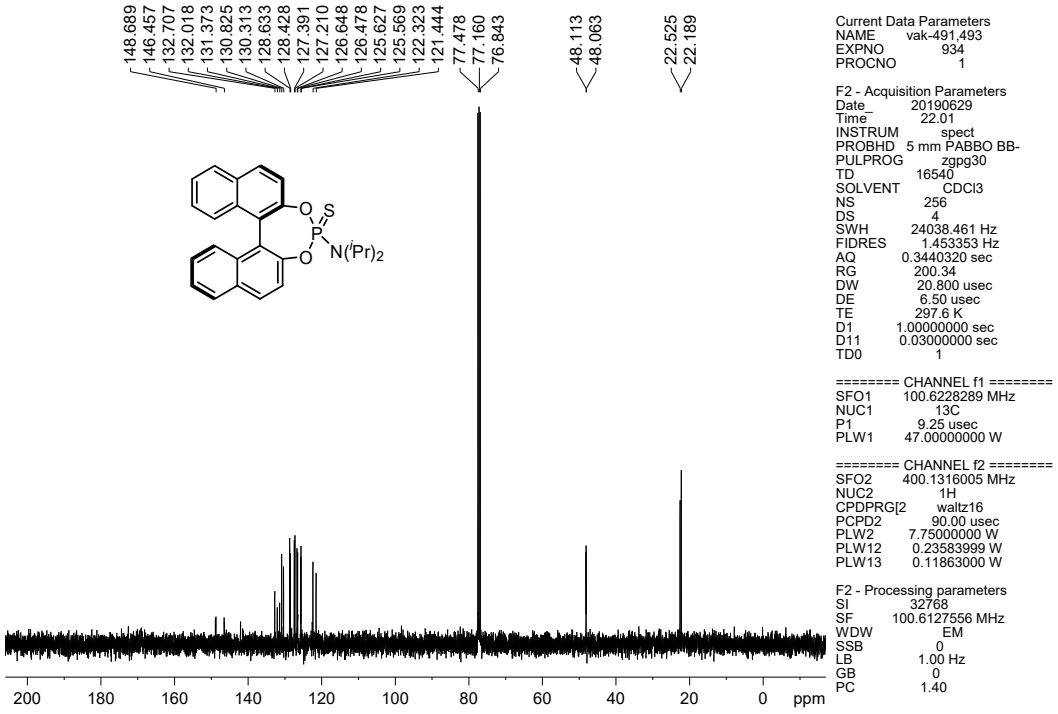


4-(Diisopropylamino)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine 4-sulfide (LB10)

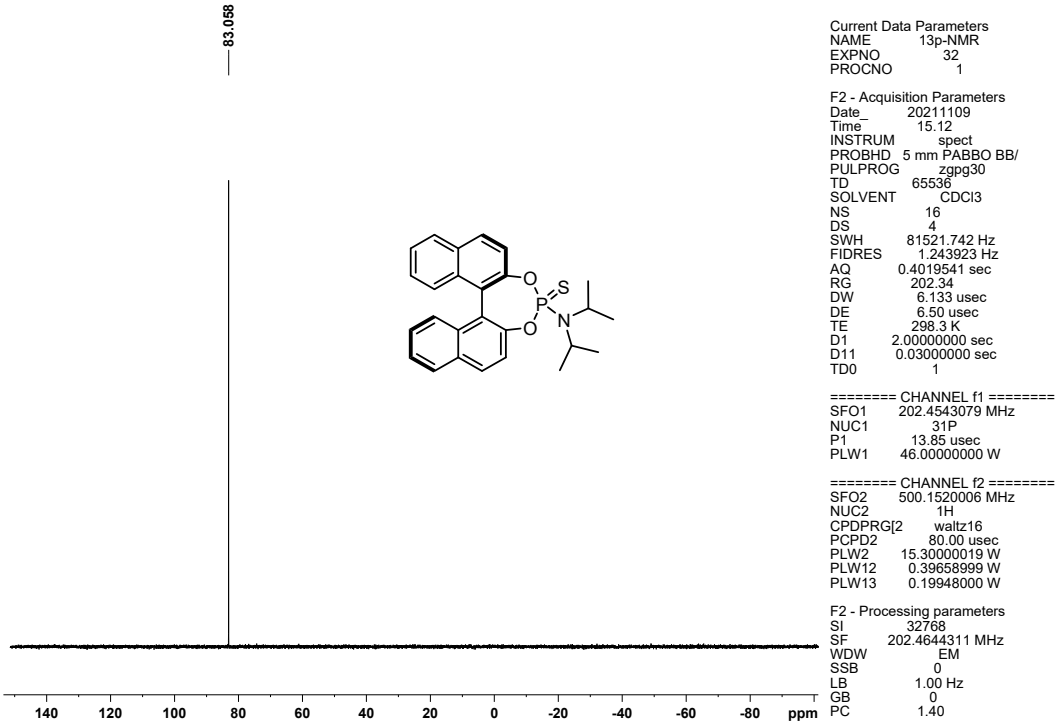
^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24˚C):

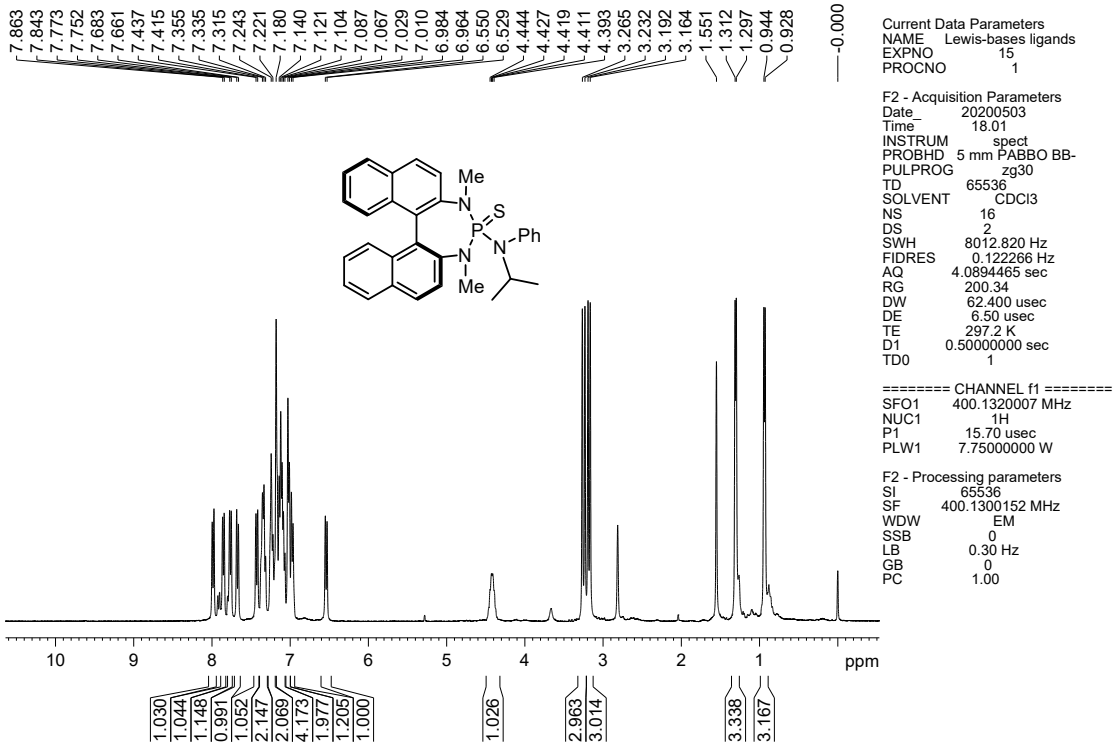


^{31}P NMR (202 MHz, $CDCl_3$, 24 °C):

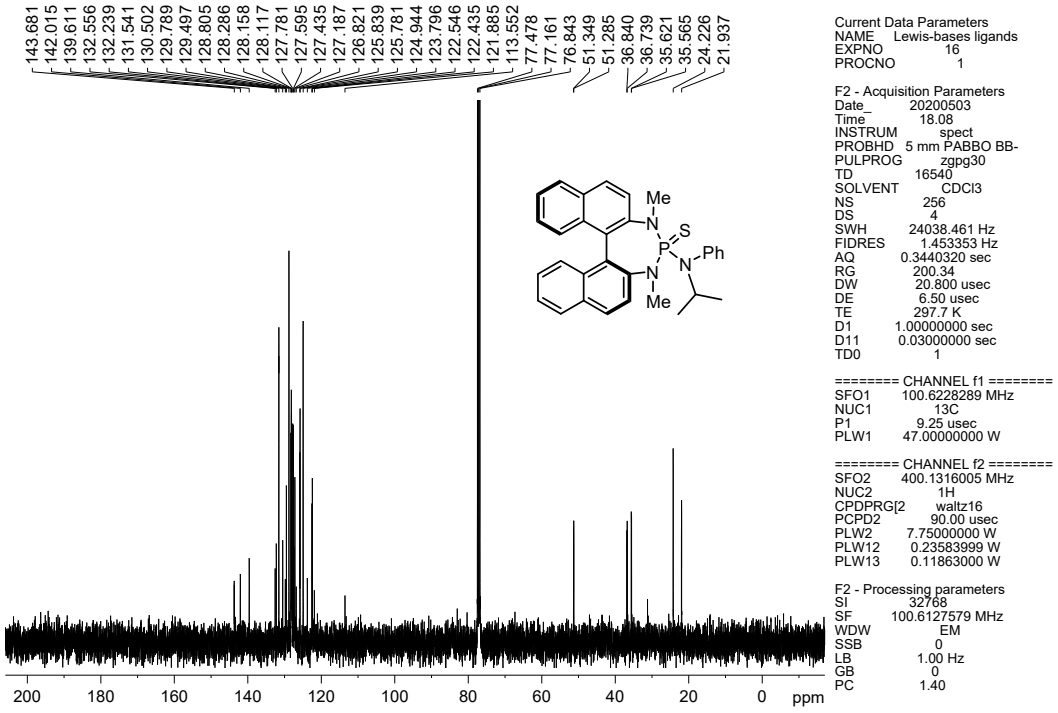


(11bS)-4-(Isopropyl(phenyl)amino)-3,5-dimethyl-3,5-dihydrodinaphtho[2,1-d:1',2'-f][1,3,2]diazaphosphepine 4-sulfide (LB11)

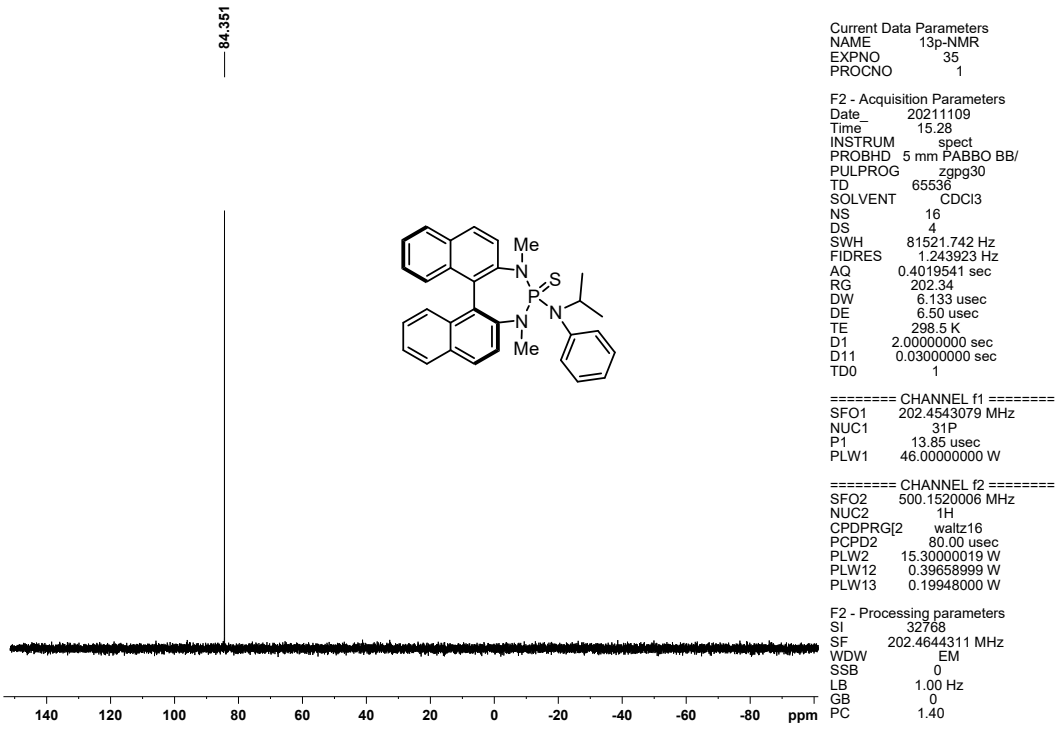
^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):



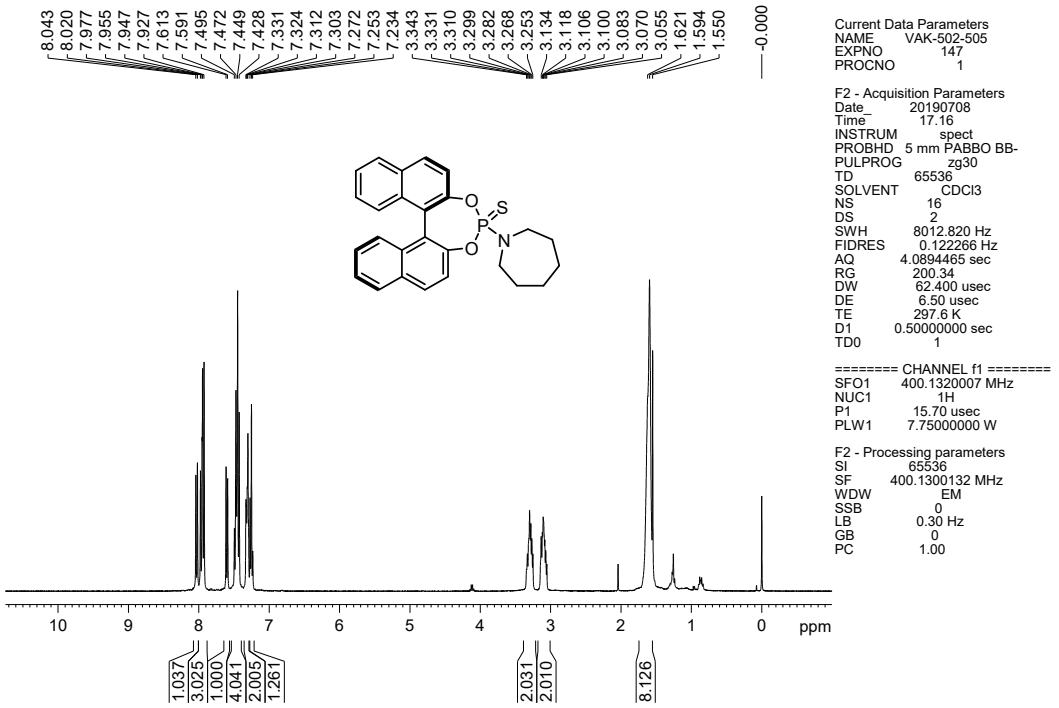
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24˚C):



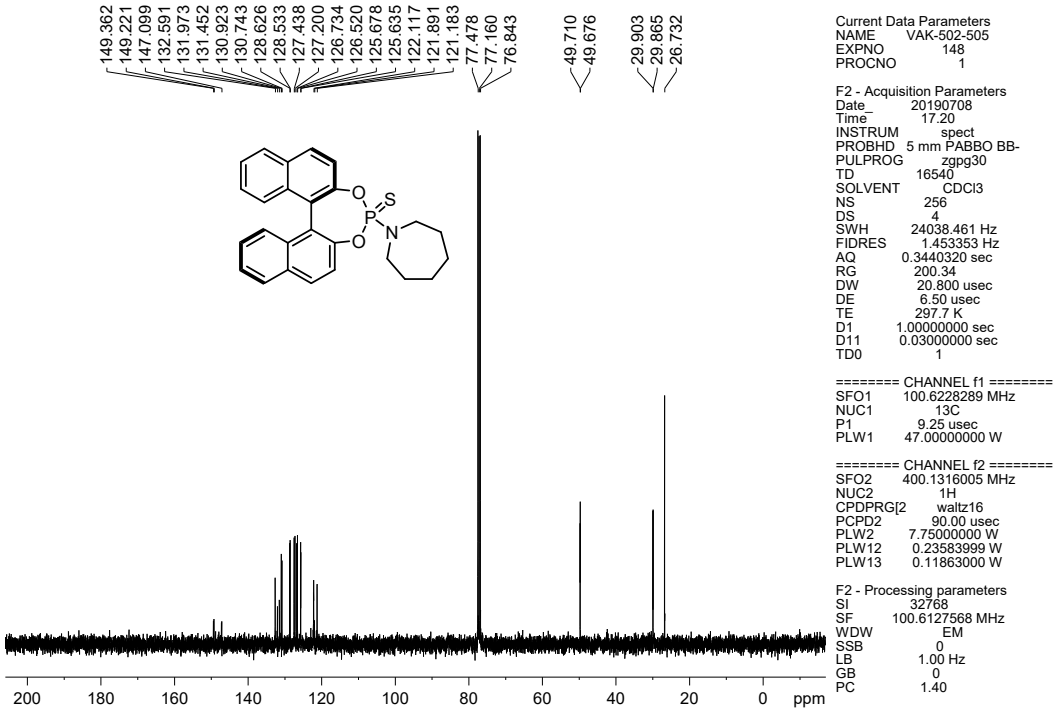
^{31}P NMR (202 MHz, $CDCl_3$, 24 °C):



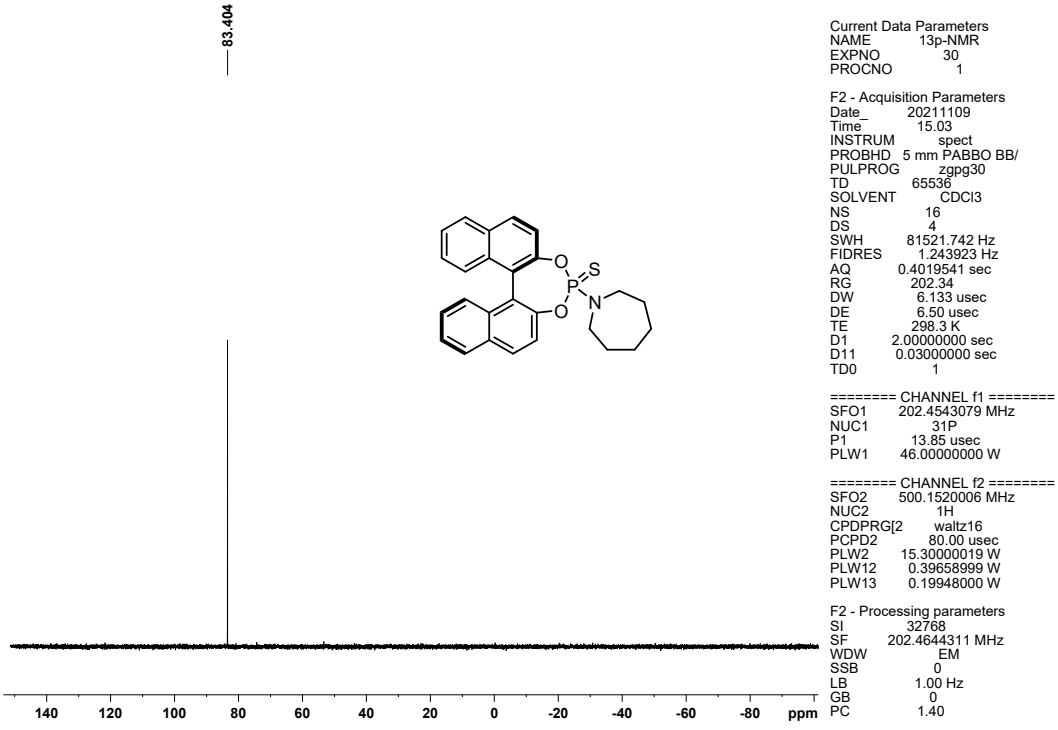
4-(Azepan-1-yl)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine 4-sulfide (LB12)
^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24˚C):

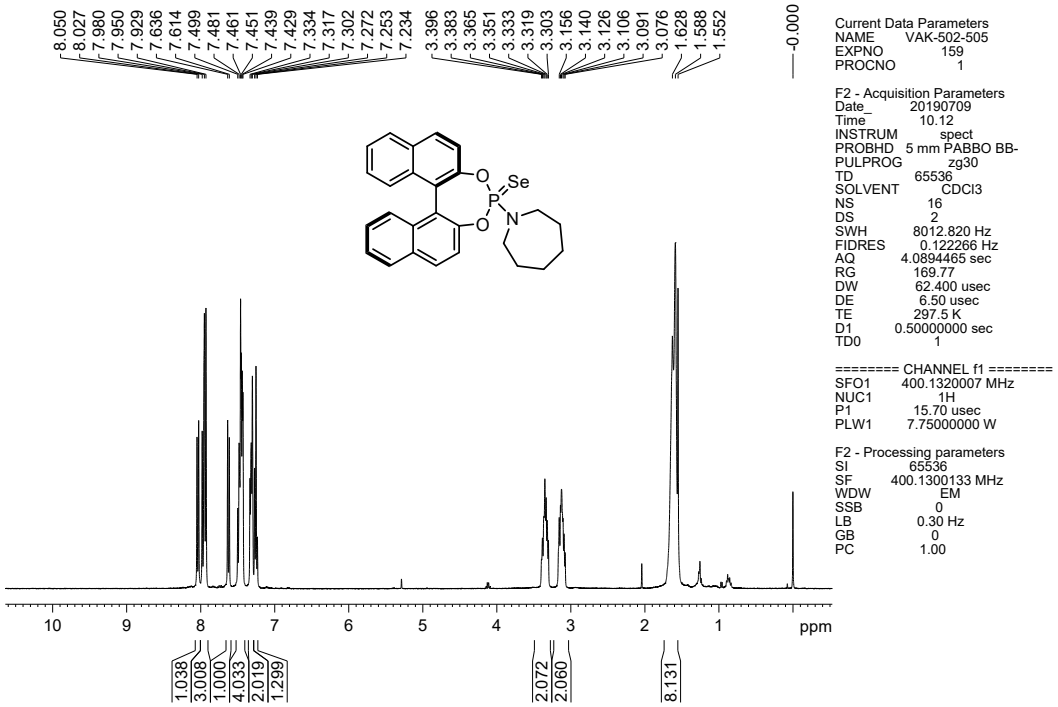


3^{31}P NMR (202 MHz, $CDCl_3$, 24 °C):

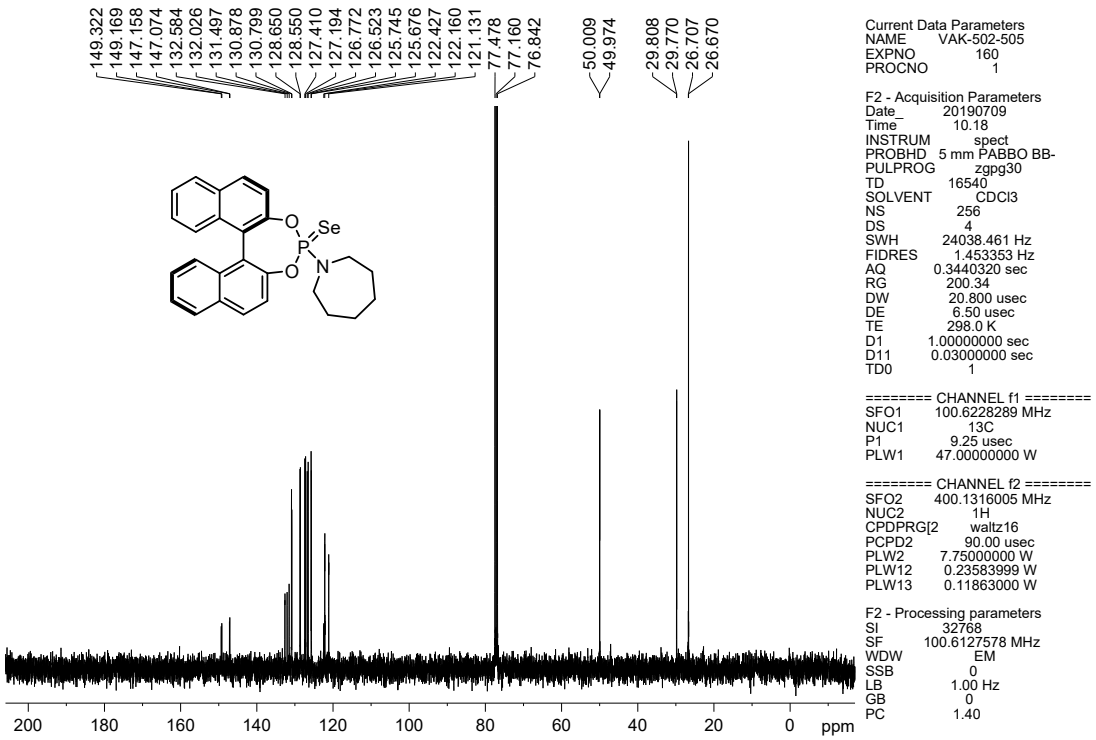


(11bS)-4-(Azepan-1-yl)-3,5-dimethyl-3,5-dihydrodinaphtho[2,1-d:1',2'-f][1,3,2]diazaphosphepine 4-selenide (LB13)

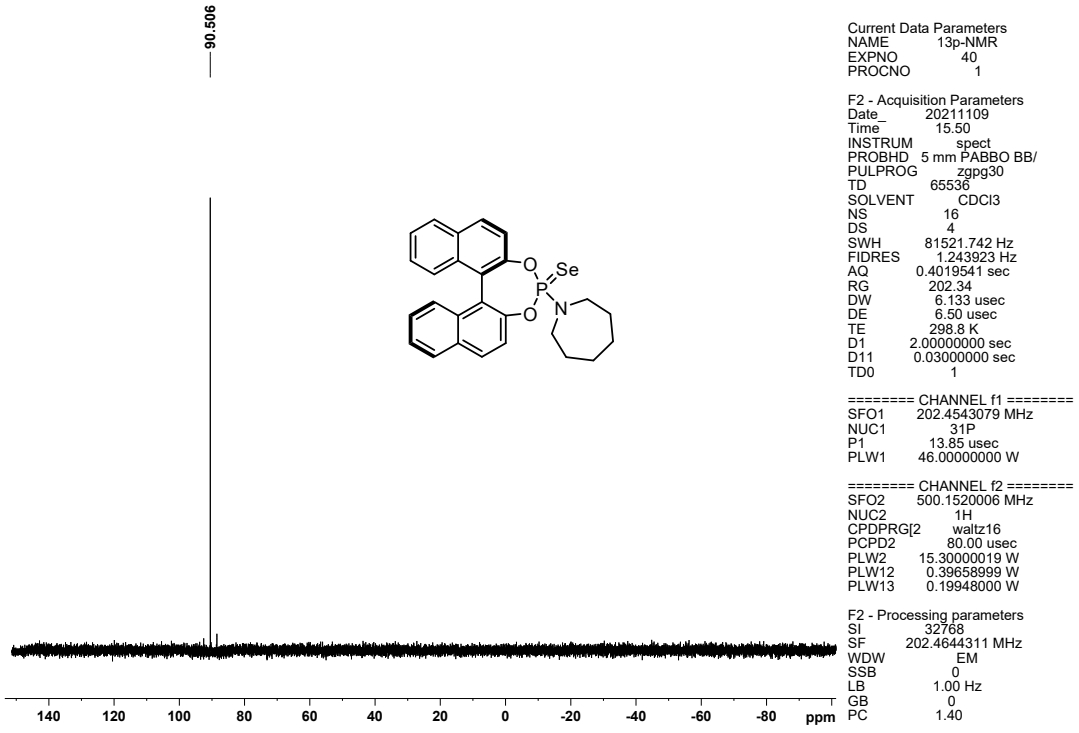
^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):



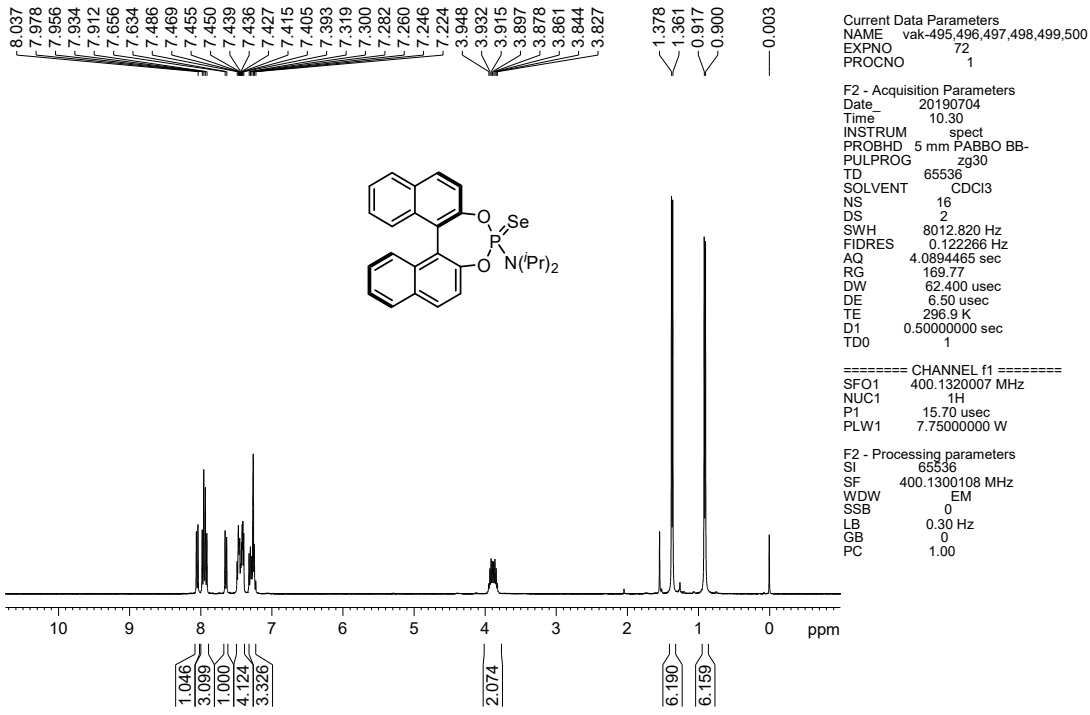
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24˚C):



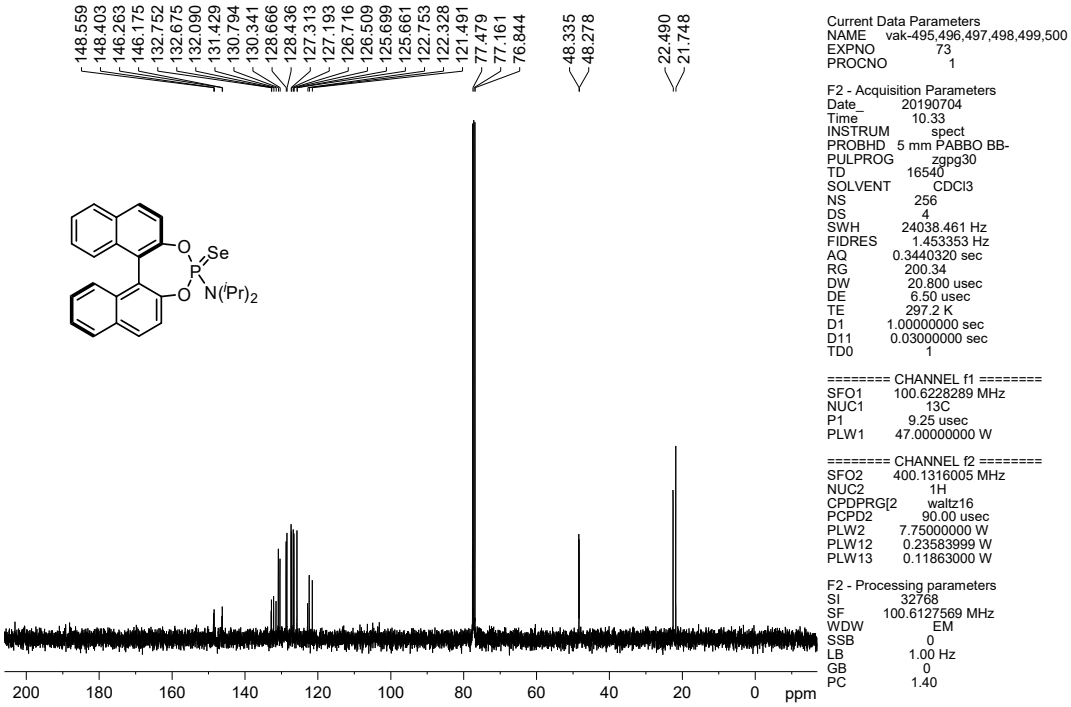
^{31}P NMR (202 MHz, $CDCl_3$, 24 °C):



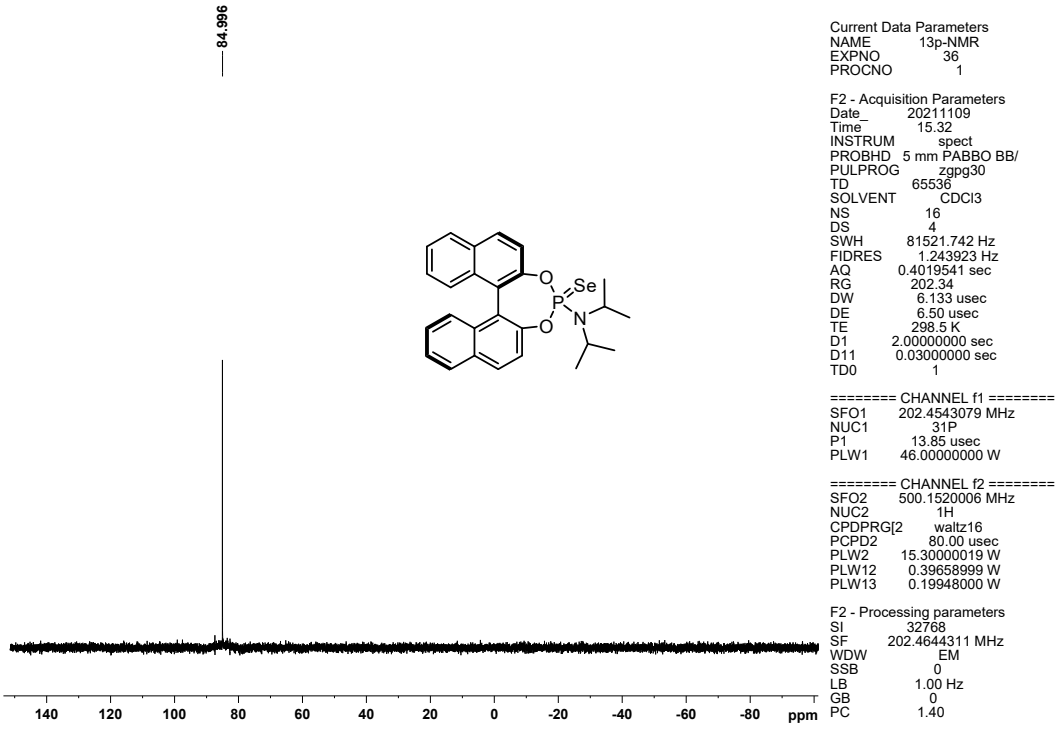
4-(Diisopropylamino)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine 4-selenide (LB14)
^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24˚C):



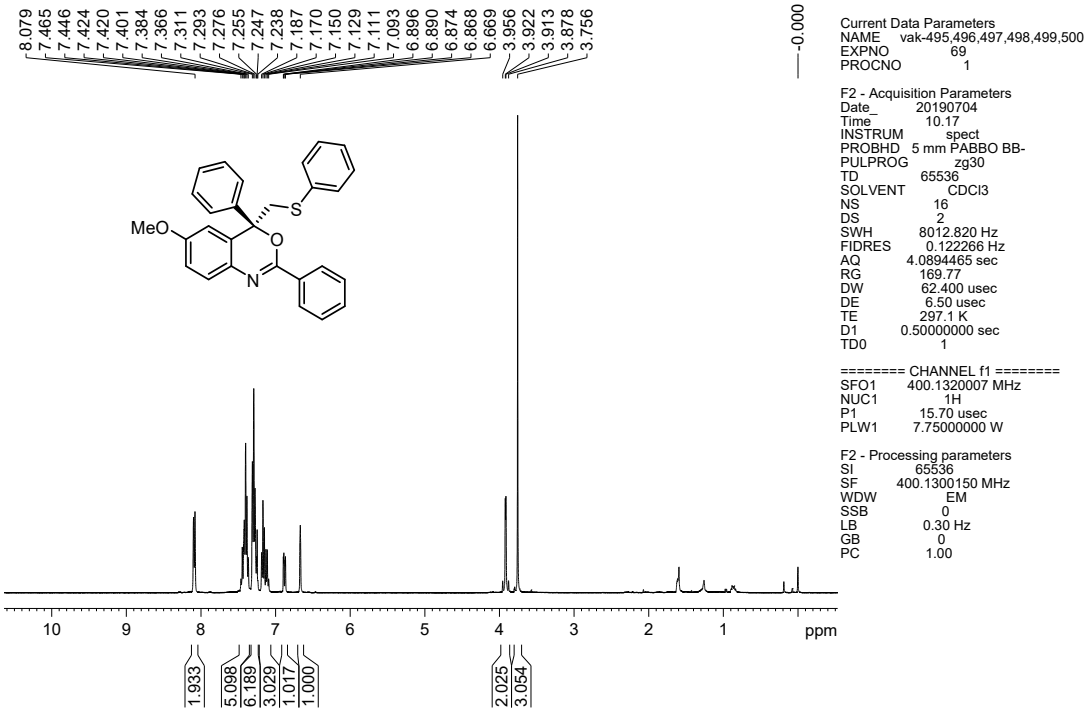
^{31}P NMR (202 MHz, $CDCl_3$, 24 °C):



13. NMR spectra of isolated compounds

(*R*)-6-Methoxy-2,4-diphenyl-4-((phenylthio)methyl)-4*H*-benzo[d][1,3]oxazine (3a)

^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):

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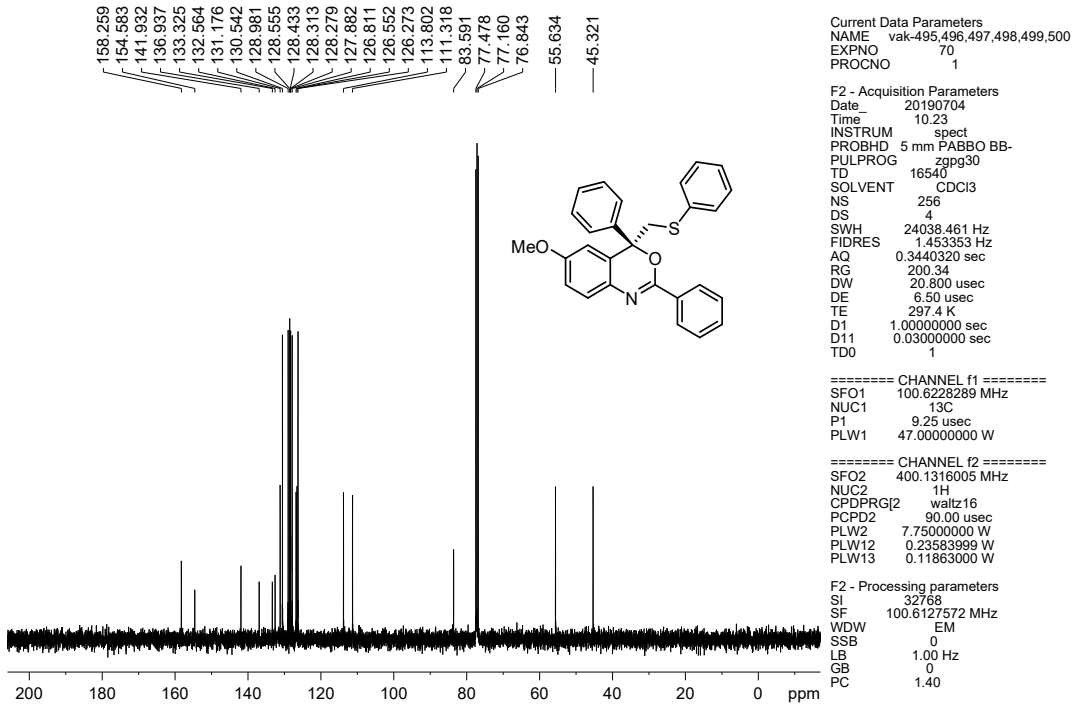
Current Data Parameters
NAME      vak-495,496,497,498,499,500
EXPNO             69
PROCNO             1

F2 - Acquisition Parameters
Date_         20190704
Time             10.17
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG          zg30
TD              65536
SOLVENT          CDCl3
NS                  16
DS                   2
SWH           8012.820 Hz
FIDRES           0.122266 Hz
AQ            4.0894465 sec
RG                169.77
DW                62.400 usec
DE                 6.50 usec
TE                297.1 K
D1            0.50000000 sec
TD0                 1

======== CHANNEL f1 ========
SFO1         400.1320007 MHz
NUC1                1H
P1                 15.70 usec
PLW1          7.75000000 W

F2 - Processing parameters
SI                 65536
SF           400.1300150 MHz
WDW                 EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                1.00
```

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24˚C):

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Current Data Parameters
NAME      vak-495,496,497,498,499,500
EXPNO             70
PROCNO             1

F2 - Acquisition Parameters
Date_         20190704
Time             10.23
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG        zgpg30
TD              16540
SOLVENT          CDCl3
NS                 256
DS                   4
SWH           24038.461 Hz
FIDRES           1.453353 Hz
AQ            0.3440320 sec
RG                200.34
DW                20.800 usec
DE                 6.50 usec
TE                297.4 K
D1            1.00000000 sec
D11           0.03000000 sec
TD0                 1

======== CHANNEL f1 ========
SFO1         100.6228289 MHz
NUC1                13C
P1                 9.25 usec
PLW1          47.00000000 W

======== CHANNEL f2 ========
SFO2         400.1316005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             90.00 usec
PLW2          7.75000000 W
PLW12         0.23583999 W
PLW13         0.11863000 W

F2 - Processing parameters
SI                 32768
SF           100.6127572 MHz
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                1.40
```
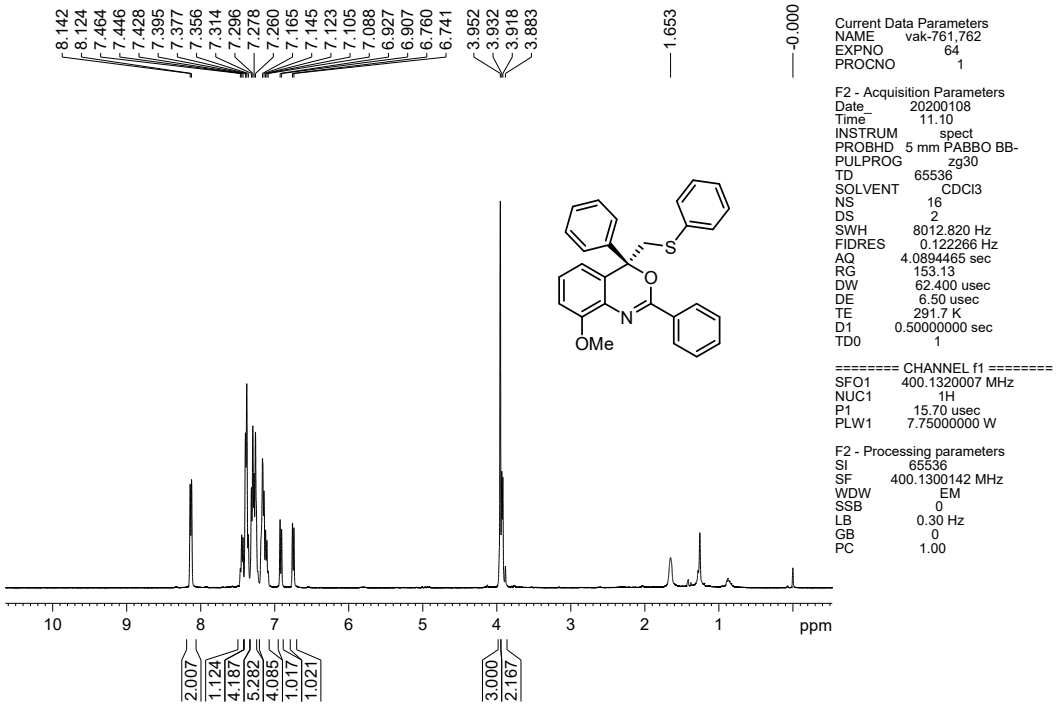
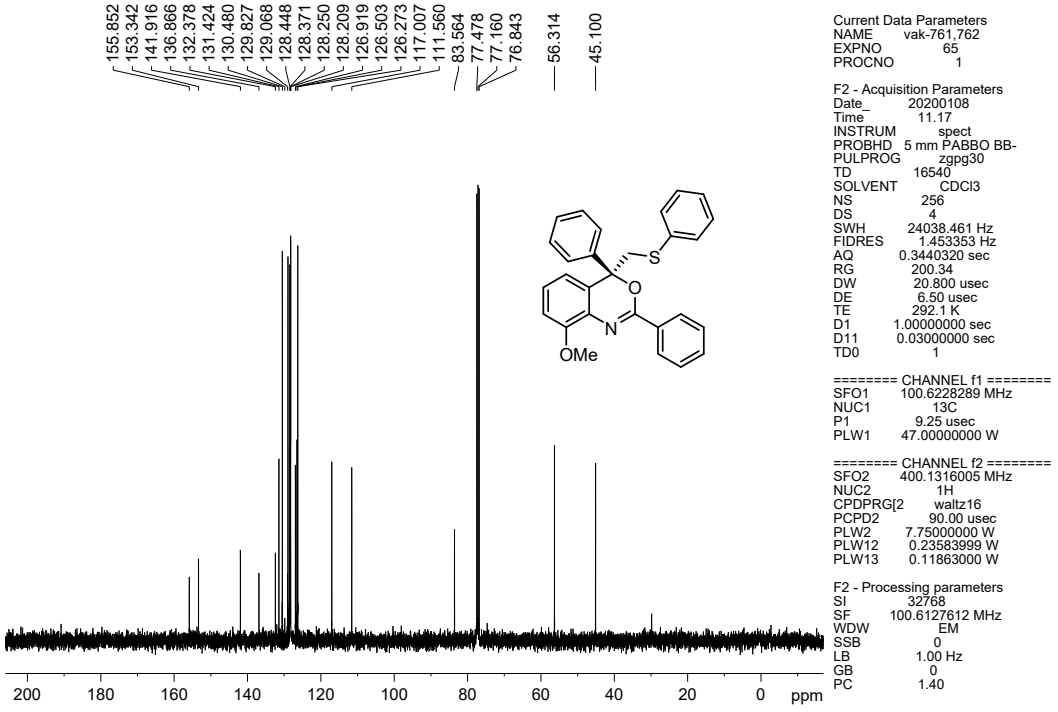

(*R*)-8-Methoxy-2,4-diphenyl-4-((phenylthio)methyl)-4*H*-benzo[d][1,3]oxazine (3b)

^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):




```
Current Data Parameters
NAME        vak-761,762
EXPNO            64
PROCNO            1

F2 - Acquisition Parameters
Date_        20200108
Time            11.10
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG          zg30
TD              65536
SOLVENT          CDCl3
NS                16
DS                 2
SWH          8012.820 Hz
FIDRES          0.122266 Hz
AQ           4.0894465 sec
RG              153.13
DW               62.400 usec
DE                6.50 usec
TE              291.7 K
D1           0.50000000 sec
TD0                1

======== CHANNEL f1 ========
SFO1       400.1320007 MHz
NUC1              1H
P1               15.70 usec
PLW1        7.75000000 W

F2 - Processing parameters
SI              65536
SF         400.1300142 MHz
WDW               EM
SSB                0
LB              0.30 Hz
GB                 0
PC              1.00
```

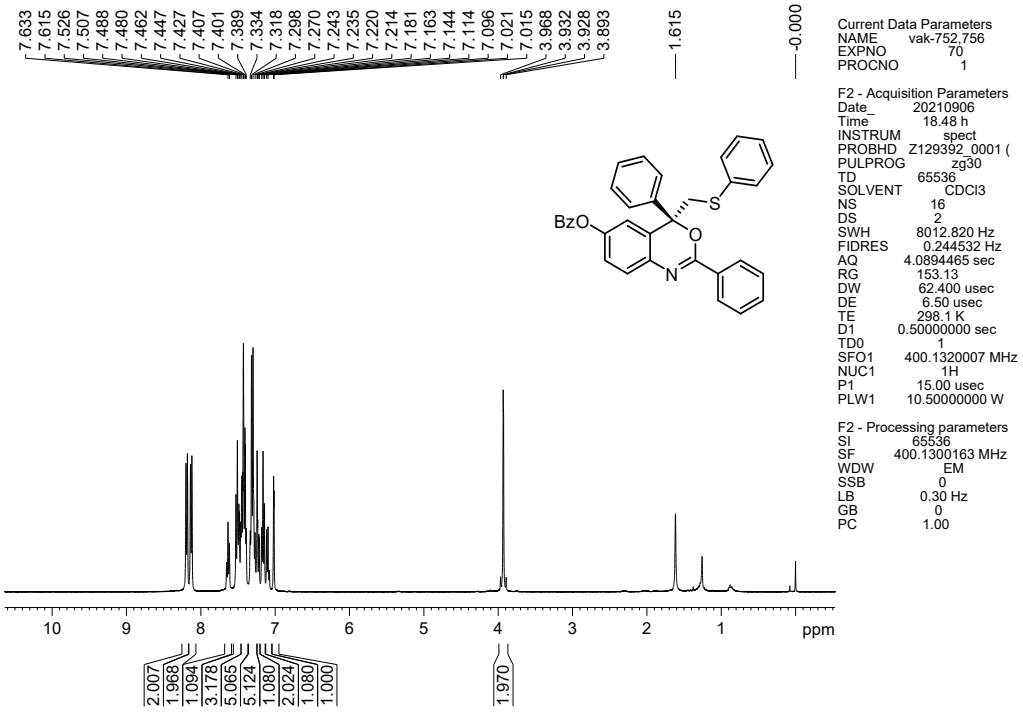
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24˚C):



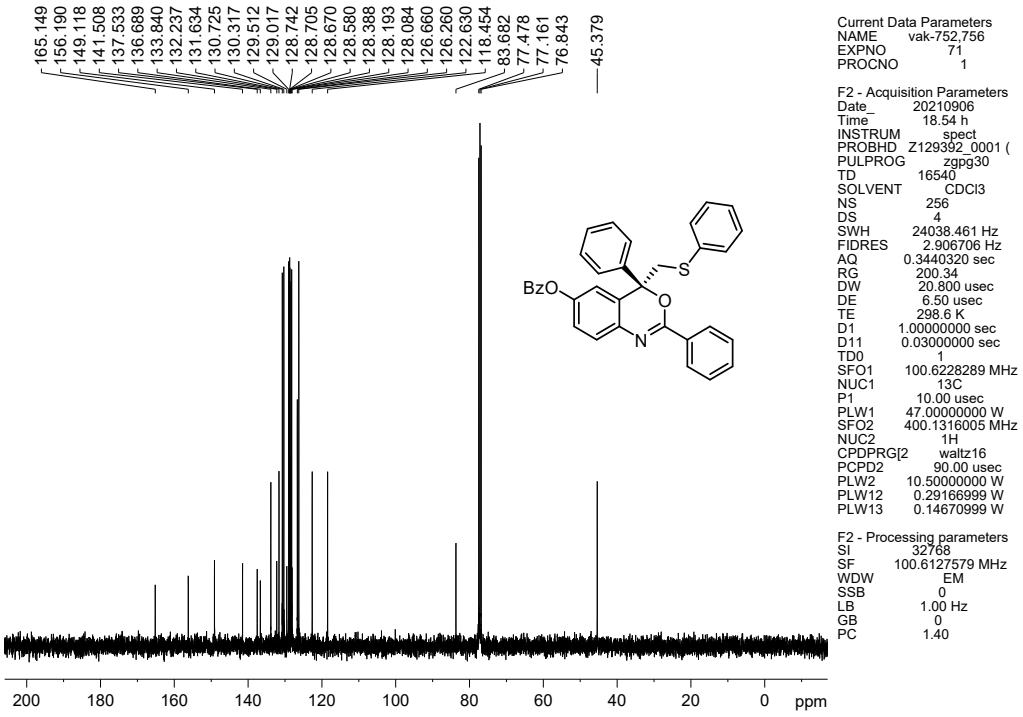

```
Current Data Parameters
NAME        vak-761,762
EXPNO            65
PROCNO            1

F2 - Acquisition Parameters
Date_        20200108
Time            11.17
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD              16540
SOLVENT          CDCl3
NS                256
DS                 4
SWH         24038.461 Hz
FIDRES          1.453353 Hz
AQ           0.3440320 sec
RG              200.34
DW               20.800 usec
DE                6.50 usec
TE              292.1 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                1

======== CHANNEL f1 ========
SFO1       100.6228289 MHz
NUC1              13C
P1                9.25 usec
PLW1       47.00000000 W

======== CHANNEL f2 ========
SFO2       400.1316005 MHz
NUC2              1H
CPDPRG[2       waltz16
PCPD2           90.00 usec
PLW2        7.75000000 W
PLW12       0.23583999 W
PLW13       0.11863000 W

F2 - Processing parameters
SI              32768
SF         100.6127612 MHz
WDW               EM
SSB                0
LB              1.00 Hz
GB                 0
PC              1.40
```

(*R*)-2,4-diphenyl-4-((phenylthio)methyl)-4*H*-benzo[d][1,3]oxazin-6-yl benzoate (3c)

^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):

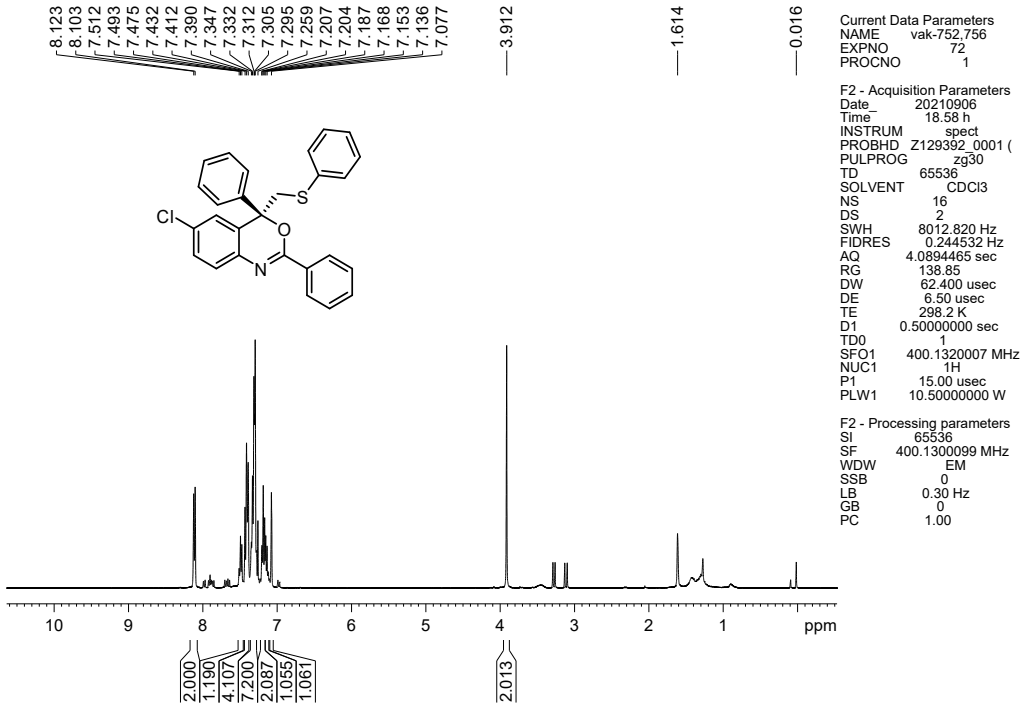


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24˚C):

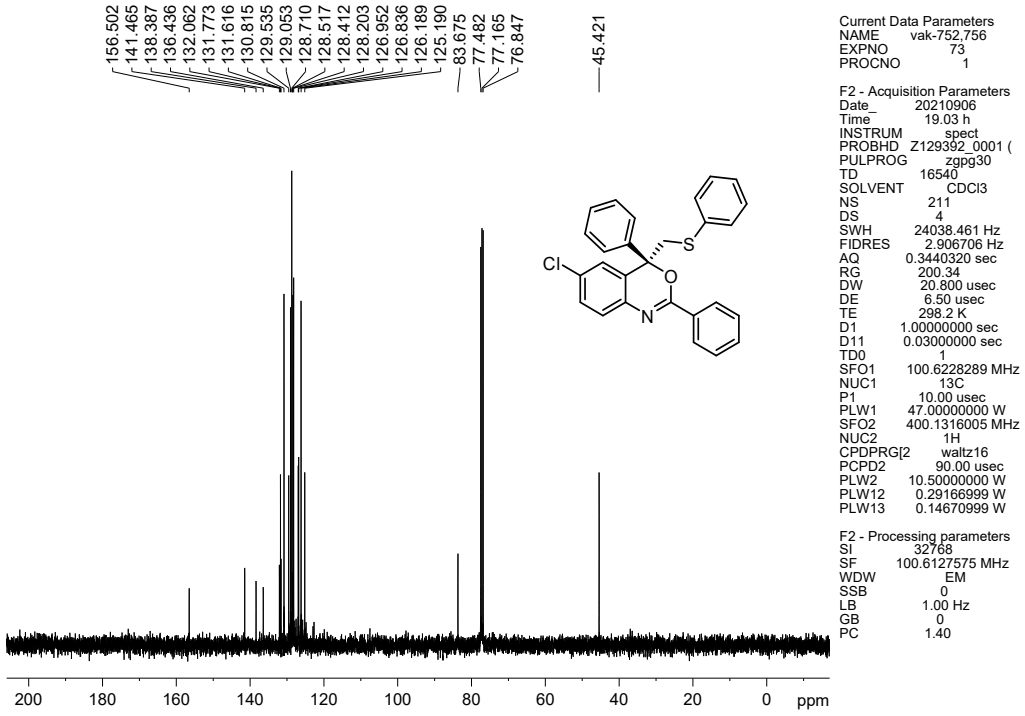


(*R*)-6-Chloro-2,4-diphenyl-4-((phenylthio)methyl)-4*H*-benzo[d][1,3]oxazine (3d)

^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):

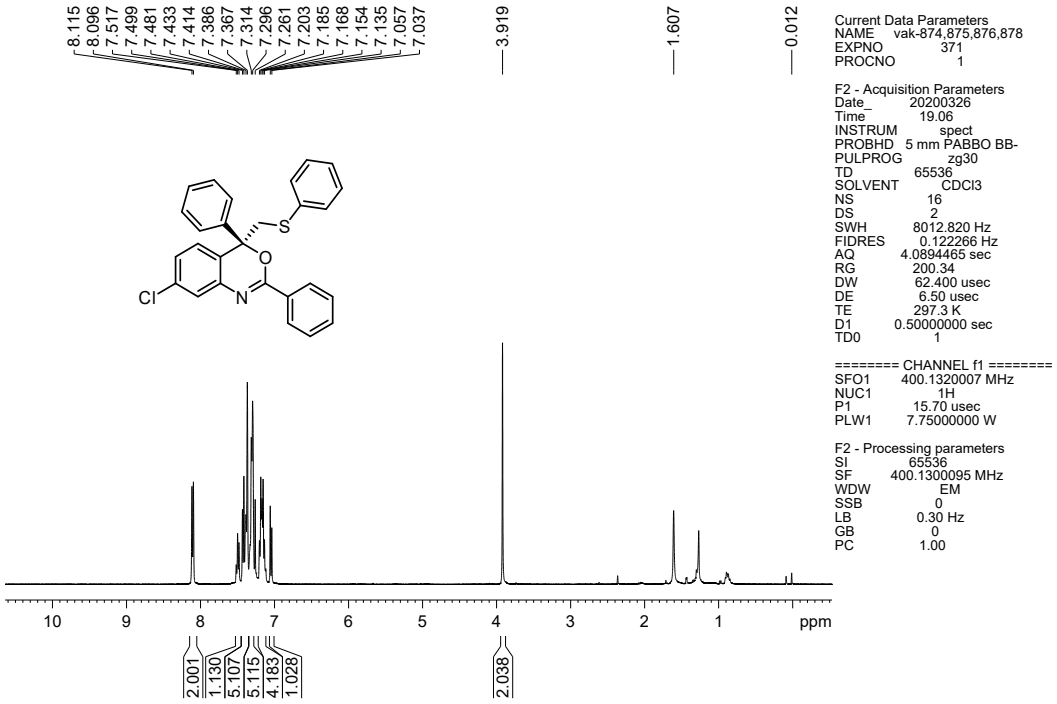


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24˚C):

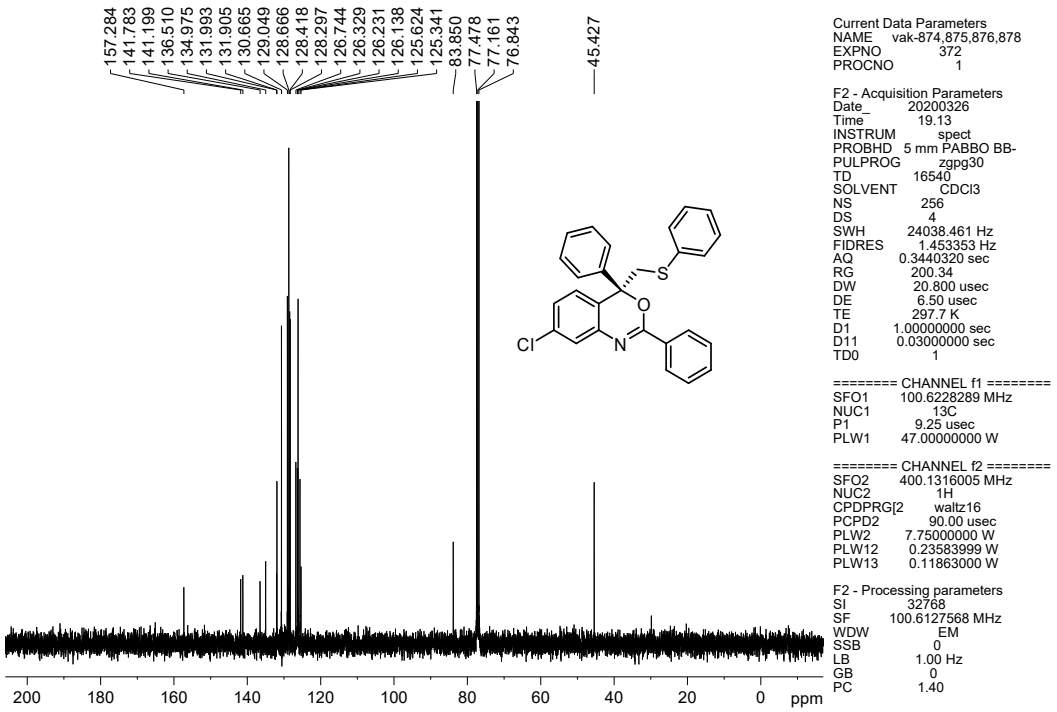


(*R*)-7-chloro-2,4-diphenyl-4-((phenylthio)methyl)-4*H*-benzo[d][1,3]oxazine (3e)

^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):

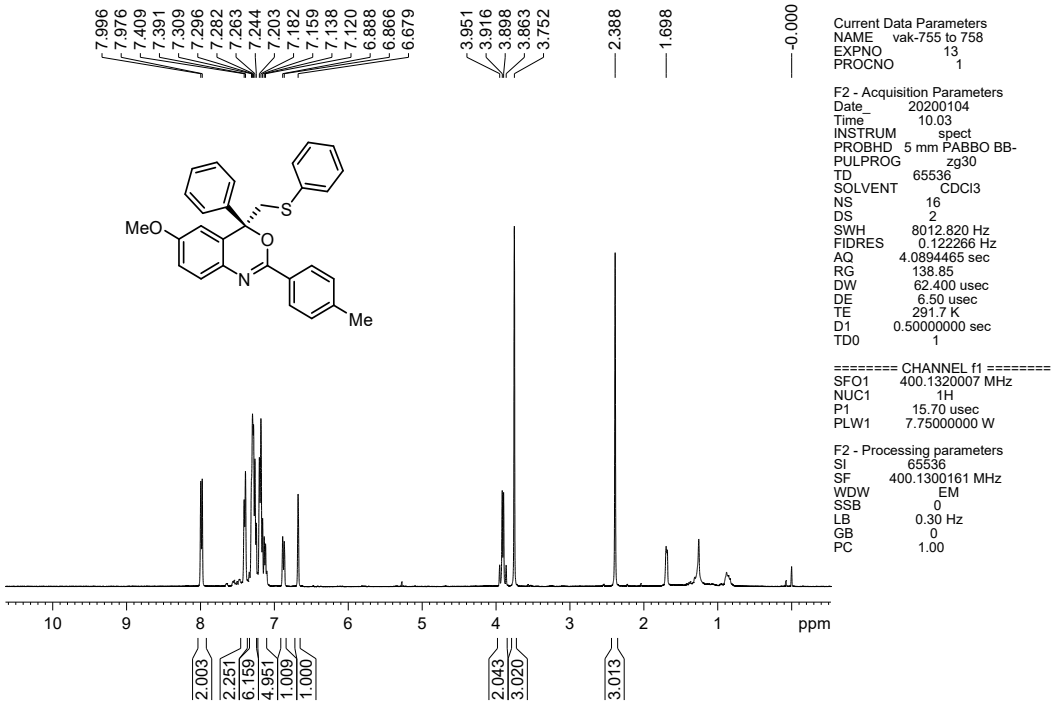


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24˚C):

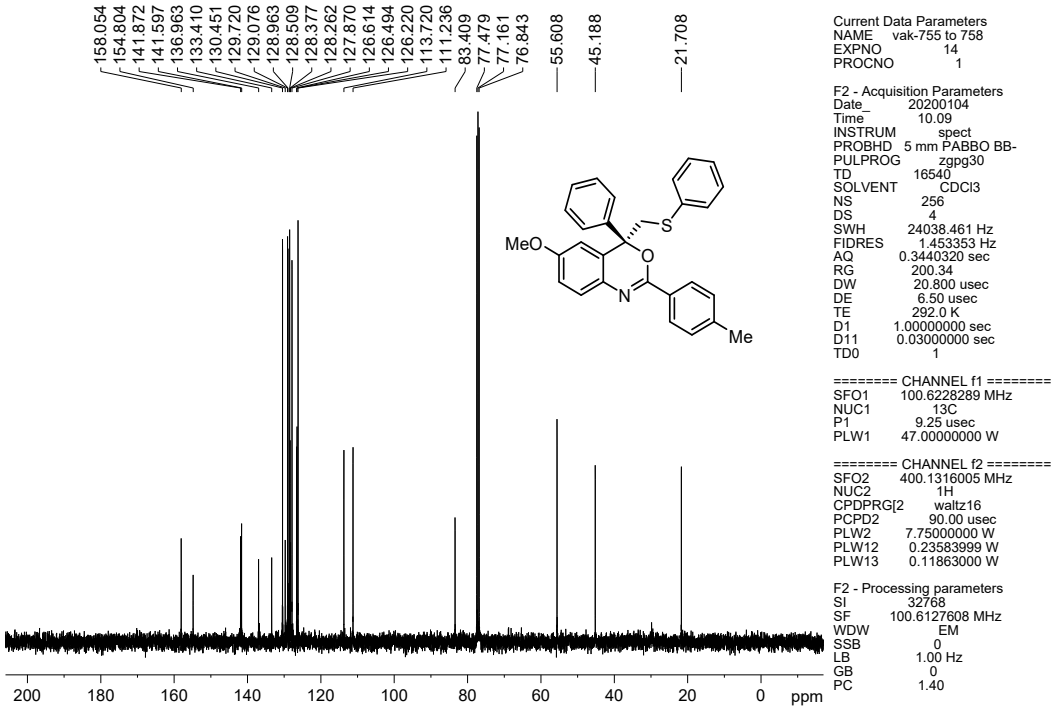


(*R*)-6-Methoxy-4-phenyl-4-((phenylthio)methyl)-2-(p-tolyl)-4*H*-benzo[d][1,3]oxazine (3f)

^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):

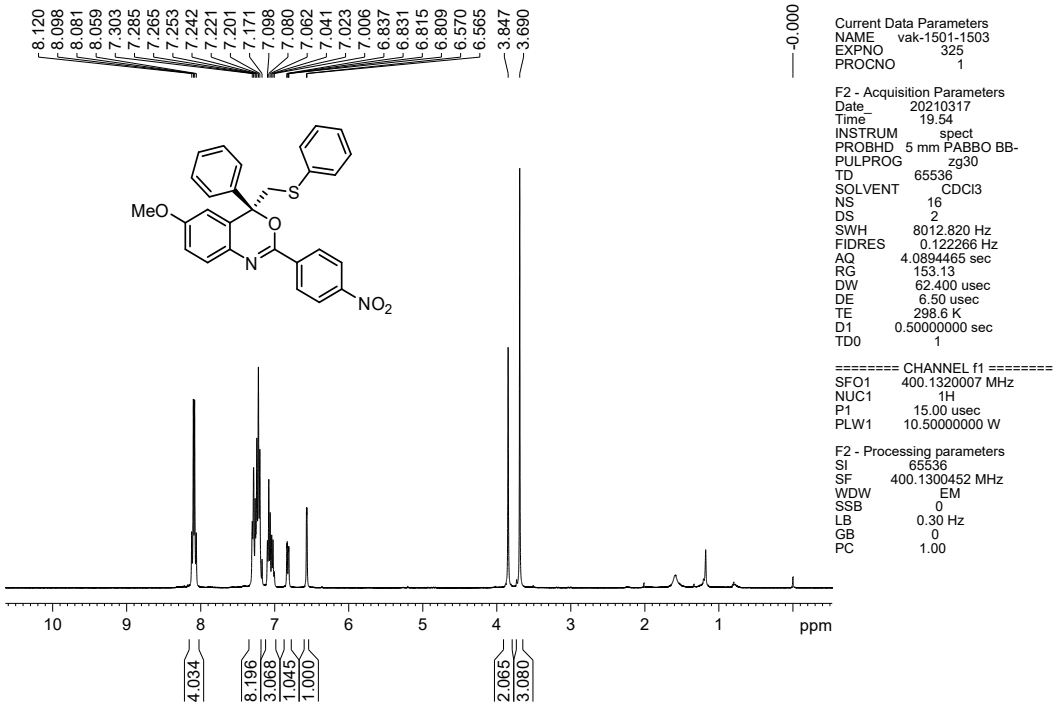


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24˚C):

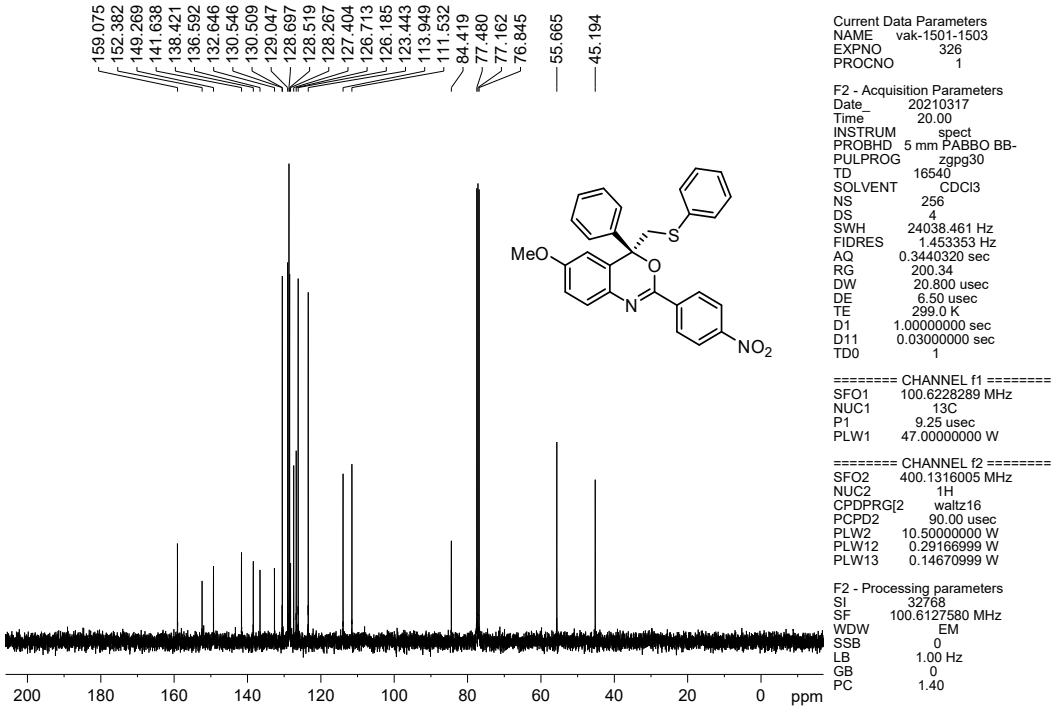


(*R*)-6-Methoxy-2-(4-nitrophenyl)-4-phenyl-4-((phenylthio)methyl)-4*H*-benzo[d][1,3]oxazine (3g)

^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):

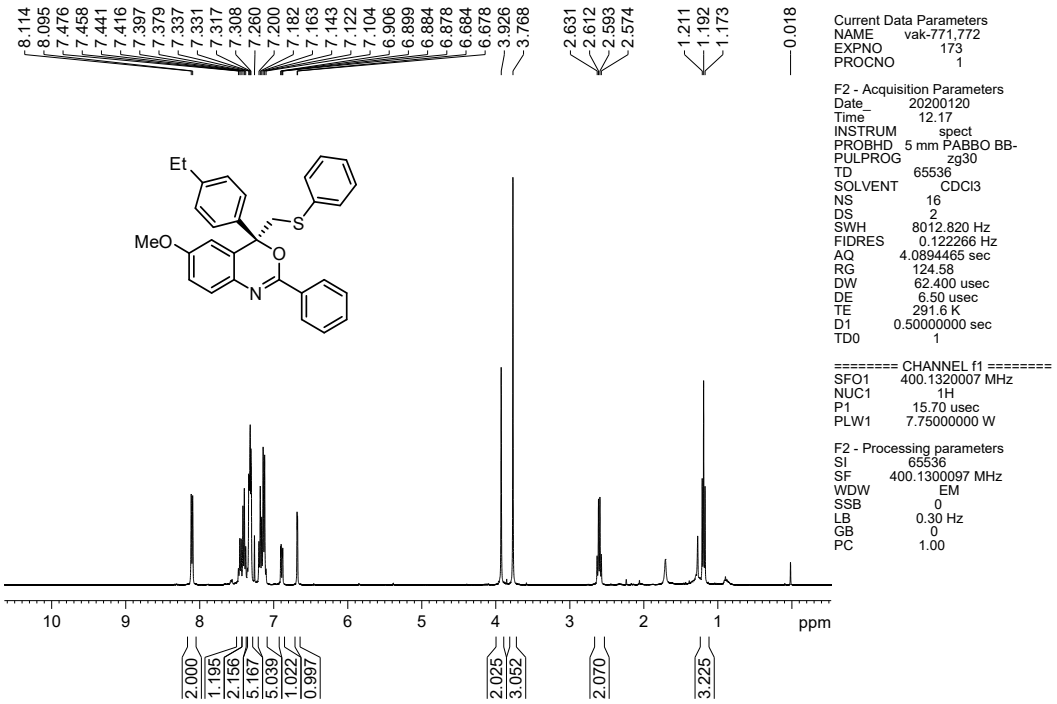


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24˚C):

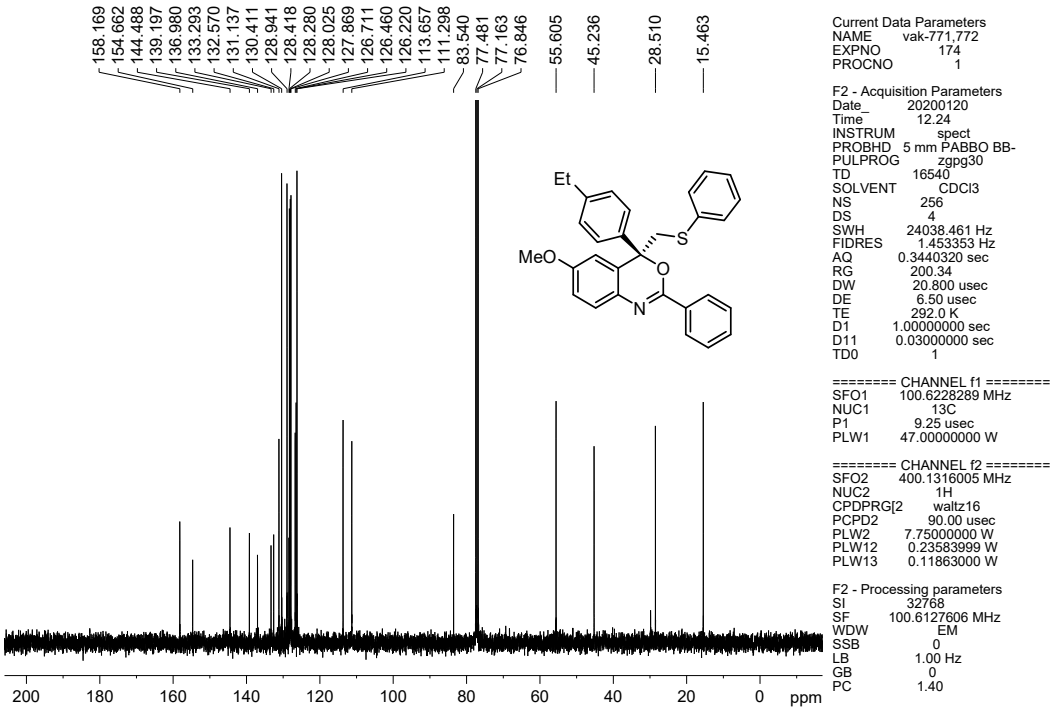


(*R*)-4-(4-Ethylphenyl)-6-methoxy-2-phenyl-4-((phenylthio)methyl)-4*H*-benzo[d][1,3]oxazine (3h)

^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):

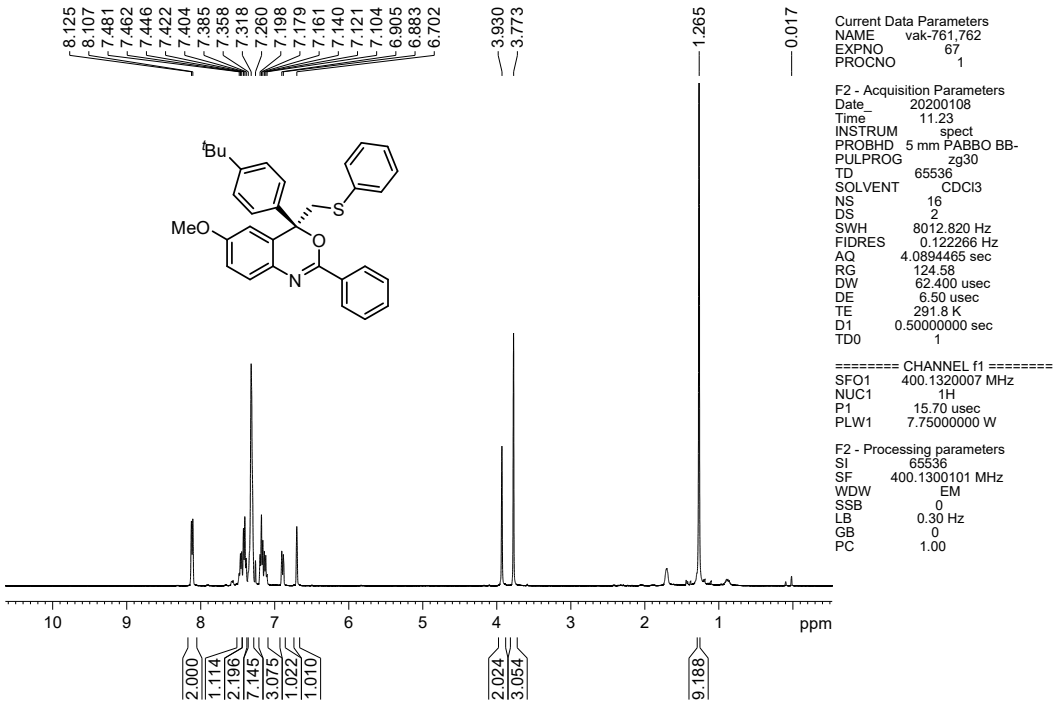


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24˚C):

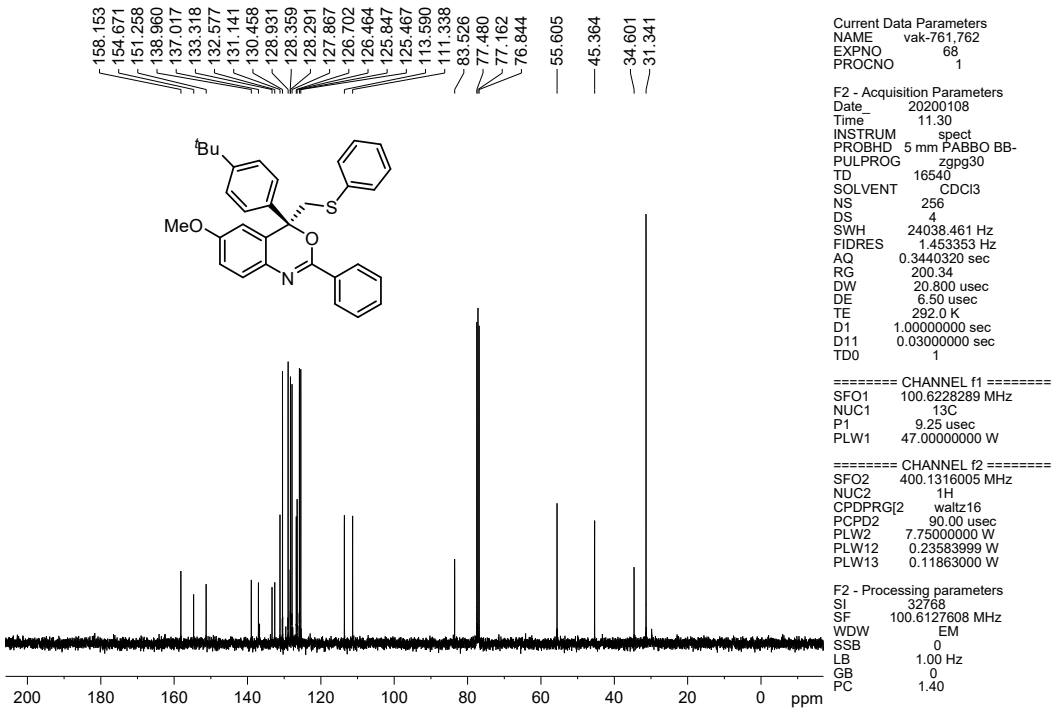


(*R*)-4-(4-(Tert-butyl)phenyl)-6-methoxy-2-phenyl-4-((phenylthio)methyl)-4*H*-benzo[d][1,3]oxazine (3i)

^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):

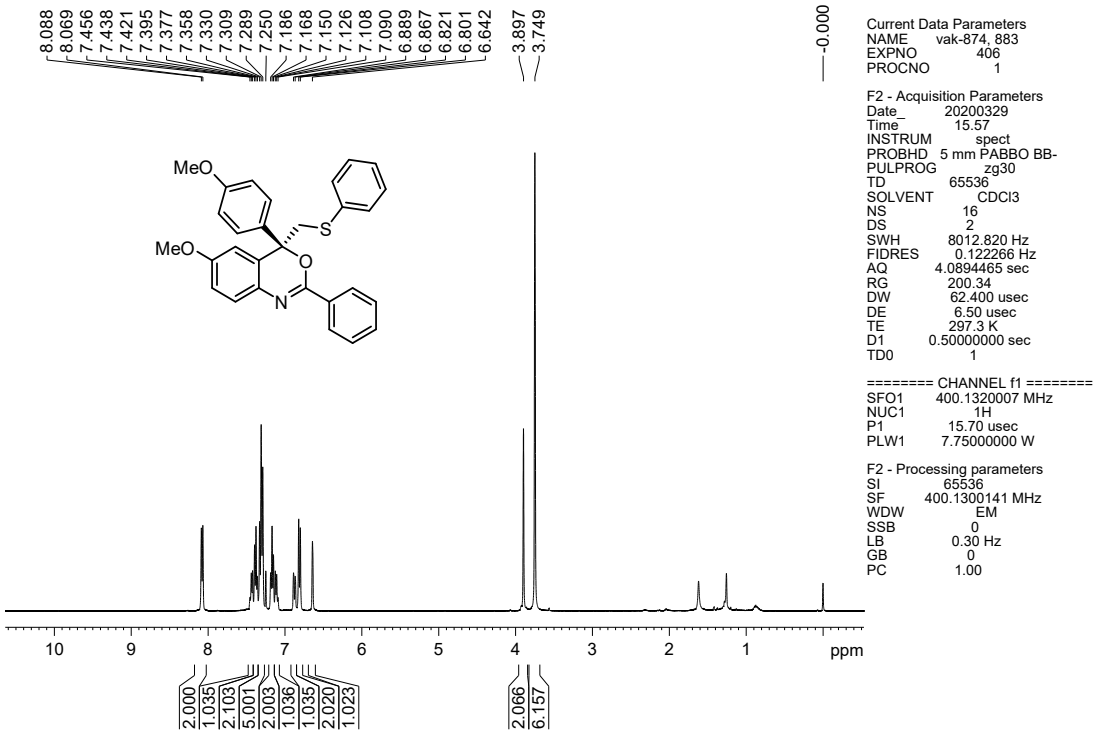


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24˚C):

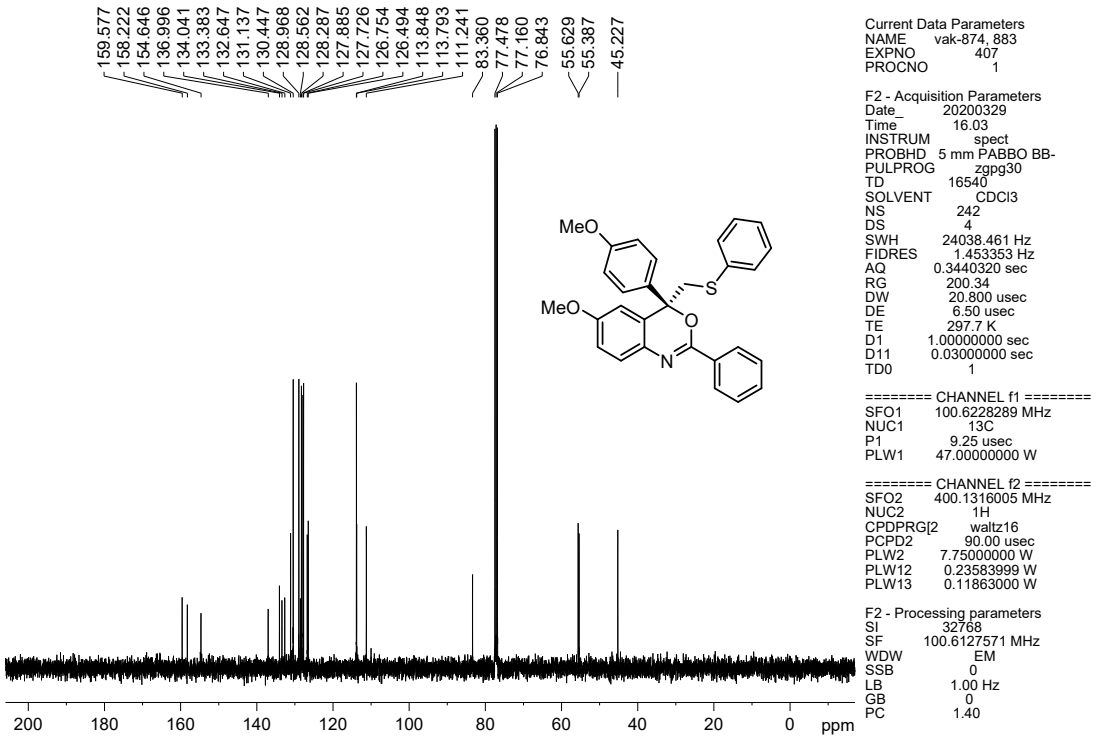


(*R*)-6-Methoxy-4-(4-methoxyphenyl)-2-phenyl-4-((phenylthio)methyl)-4*H*-benzo[d][1,3]oxazine (3j)

^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):

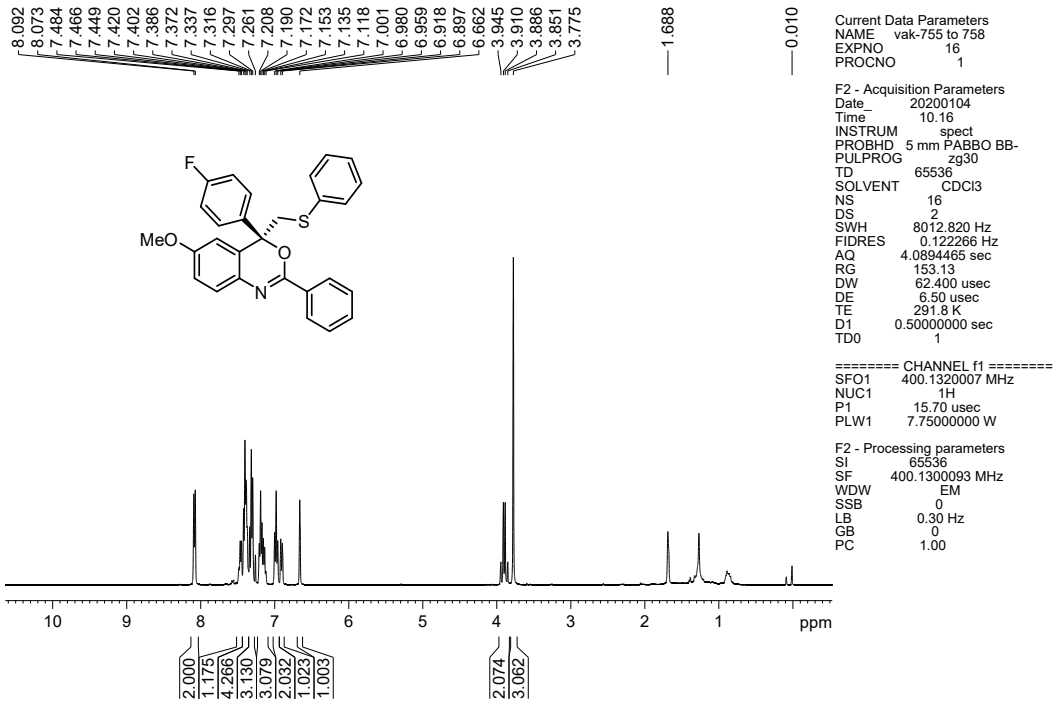


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24˚C):

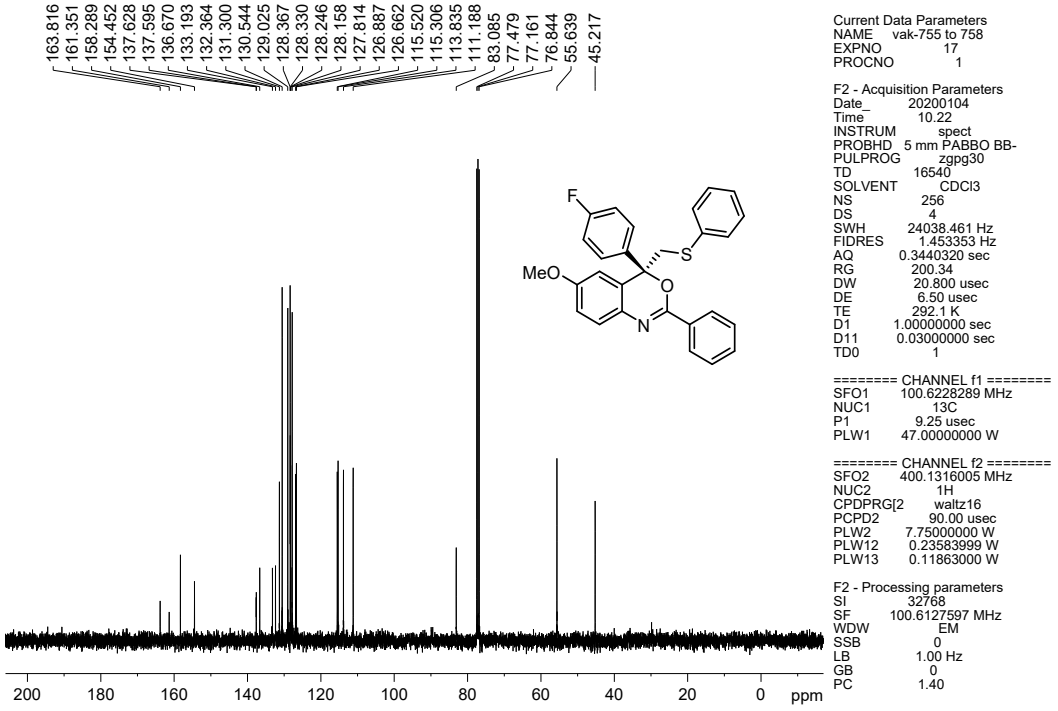


(*R*)-4-(4-Fluorophenyl)-6-methoxy-2-phenyl-4-((phenylthio)methyl)-4*H*-benzo[d][1,3]oxazine (3k)

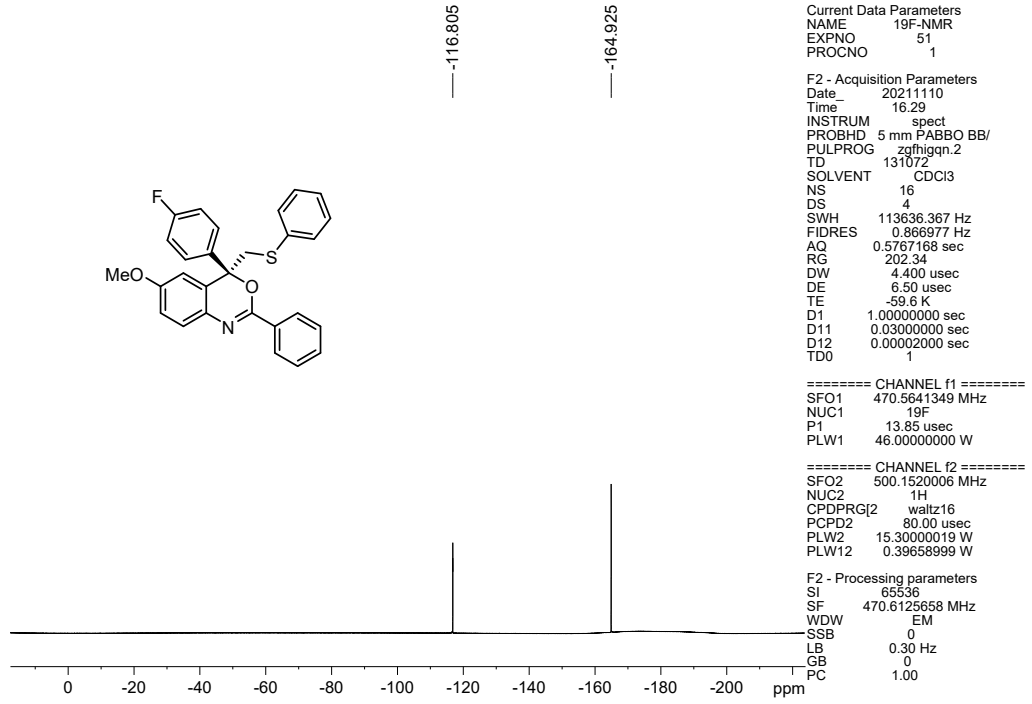
^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):



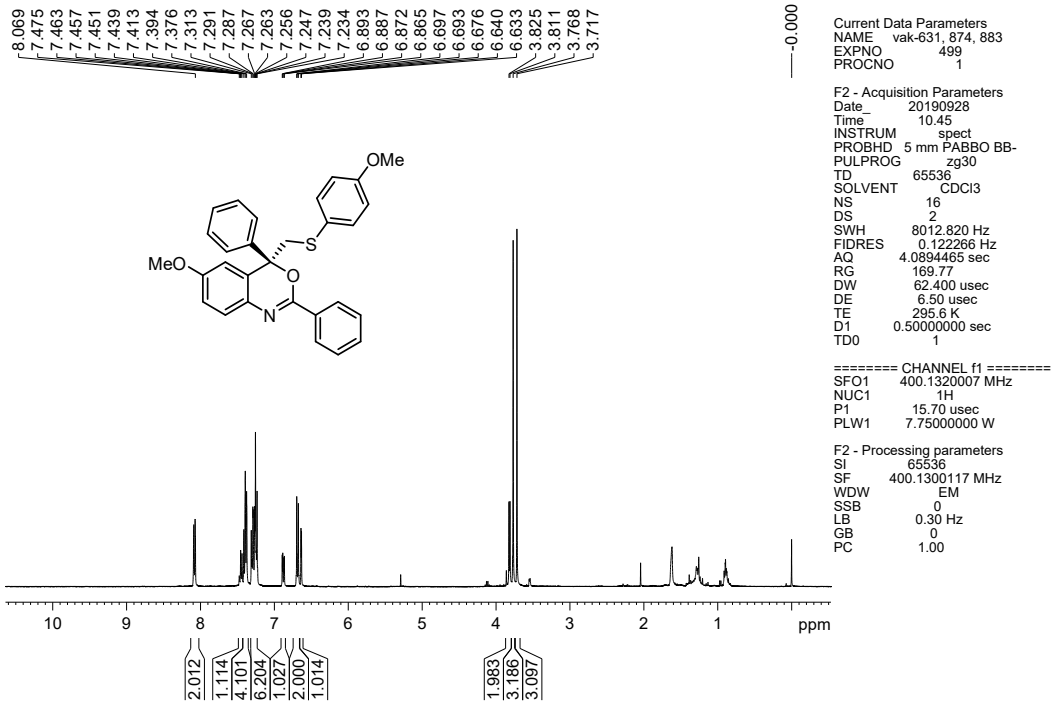
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24˚C):



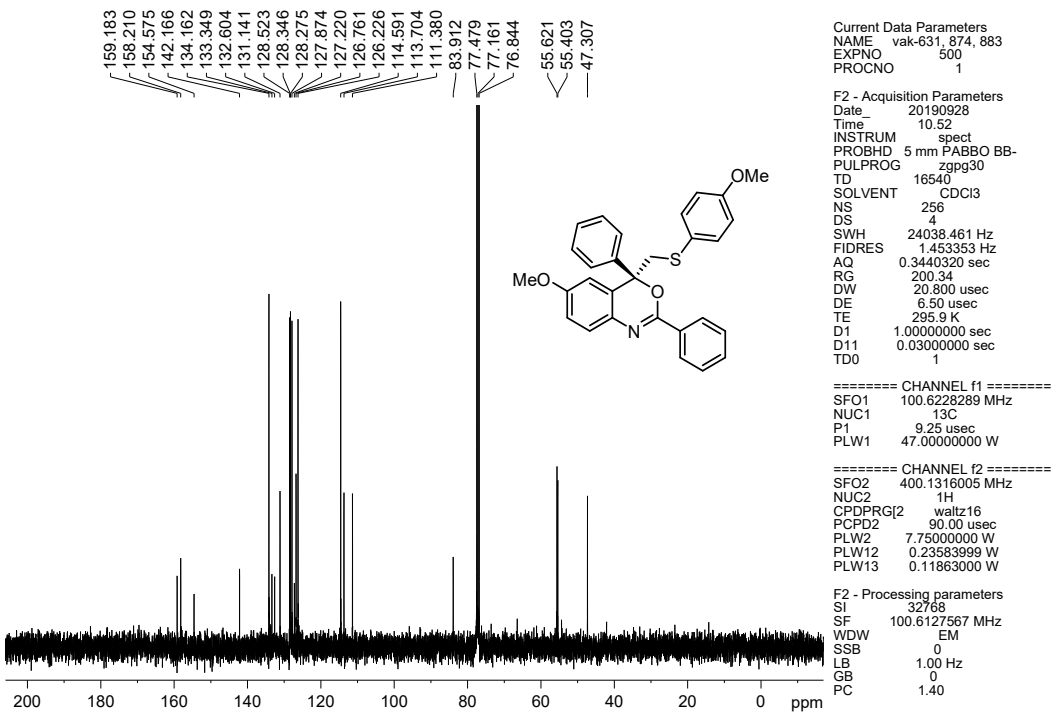
^{19}F NMR (470 MHz, $CDCl_3$, 24˚C):



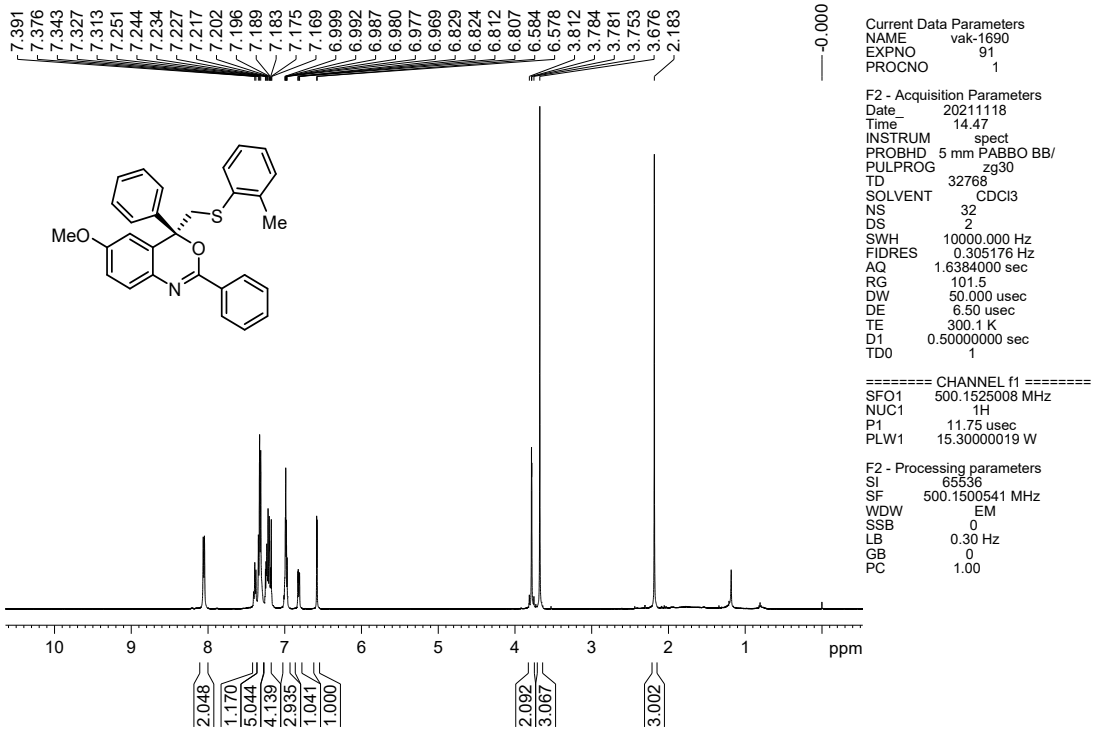
(*R*)-6-Methoxy-4-(((4-methoxyphenyl)thio)methyl)-2,4-diphenyl-4*H*-benzo[d][1,3]oxazine (3l)
^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):



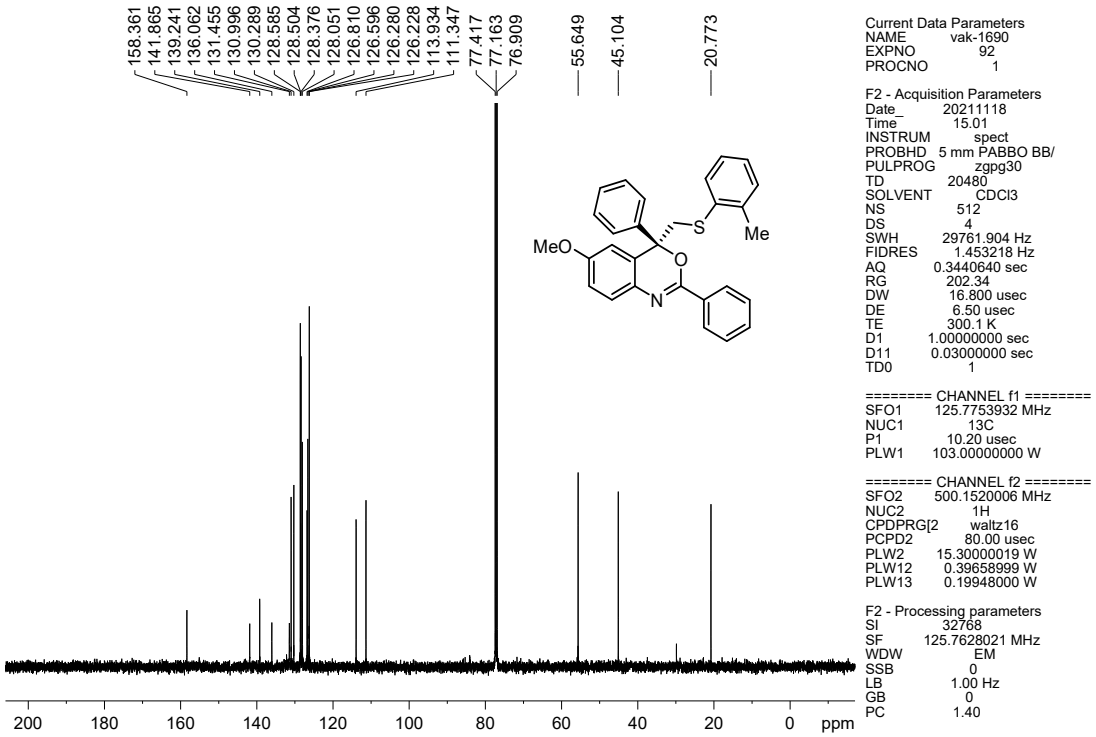
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24˚C):



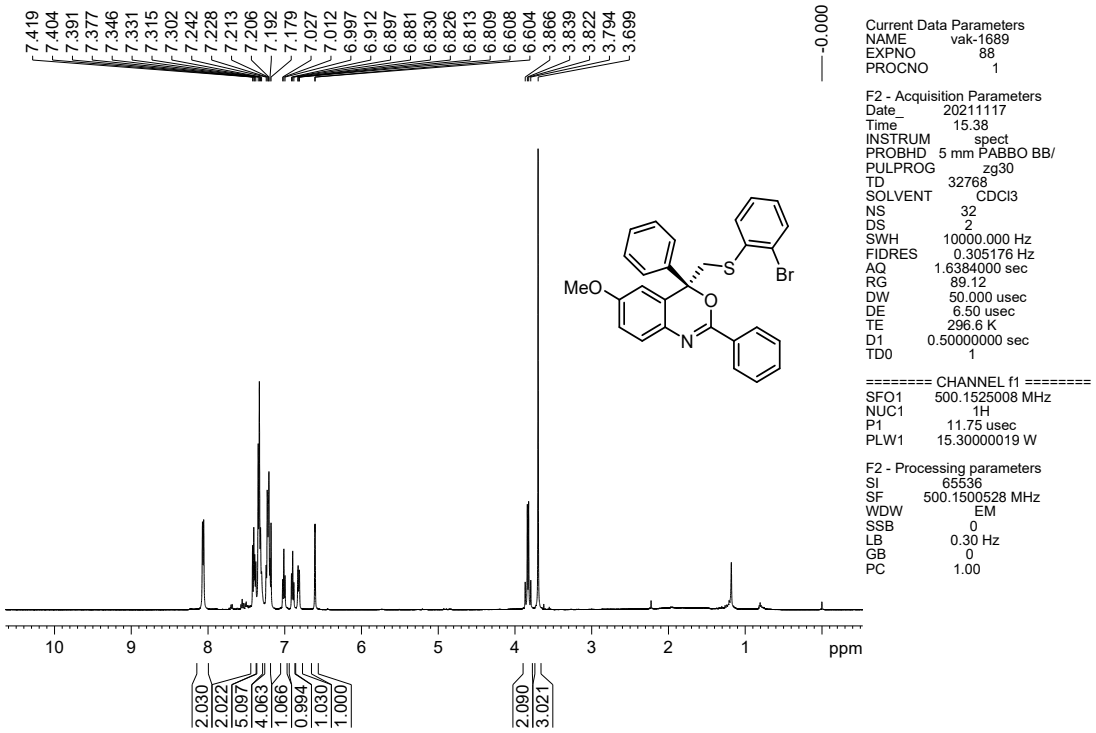
(*R*)-6-Methoxy-2,4-diphenyl-4-((o-tolylthio)methyl)-4*H*-benzo[d][1,3]oxazine (3m):
^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):



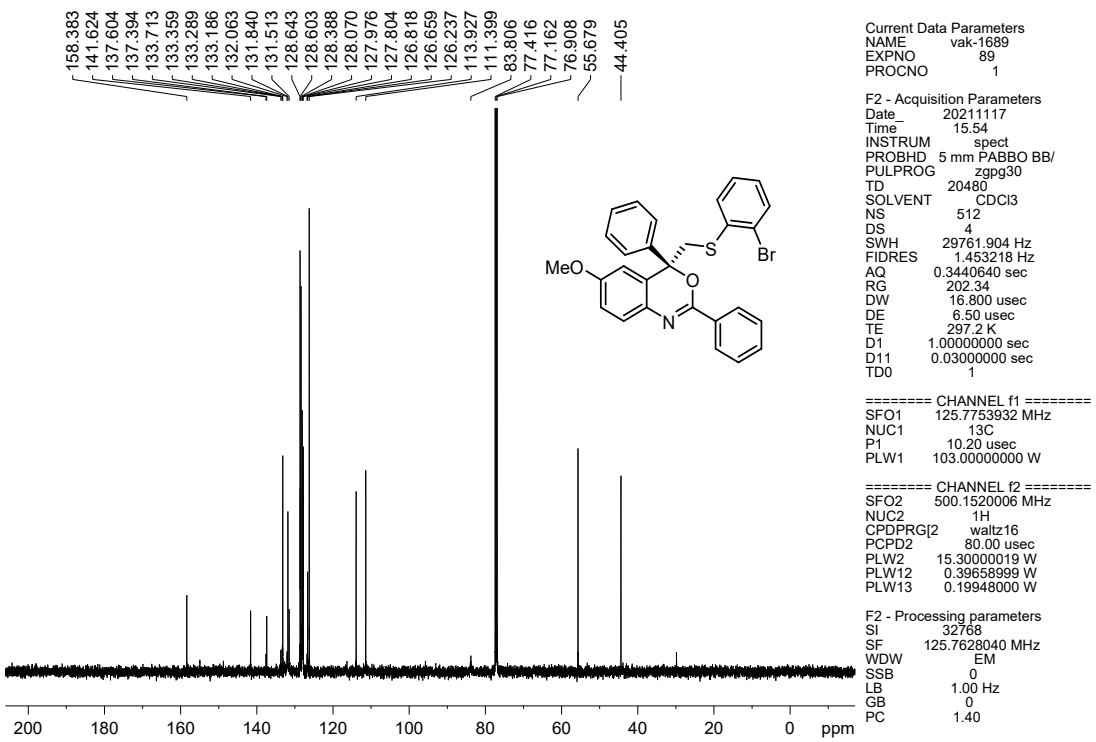
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24˚C):



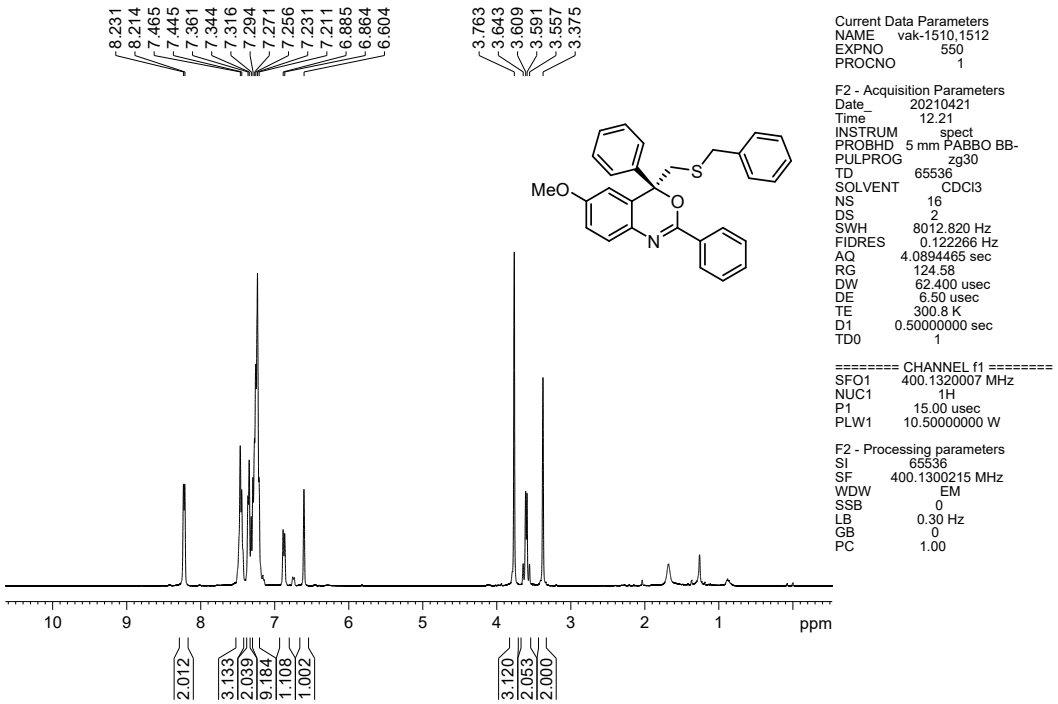
(*R*)-4-(((2-Bromophenyl)thio)methyl)-6-methoxy-2,4-diphenyl-4*H*-benzo[d][1,3]oxazine (3n):
^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):



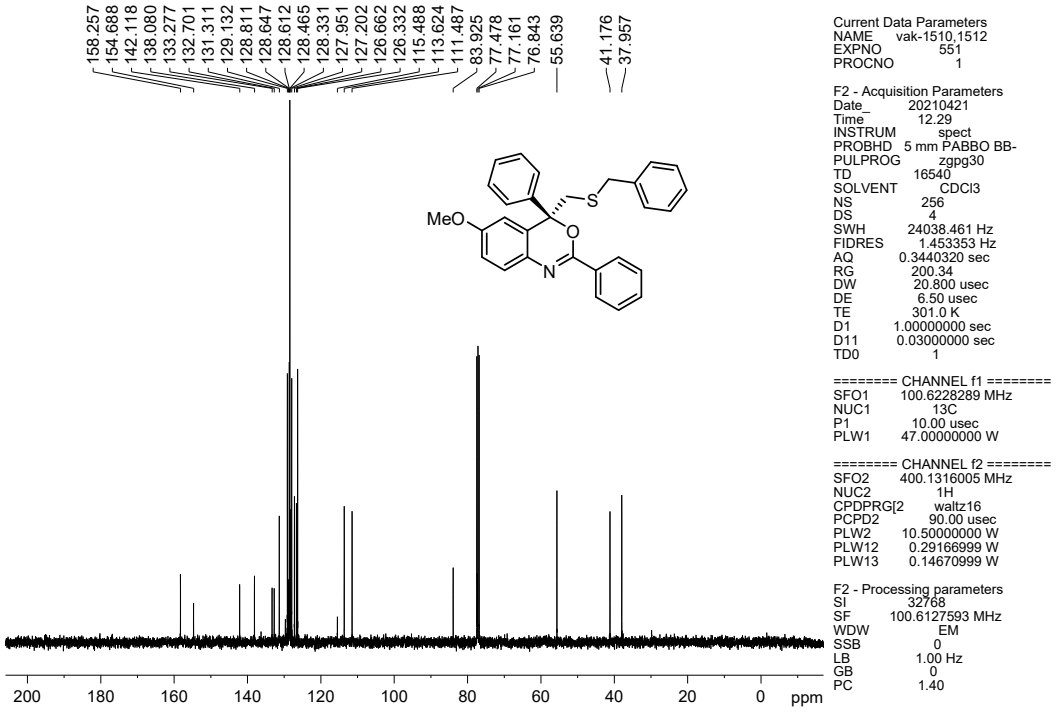
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24˚C):



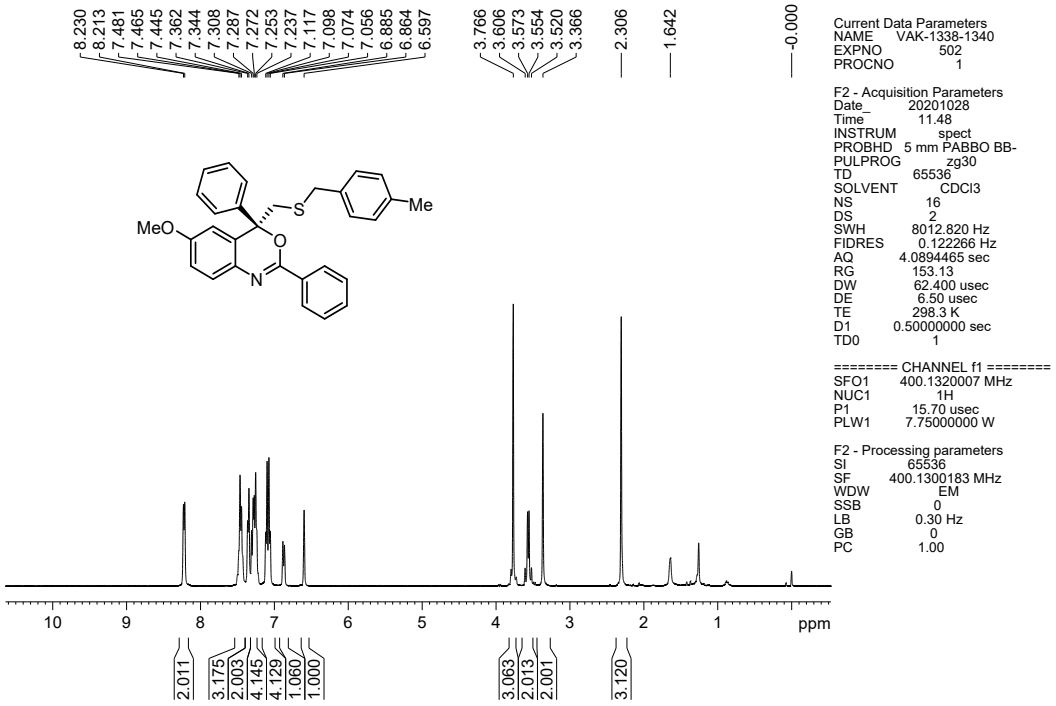
(*R*)-4-((Benzylthio)methyl)-6-methoxy-2,4-diphenyl-4*H*-benzo[d][1,3]oxazine (3o)
^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):



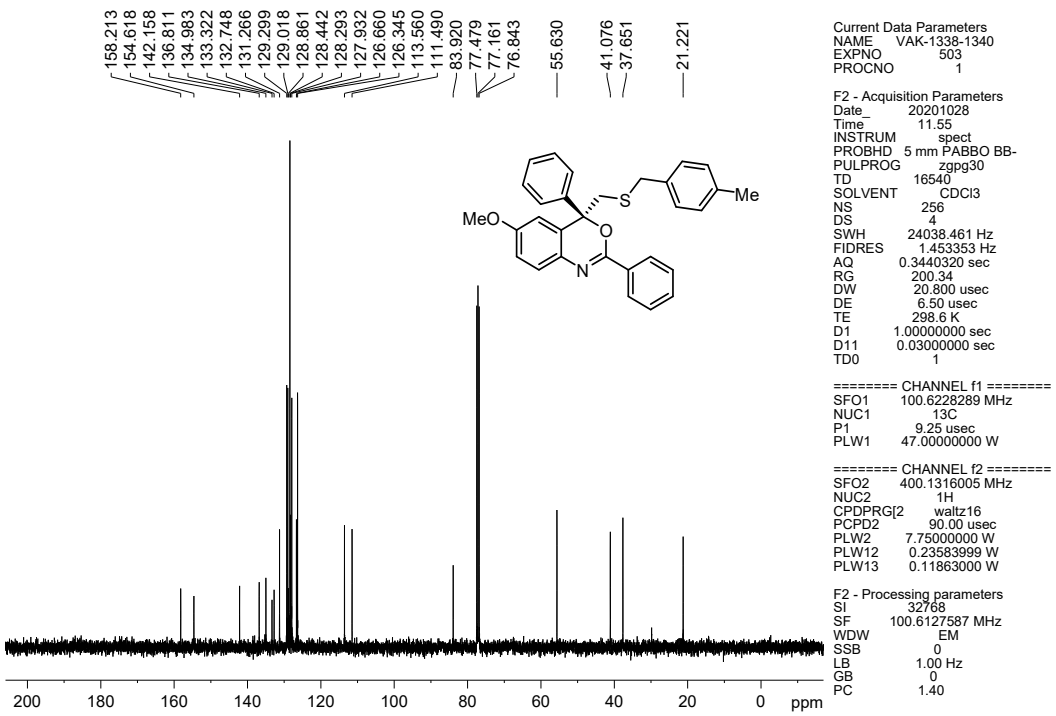
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24˚C):



(*R*)-6-Methoxy-4-(((4-methylbenzyl)thio)methyl)-2,4-diphenyl-4*H*-benzo[d][1,3]oxazine (3p)
^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):

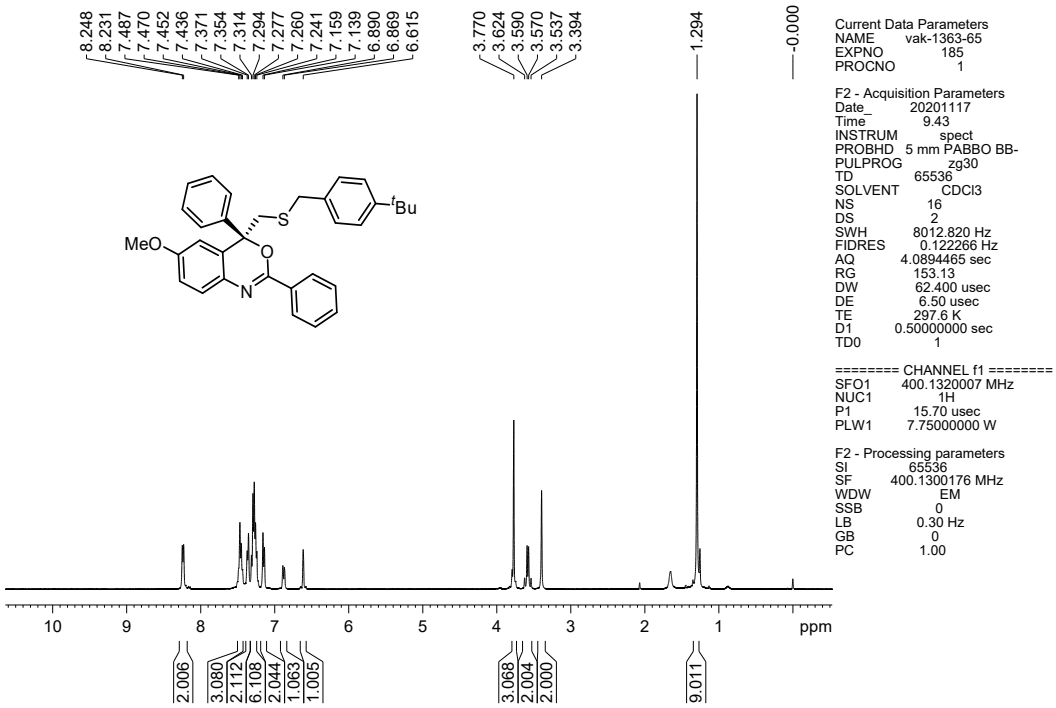


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24˚C):

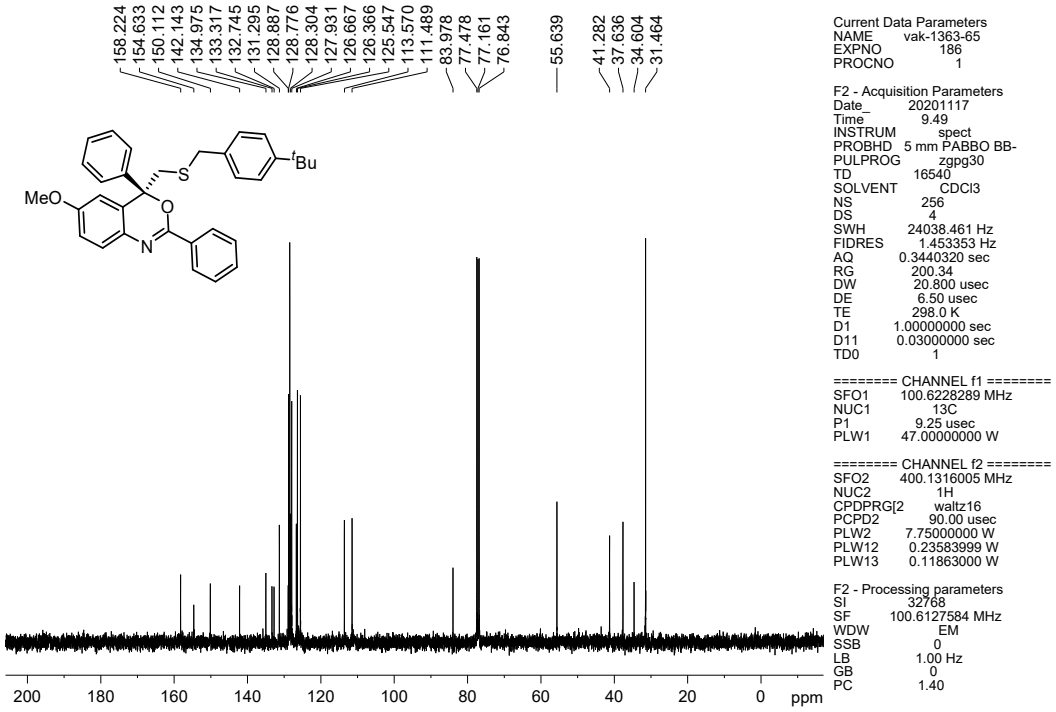


(*R*)-4-(((4-(Tert-butyl)benzyl)thio)methyl)-6-methoxy-2,4-diphenyl-4*H*-benzo[d][1,3]oxazine (3q)

^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):

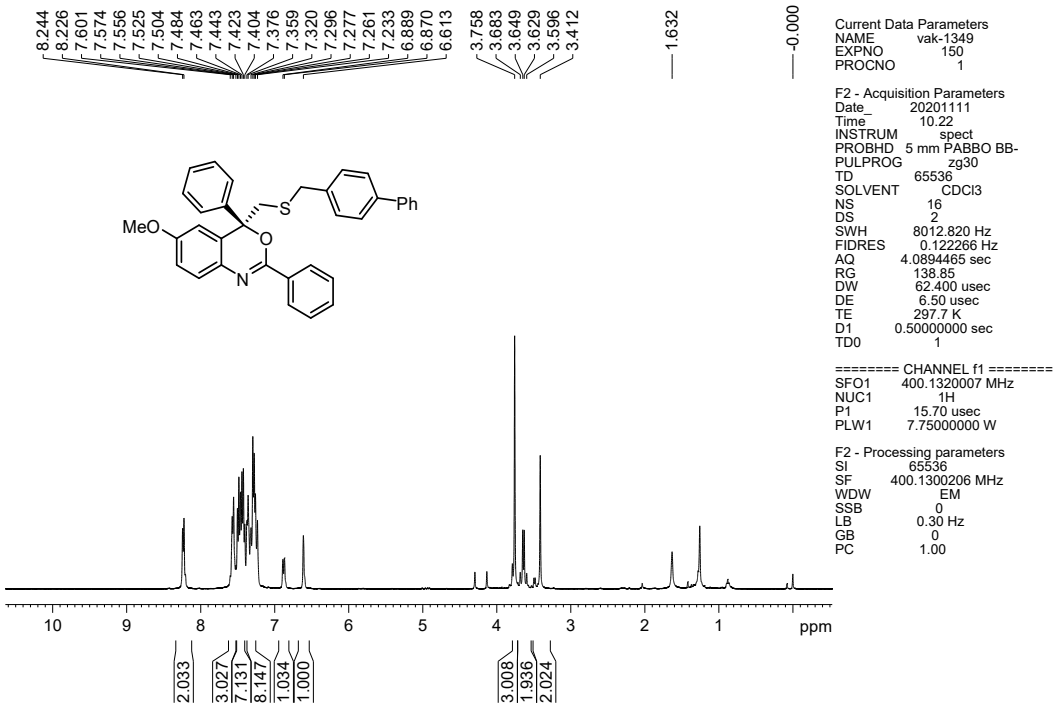


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24˚C):

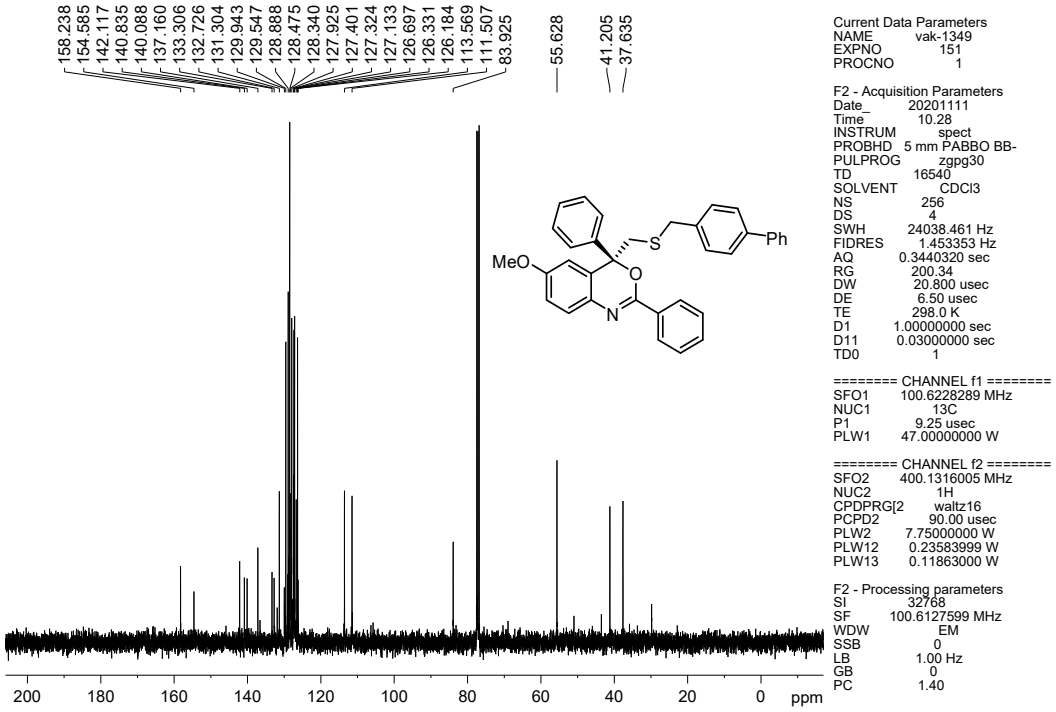


(*R*)-4-((([1,1'-Biphenyl]-4-ylmethyl)thio)methyl)-6-methoxy-2,4-diphenyl-4*H*-benzo[d][1,3]oxazine (3r)

^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):

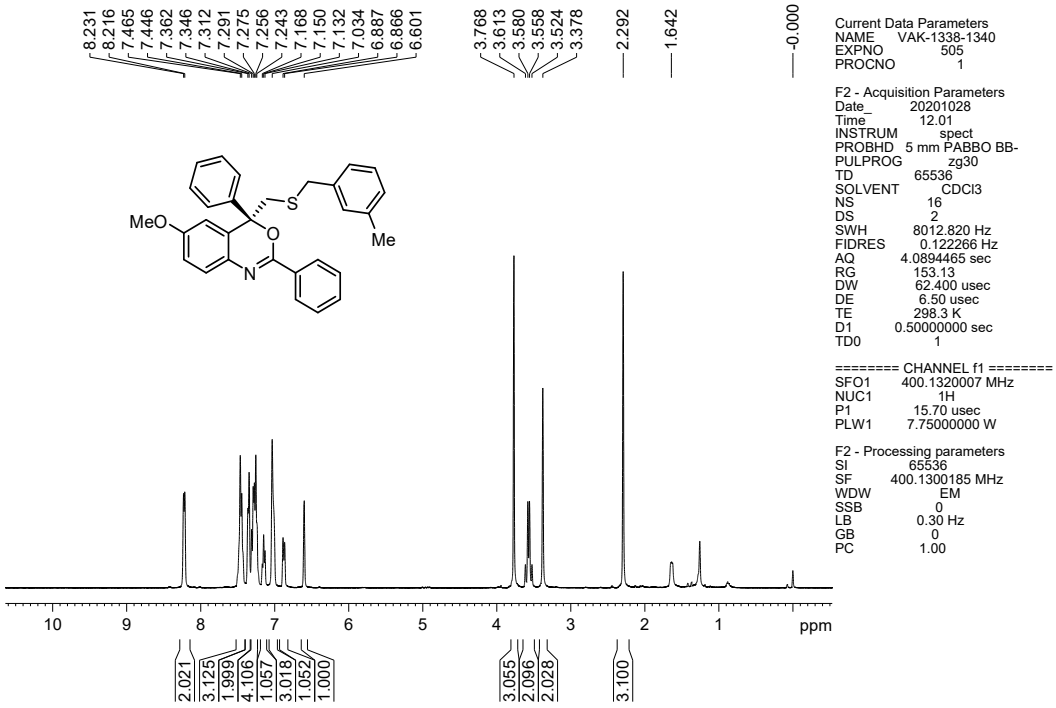


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24˚C):

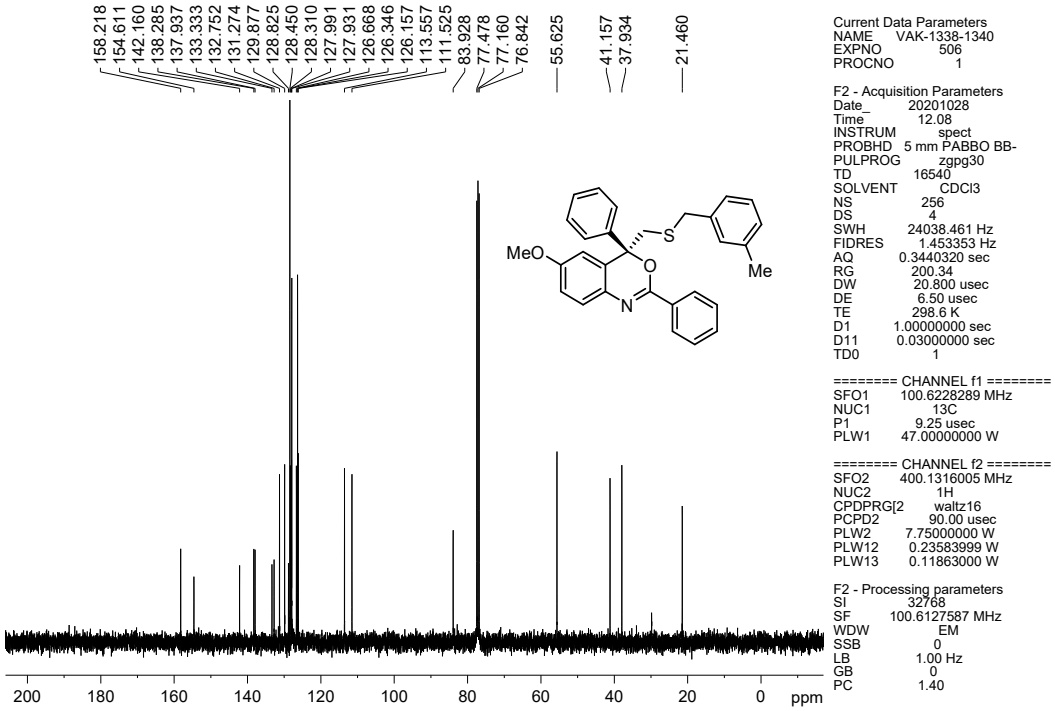


(*R*)-6-Methoxy-4-(((3-methylbenzyl)thio)methyl)-2,4-diphenyl-4*H*-benzo[d][1,3]oxazine (3s)

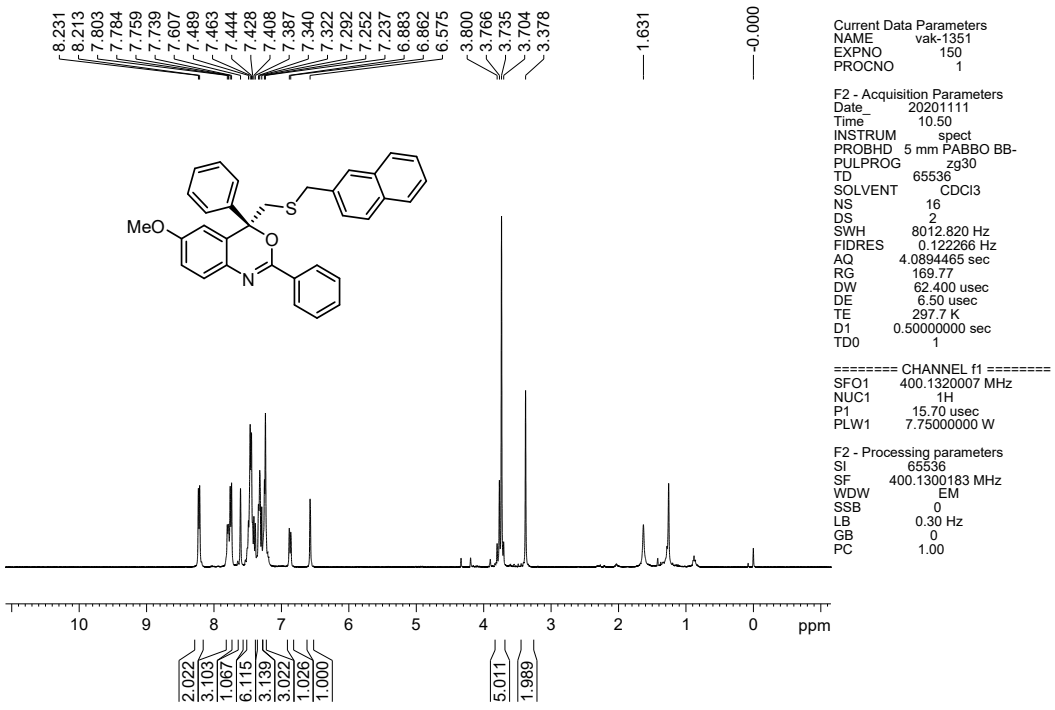
^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):



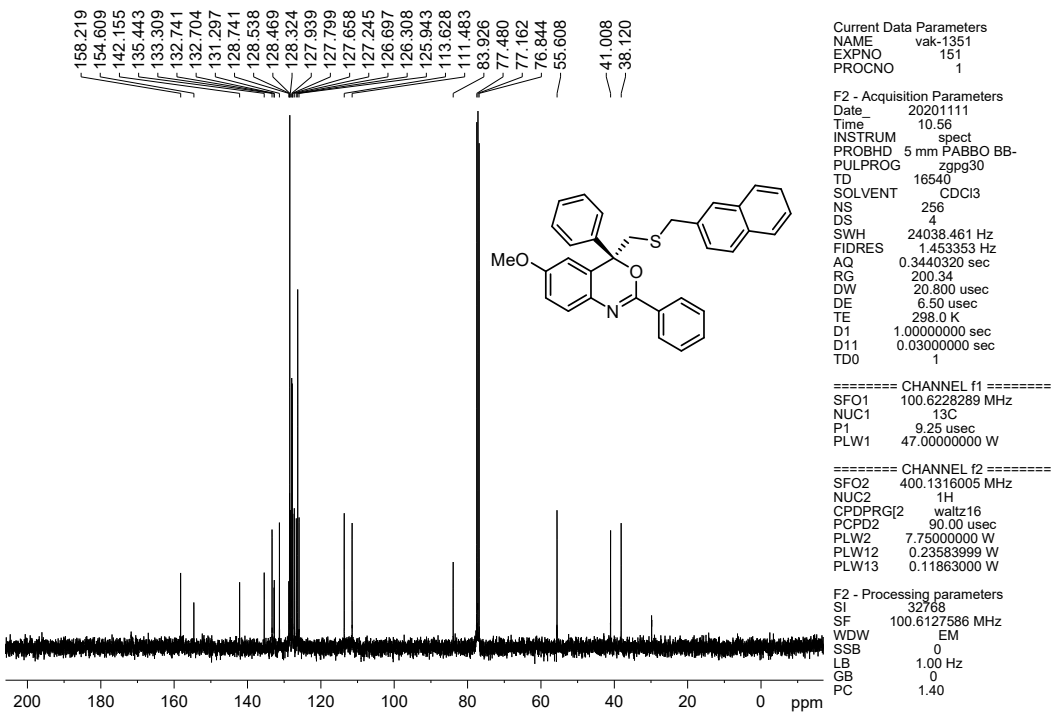
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24˚C):



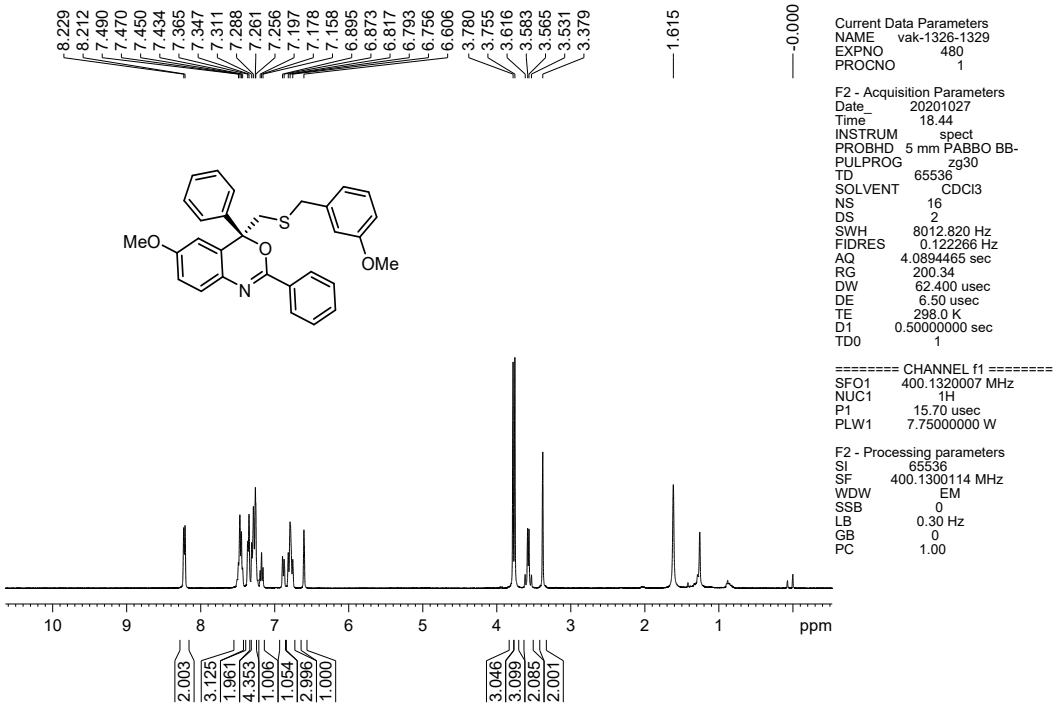
(*R*)-6-Methoxy-4-(((naphthalen-2-ylmethyl)thio)methyl)-2,4-diphenyl-4*H*-benzo[d][1,3]oxazine (3t)
^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):



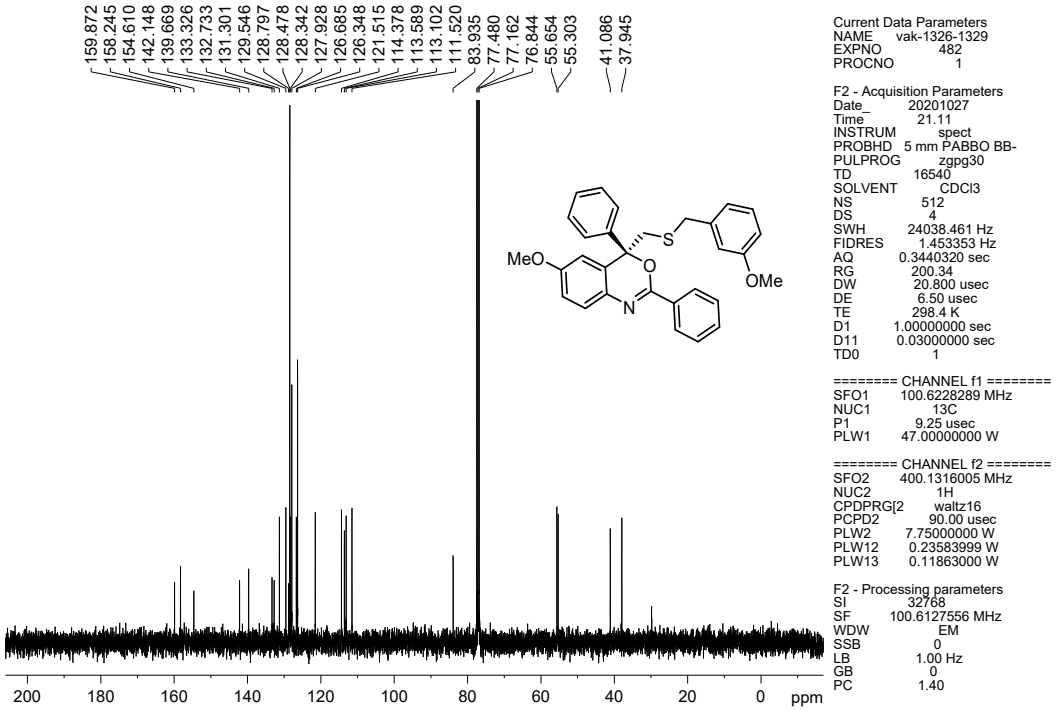
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24˚C):



(*R*)-6-Methoxy-4-(((3-methoxybenzyl)thio)methyl)-2,4-diphenyl-4*H*-benzo[d][1,3]oxazine (3u)
^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):

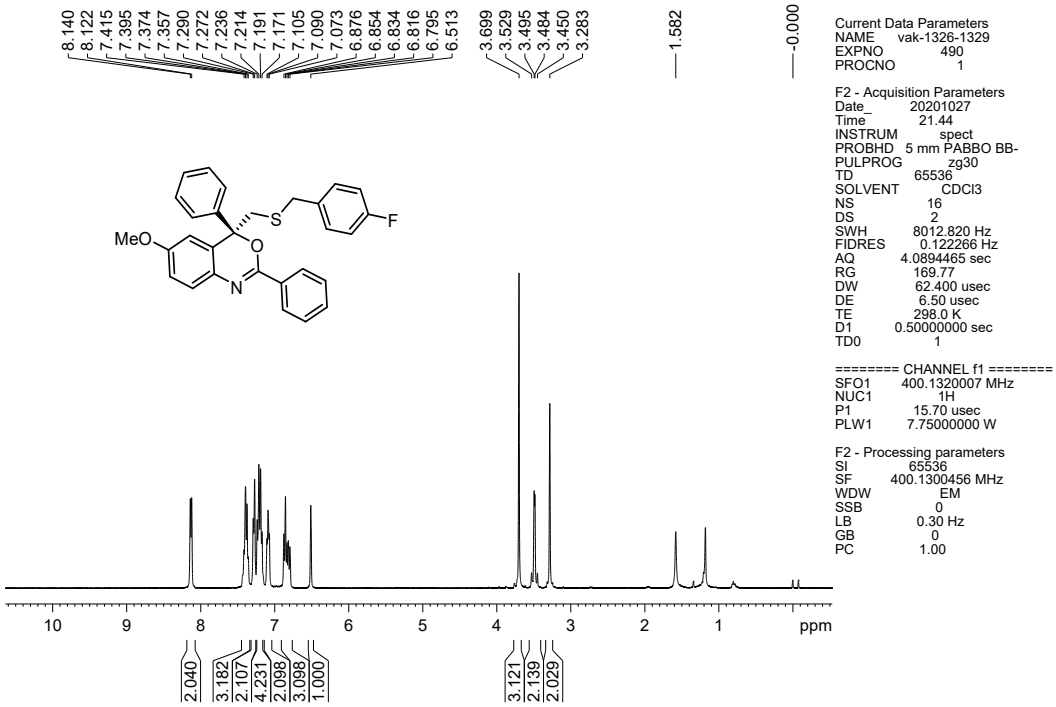


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24˚C):

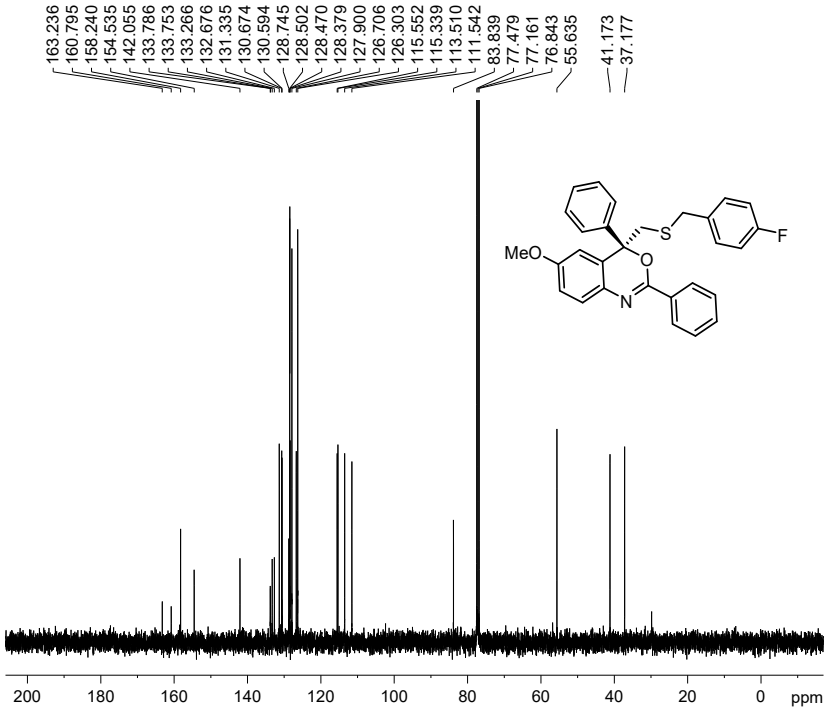


(*R*)-4-(((4-Fluorobenzyl)thio)methyl)-6-methoxy-2,4-diphenyl-4*H*-benzo[d][1,3]oxazine (3v)

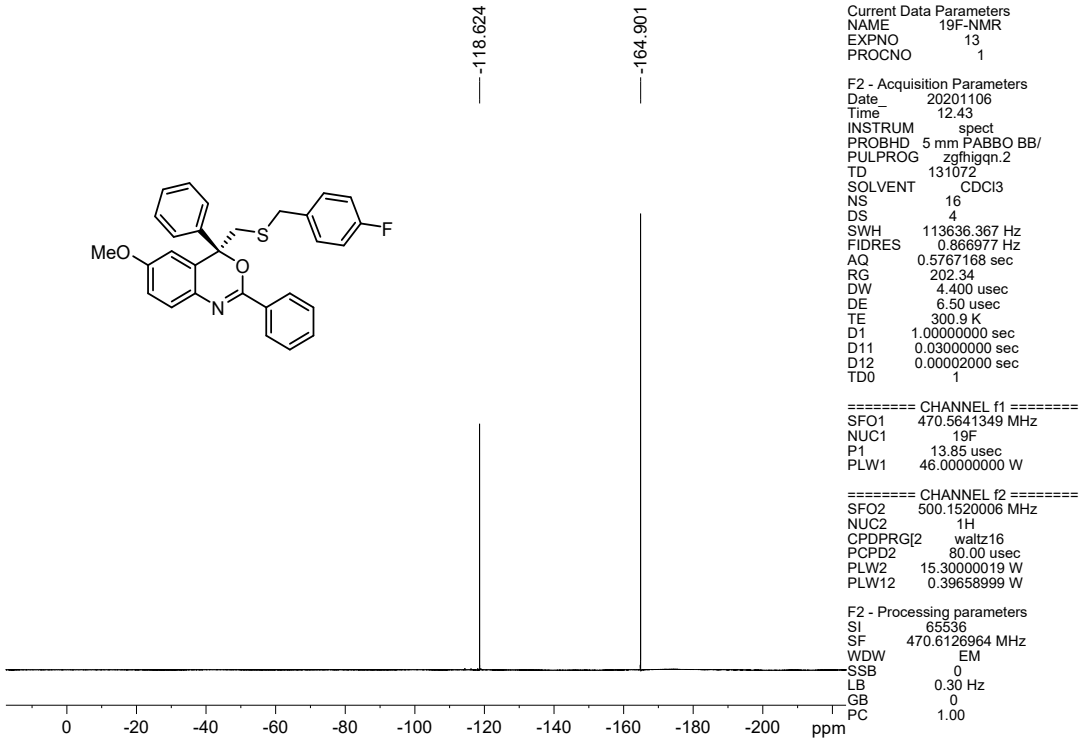
^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24˚C):

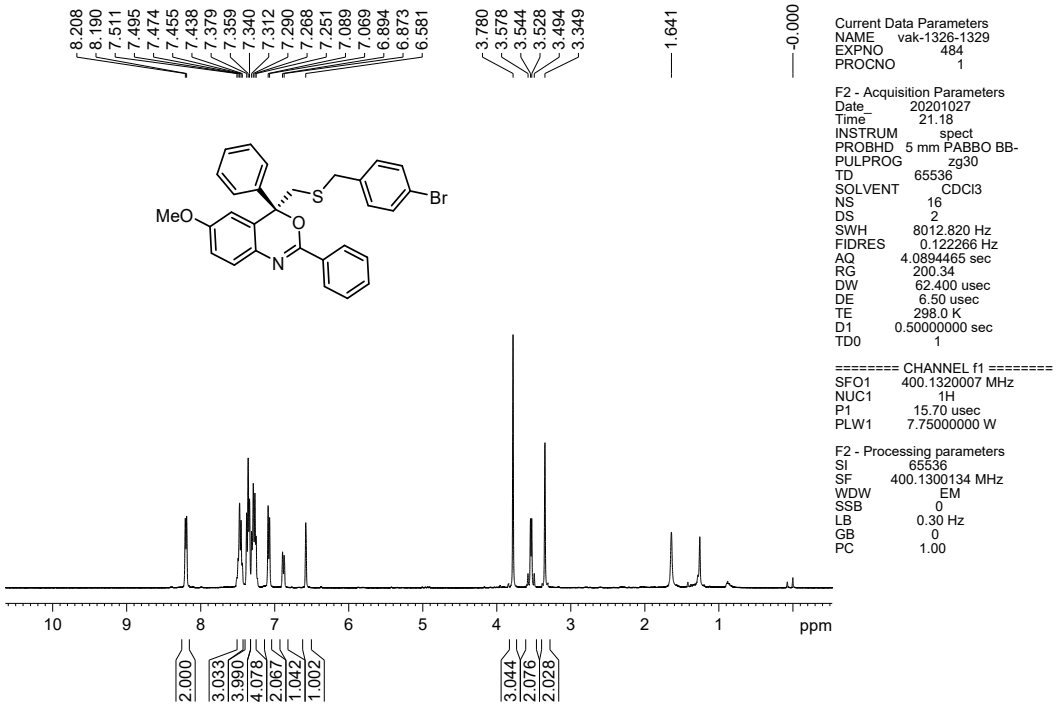


^{19}F NMR (470 MHz, $CDCl_3$, 24˚C):

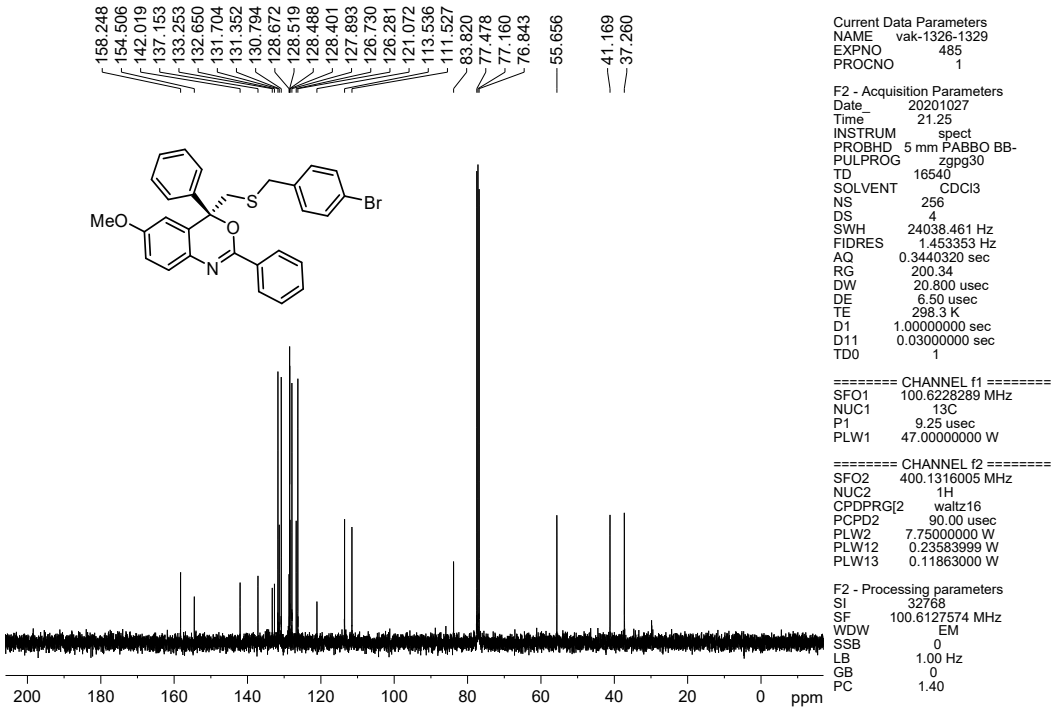


(*R*)-4-(((4-Bromobenzyl)thio)methyl)-6-methoxy-2,4-diphenyl-4*H*-benzo[d][1,3]oxazine (3w)

^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):

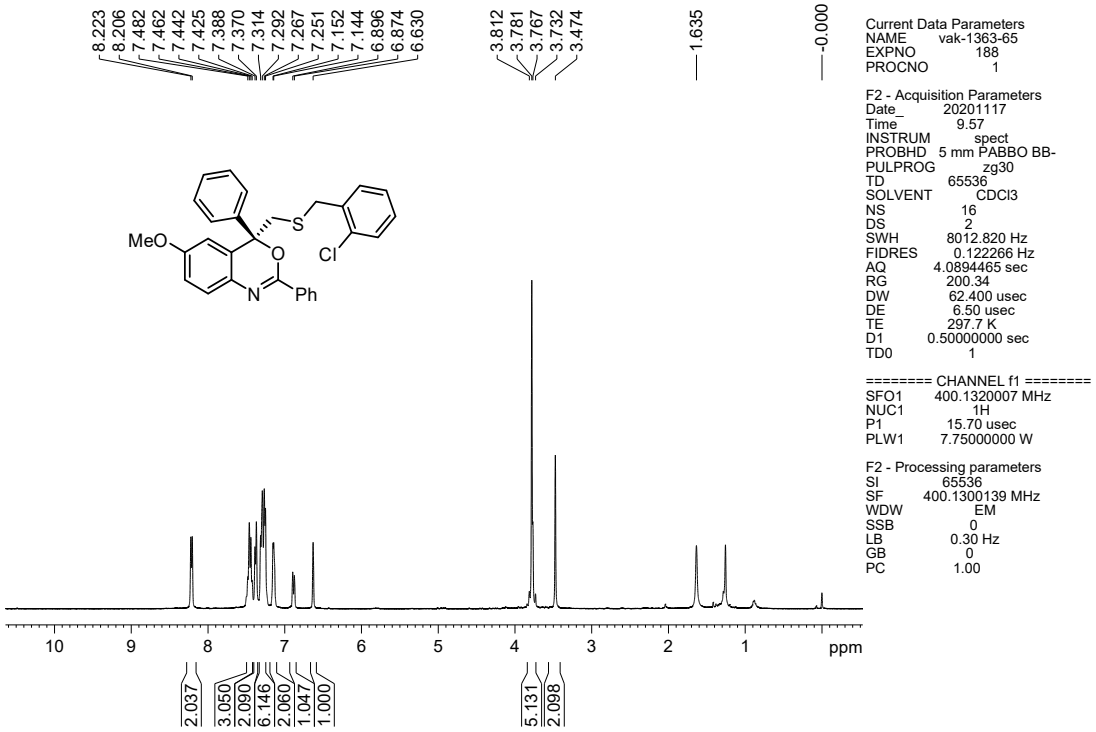


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24˚C):

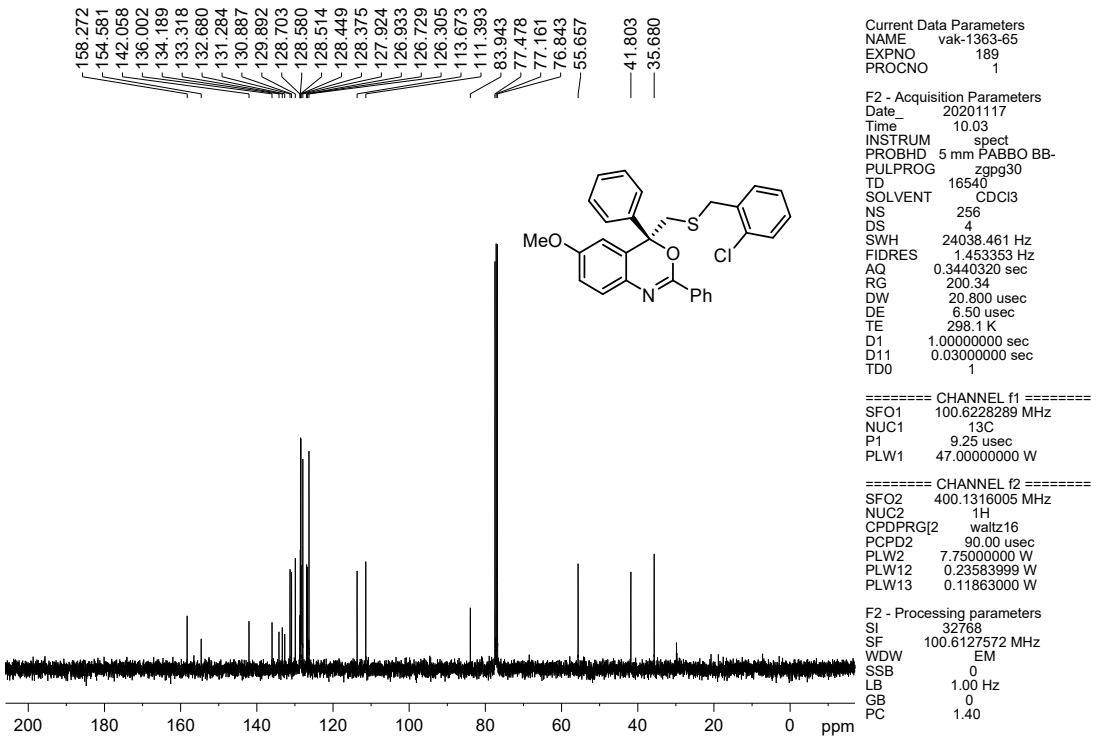


(*R*)-4-(((2-Chlorobenzyl)thio)methyl)-6-methoxy-2,4-diphenyl-4*H*-benzo[d][1,3]oxazine (3x):

^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):

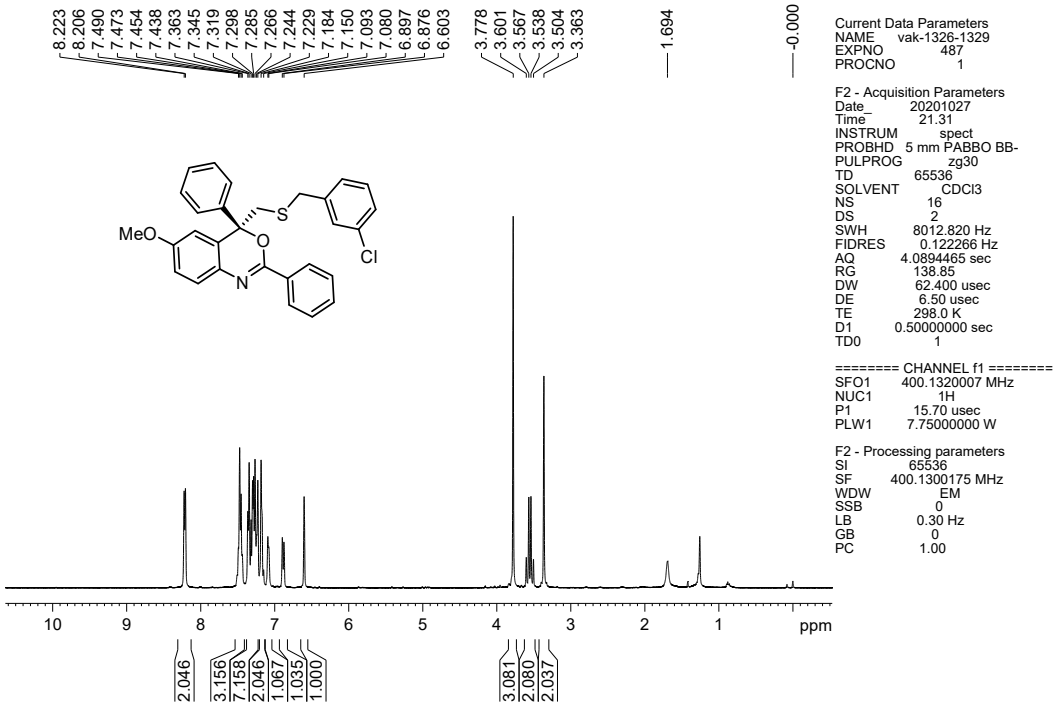


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24˚C):

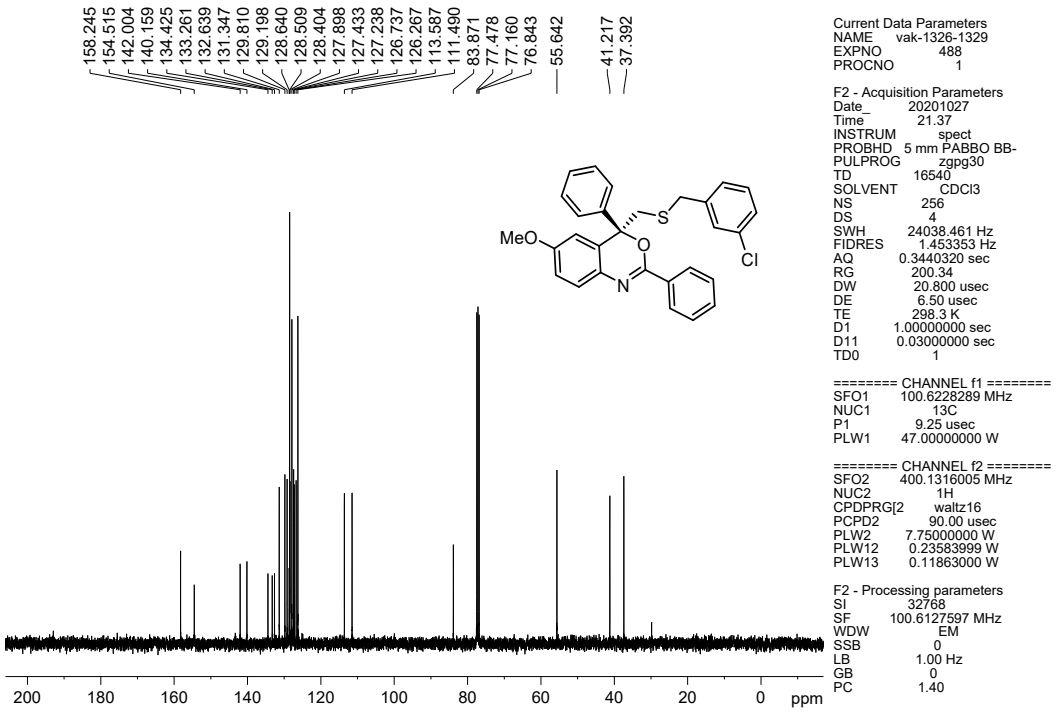


(*R*)-4-(((3-Chlorobenzyl)thio)methyl)-6-methoxy-2,4-diphenyl-4*H*-benzo[d][1,3]oxazine (3y)

^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):

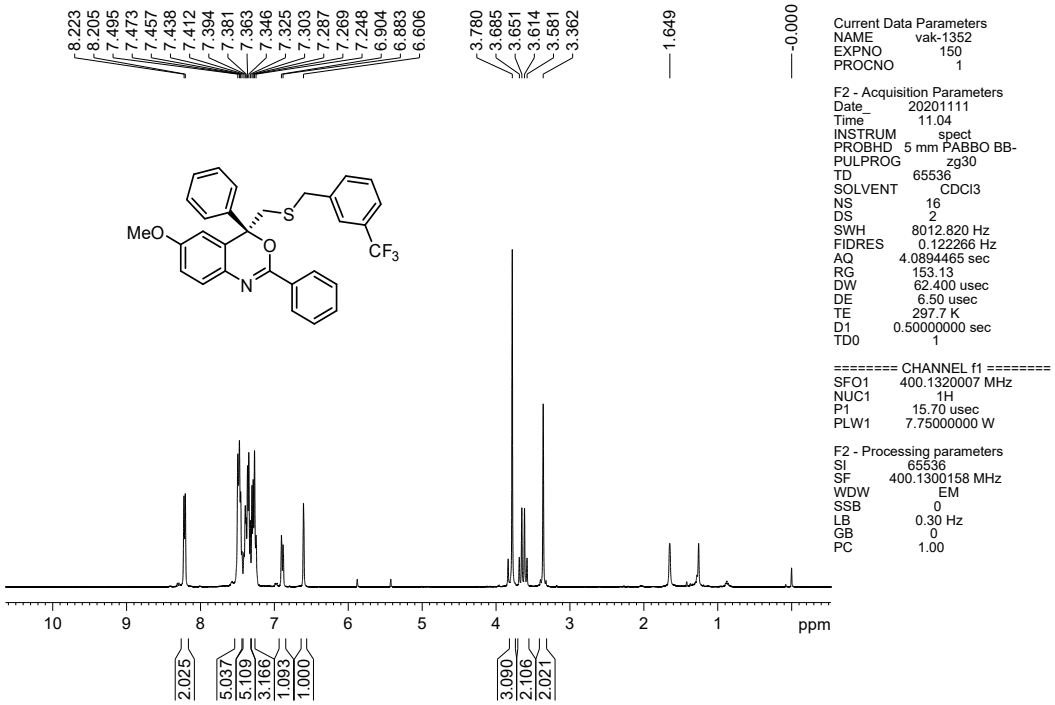


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24˚C):

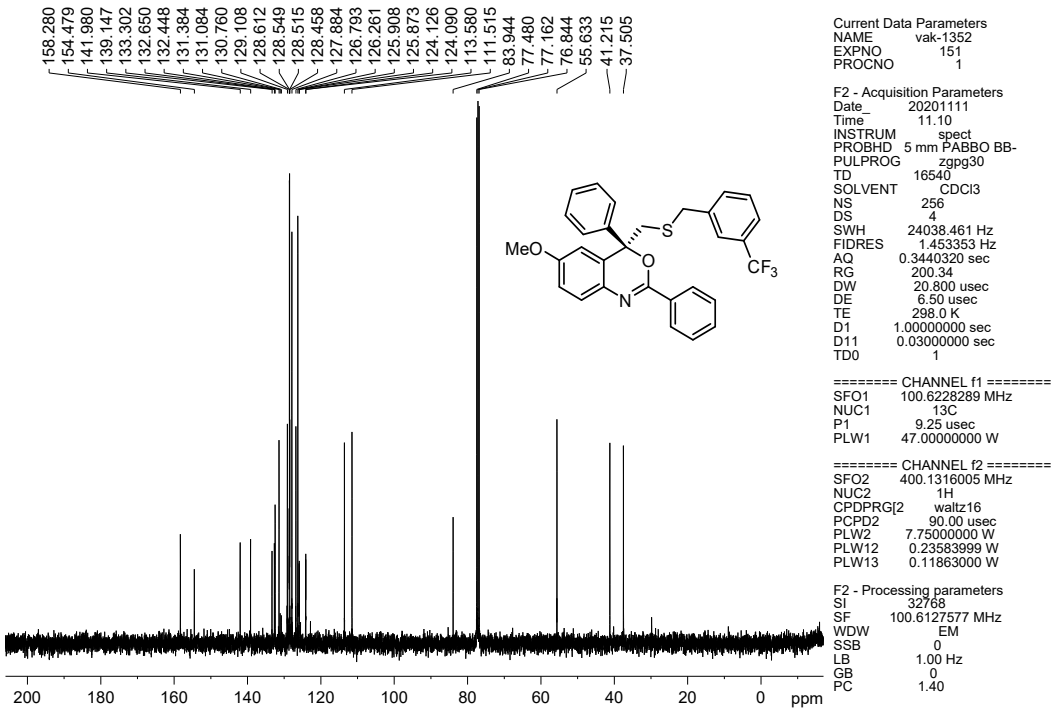


(*R*)-6-Methoxy-2,4-diphenyl-4-(((3-(trifluoromethyl)benzyl)thio)methyl)-4*H*-benzo[d][1,3]oxazine (3z)

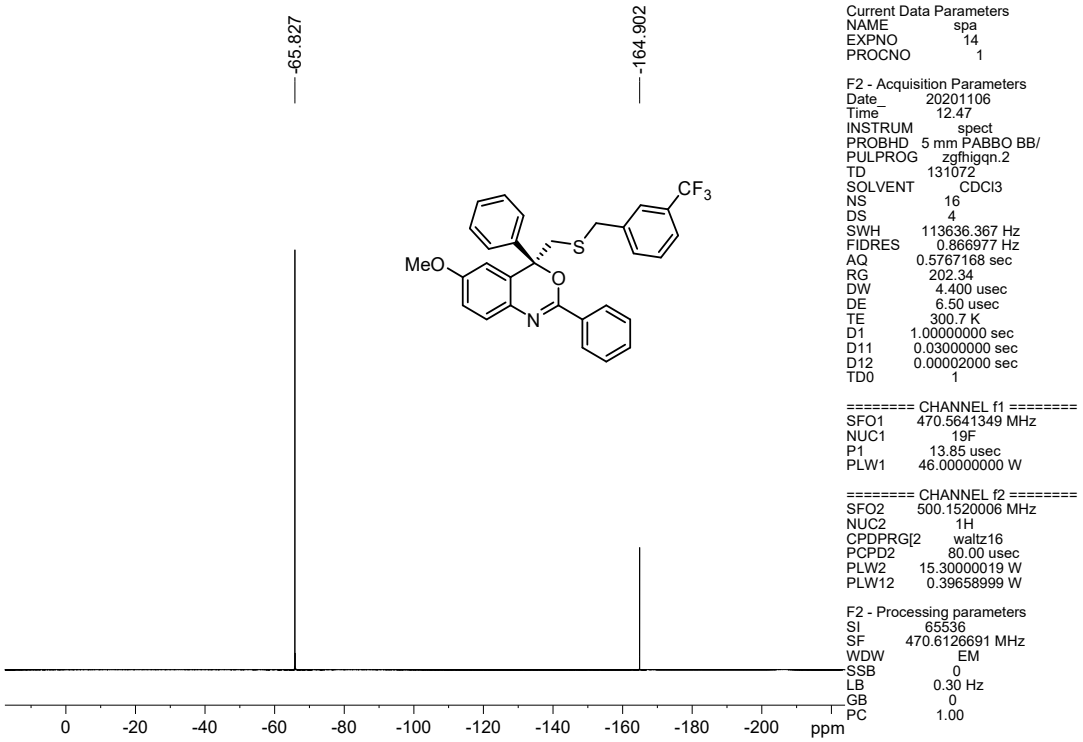
^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):



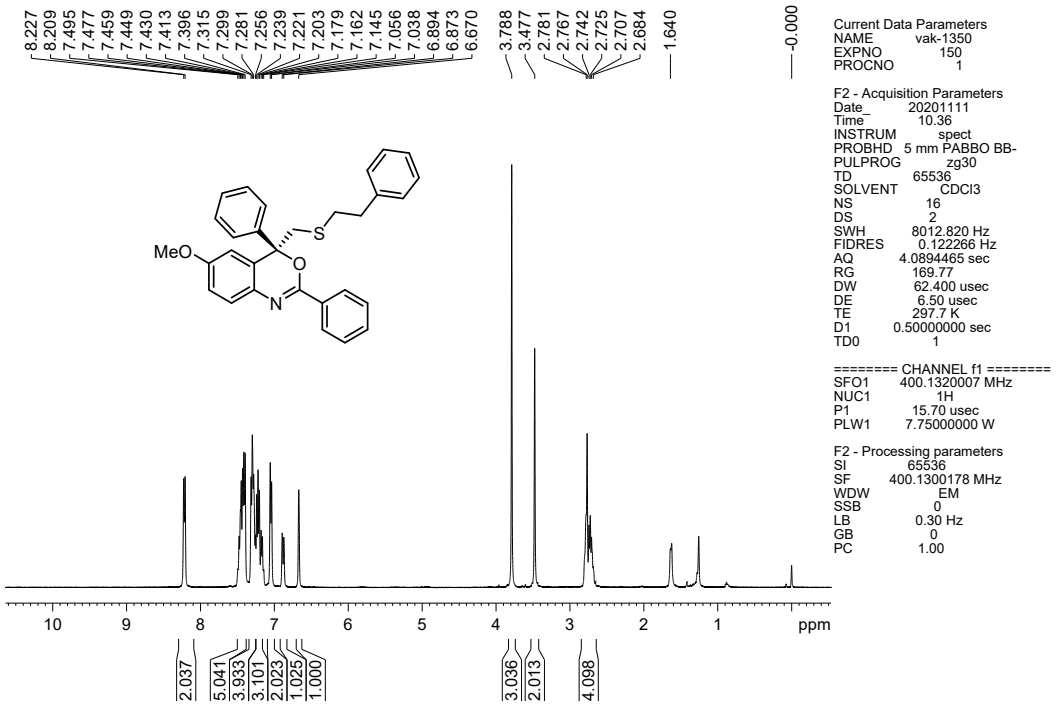
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24˚C):



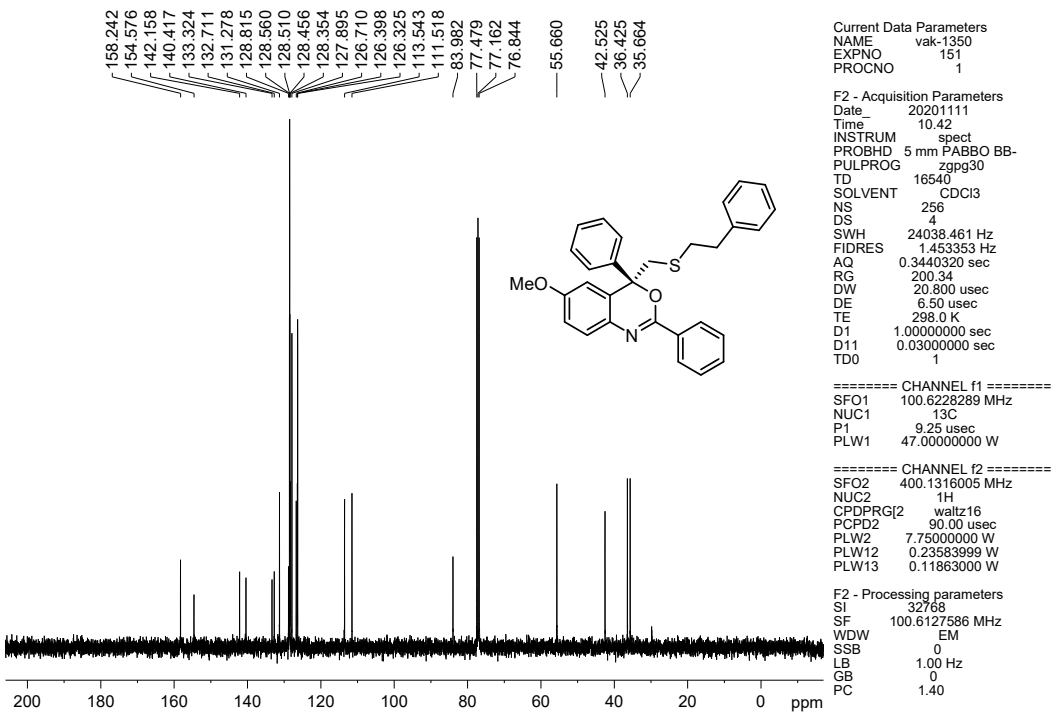
^{19}F NMR (470 MHz, $CDCl_3$, 24˚C):



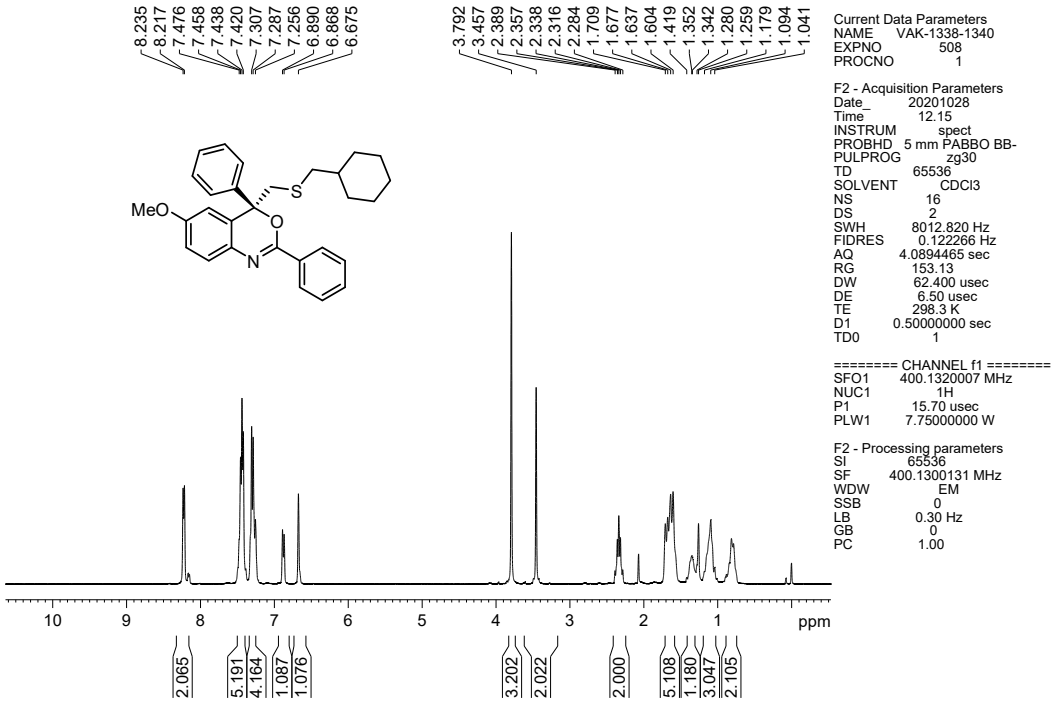
(*R*)-6-Methoxy-4-((phenethylthio)methyl)-2,4-diphenyl-4*H*-benzo[d][1,3]oxazine (3aa)
^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):



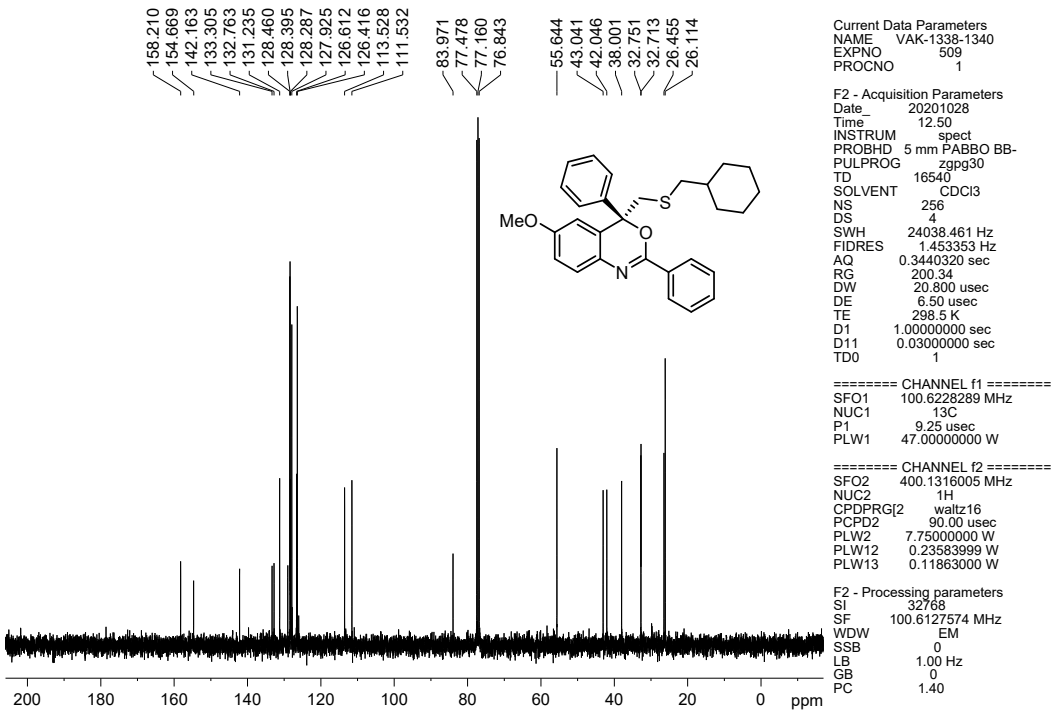
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24˚C):



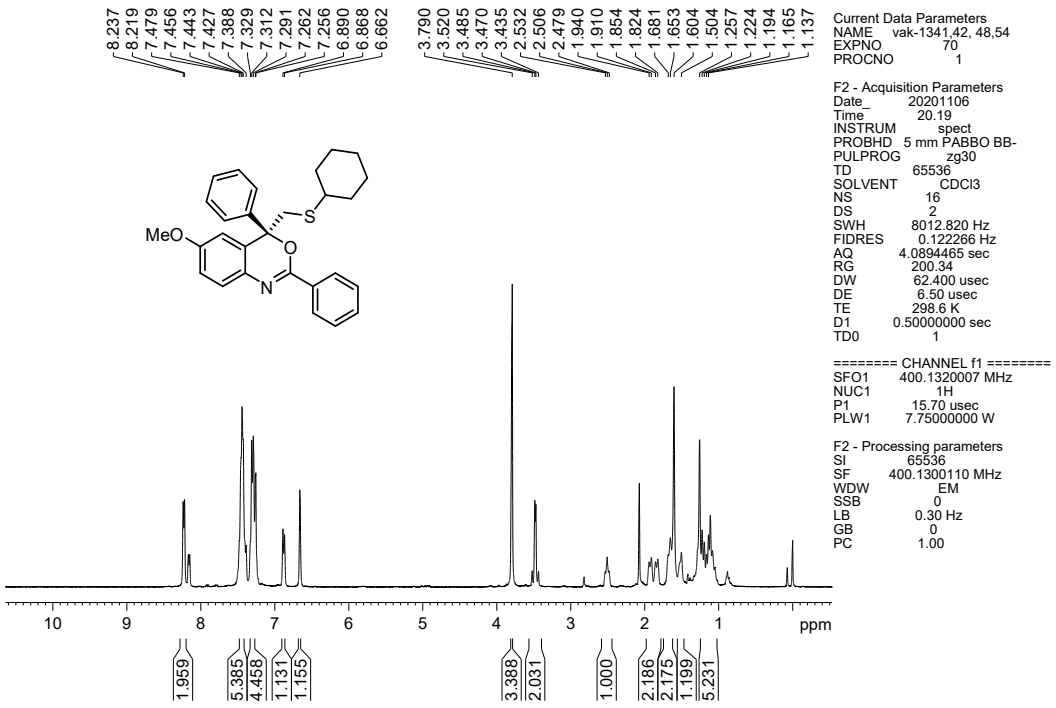
(*R*)-4-(((Cyclohexylmethyl)thio)methyl)-6-methoxy-2,4-diphenyl-4*H*-benzo[d][1,3]oxazine (3ab)
^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):



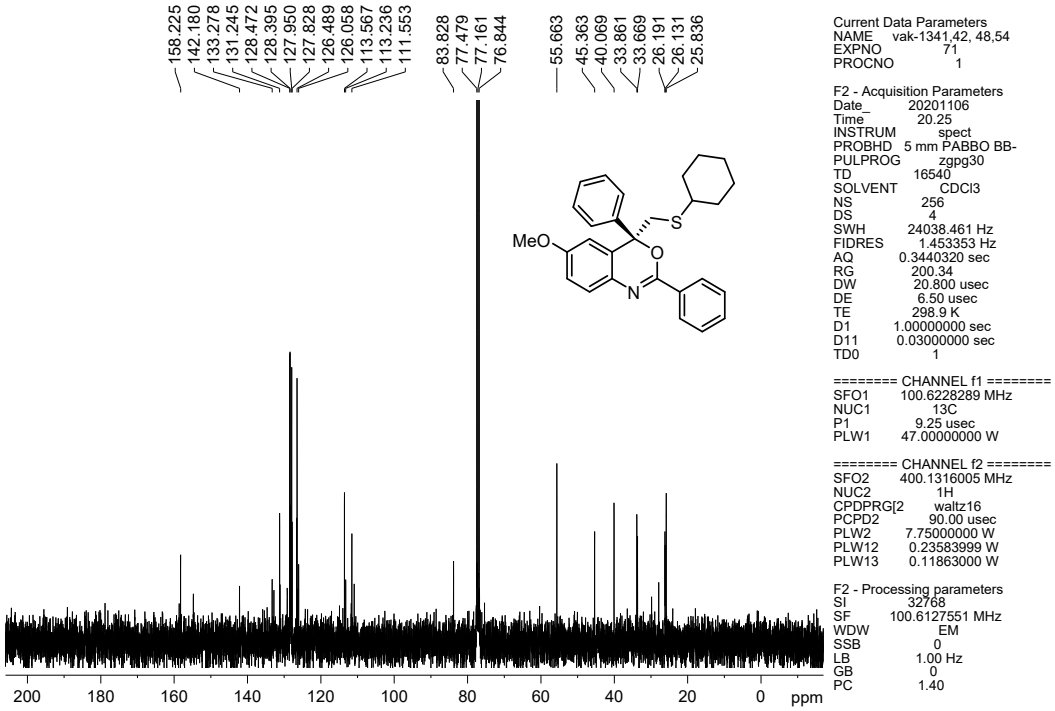
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24˚C):



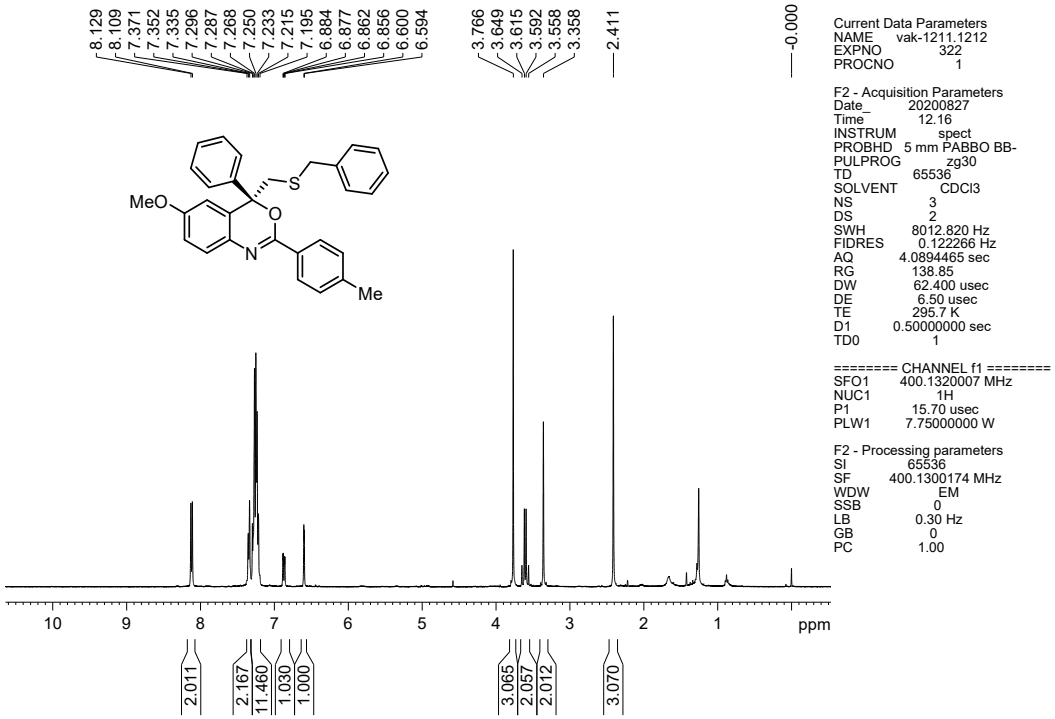
(*R*)-4-((Cyclohexylthio)methyl)-6-methoxy-2,4-diphenyl-4*H*-benzo[d][1,3]oxazine (3ac)
^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):



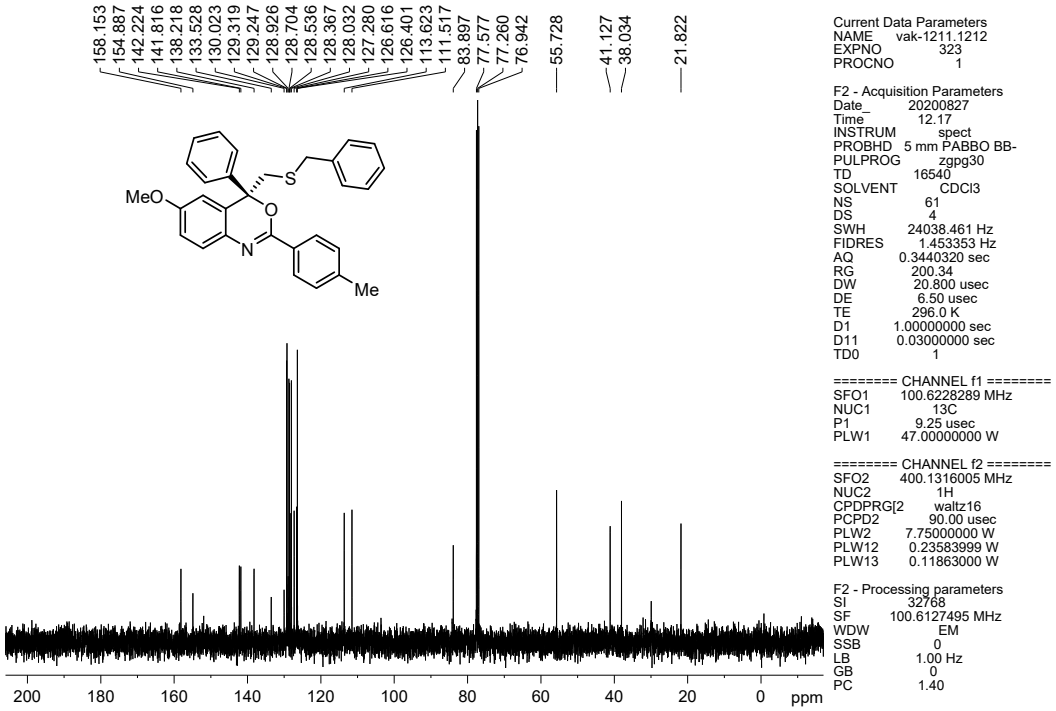
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24˚C):



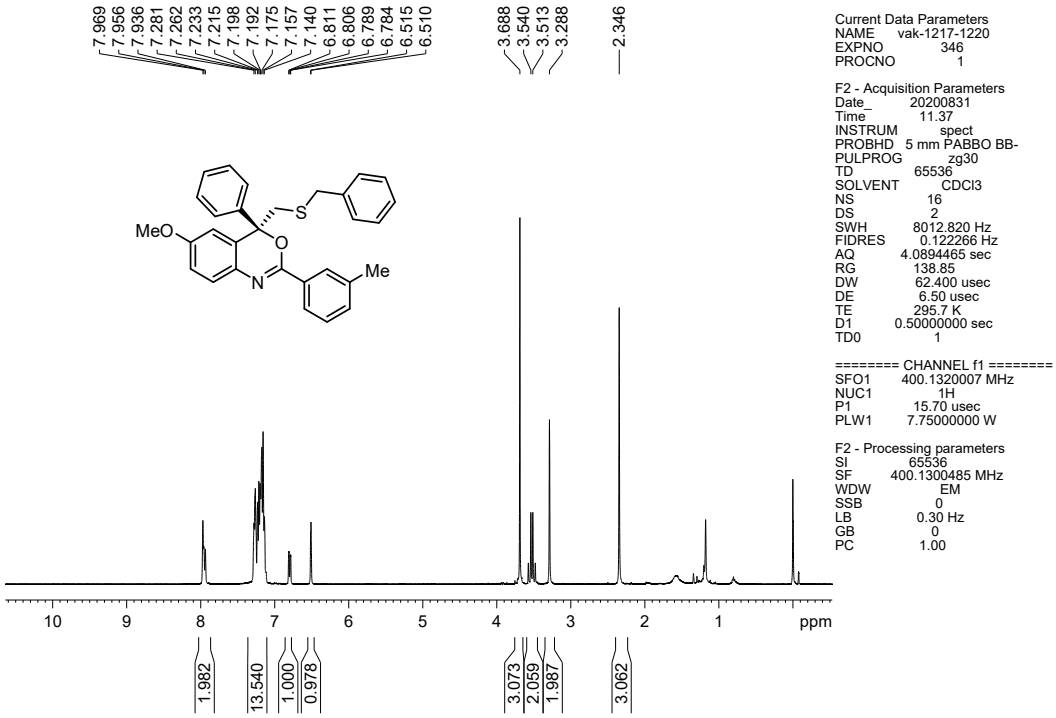
(*R*)-4-((Benzylthio)methyl)-6-methoxy-4-phenyl-2-(p-tolyl)-4*H*-benzo[d][1,3]oxazine (3ad)
^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):



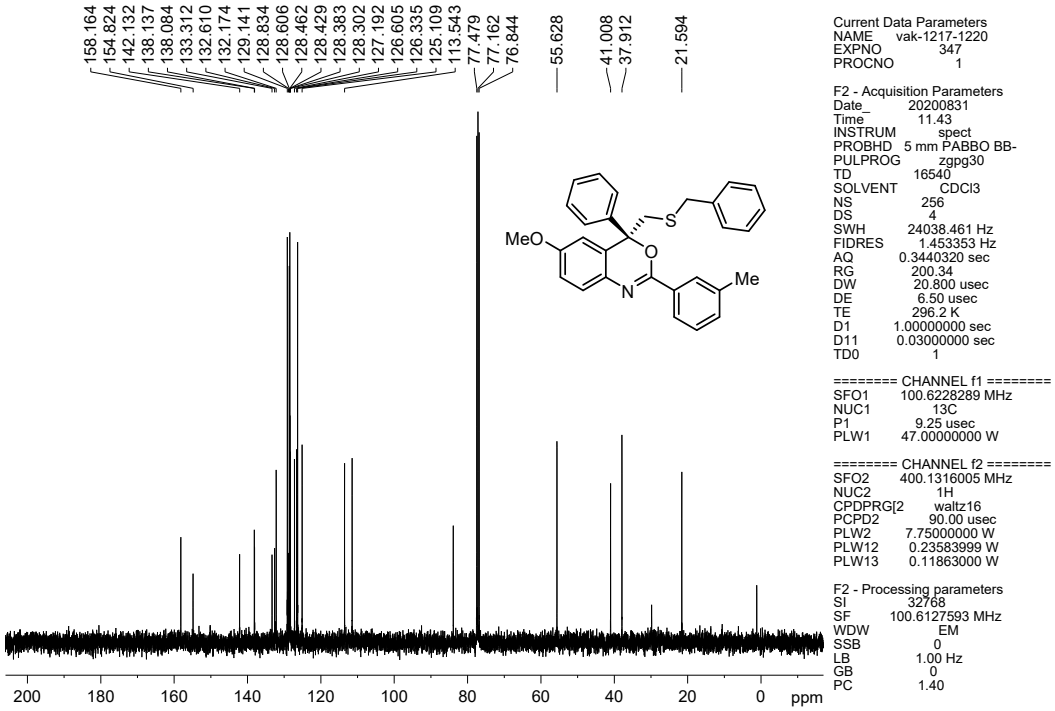
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24˚C):



(*R*)-4-((Benzylthio)methyl)-6-methoxy-4-phenyl-2-(m-tolyl)-4*H*-benzo[d][1,3]oxazine (3ae)
^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):

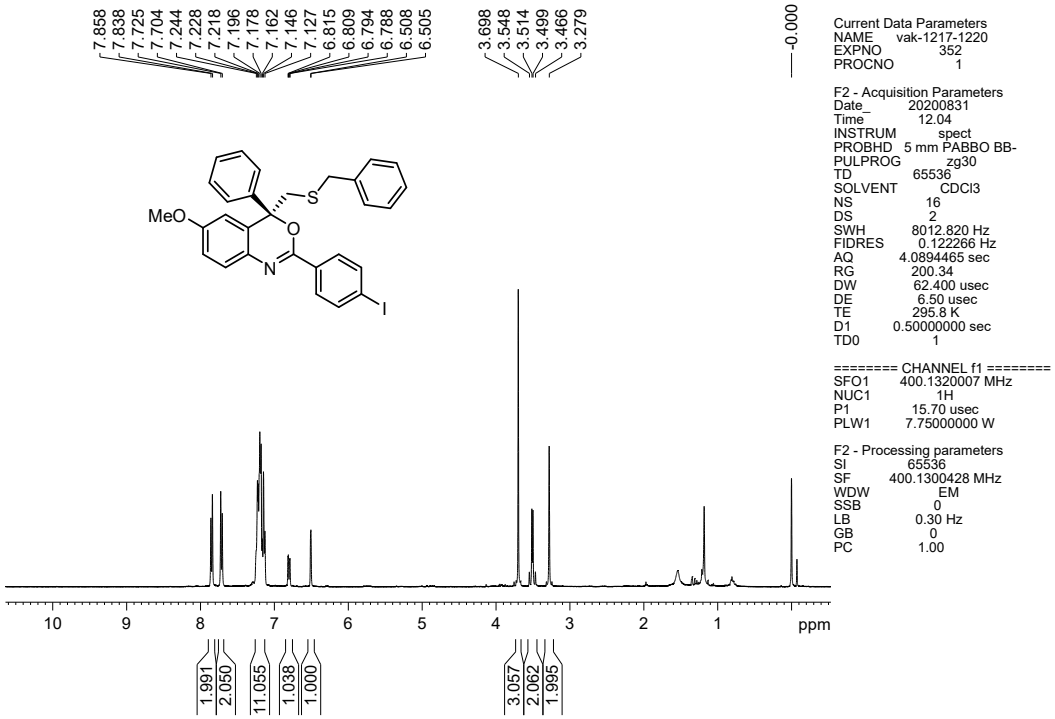


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24˚C):

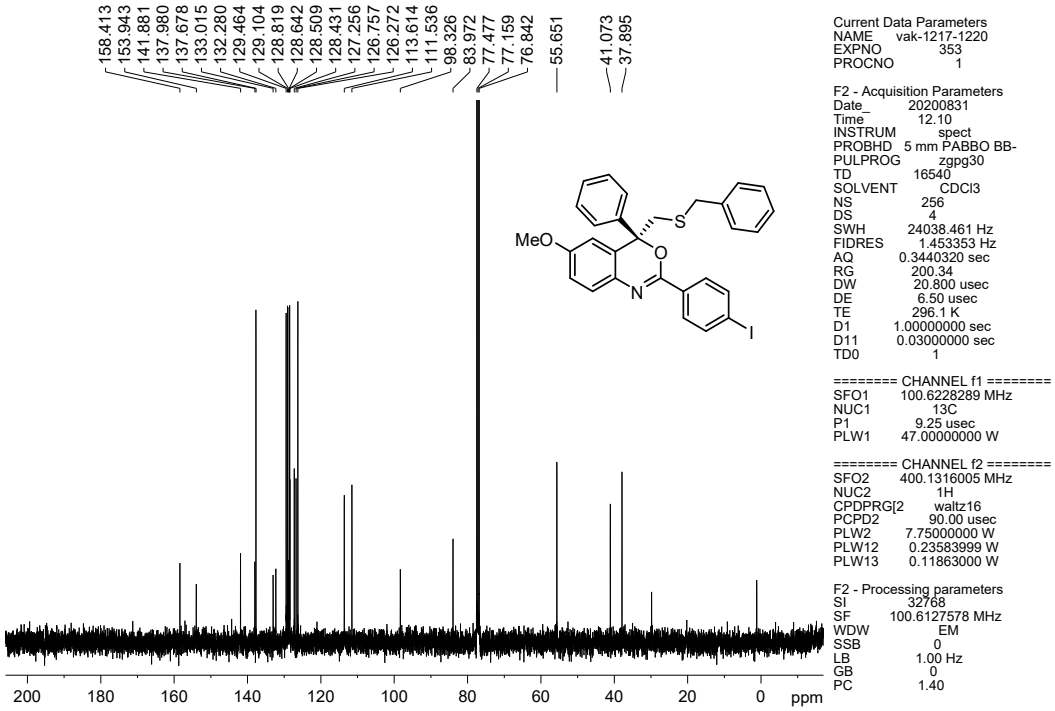


(*R*)-4-((Benzylthio)methyl)-2-(4-iodophenyl)-6-methoxy-4-phenyl-4*H*-benzo[d][1,3]oxazine (3af)

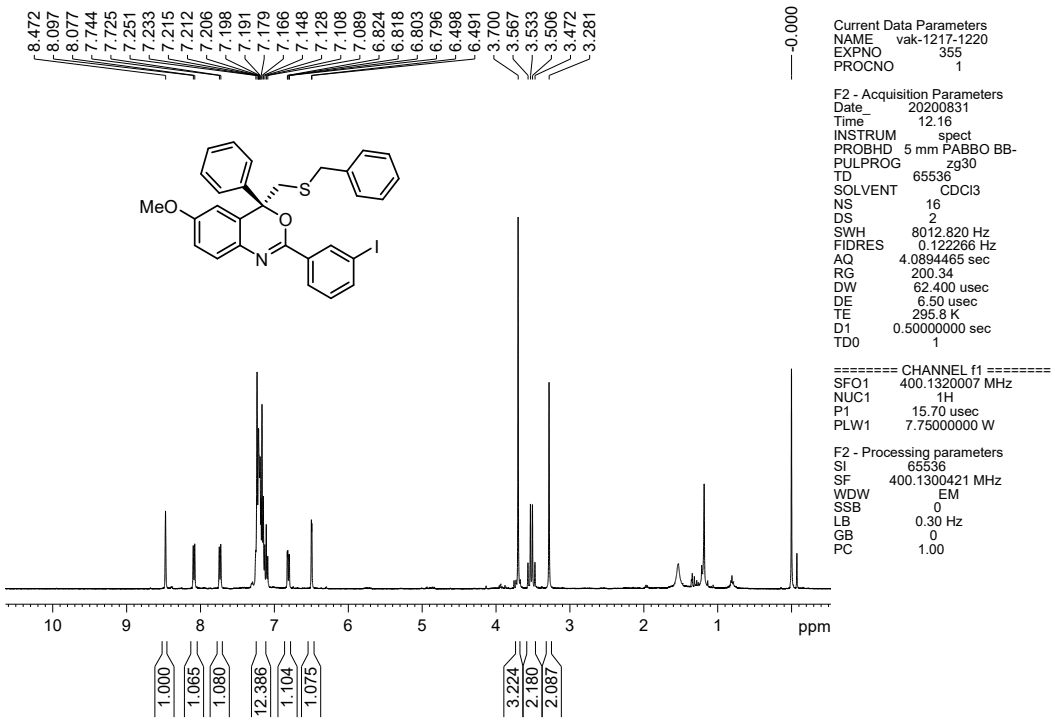
^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):



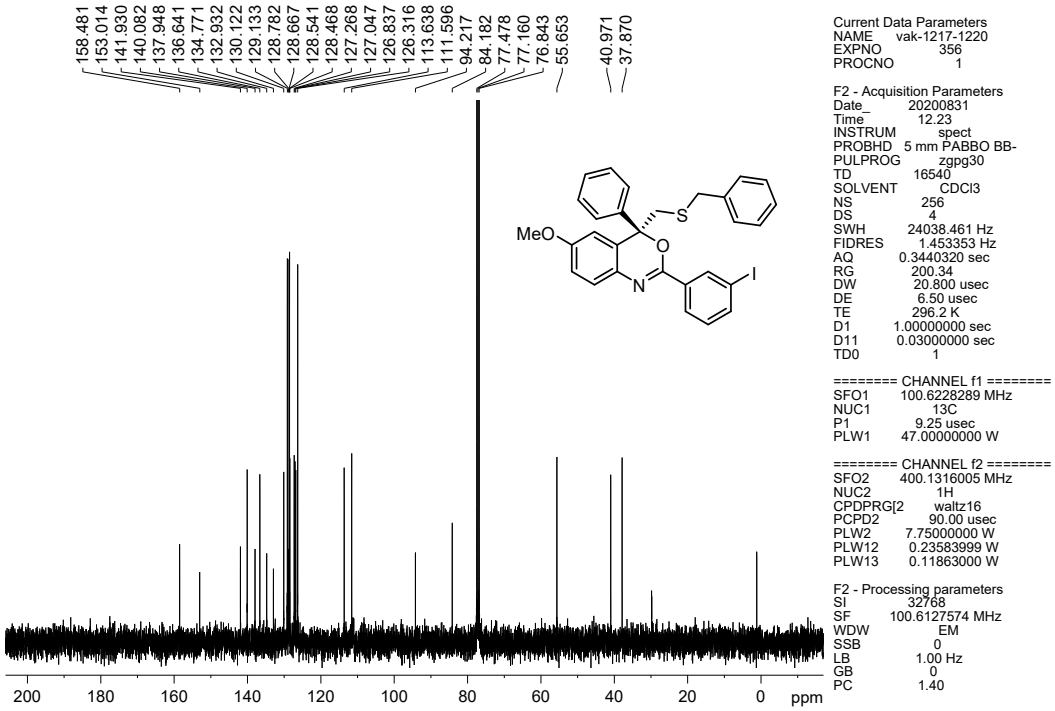
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24˚C):



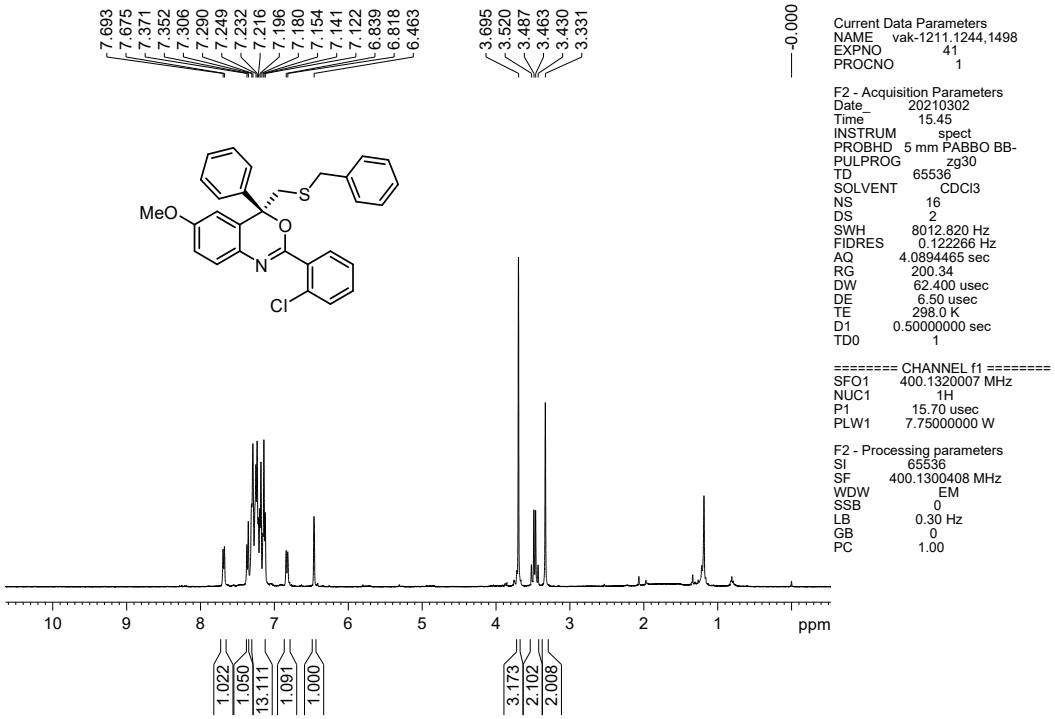
(*R*)-4-((Benzylthio)methyl)-2-(3-iodophenyl)-6-methoxy-4-phenyl-4*H*-benzo[d][1,3]oxazine (3ag)
^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):



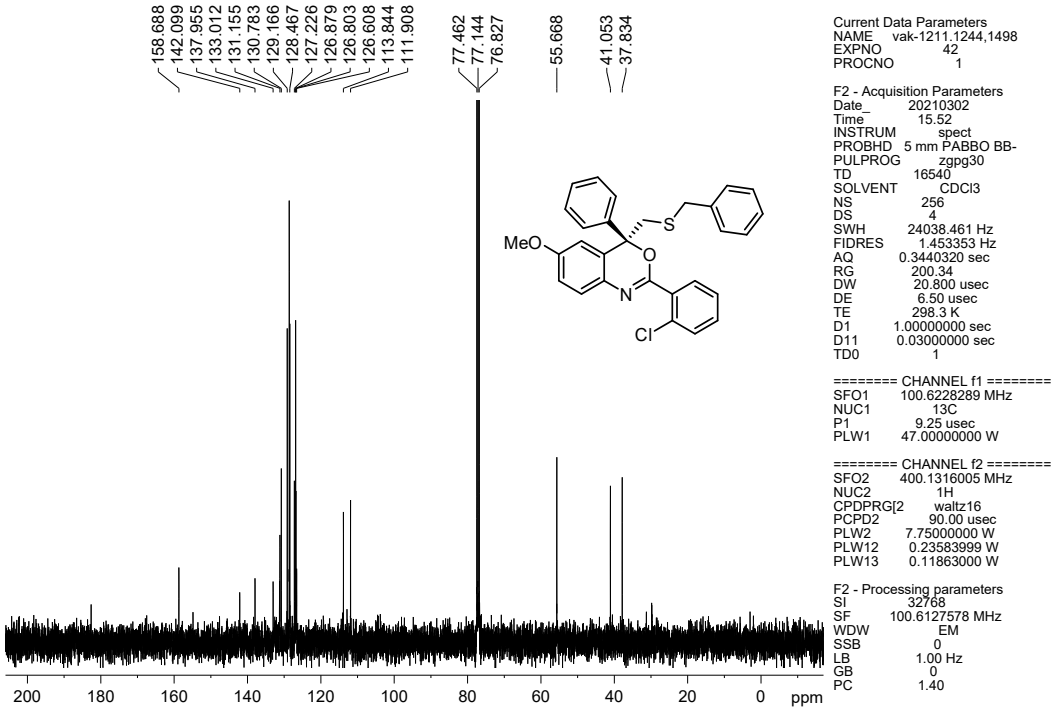
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24˚C):



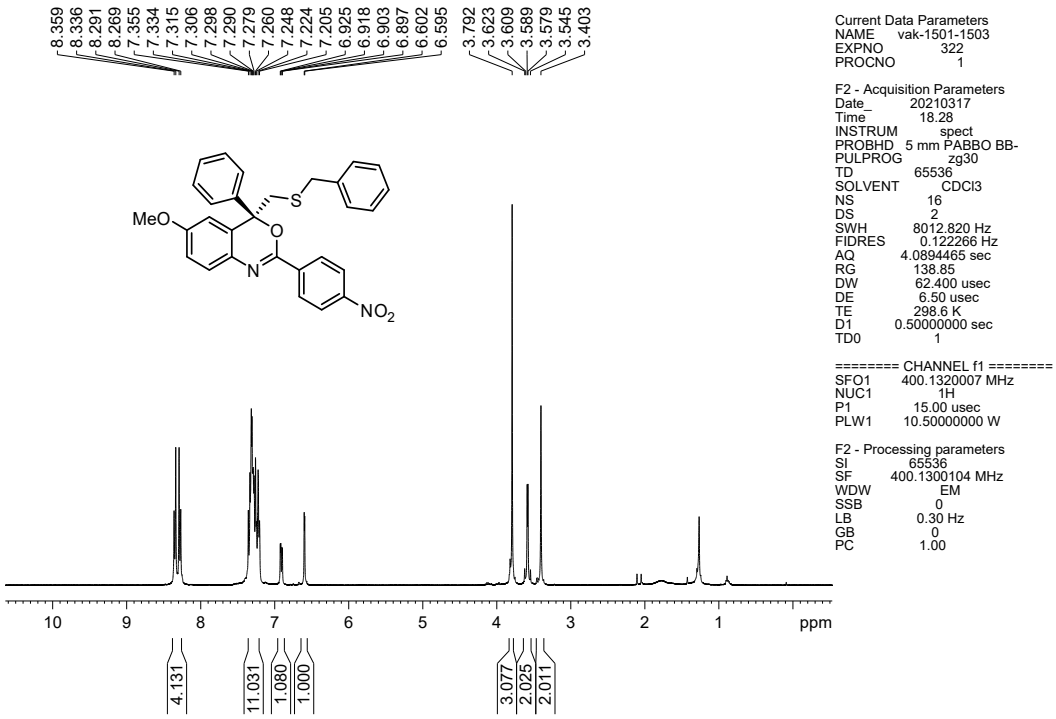
(*R*)-4-((Benzylthio)methyl)-2-(2-chlorophenyl)-6-methoxy-4-phenyl-4*H*-benzo[d][1,3]oxazine (3ah)
^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):



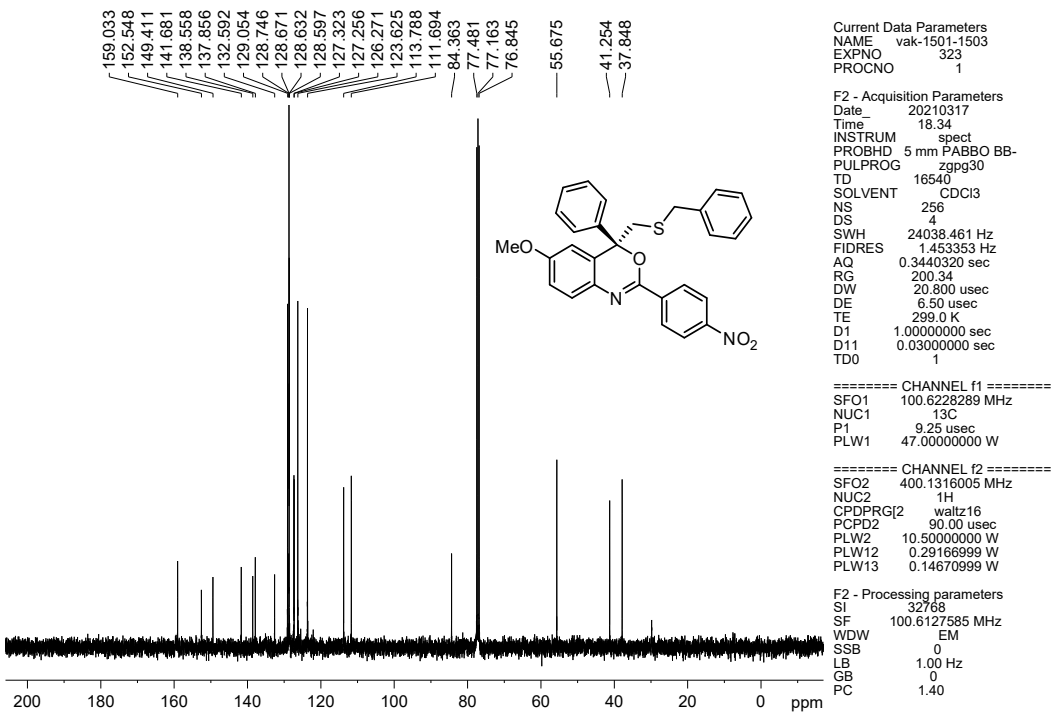
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24˚C):



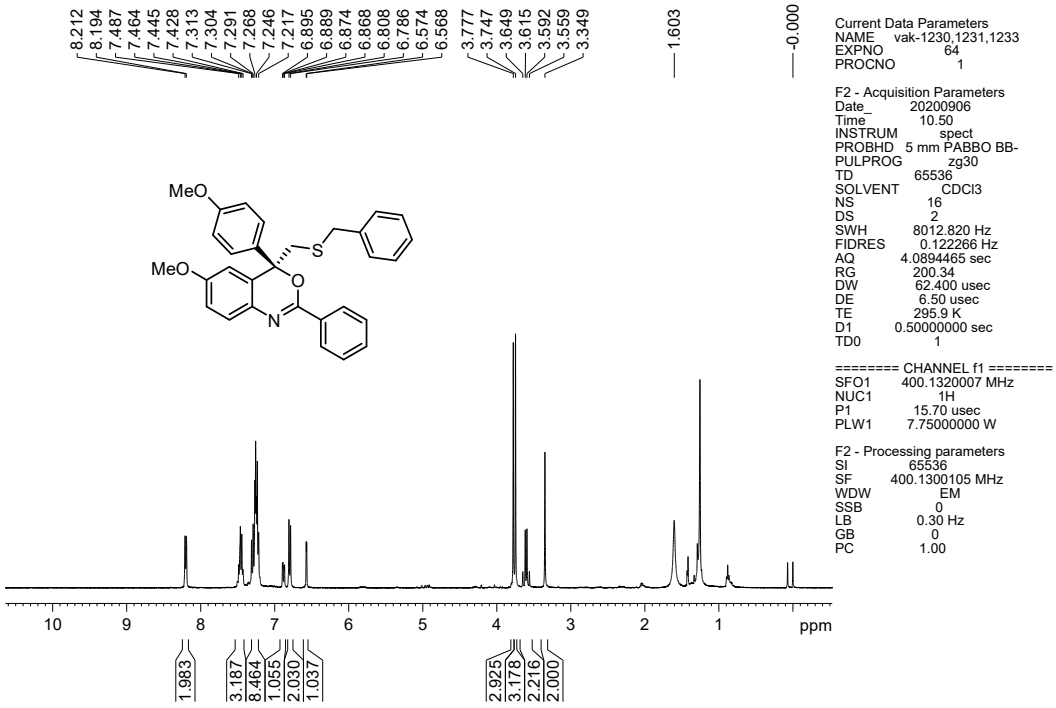
(*R*)-4-((Benzylthio)methyl)-6-methoxy-2-(4-nitrophenyl)-4-phenyl-4*H*-benzo[d][1,3]oxazine (3ai)
^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):



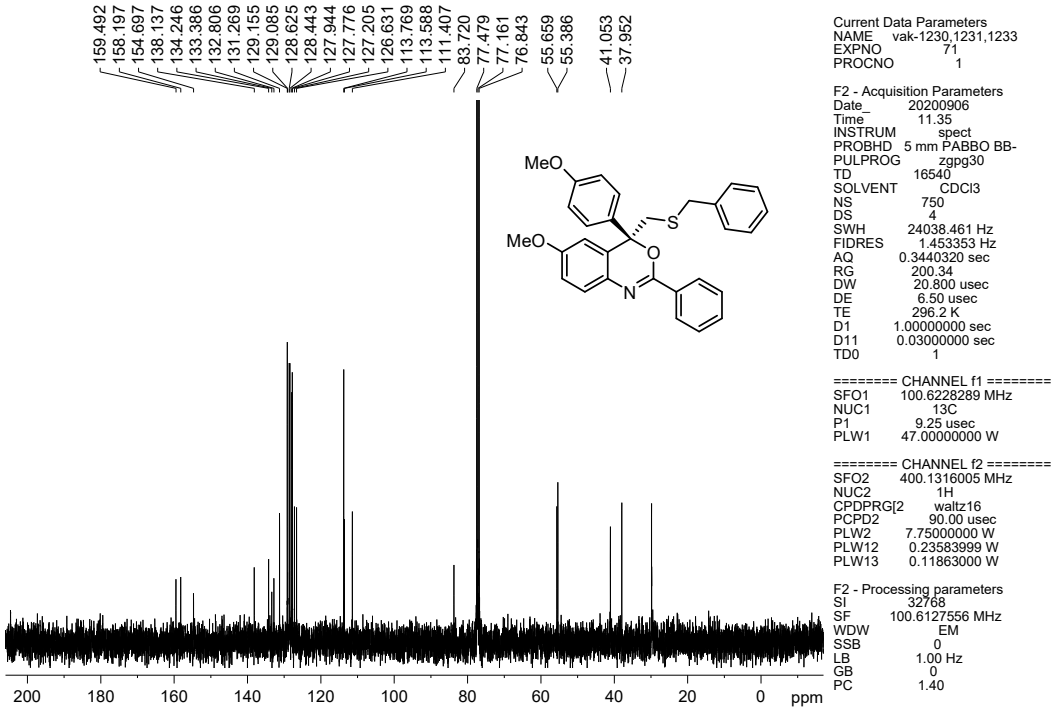
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24˚C):



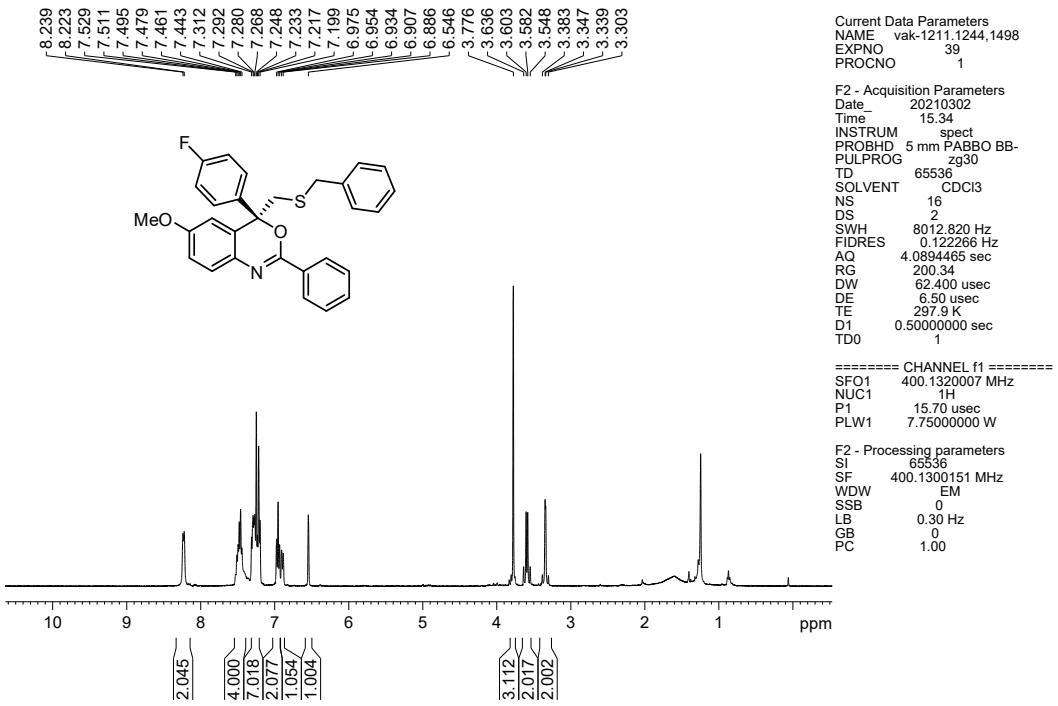
(*R*)-4-((Benzylthio)methyl)-6-methoxy-4-(4-methoxyphenyl)-2-phenyl-4*H*-benzo[d][1,3]oxazine (3aj)
^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):



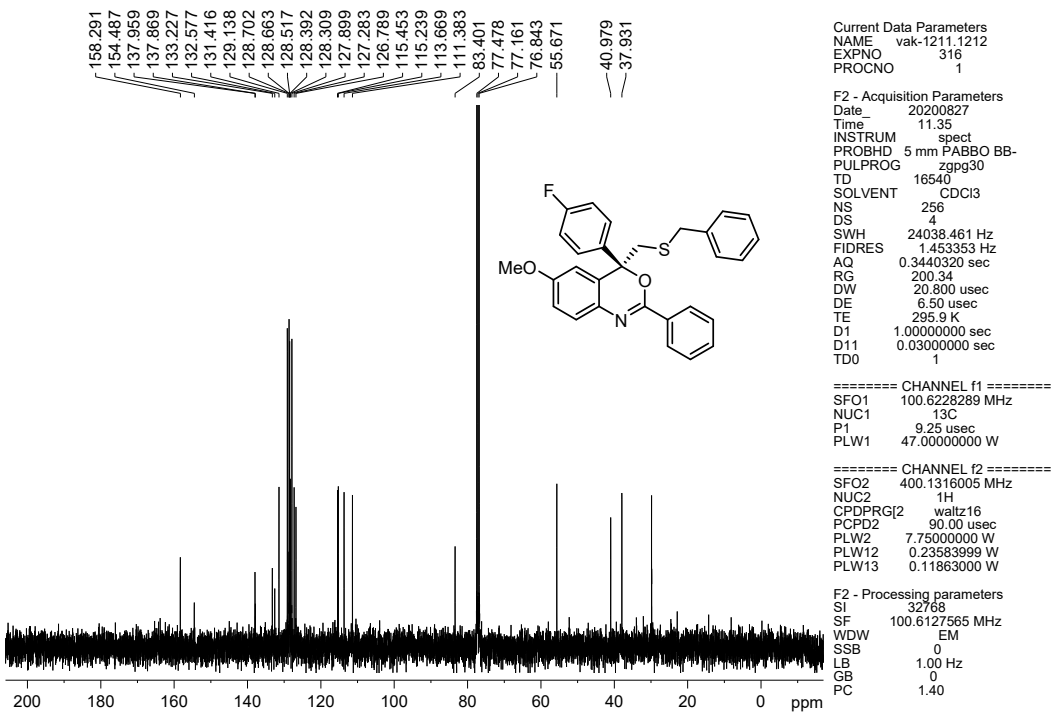
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24˚C):



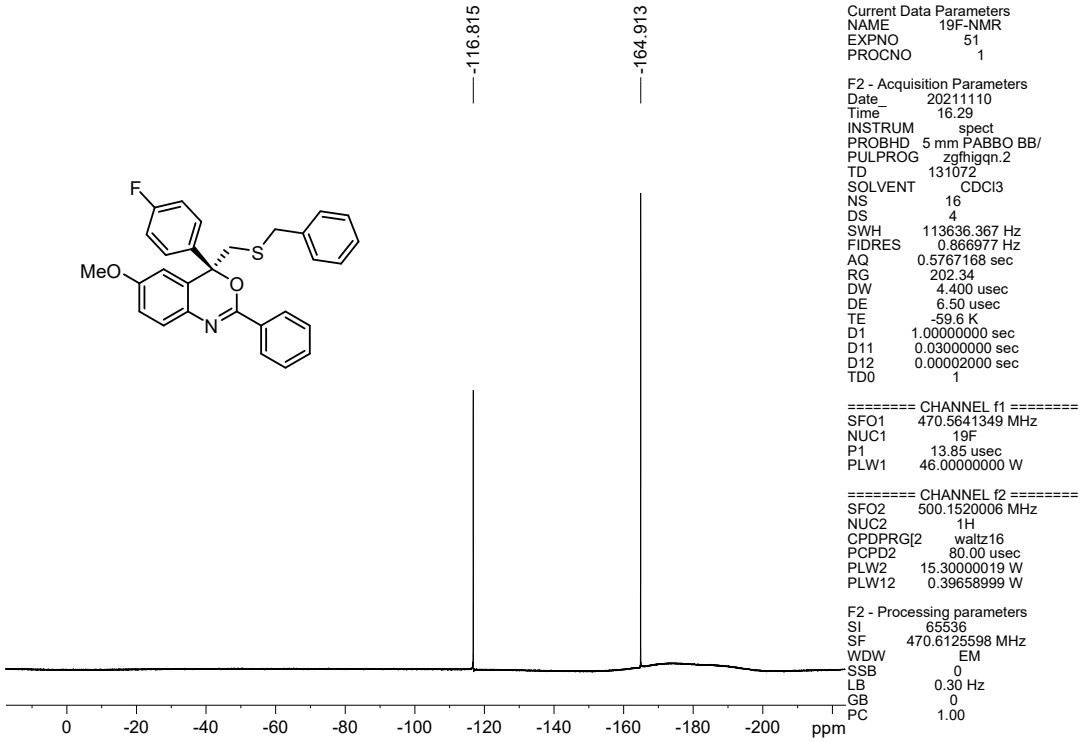
(*R*)-4-((Benzylthio)methyl)-4-(4-fluorophenyl)-6-methoxy-2-phenyl-4*H*-benzo[d][1,3]oxazine (3ak)
^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24˚C):

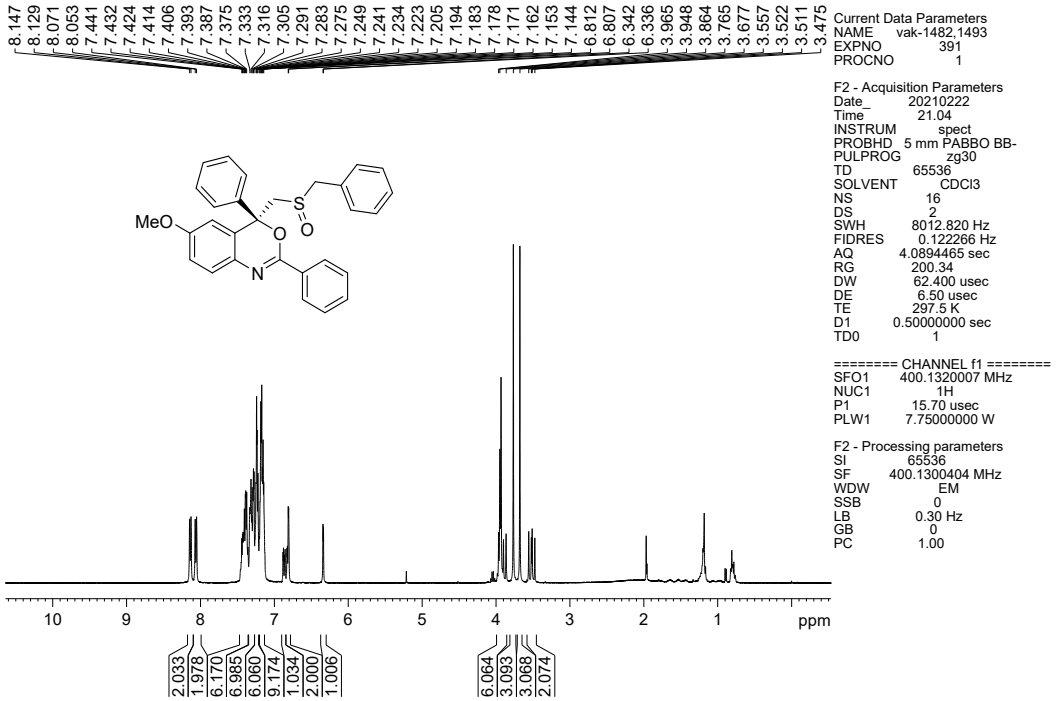


^{19}F NMR (470 MHz, $CDCl_3$, 24˚C):

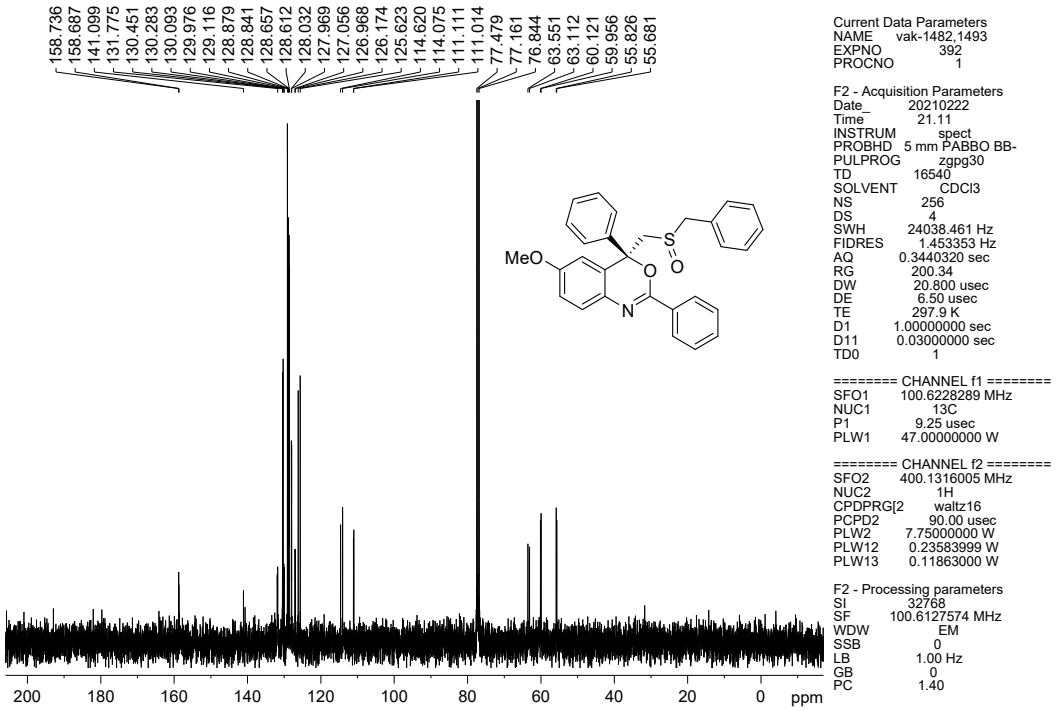


(4*R*)-4-((Benzylsulfinyl)methyl)-6-methoxy-2,4-diphenyl-4*H*-benzo[d][1,3]oxazine (4):

^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):

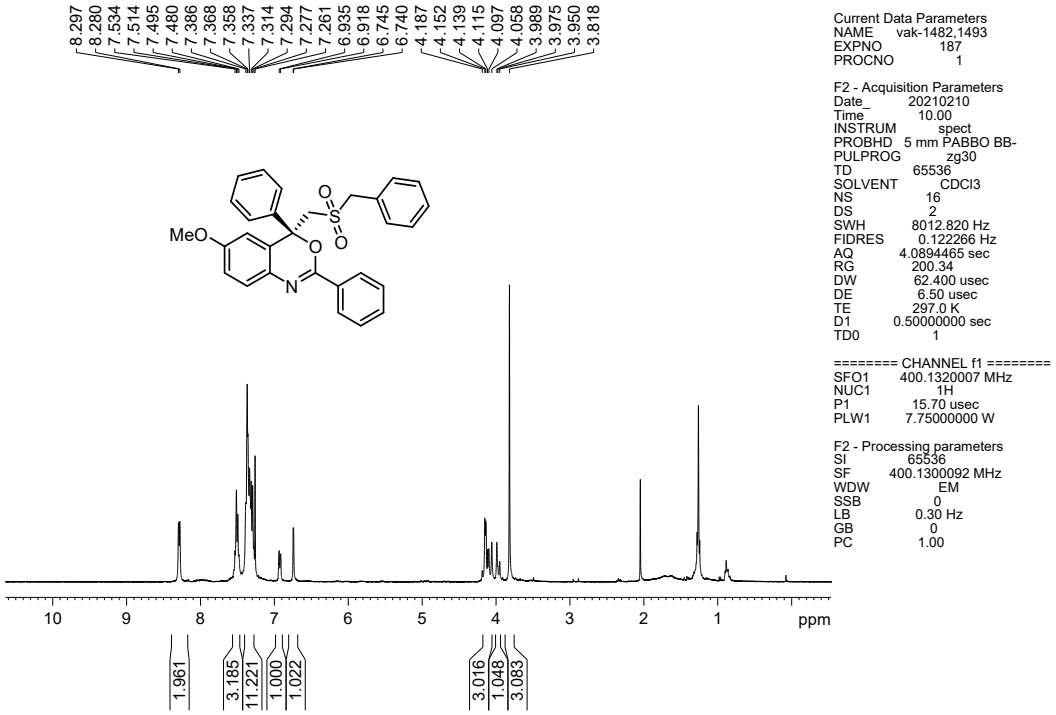


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24˚C):

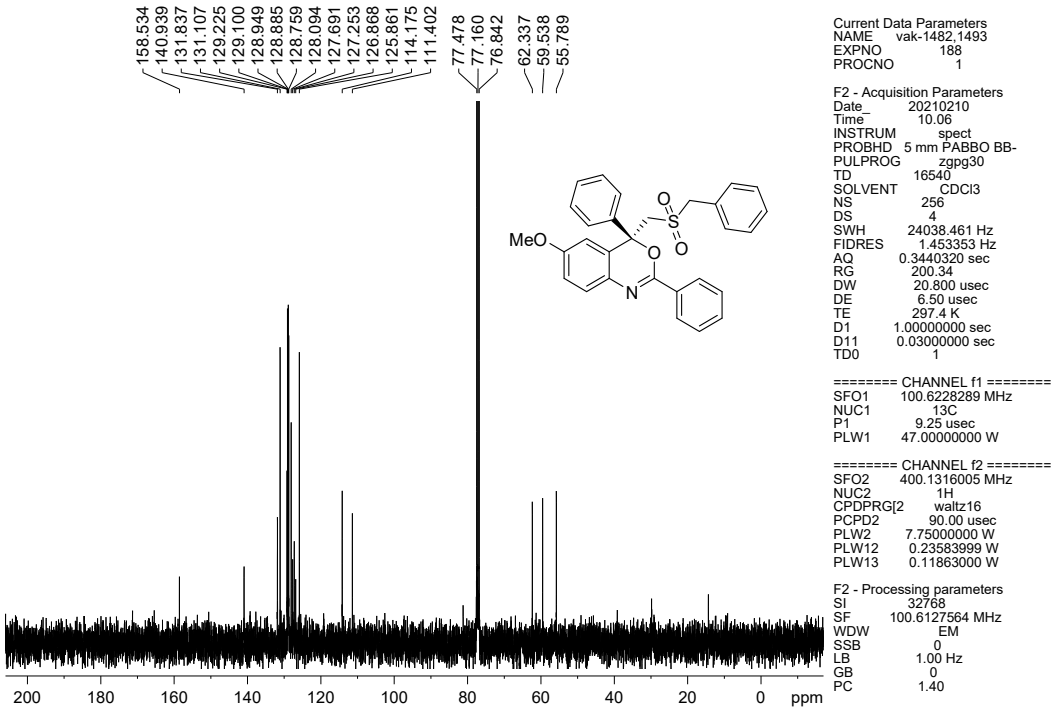


(*R*)-4-((Benzylsulfonyl)methyl)-6-methoxy-2,4-diphenyl-4*H*-benzo[d][1,3]oxazine (5):

^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):

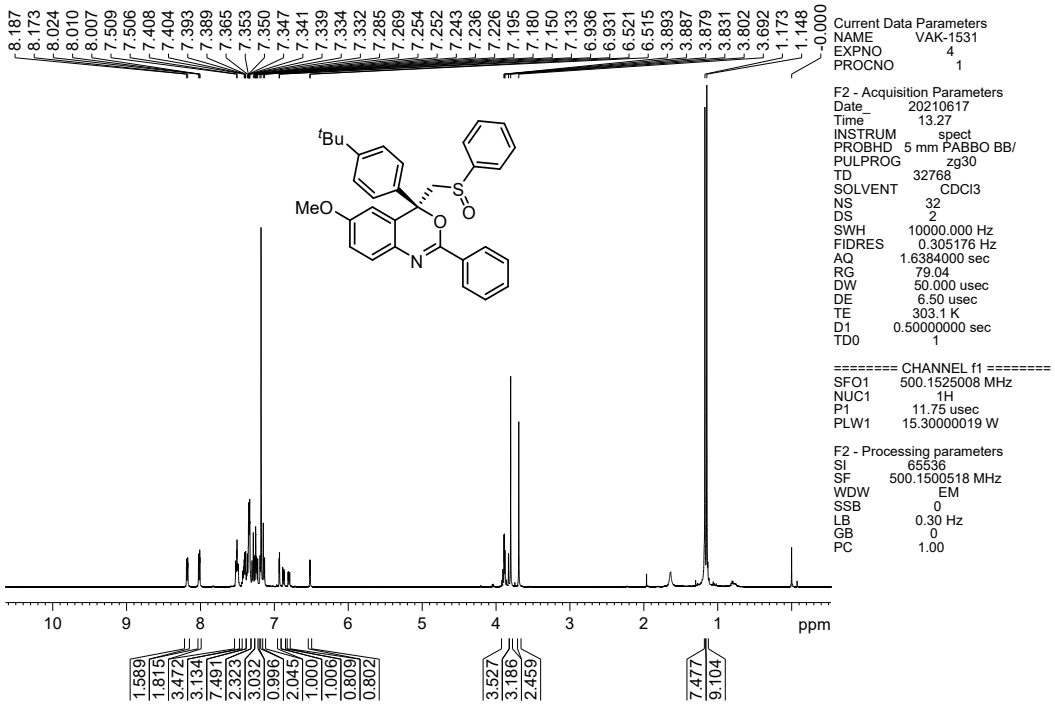


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24˚C):

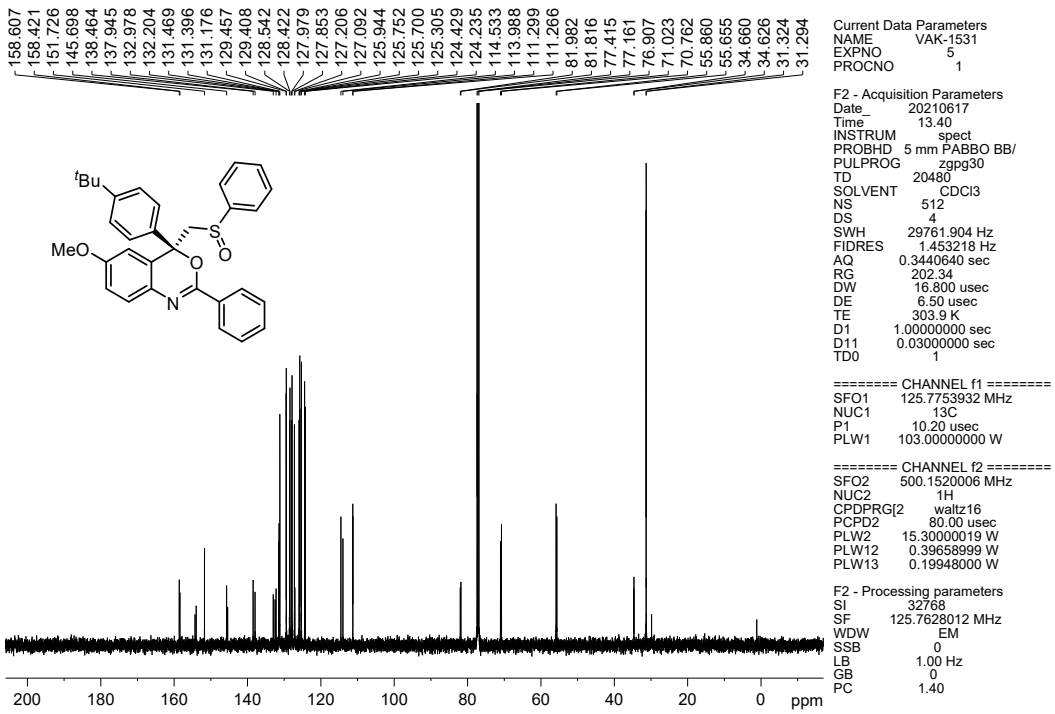


(*R*)-4-(4-(Tert-butyl)phenyl)-6-methoxy-2-phenyl-4-((phenylsulfinyl)methyl)-4*H*-benzo[d][1,3]oxazine

^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):

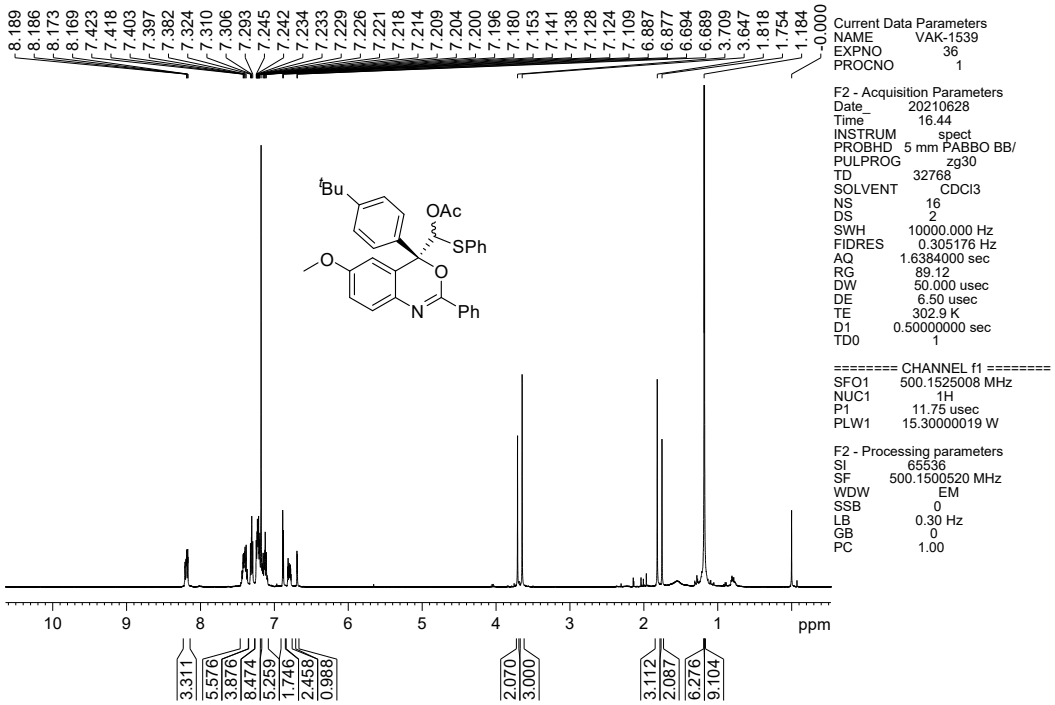


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24˚C):

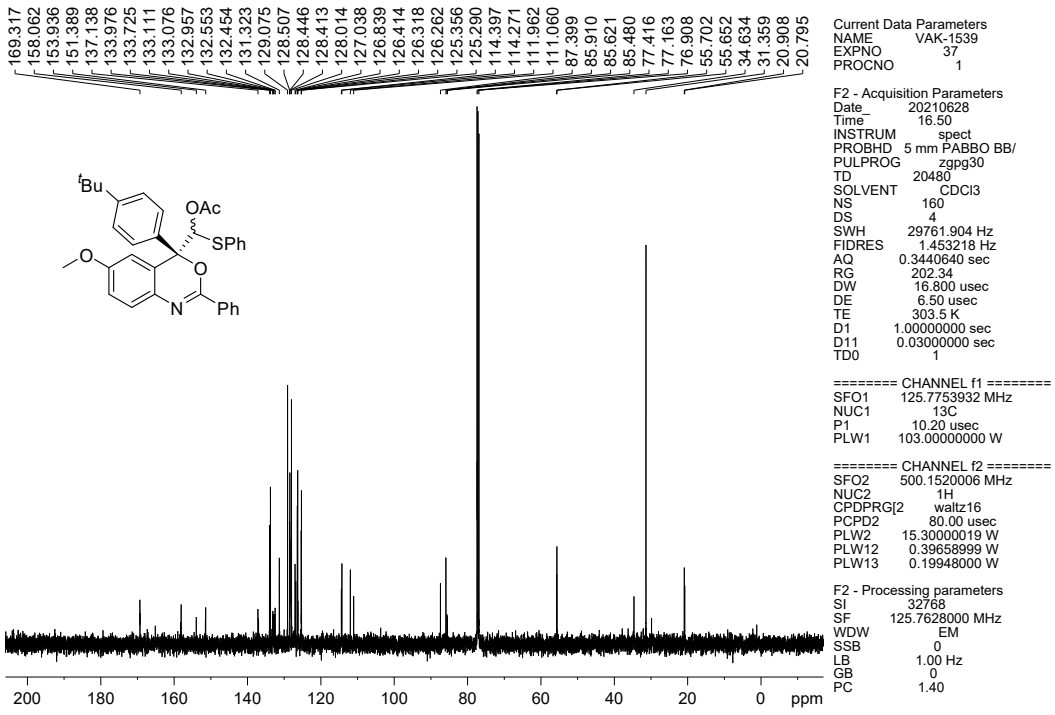


(*R*)-4-(4-(Tert-butyl)phenyl)-6-methoxy-2-phenyl-4*H*-benzo[d][1,3]oxazin-4-yl)(phenylthio)methyl acetate (6)

^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):

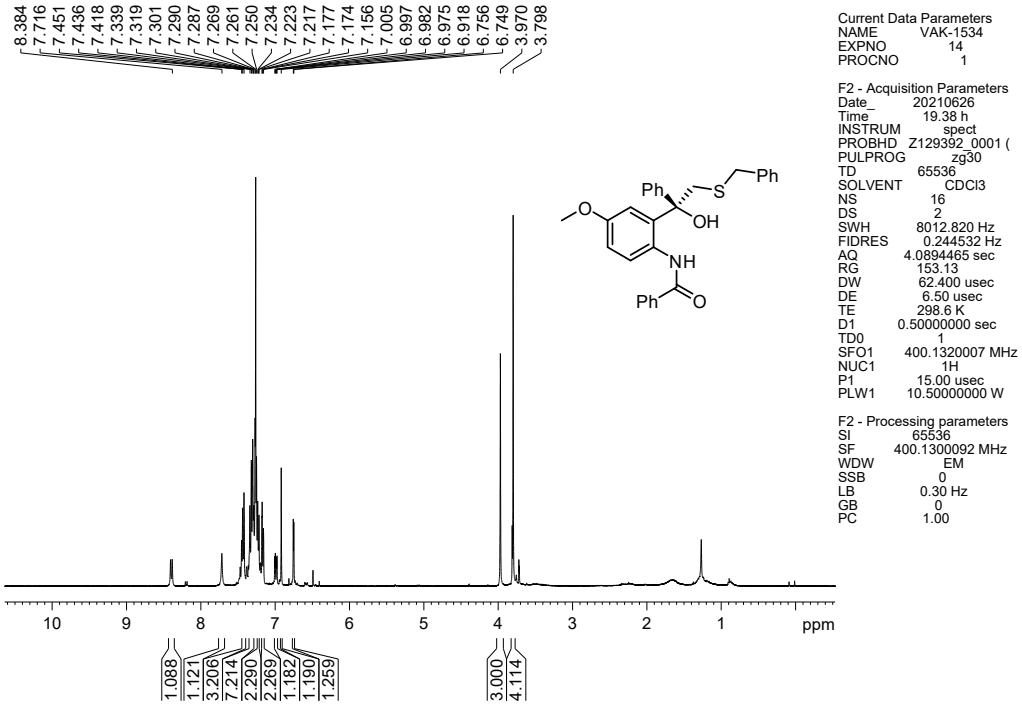


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24˚C):

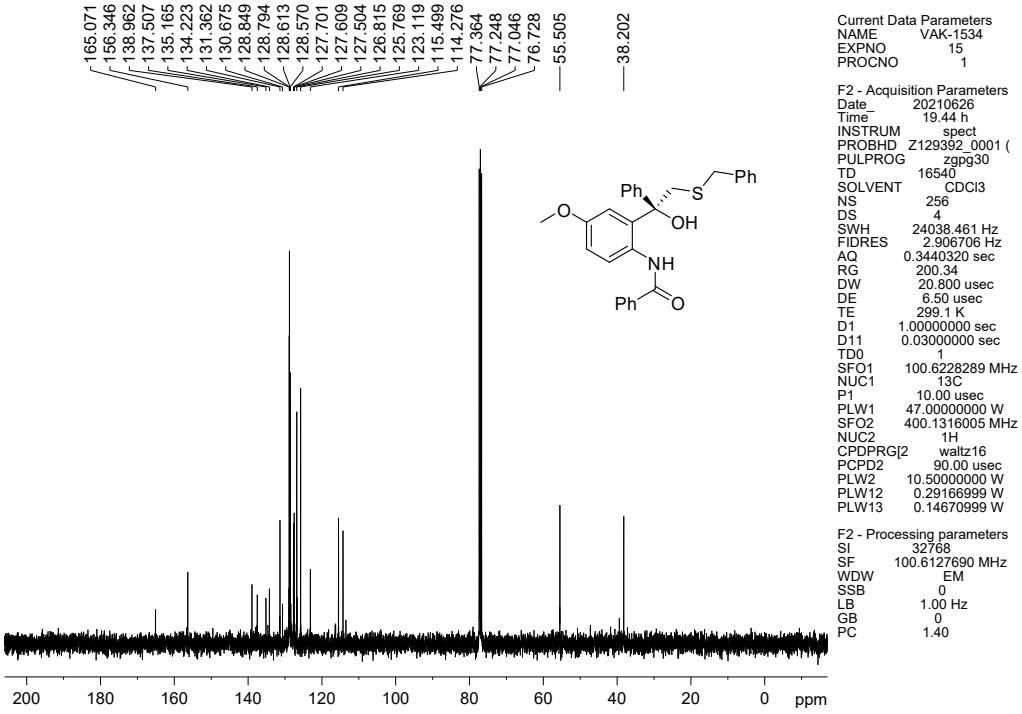


(*R*)-*N*-(2-(2-(Benzylthio)-1-hydroxy-1-phenylethyl)-4-methoxyphenyl)benzamide (7)

^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):

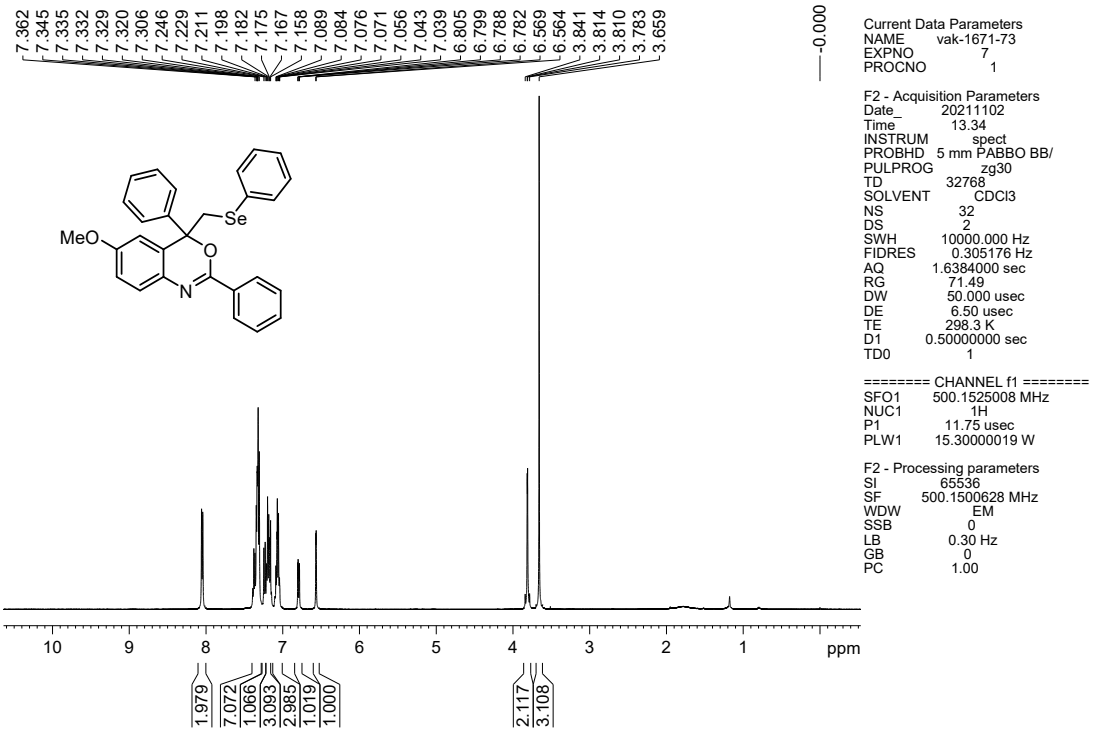


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24˚C):

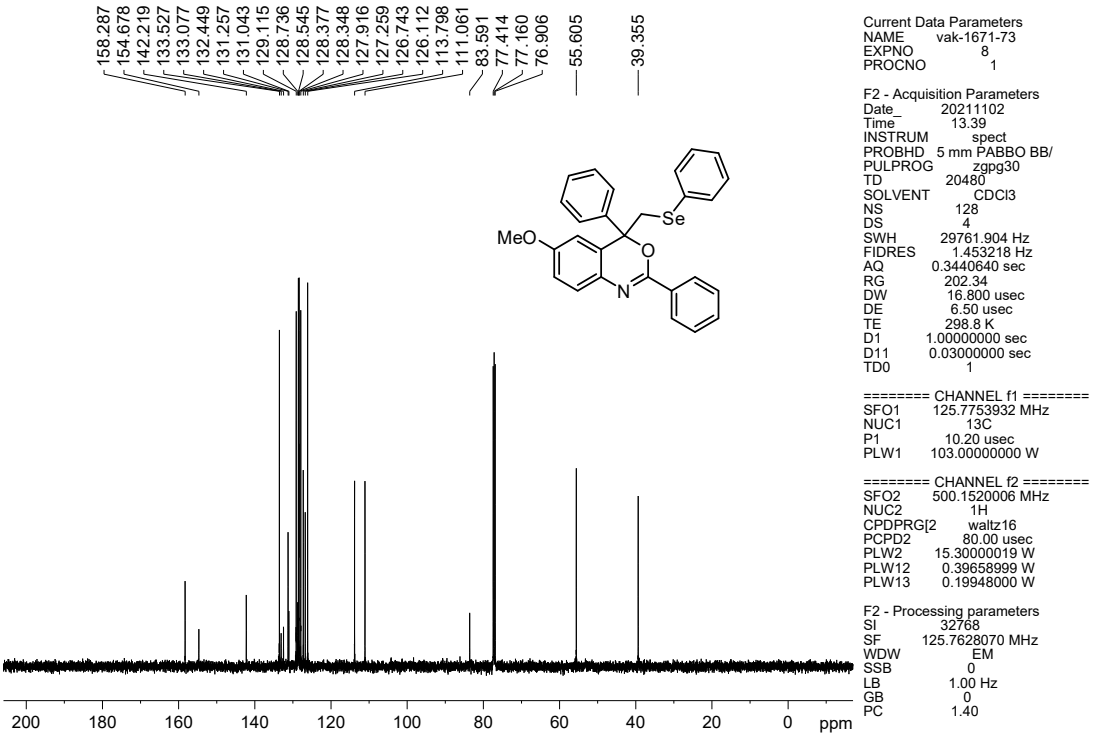


6-Methoxy-2,4-diphenyl-4-((phenylselanyl)methyl)-4*H*-benzo[d][1,3]oxazine:

^{1}H NMR (400 MHz, $CDCl_3$, 24˚C):

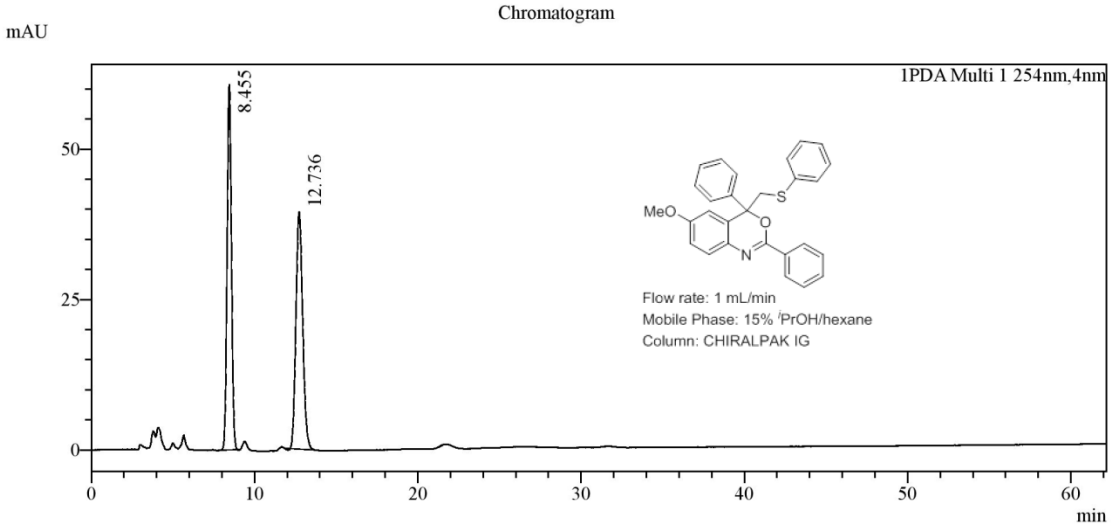


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24˚C):



14. HPLC Chromatogram of isolated compounds

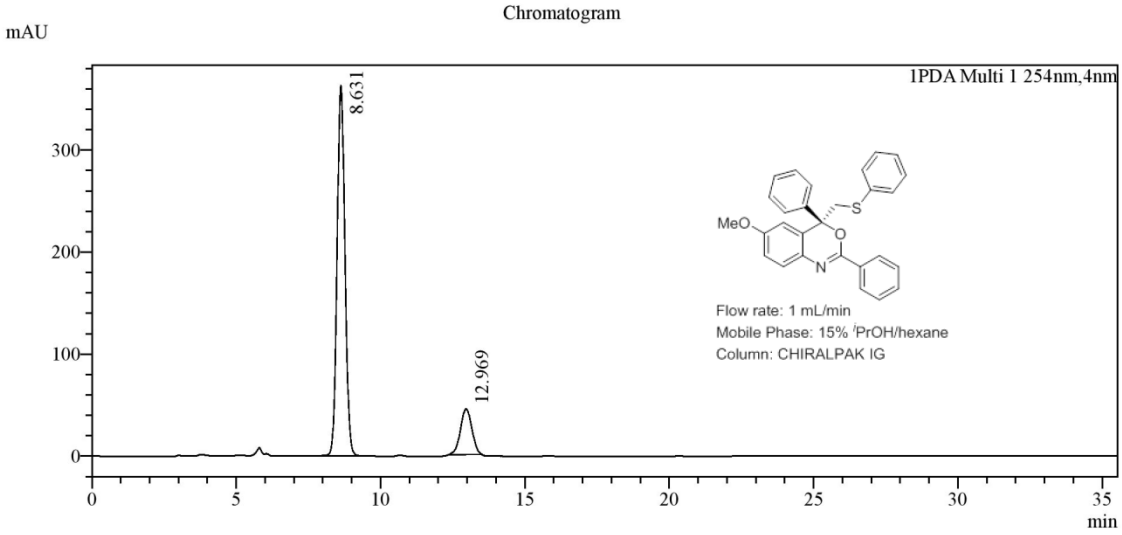
HPLC Chromatogram of compound 3a



Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:8.455	8.455	1116911	49.617	60700	60.619
2	RT:12.736	12.736	1134153	50.383	39434	39.381
Total			2251064	100.000	100134	100.000

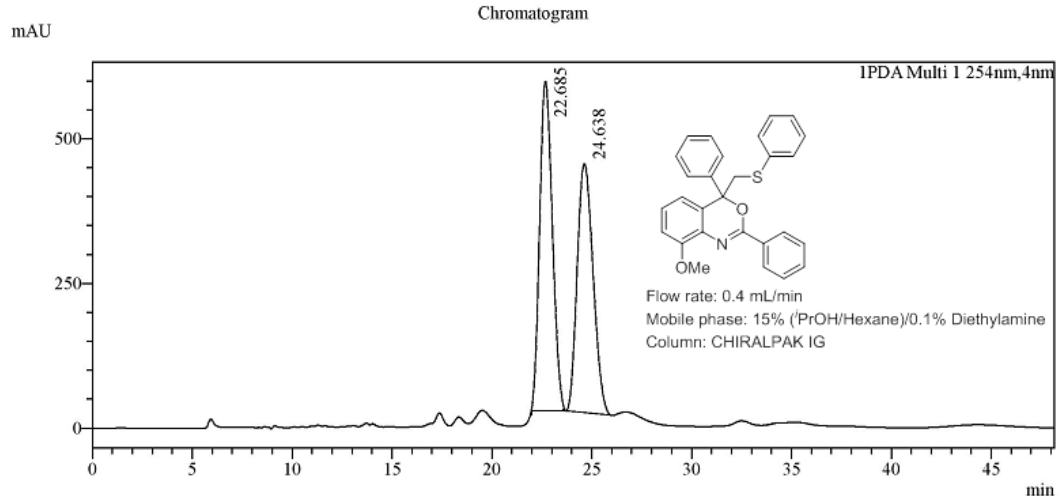


Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:8.631	8.631	6876608	84.805	362884	89.023
2	RT:12.969	12.969	1232135	15.195	44746	10.977
Total			8108743	100.000	407630	100.000

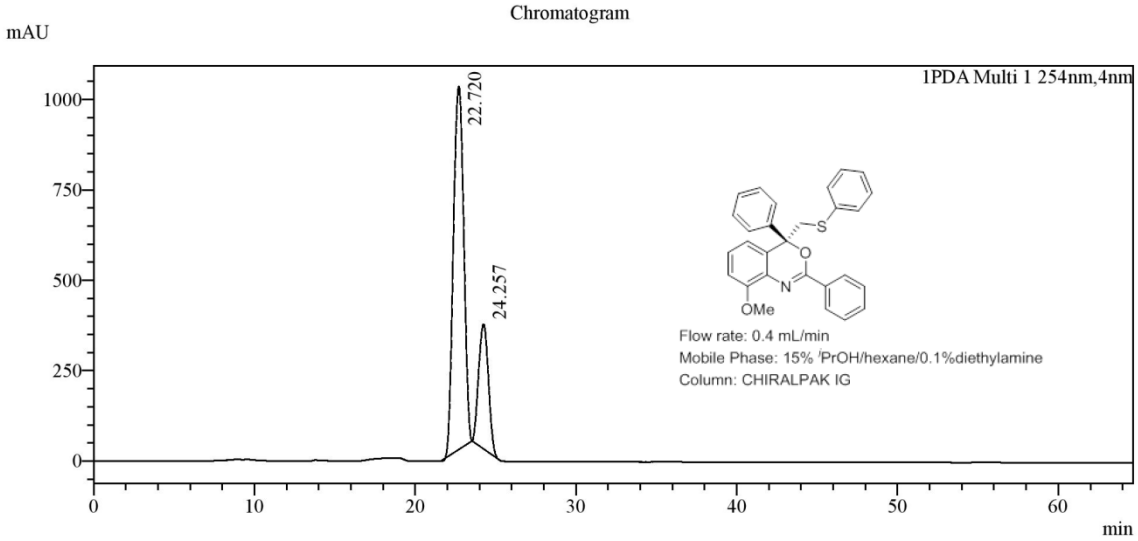
HPLC Chromatogram of compound 3b



Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:22.685	22.685	24327028	50.606	559789	56.565
2	RT:24.638	24.638	23743947	49.394	429853	43.435
Total			48070975	100.000	989642	100.000

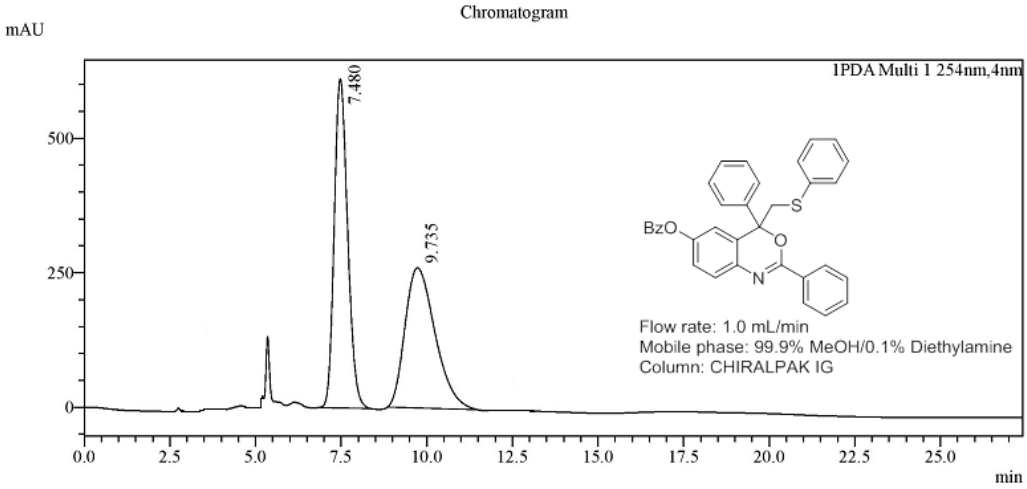


Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:22.720	22.720	44968378	75.449	1003685	74.414
2	RT:24.257	24.257	14632856	24.551	345098	25.586
Total			59601234	100.000	1348784	100.000

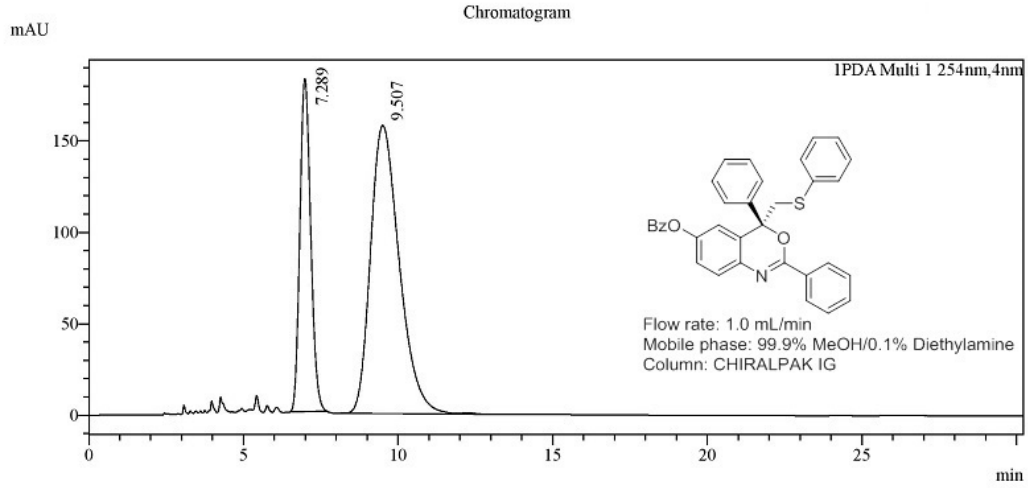
HPLC Chromatogram of compound 3c



Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:7.480	7.480	16691725	51.102	612305	70.125
2	RT:9.735	9.735	15971785	48.898	260852	29.875
Total			32663511	100.000	873157	100.000

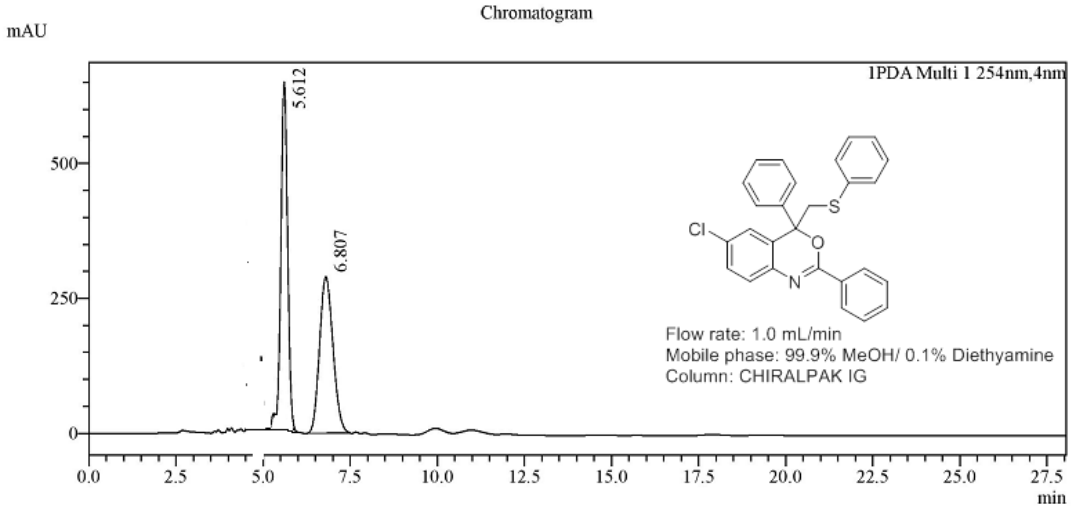


Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:7.289	7.289	4421424	30.140	182092	53.602
2	RT:9.507	9.507	10248283	69.860	157622	46.398
Total			14669707	100.000	339713	100.000

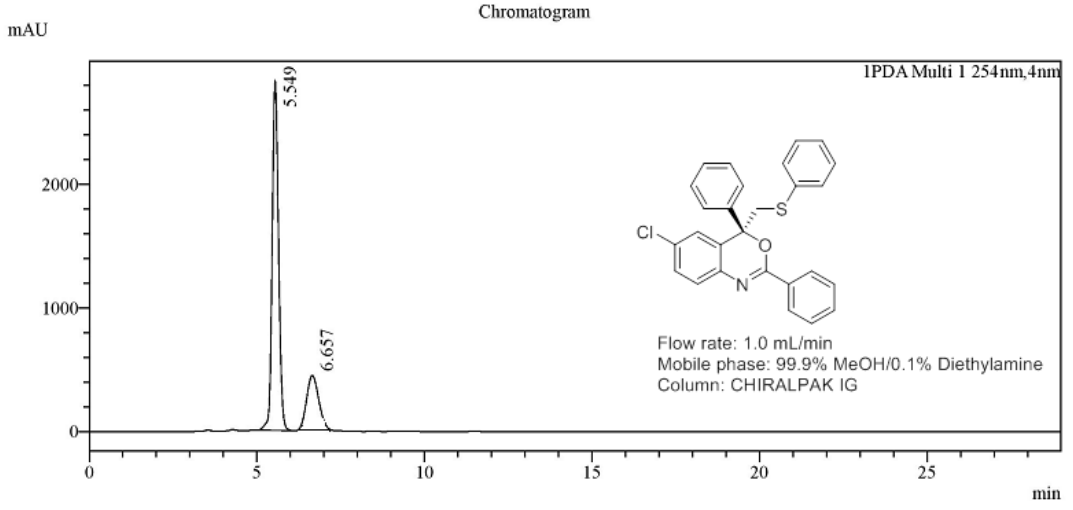
HPLC Chromatogram of compound 3d



Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:5.612	5.612	7990215	50.609	629599	68.477
2	RT:6.807	6.807	7797920	49.391	289826	31.523
Total			15788135	100.000	919425	100.000

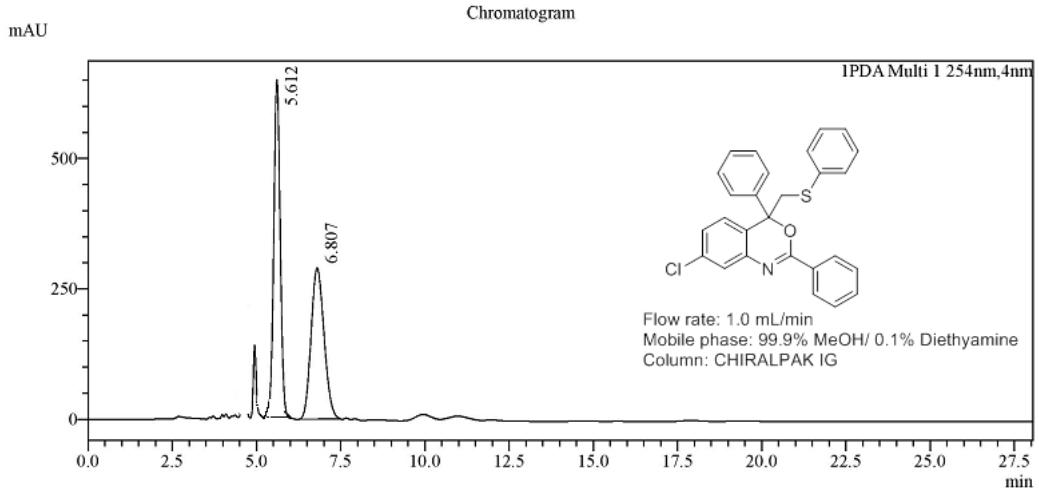


Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:5.549	5.549	37074067	80.415	2828991	87.603
2	RT:6.657	6.657	9029129	19.585	400358	12.397
Total			46103196	100.000	3229349	100.000

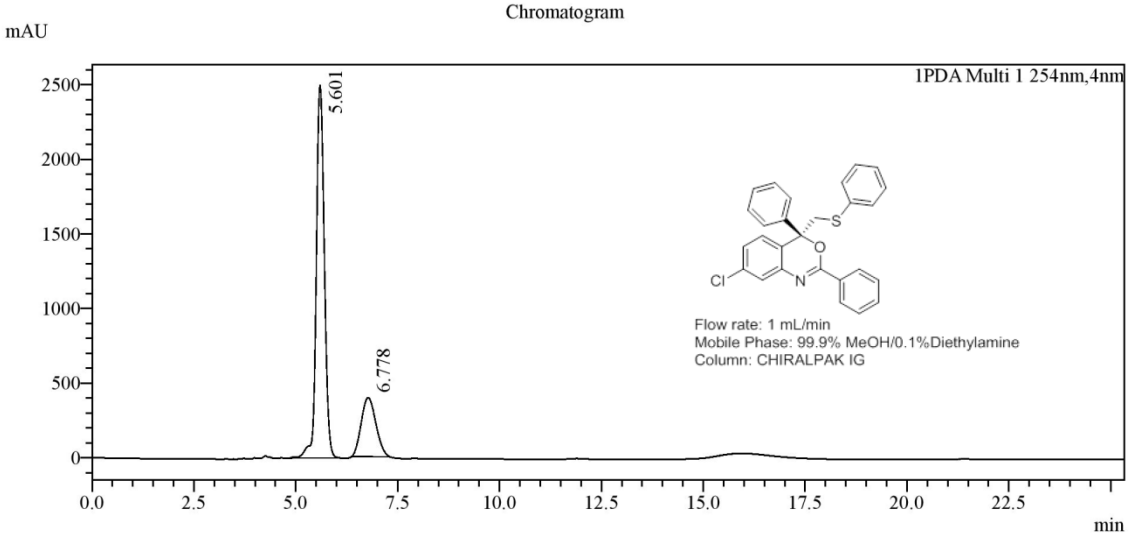
HPLC Chromatogram of compound 3e



Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:5.612	5.612	7816410	50.059	623980	68.284
2	RT:6.807	6.807	7797920	49.941	289826	31.716
Total			15614330	100.000	913806	100.000

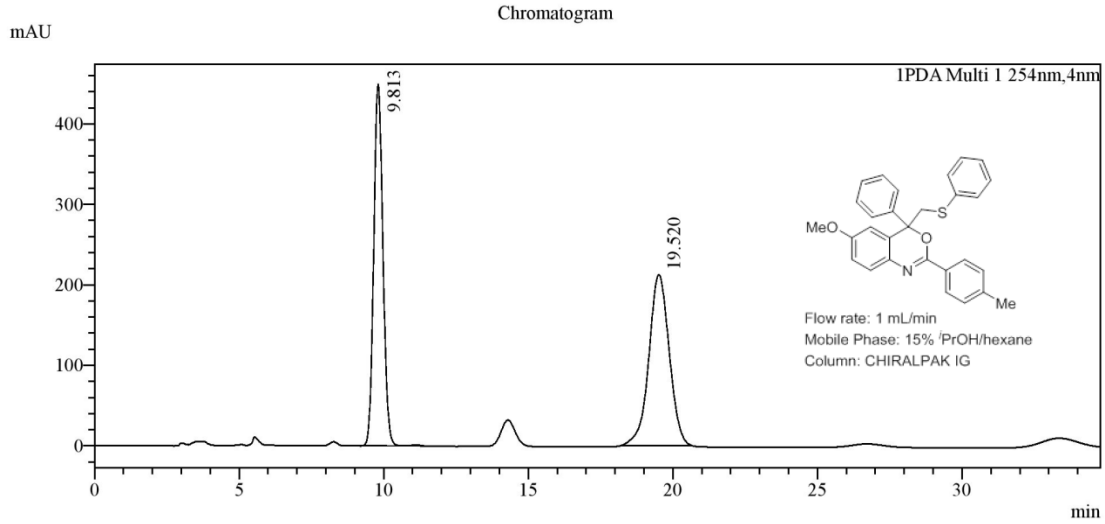


Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:5.601	5.601	34392140	77.612	2495307	86.319
2	RT:6.778	6.778	9920797	22.388	395505	13.681
Total			44312937	100.000	2890812	100.000

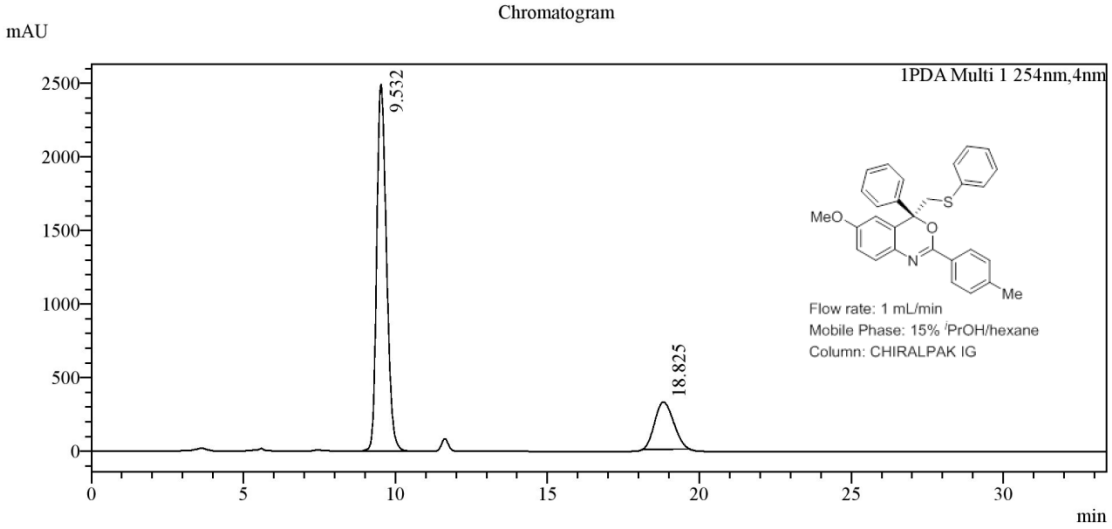
HPLC Chromatogram of compound 3f



Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:9.813	9.813	9936507	48.833	448979	67.877
2	RT:19.520	19.520	10411381	51.167	212478	32.123
Total			20347888	100.000	661456	100.000

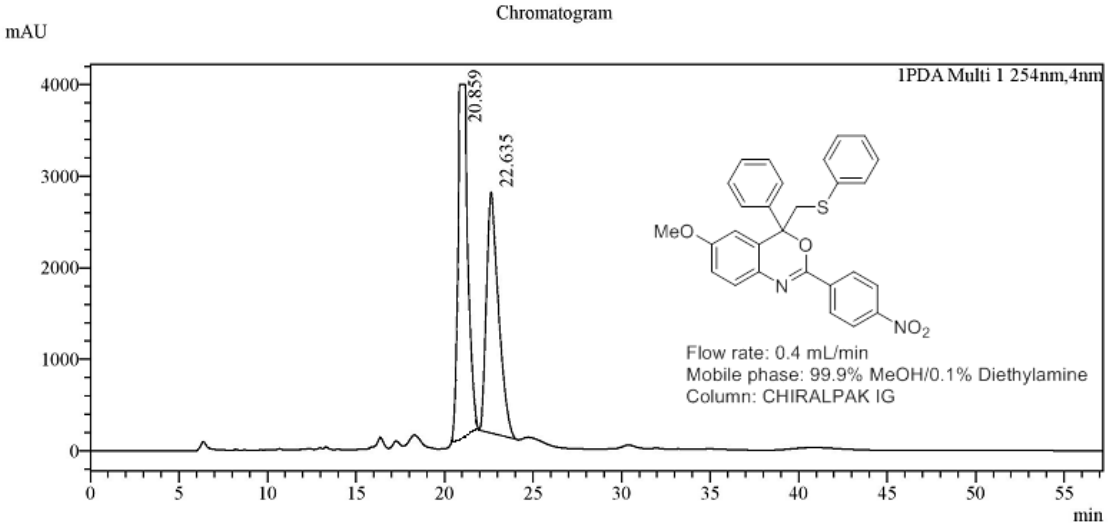


Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:9.532	9.532	55521549	80.026	2491191	88.583
2	RT:18.825	18.825	13858155	19.974	321086	11.417
Total			69379705	100.000	2812278	100.000

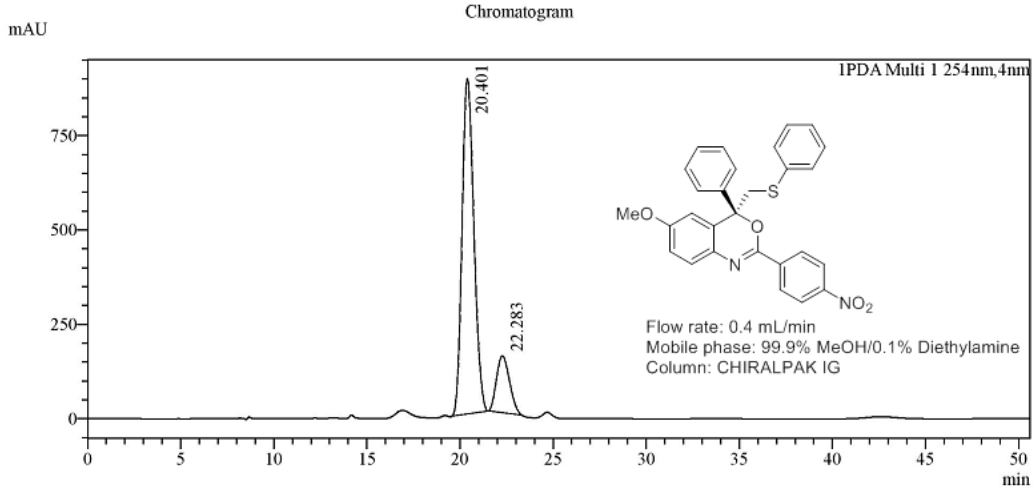
HPLC Chromatogram of compound 3g



Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:20.859	20.859	123182979	49.871	3306158	55.698
2	RT:22.635	22.635	123821672	50.129	2629682	44.302
Total			247004652	100.000	5935840	100.000

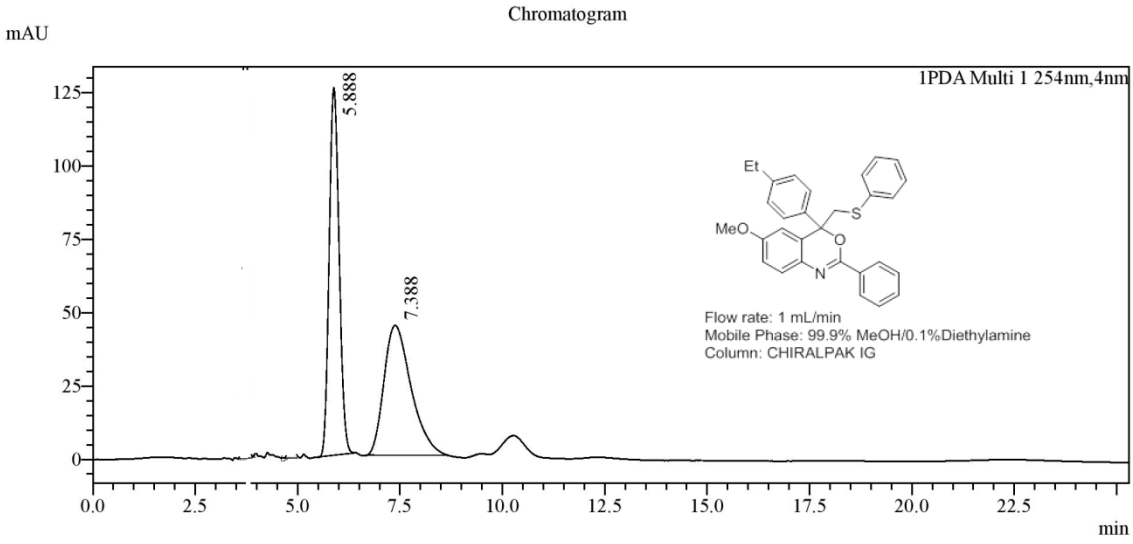


Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:20.401	20.401	39144774	84.205	888516	85.524
2	RT:22.282	22.283	7342935	15.795	150389	14.476
Total			46487709	100.000	1038905	100.000

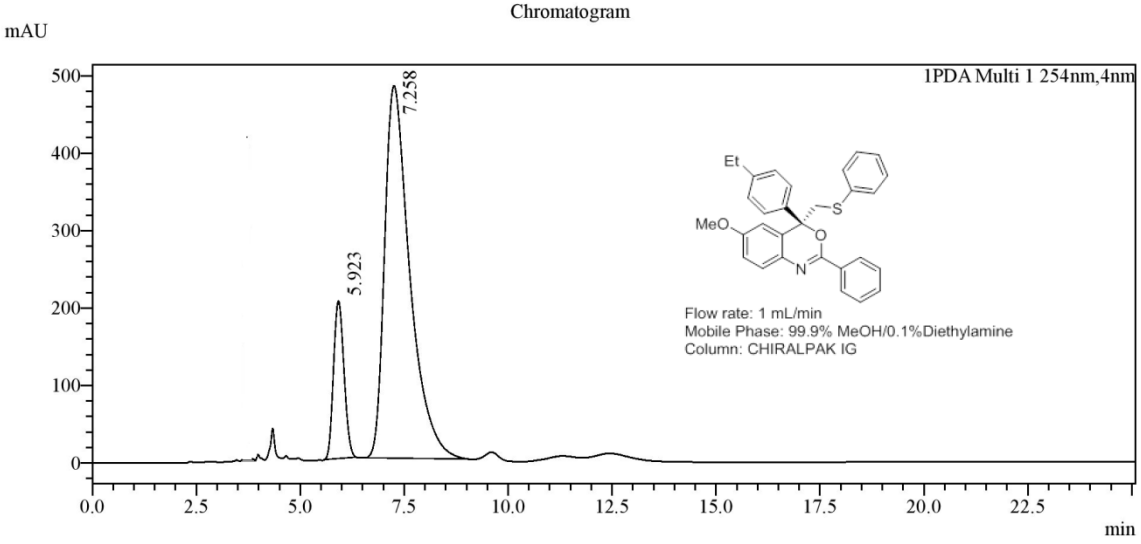
HPLC Chromatogram of compound 3h



Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:5.888	5.888	2110270	50.854	125220	73.909
2	RT:7.388	7.388	2039375	49.146	44204	26.091
Total			4149645	100.000	169424	100.000

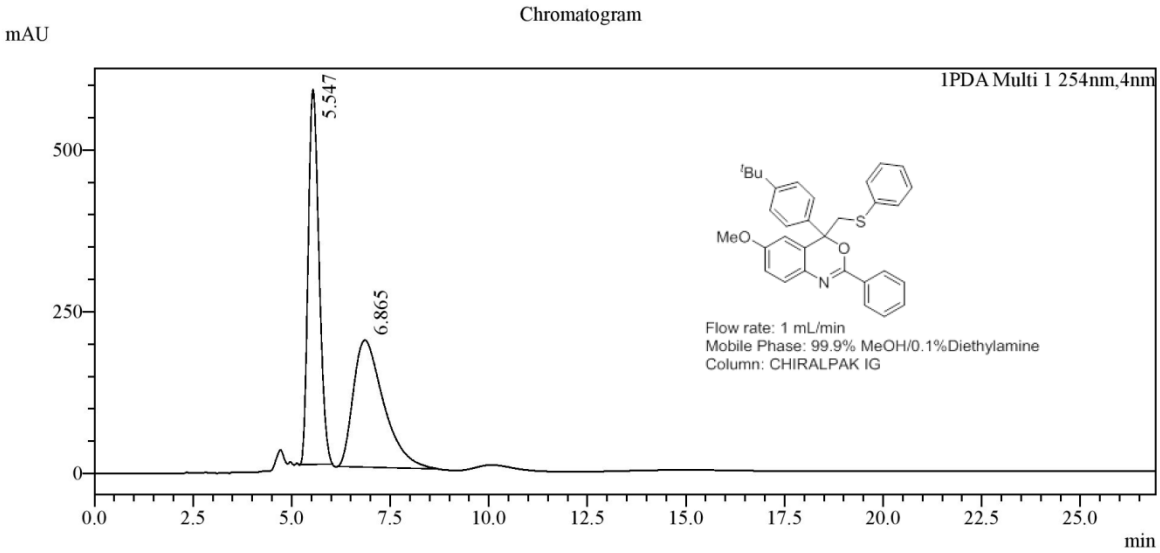


Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:5.923	5.923	3576486	14.979	203301	29.708
2	RT:7.258	7.258	20300483	85.021	481027	70.292
Total			23876969	100.000	684328	100.000

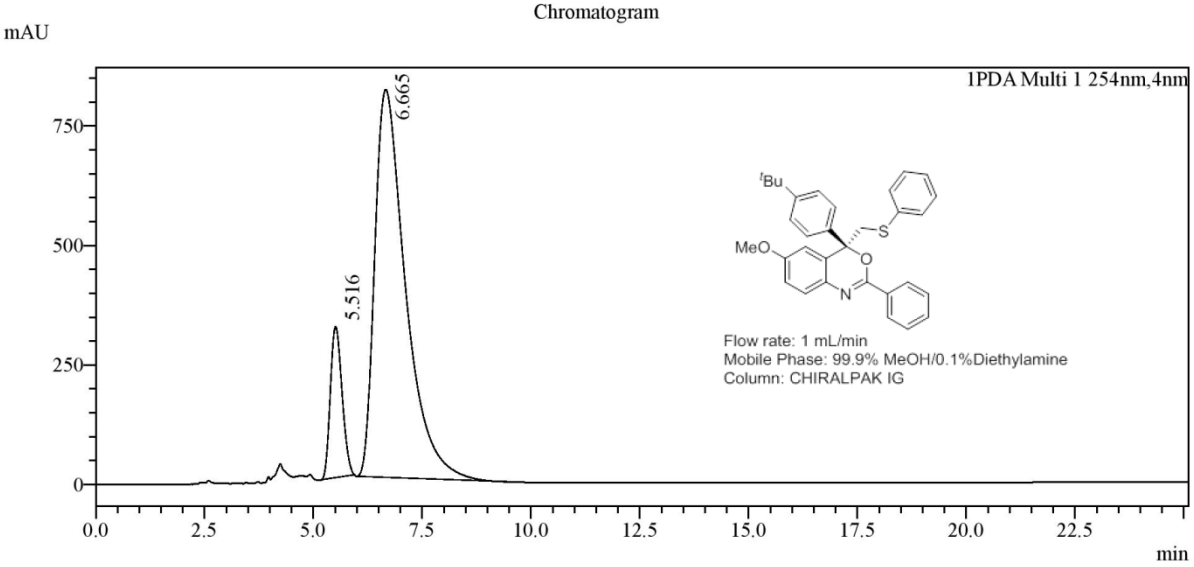
HPLC Chromatogram of compound 3i



Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:5.547	5.547	11073892	51.111	579174	74.664
2	RT:6.865	6.865	10592258	48.889	196535	25.336
Total			21666150	100.000	775709	100.000

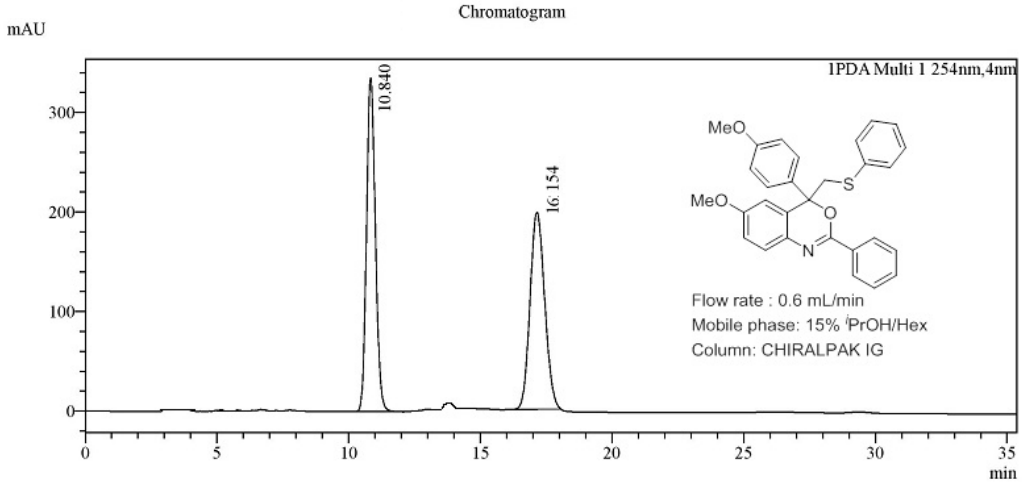


Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:5.516	5.516	5946273	12.986	316453	28.064
2	RT:6.665	6.665	39843659	87.014	811155	71.936
Total			45789932	100.000	1127608	100.000

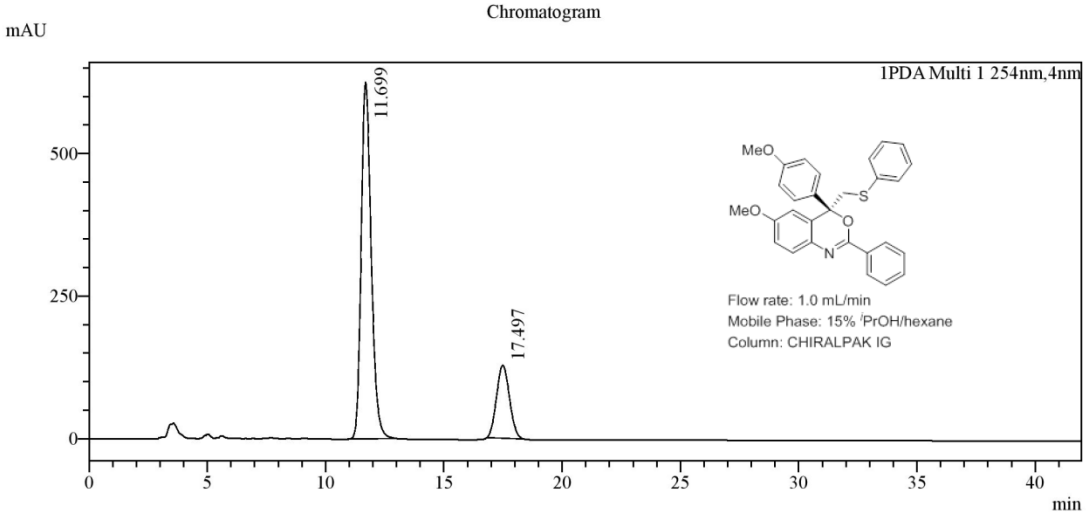
HPLC Chromatogram of compound 3j



Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:10.840	10.840	7849557	50.634	335401	62.887
2	RT:16.154	16.154	7653065	49.366	197934	37.113
Total			15502621	100.000	533336	100.000

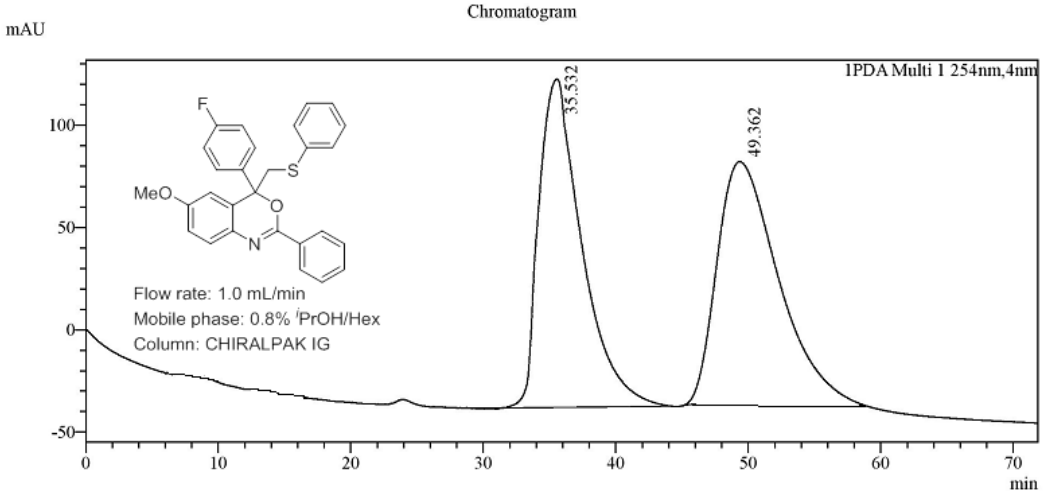


Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:11.699	11.699	18422151	79.082	625158	83.024
2	RT:17.497	17.497	4872743	20.918	127827	16.976
Total			23294894	100.000	752984	100.000

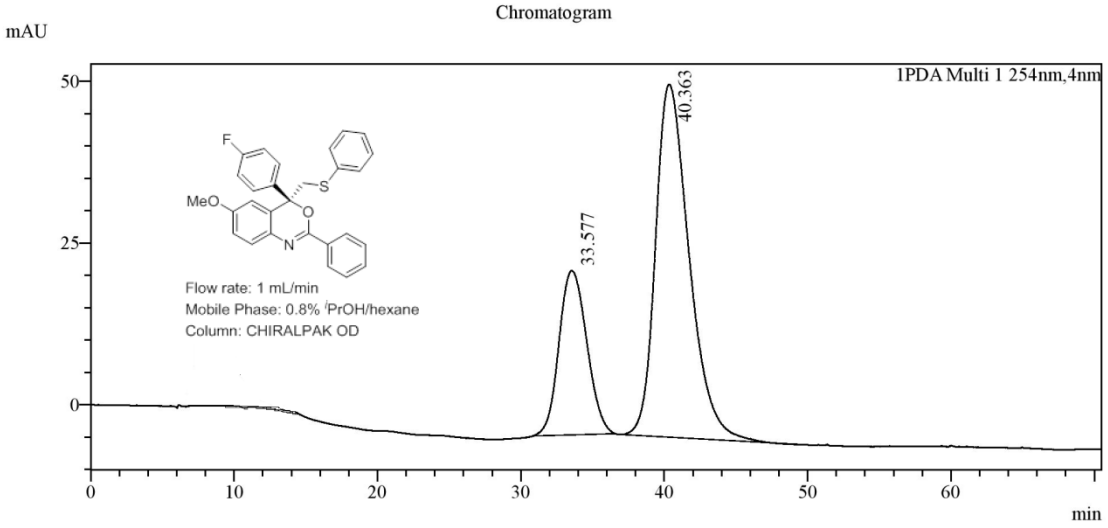
HPLC Chromatogram of compound 3k



Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:35.532	35.532	36035440	50.056	160380	57.853
2	RT:49.362	49.362	35954346	49.944	116840	42.147
Total			71989787	100.000	277221	100.000

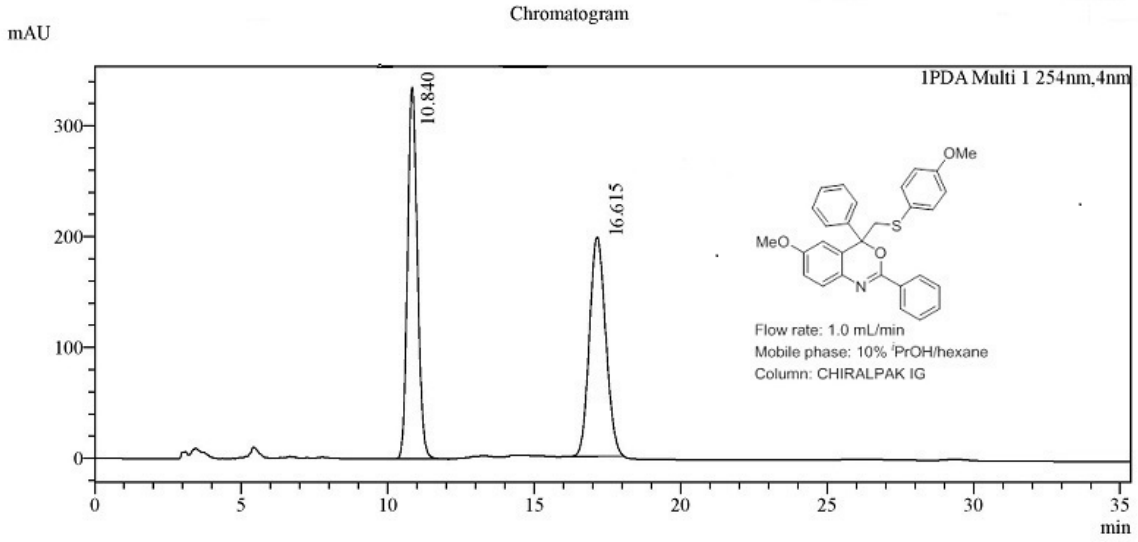


Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:33.577	33.577	3425877	27.798	25398	31.763
2	RT:40.363	40.363	8898381	72.202	54564	68.237
Total			12324258	100.000	79962	100.000

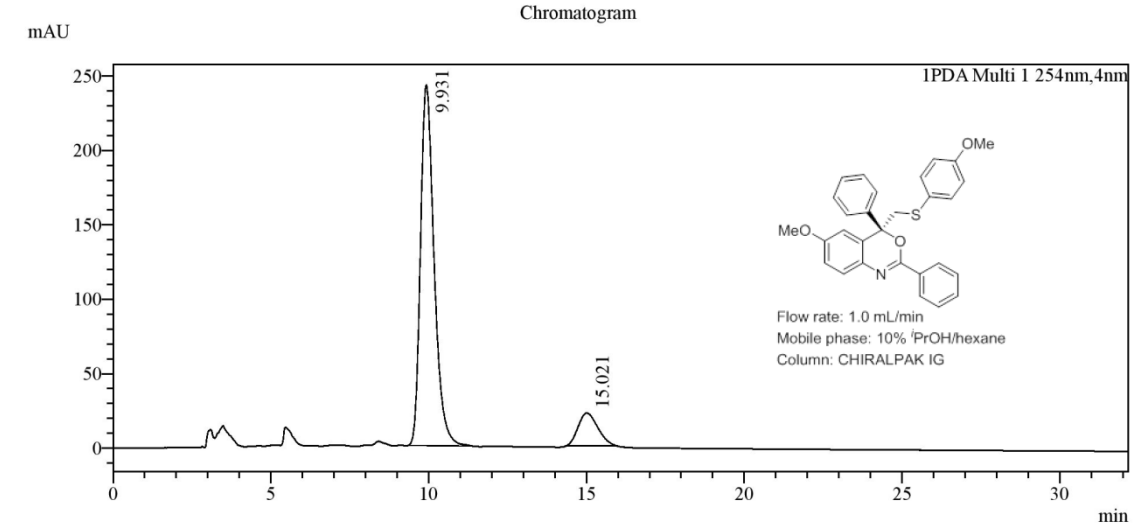
HPLC Chromatogram of compound 3l



Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:10.840	10.840	7849557	50.634	335401	62.887
2	RT:16.615	16.615	7653065	49.366	197934	37.113
Total			15502621	100.000	533336	100.000

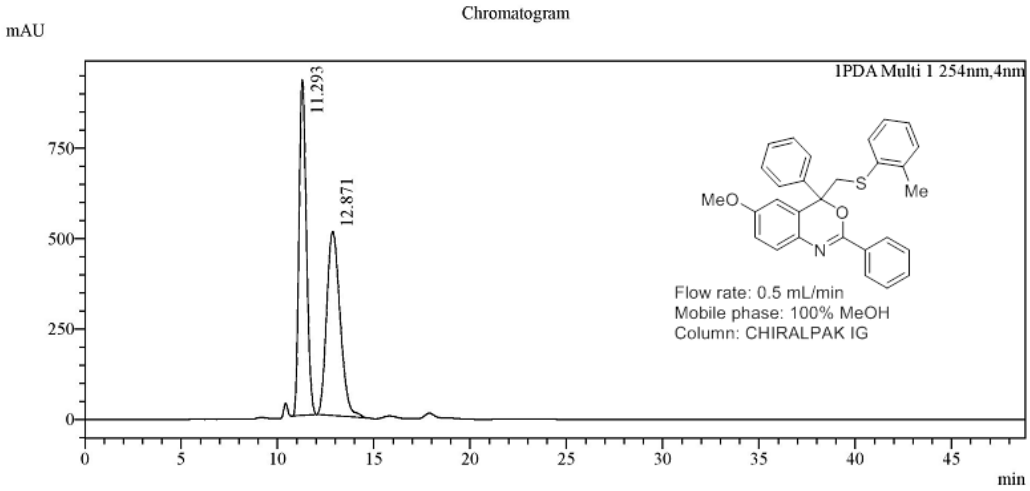


Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:9.931	9.931	7283700	88.405	242462	91.679
2	RT:15.021	15.021	955348	11.595	22006	8.321
Total			8239047	100.000	264468	100.000

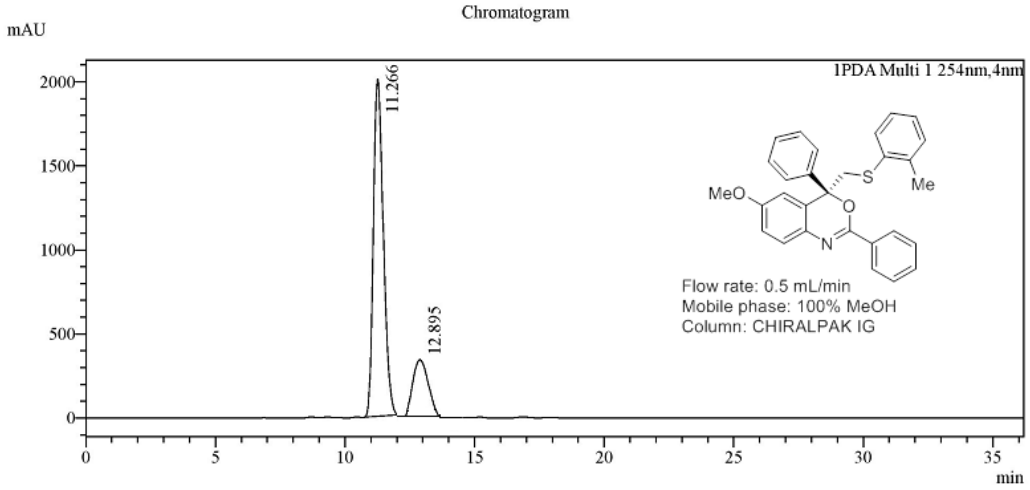
HPLC Chromatogram of compound 3m



Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:11.293	11.293	24681892	49.915	927969	64.609
2	RT:12.871	12.871	24765881	50.085	508325	35.391
Total			49447773	100.000	1436294	100.000

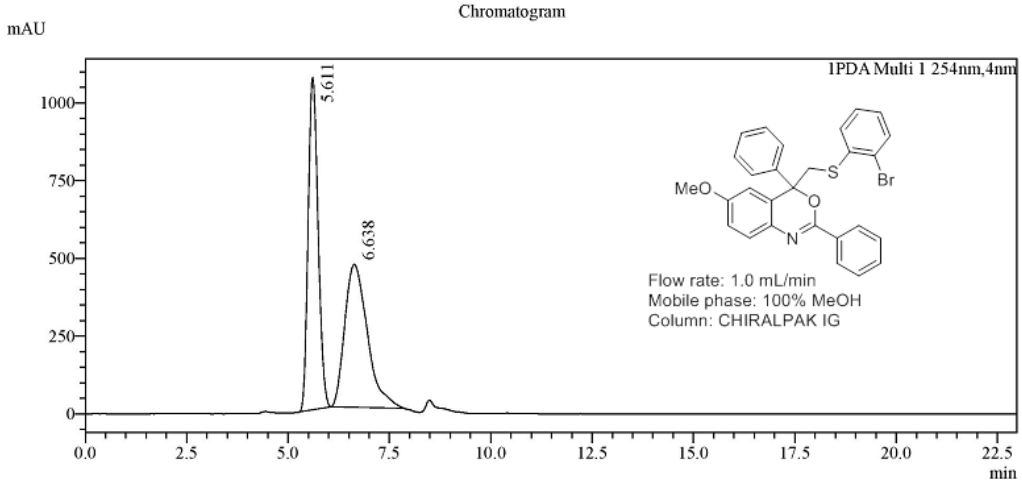


Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:11.266	11.266	53565417	82.591	2006812	86.944
2	RT:12.895	12.895	11291118	17.409	301348	13.056
Total			64856535	100.000	2308161	100.000

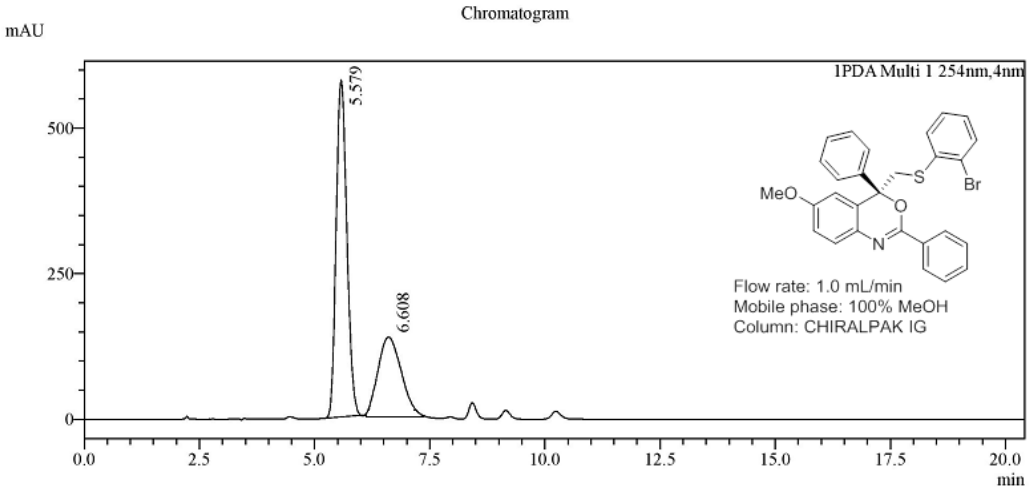
HPLC Chromatogram of compound 3n



Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:5.611	5.611	18164252	50.347	1068369	69.949
2	RT:6.638	6.638	17913689	49.653	458978	30.051
Total			36077941	100.000	1527348	100.000

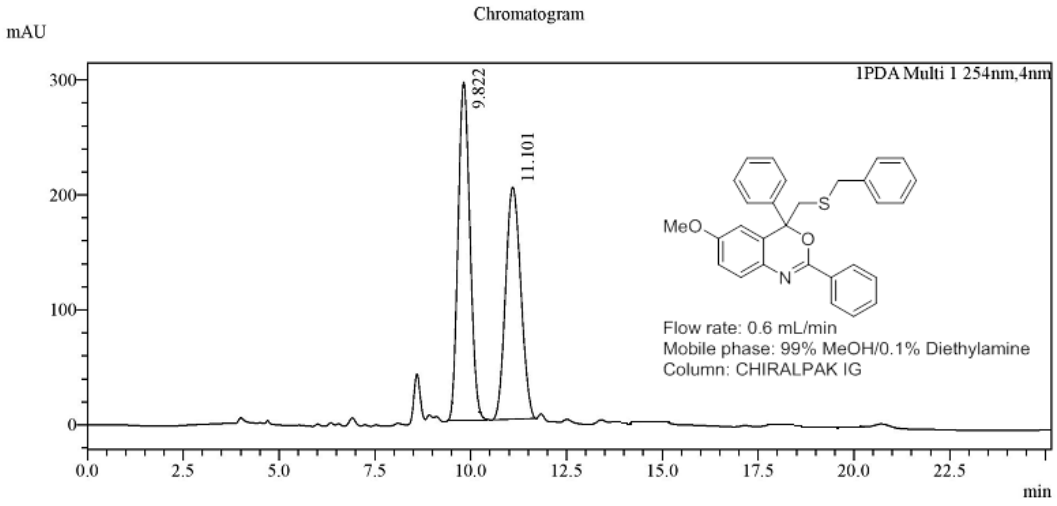


Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:5.579	5.579	9328279	69.644	578757	82.168
2	RT:6.608	6.608	4065908	30.356	125605	17.832
Total			13394187	100.000	704362	100.000

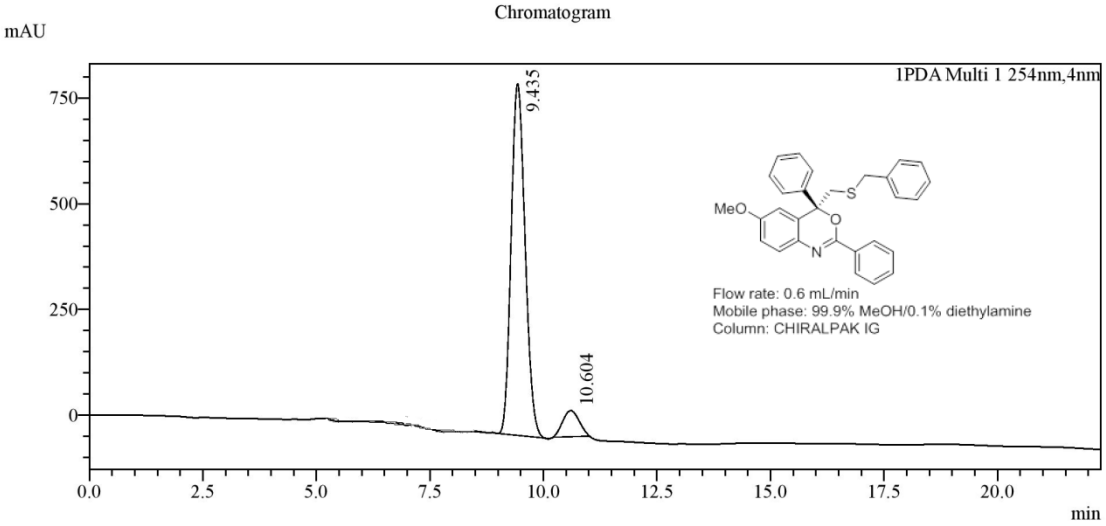
HPLC Chromatogram of compound 3o



Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:9.822	9.822	5773160	50.882	282391	58.329
2	RT:11.101	11.101	5573035	49.118	201743	41.671
Total			11346195	100.000	484134	100.000

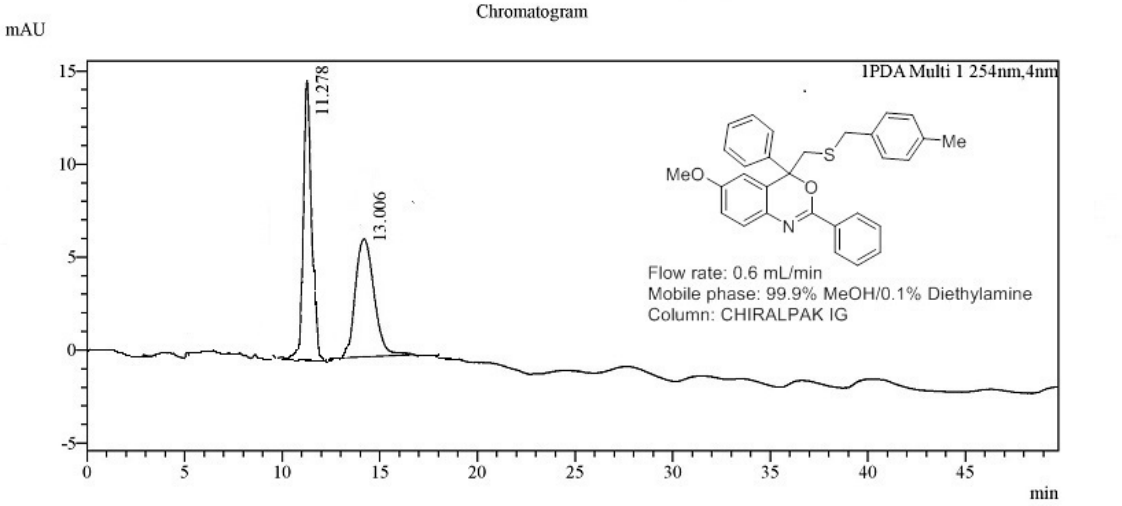


Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:9.435	9.435	17759975	91.959	830776	93.107
2	RT:10.604	10.604	1552858	8.041	61508	6.893
Total			19312833	100.000	892284	100.000

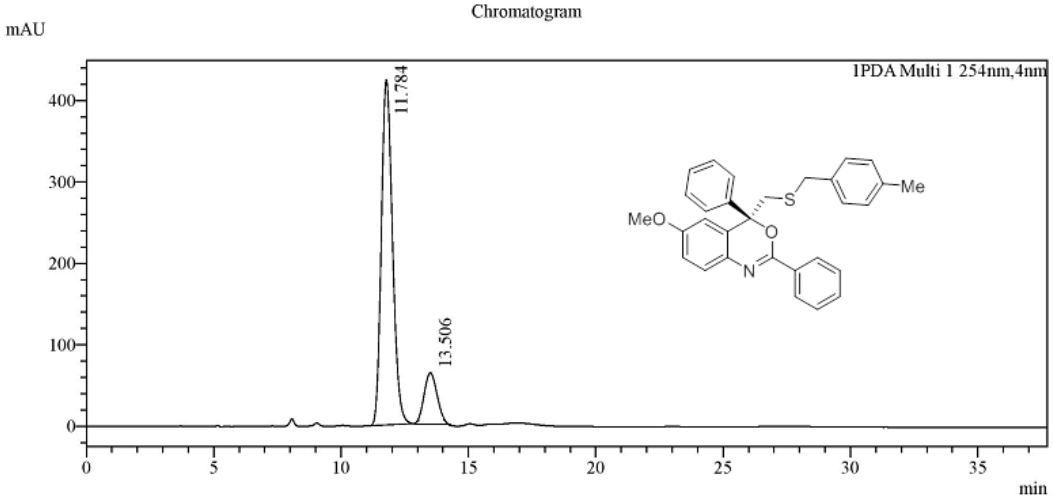
HPLC Chromatogram of compound 3p



Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:11.278	11.278	437163	50.497	14397	69.413
2	RT:13.006	13.006	428550	49.503	6344	30.587
Total			865713	100.000	20742	100.000

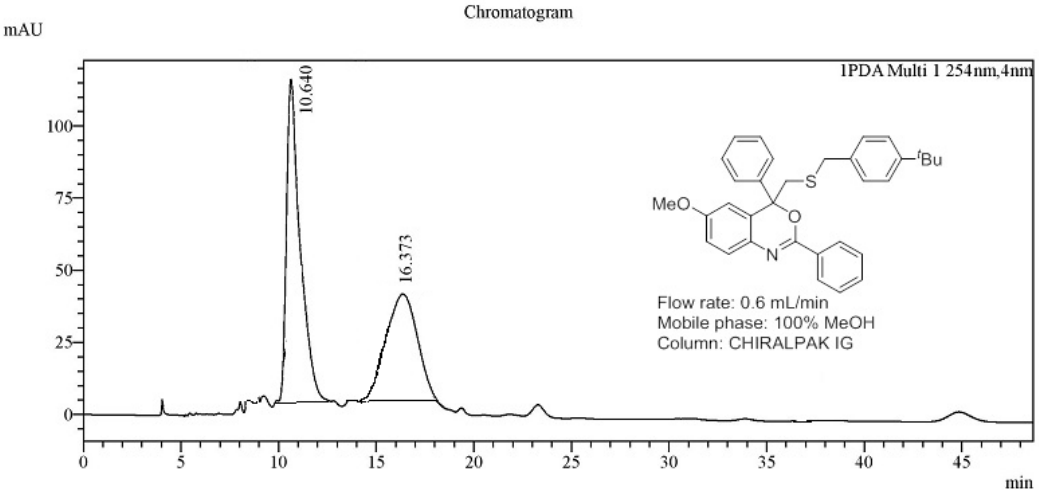


Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:11.784	11.784	12858898	87.023	423954	87.866
2	RT:13.506	13.506	1917559	12.977	58546	12.134
Total			14776457	100.000	482501	100.000

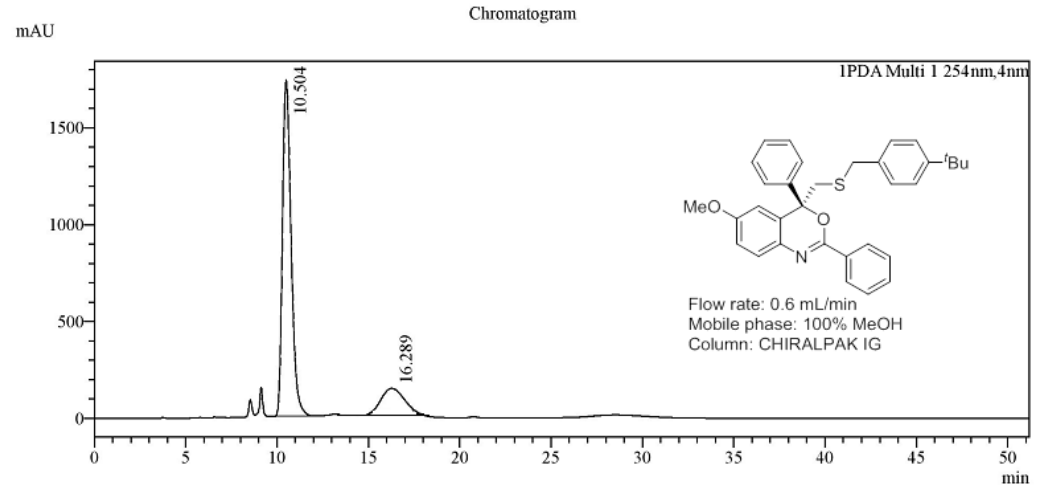
HPLC Chromatogram of compound 3q



Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:10.640	10.640	2519917	49.126	83806	75.367
2	RT:16.373	16.373	2609606	50.874	27391	24.633
Total			5129523	100.000	111197	100.000

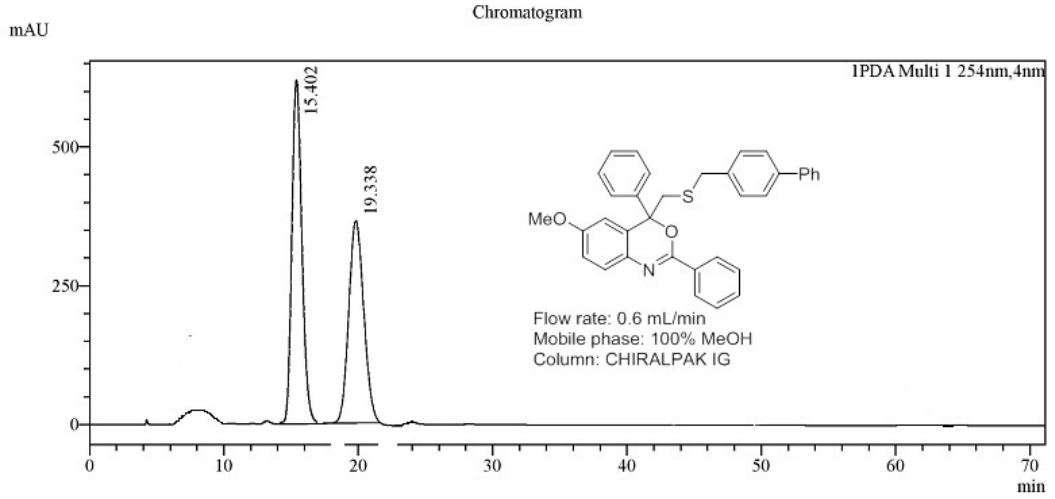


Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:10.504	10.504	57172062	85.949	1735880	93.587
2	RT:16.289	16.289	9346860	14.051	118959	6.413
Total			66518922	100.000	1854840	100.000

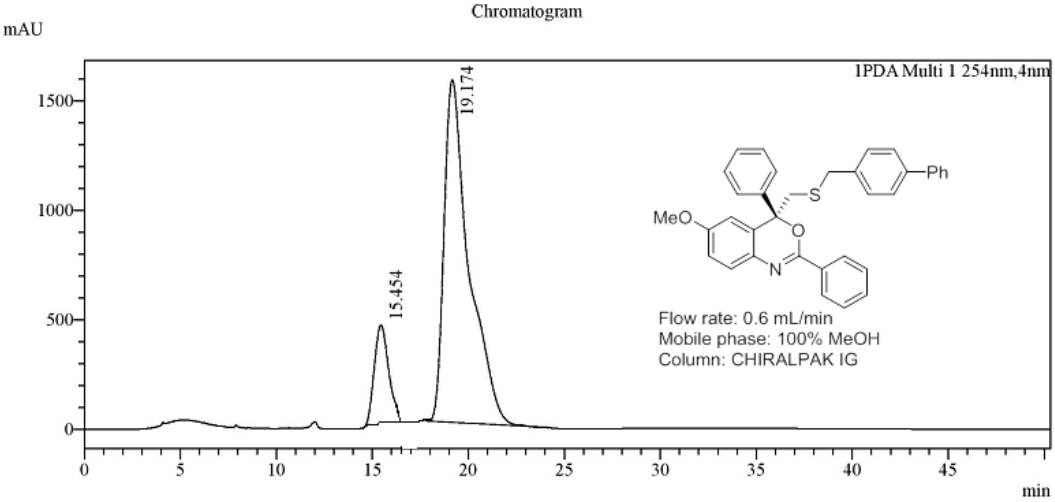
HPLC Chromatogram of compound 3r



Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:15.402	15.402	32116949	50.538	619678	70.401
2	RT:19.338	19.338	31433607	49.462	260531	29.599
Total			63550556	100.000	880209	100.000

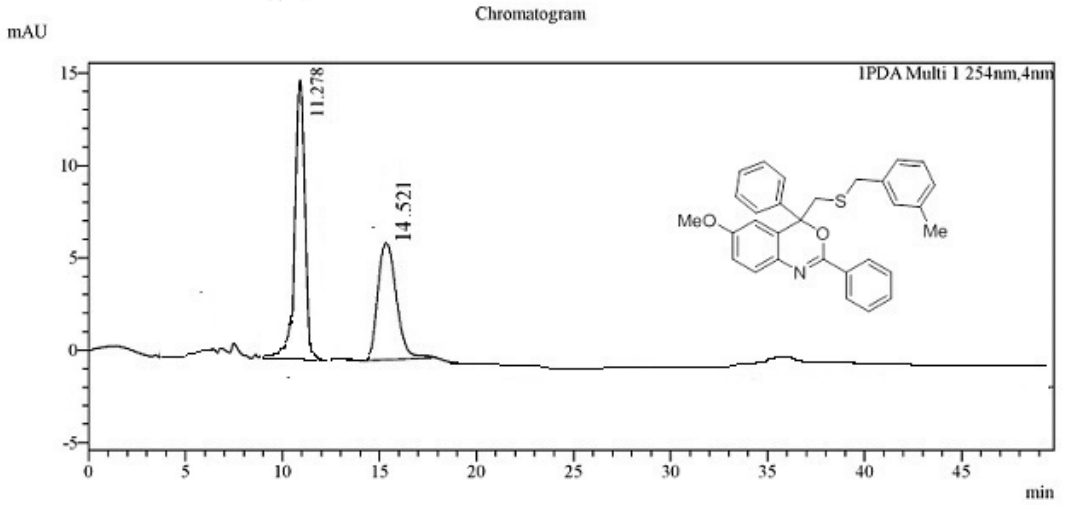


Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:15.454	15.454	20100847	12.511	420420	21.193
2	RT:19.174	19.174	140565305	87.489	1563345	78.807
Total			160666152	100.000	1983765	100.000

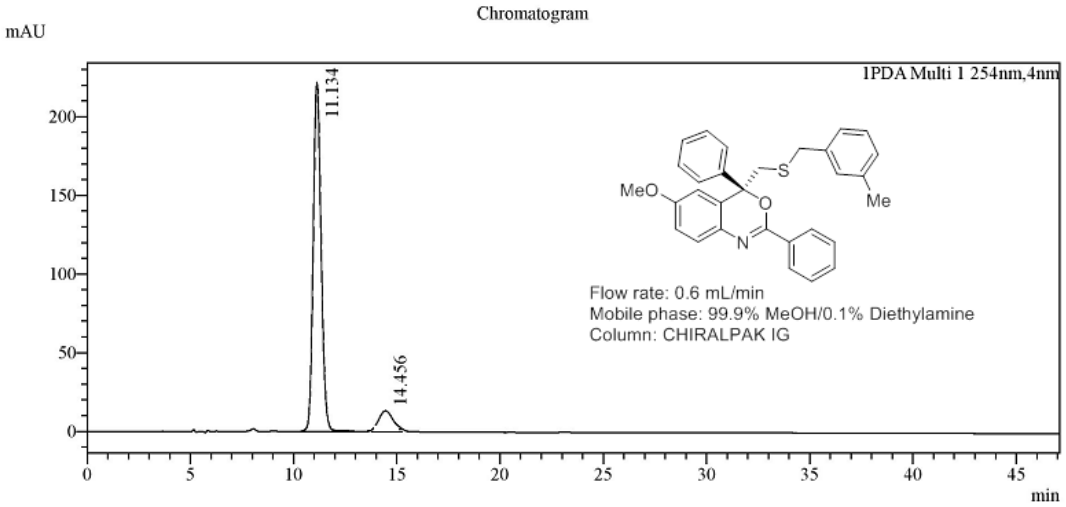
HPLC Chromatogram of compound 3s



Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:11.278	11.278	437163	50.497	14397	69.413
2	RT:14.521	14.521	428550	49.503	6344	30.587
Total			865713	100.000	20742	100.000

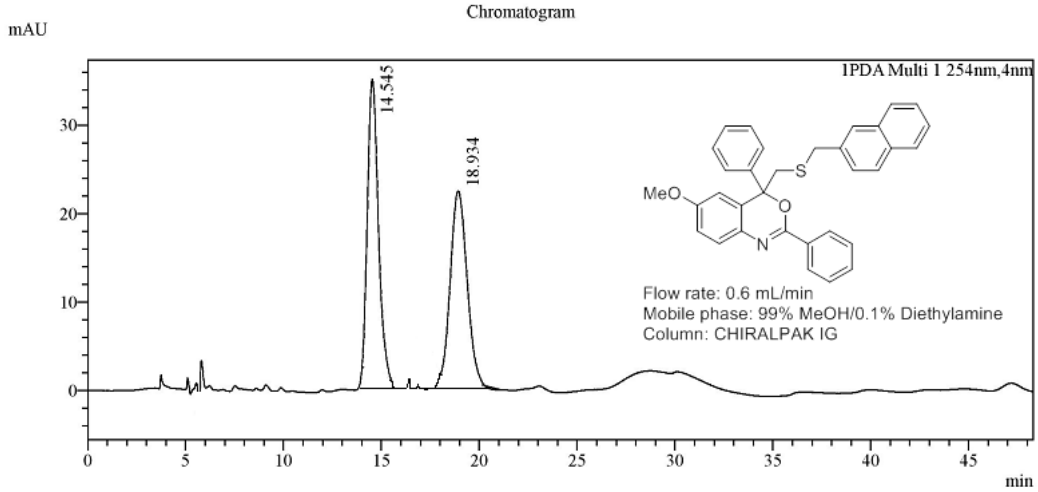


Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:11.134	11.134	5923825	91.730	221941	94.926
2	RT:14.456	14.456	534088	8.270	11863	5.074
Total			6457914	100.000	233804	100.000

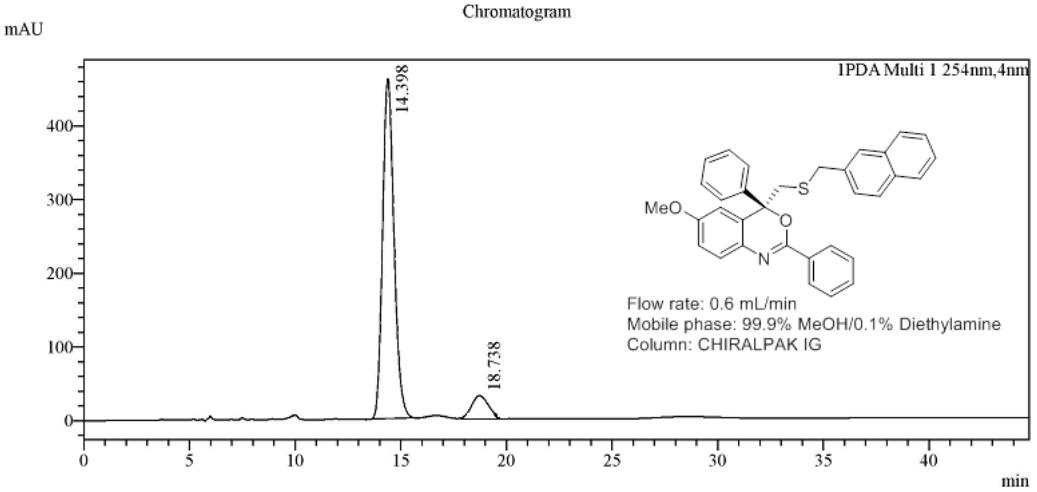
HPLC Chromatogram of compound 3t



Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:14.545	14.545	1239785	50.707	33113	60.900
2	RT:18.934	18.934	1205196	49.293	21260	39.100
Total			2444981	100.000	54373	100.000

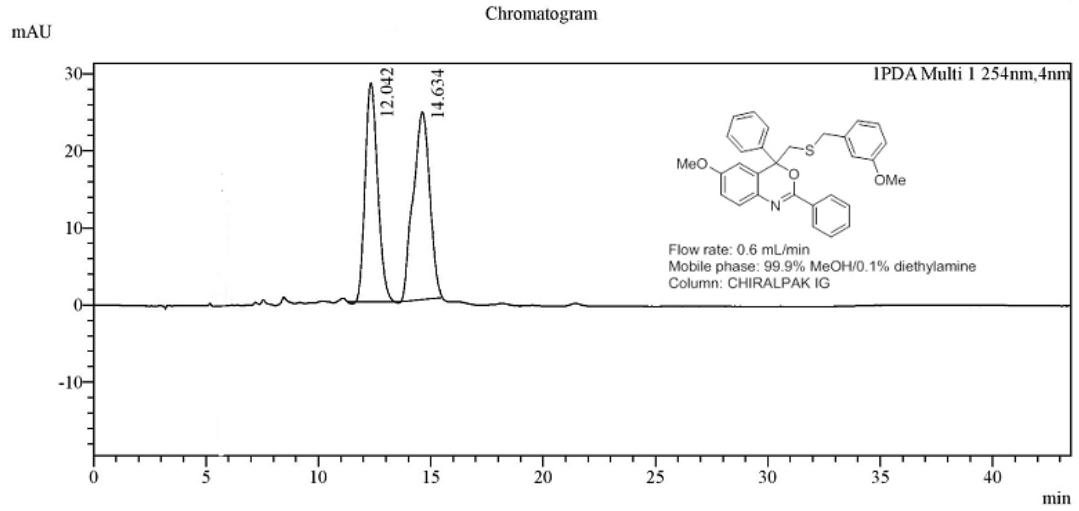


Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:14.398	14.398	17299305	92.988	461294	94.477
2	RT:18.738	18.738	1304590	7.012	26967	5.523
Total			18603895	100.000	488261	100.000

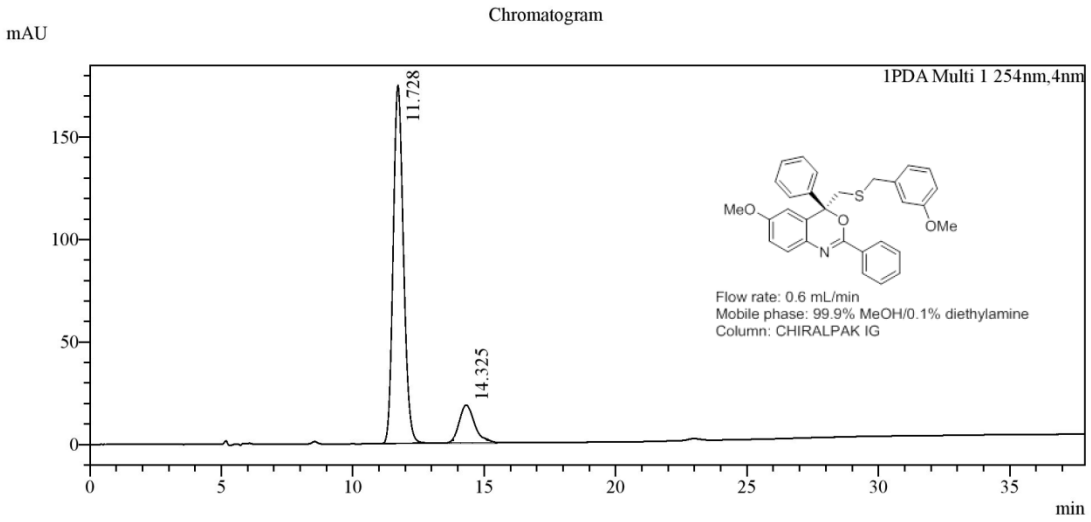
HPLC Chromatogram of compound 3u



Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:12.042	12.042	1096966	46.755	28388	53.875
2	RT:14.634	14.634	1249225	53.245	24304	46.125
Total			2346191	100.000	52692	100.000

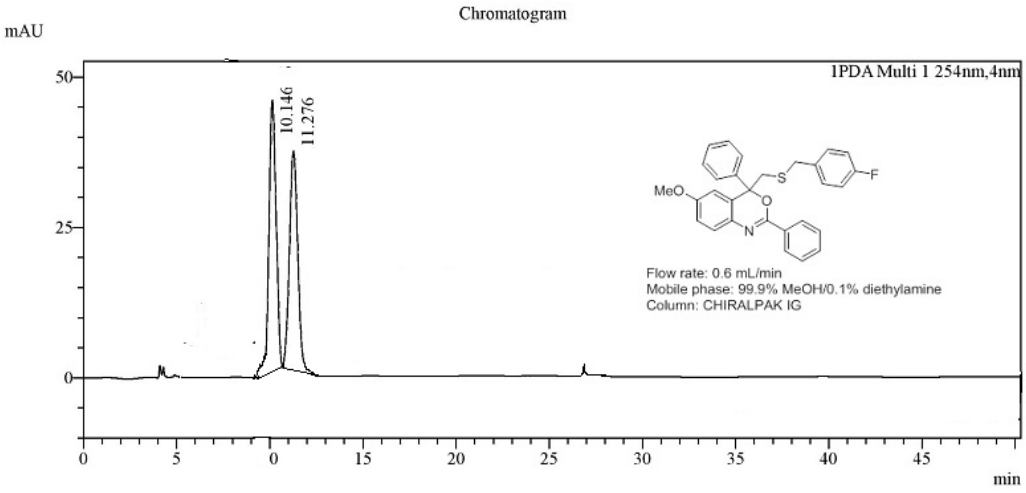


Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:11.728	11.728	4714791	88.319	174641	91.092
2	RT:14.325	14.325	623566	11.681	17079	8.908
Total			5338357	100.000	191720	100.000

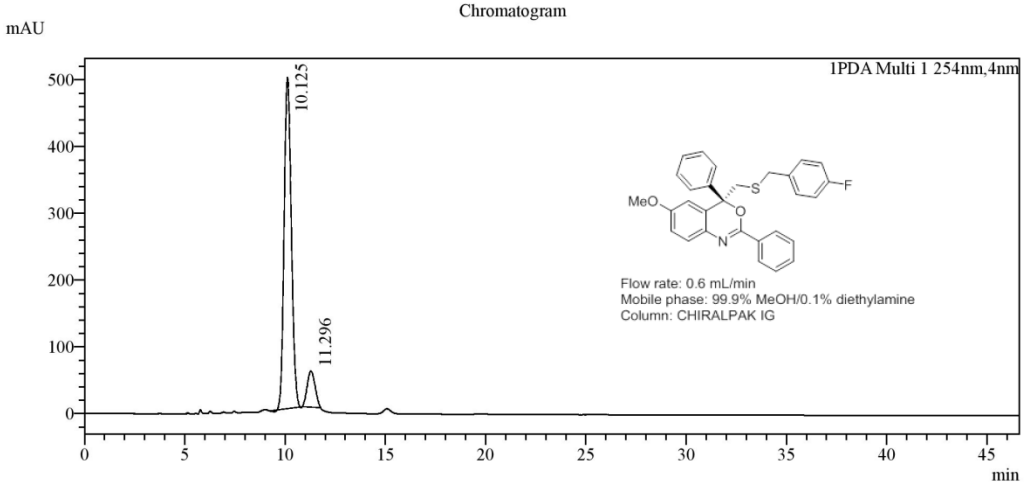
HPLC Chromatogram of compound 3v



Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:10.146	10.146	1177372	50.970	45245	55.439
2	RT:11.276	11.276	1132560	49.030	36367	44.561
Total			2309932	100.000	81612	100.000

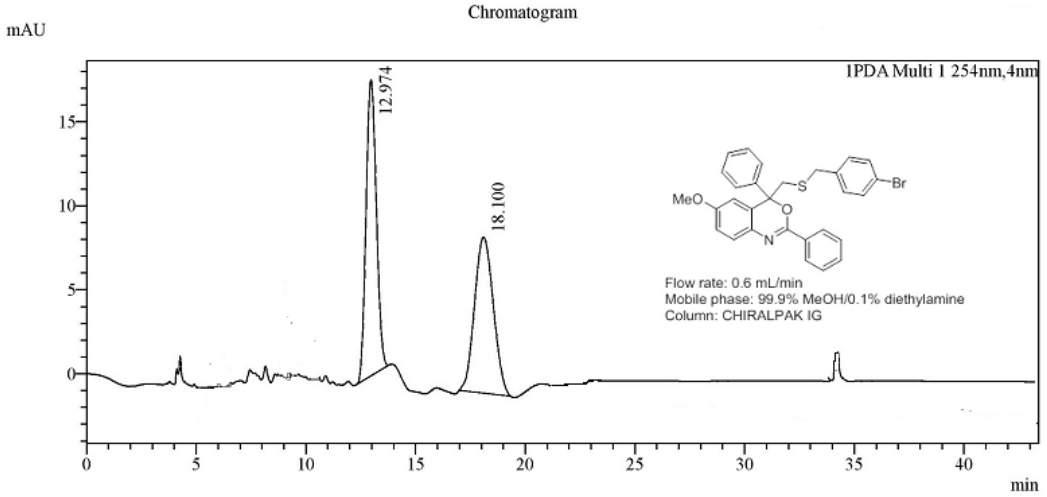


Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:10.125	10.125	12351910	89.270	496348	90.184
2	RT:11.296	11.296	1484616	10.730	54025	9.816
Total			13836526	100.000	550373	100.000

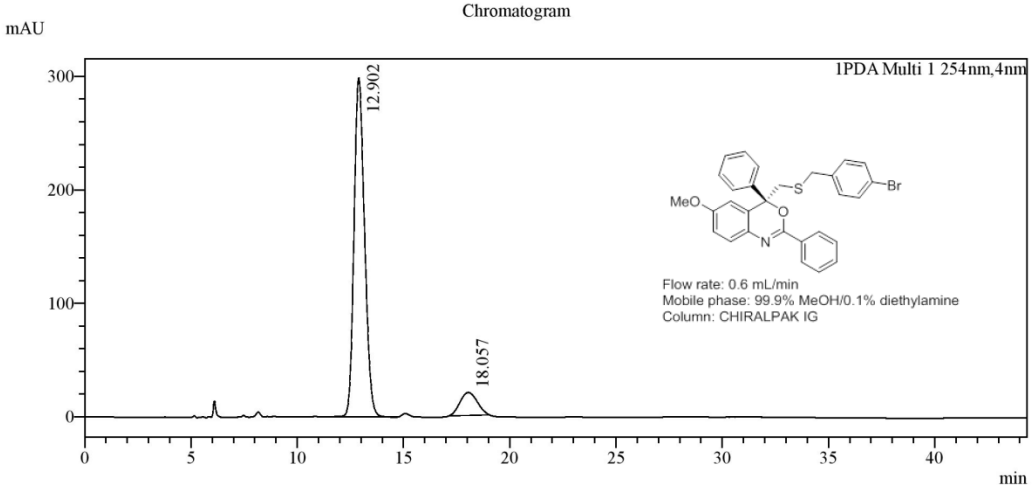
HPLC Chromatogram of compound 3w



Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:12.974	12.974	574686	50.880	17631	65.467
2	RT:18.100	18.100	554817	49.120	9300	34.533
Total			1129503	100.000	26932	100.000

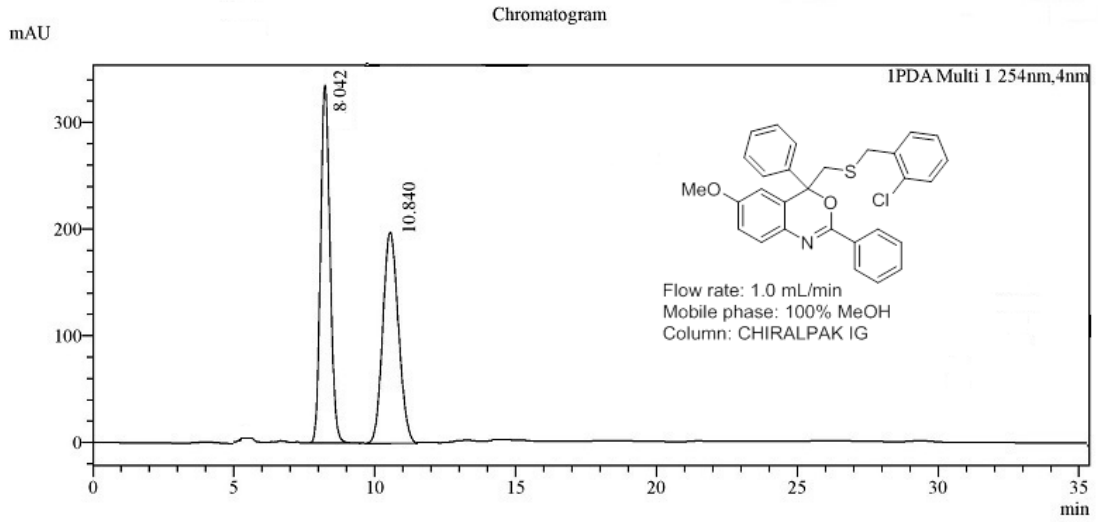


Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:12.902	12.902	10297943	90.071	298949	93.697
2	RT:18.057	18.057	1135240	9.929	20110	6.303
Total			11433183	100.000	319059	100.000

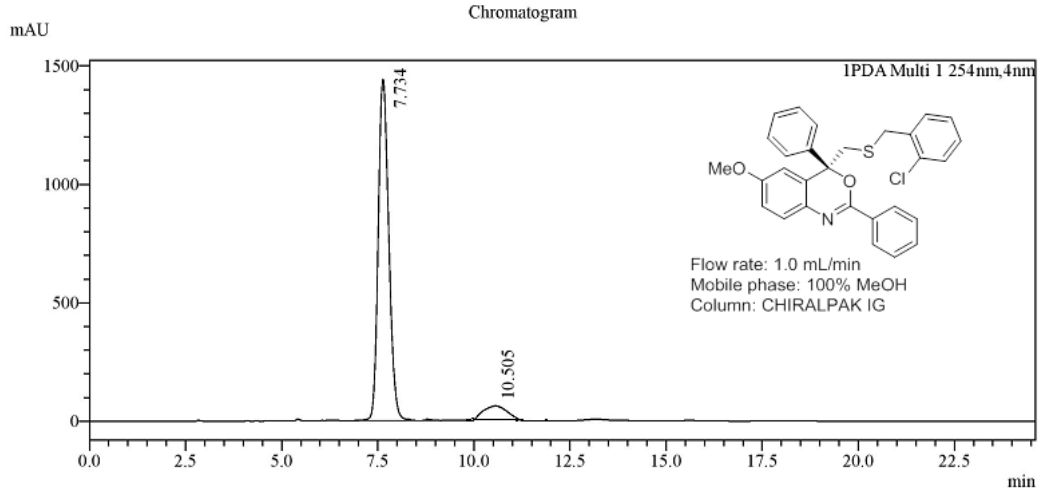
HPLC Chromatogram of compound 3x



Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT: 8.042	8.042	7849557	50.634	335401	62.887
2	RT: 10.840	10.840	7653065	49.366	197934	37.113
Total			15502621	100.000	533336	100.000

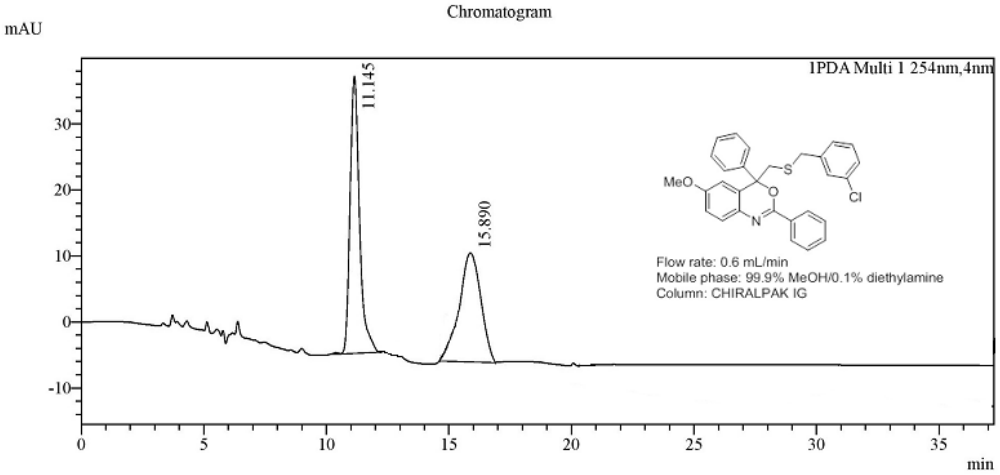


Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:7.734	7.734	27721114	92.232	1440307	96.240
2	RT:10.505	10.505	2334659	7.768	56273	3.760
Total			30055773	100.000	1496581	100.000

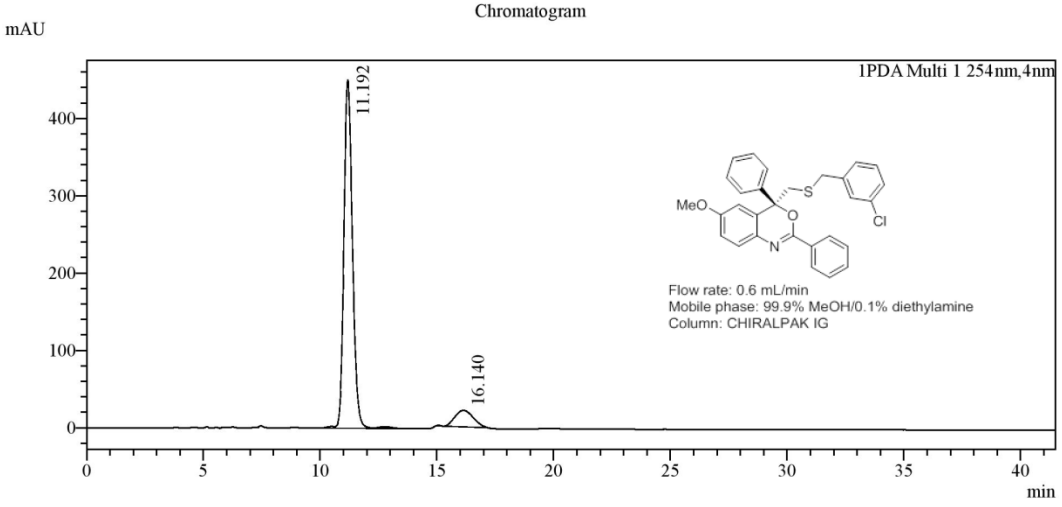
HPLC Chromatogram of compound 3y



Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:11.145	11.145	1121429	50.599	41923	71.773
2	RT:15.890	15.890	1094861	49.401	16488	28.227
Total			2216290	100.000	58411	100.000

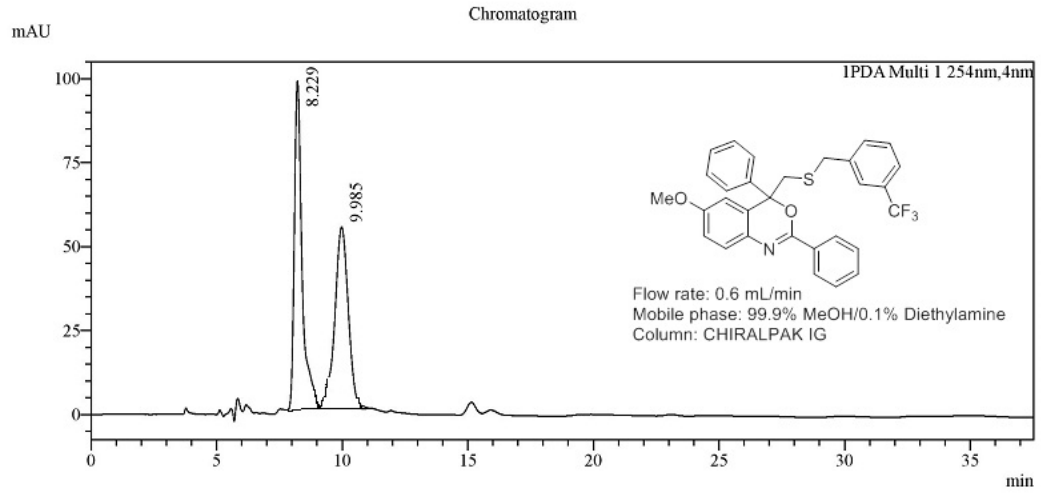


Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:11.192	11.192	11577710	90.612	450526	95.444
2	RT:16.140	16.140	1199530	9.388	21506	4.556
Total			12777240	100.000	472032	100.000

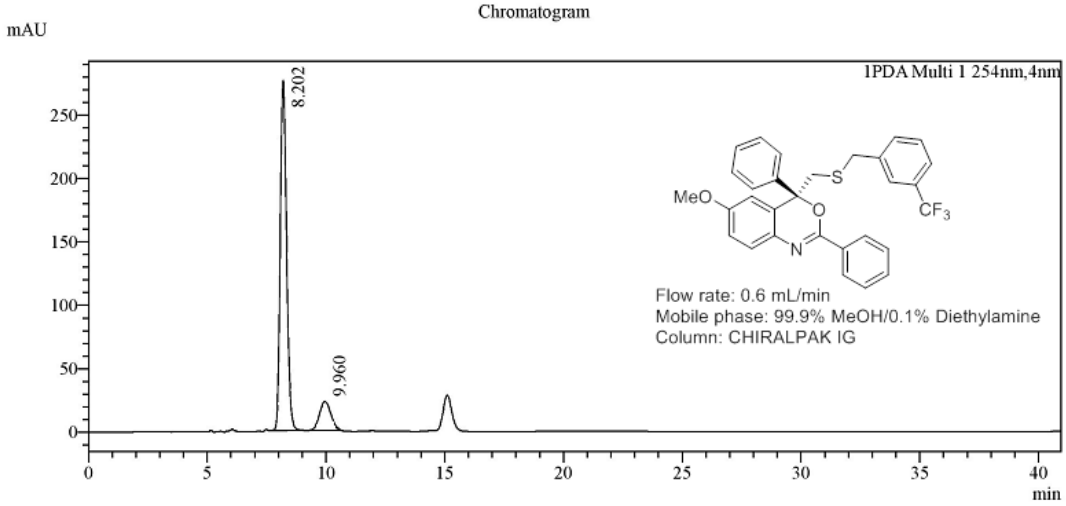
HPLC Chromatogram of compound 3z



Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:8.229	8.229	1800349	50.204	93593	64.719
2	RT:9.985	9.985	1785748	49.796	51022	35.281
Total			3586097	100.000	144615	100.000

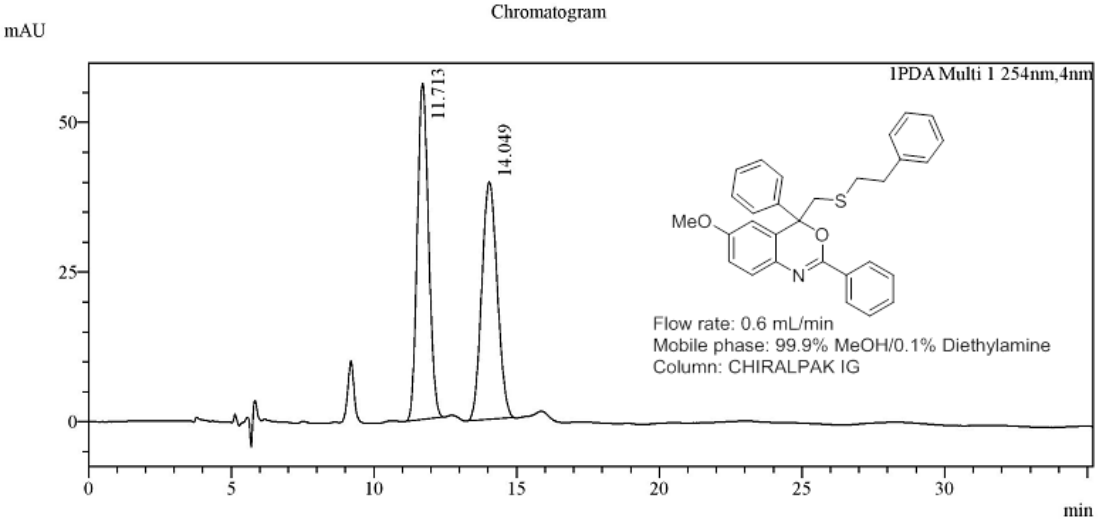


Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:8.202	8.202	5090927	89.450	276028	93.181
2	RT:9.960	9.960	600435	10.550	20201	6.819
Total			5691362	100.000	296228	100.000

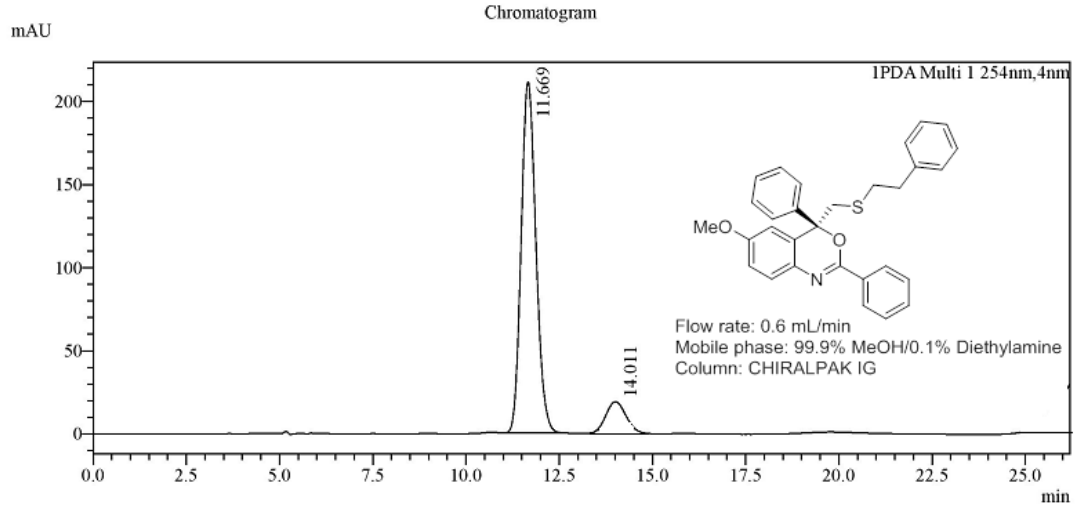
HPLC Chromatogram of compound 3aa



Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:11.713	11.713	1539495	50.686	56150	58.604
2	RT:14.049	14.049	1497796	49.314	39663	41.396
Total			3037291	100.000	95813	100.000

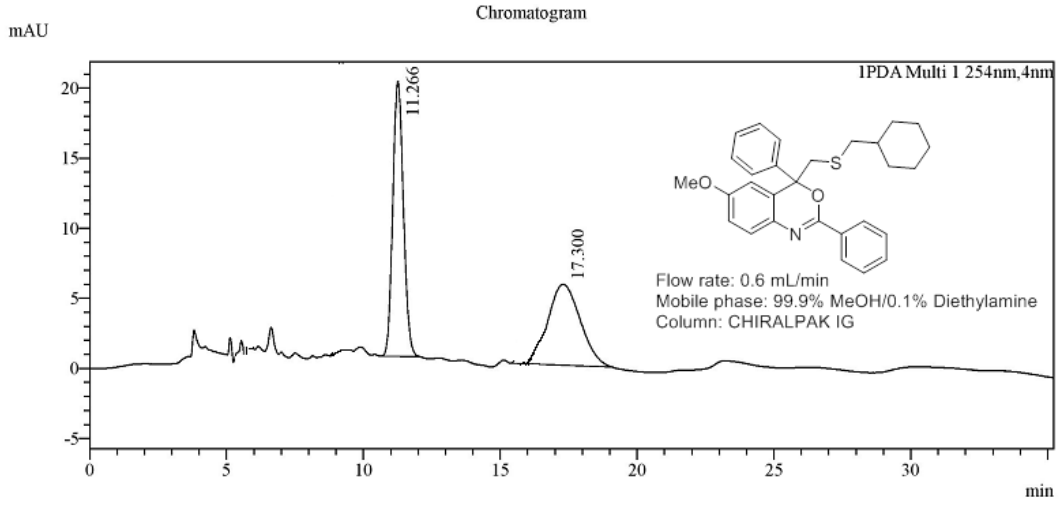


Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:11.669	11.669	5813199	91.396	211372	92.668
2	RT:14.011	14.011	547277	8.604	16724	7.332
Total			6360476	100.000	228095	100.000

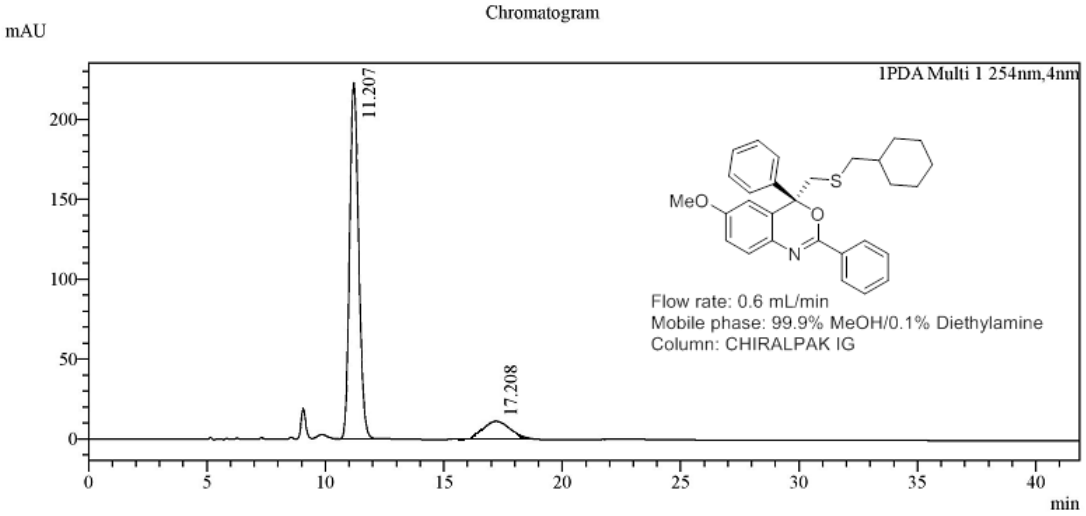
HPLC Chromatogram of compound 3ab



Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:11.266	11.266	529272	50.345	19637	77.285
2	RT:17.300	17.300	522019	49.655	5772	22.715
Total			1051291	100.000	25408	100.000

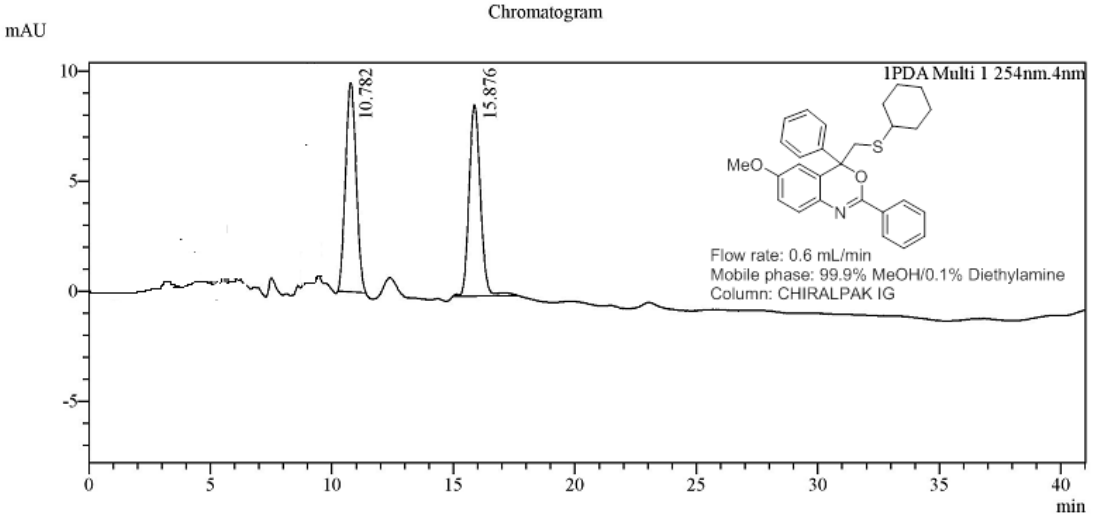


Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:11.207	11.207	5918566	91.679	222653	96.333
2	RT:17.208	17.208	537167	8.321	8475	3.667
Total			6455733	100.000	231129	100.000

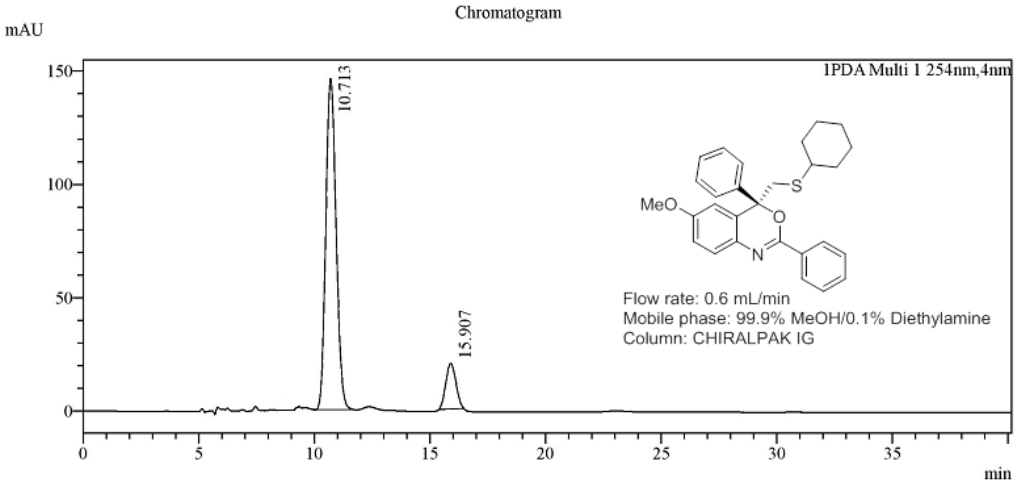
HPLC Chromatogram of compound 3ac



Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:10.782	10.782	289325	50.515	9511	52.215
2	RT:15.876	15.876	283429	49.485	8704	47.785
Total			572754	100.000	18215	100.000

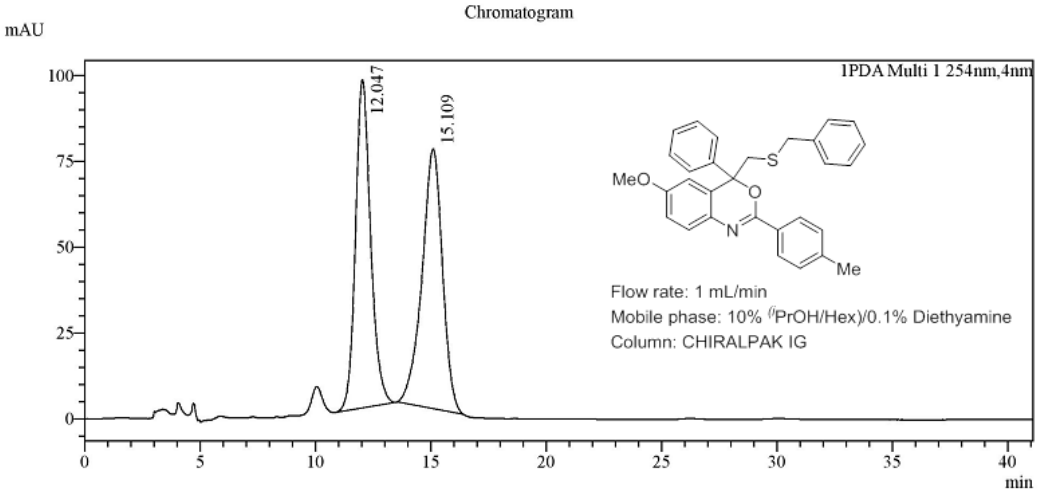


Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:10.713	10.713	4516089	88.084	146065	87.894
2	RT:15.907	15.907	610925	11.916	20118	12.106
Total			5127015	100.000	166183	100.000

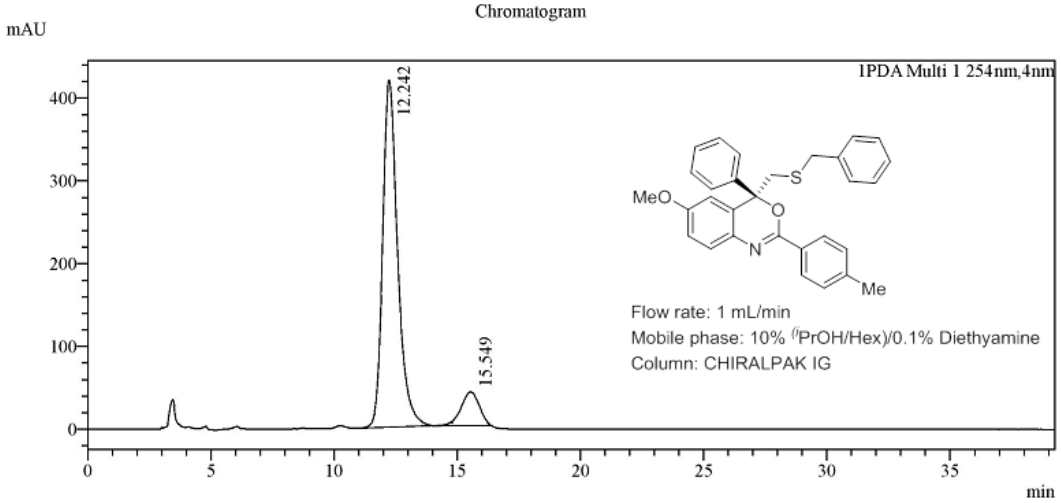
HPLC Chromatogram of compound 3ad



Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:12.047	12.047	4351882	48.299	95656	55.842
2	RT:15.109	15.109	4658495	51.701	75640	44.158
Total			9010377	100.000	171295	100.000

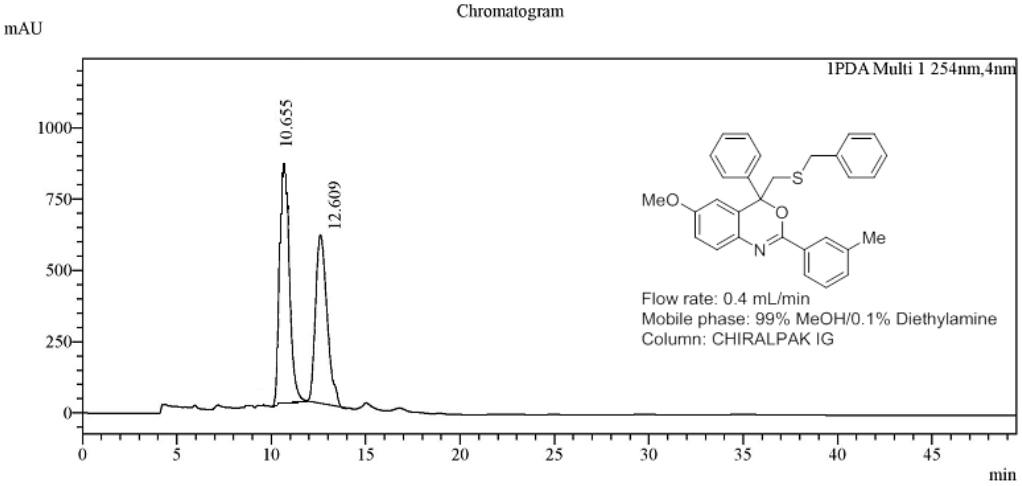


Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:12.242	12.242	17687528	90.739	419289	91.727
2	RT:15.549	15.549	1805293	9.261	37816	8.273
Total			19492821	100.000	457105	100.000

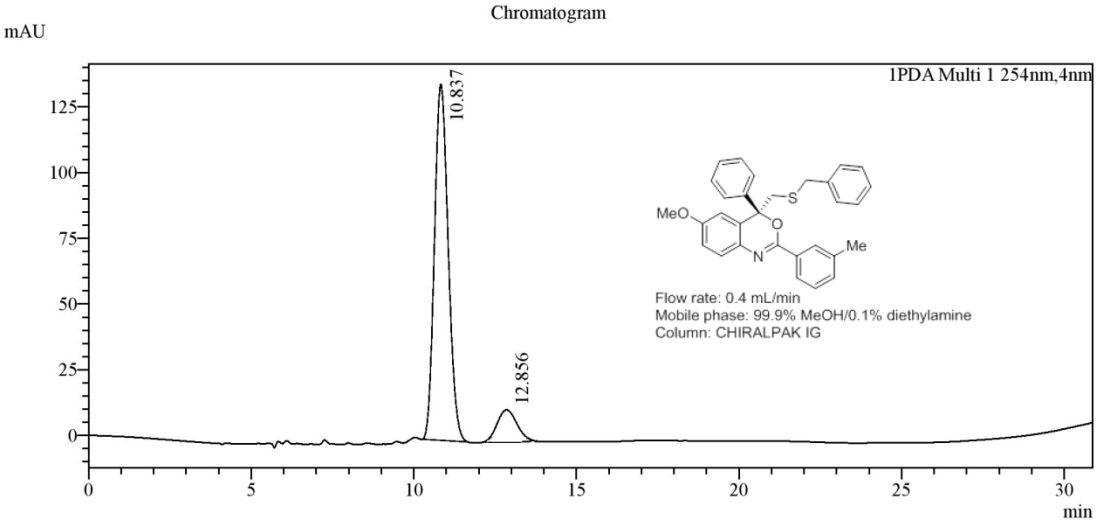
HPLC Chromatogram of compound 3ae



Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:10.655	10.655	25687873	50.598	970752	62.183
2	RT:12.609	12.609	25080548	49.402	590359	37.817
Total			50768421	100.000	1561111	100.000

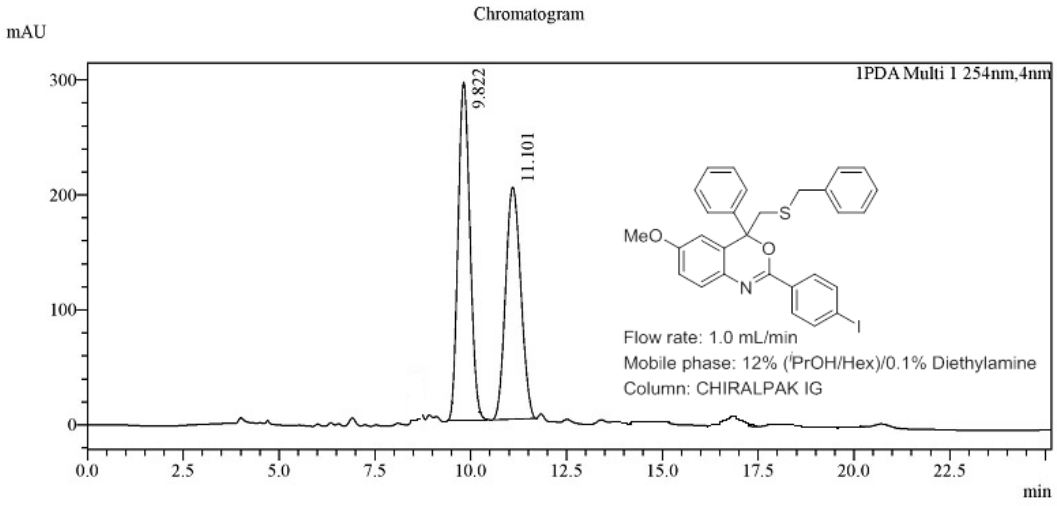


Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:10.837	10.837	3976823	90.751	135543	92.608
2	RT:12.856	12.856	405303	9.249	10819	7.392
Total			4382126	100.000	146362	100.000

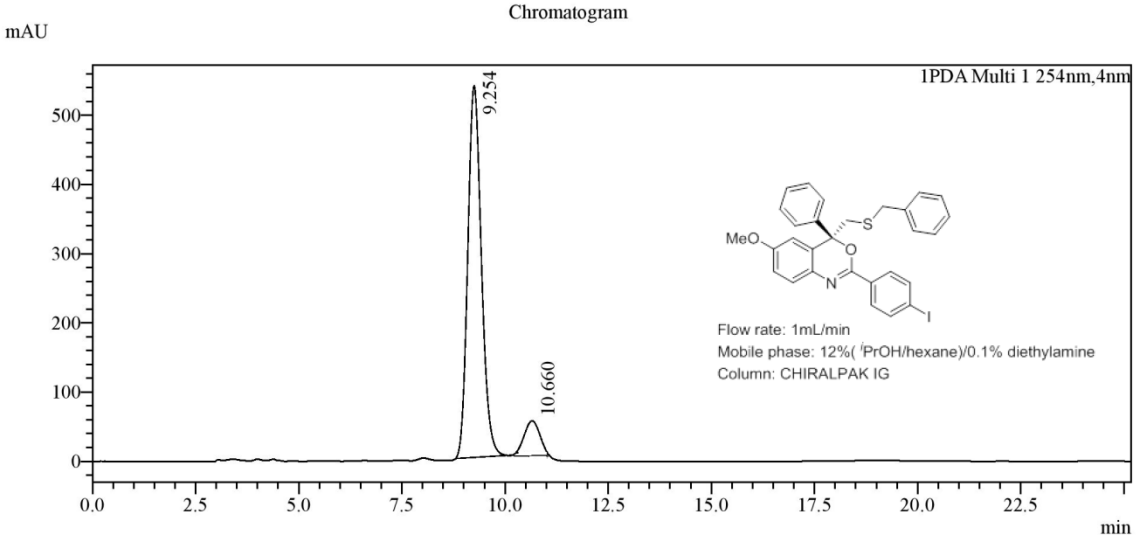
HPLC Chromatogram of compound 3af



Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:9.822	9.822	5773160	50.882	282391	58.329
2	RT:11.101	11.101	5573035	49.118	201743	41.671
Total			11346195	100.000	484134	100.000

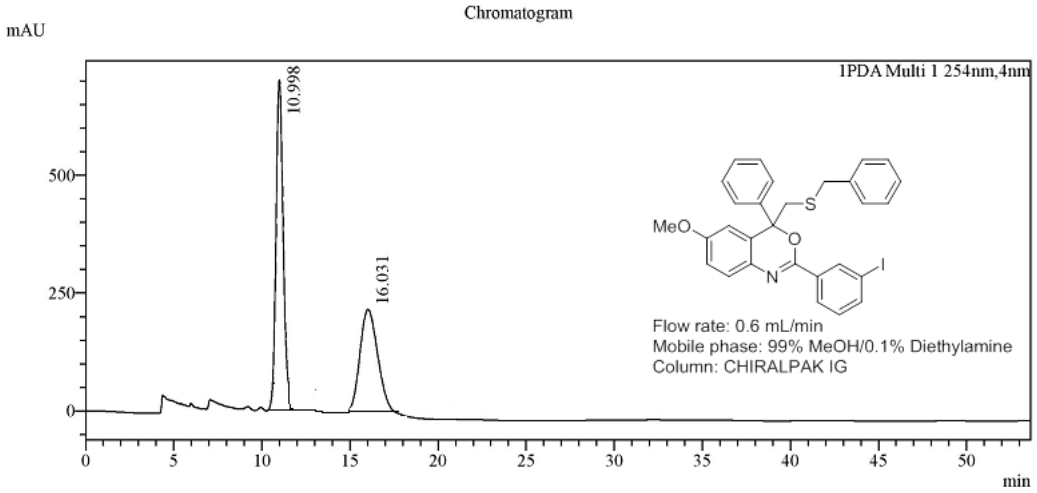


Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:9.254	9.254	12272511	91.055	536386	91.839
2	RT:10.660	10.660	1205623	8.945	47661	8.161
Total			13478134	100.000	584047	100.000

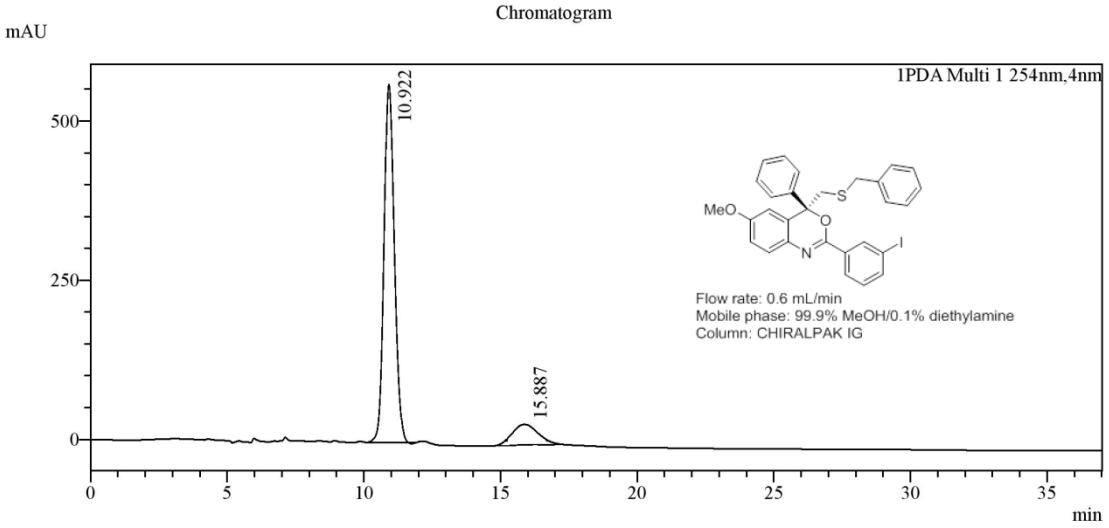
HPLC Chromatogram of compound 3ag



Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:10.998	10.998	15816106	50.231	636488	74.424
2	RT:16.031	16.031	15670698	49.769	218726	25.576
Total			31486804	100.000	855214	100.000

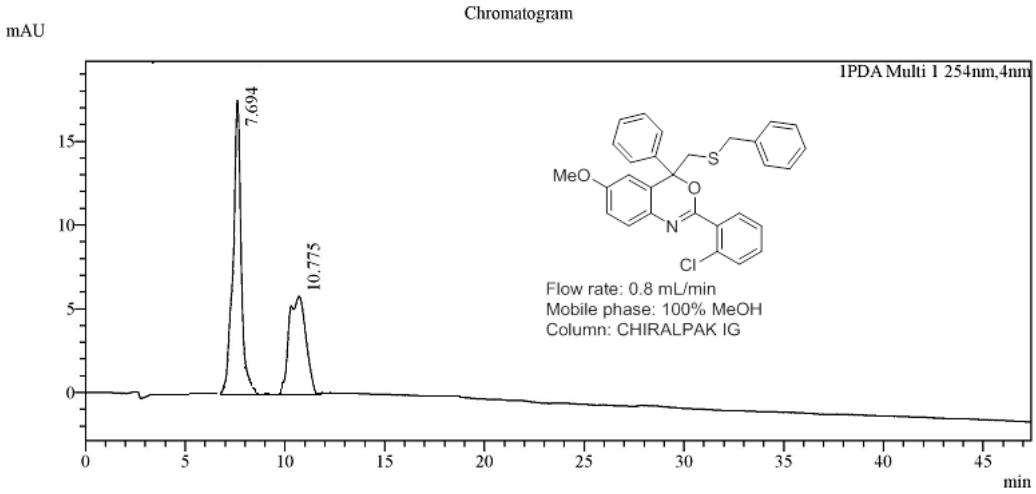


Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:10.922	10.922	14834222	91.133	562238	95.535
2	RT:15.887	15.887	1443269	8.867	26280	4.465
Total			16277491	100.000	588518	100.000

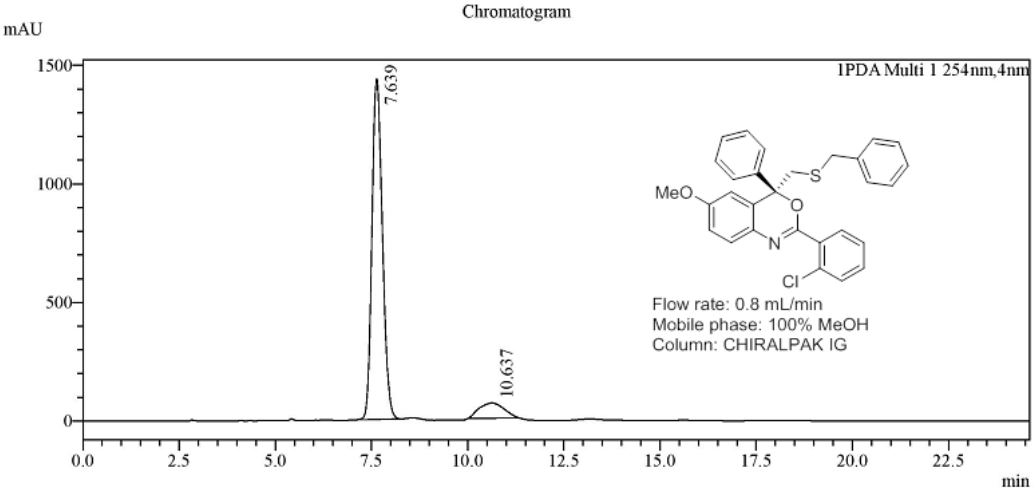
HPLC Chromatogram of compound 3ah



Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:7.694	7.694	407221	50.253	16377	73.367
2	RT:10.775	10.775	403127	49.747	5945	26.633
Total			810348	100.000	22322	100.000

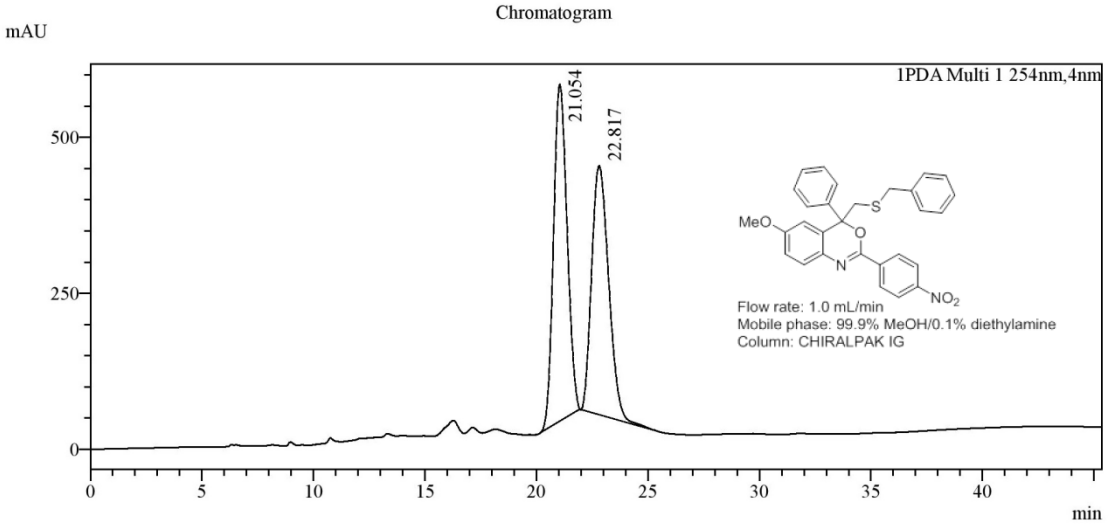


Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:7.639	7.639	27178348	90.381	1436851	95.728
2	RT:10.637	10.637	2892515	9.619	64126	4.272
Total			30070863	100.000	1500976	100.000

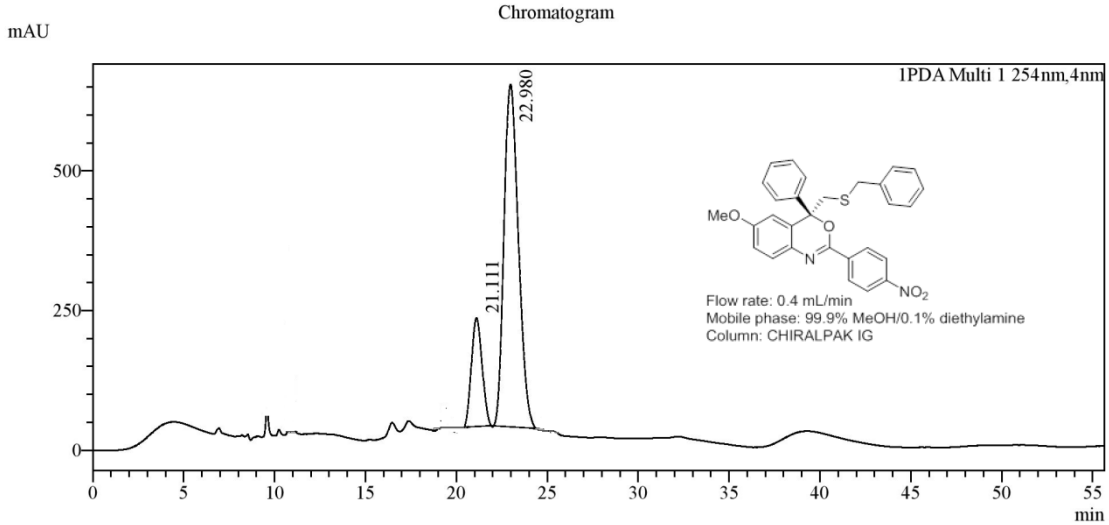
HPLC Chromatogram of compound 3ai



Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:21.054	21.054	22802682	51.845	539985	57.515
2	RT:22.817	22.817	21179437	48.155	398869	42.485
Total			43982119	100.000	938854	100.000

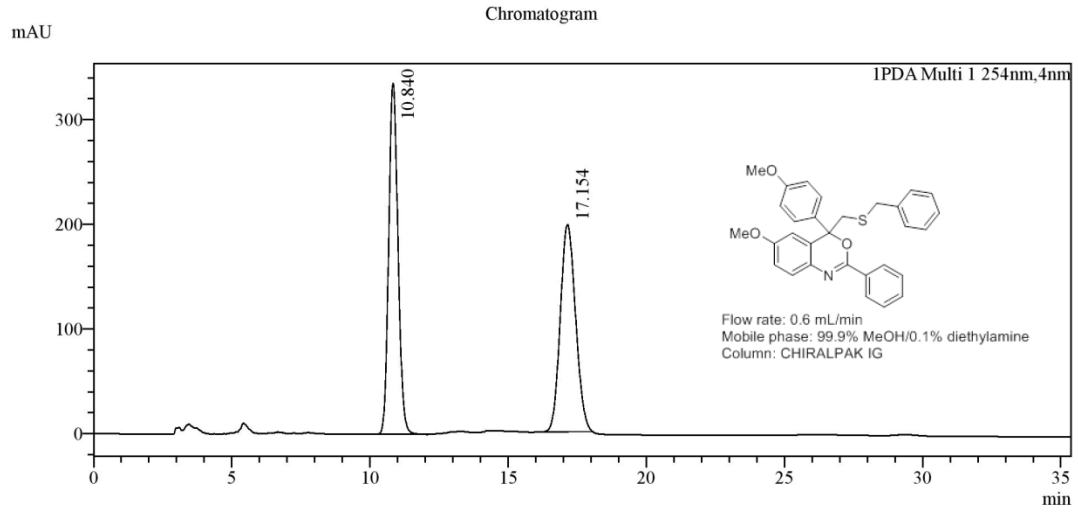


Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:21.111	21.111	7954570	19.038	194335	24.059
2	RT:22.980	22.980	33827254	80.962	613412	75.941
Total			41781824	100.000	807747	100.000

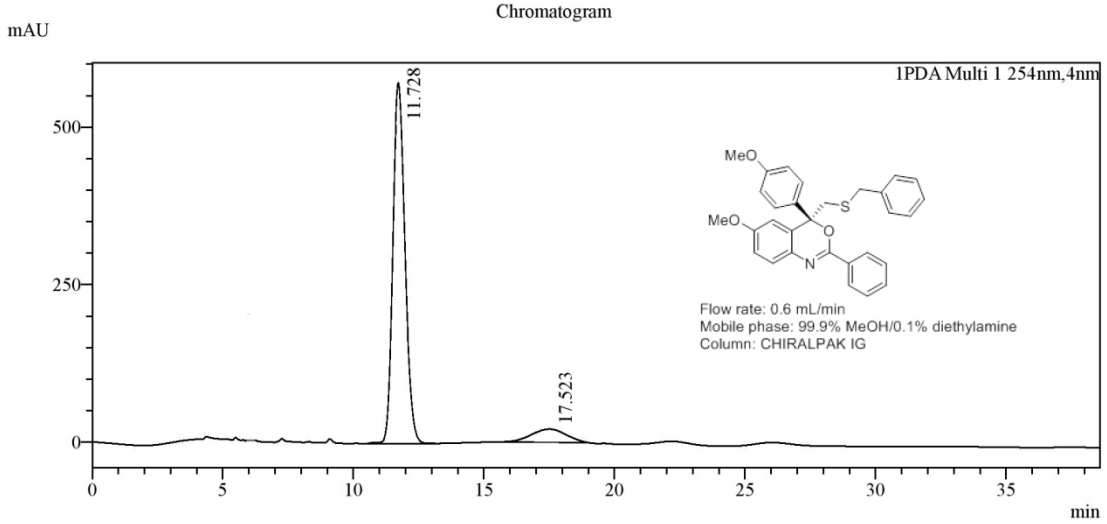
HPLC Chromatogram of compound 3aj



Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:10.840	10.840	7849557	50.634	335401	62.887
2	RT:17.154	17.154	7653065	49.366	197934	37.113
Total			15502621	100.000	533336	100.000

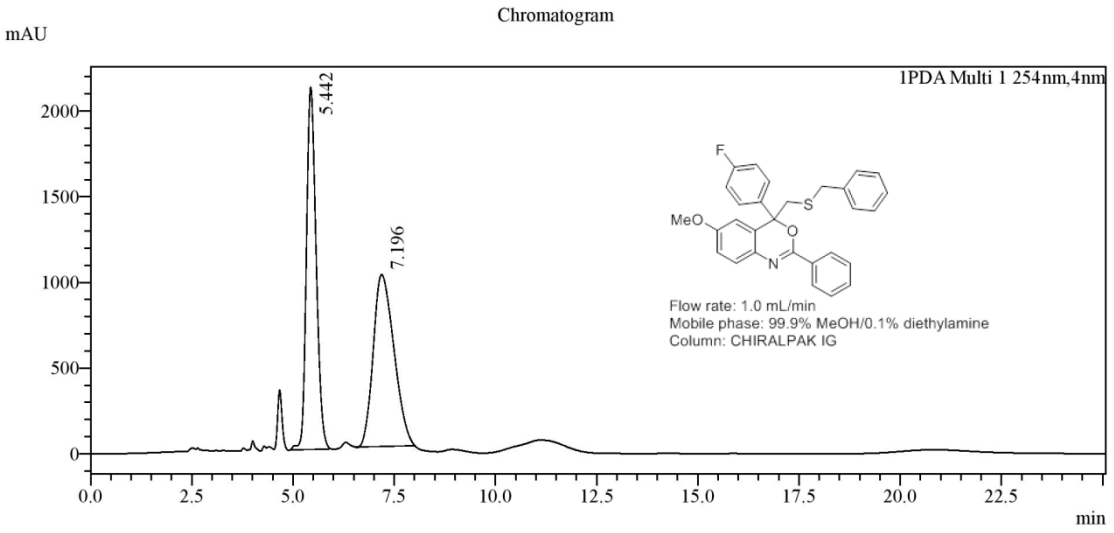


Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:11.728	11.728	18469478	90.566	572420	96.479
2	RT:17.523	17.523	1923975	9.434	20889	3.521
Total			20393452	100.000	593309	100.000

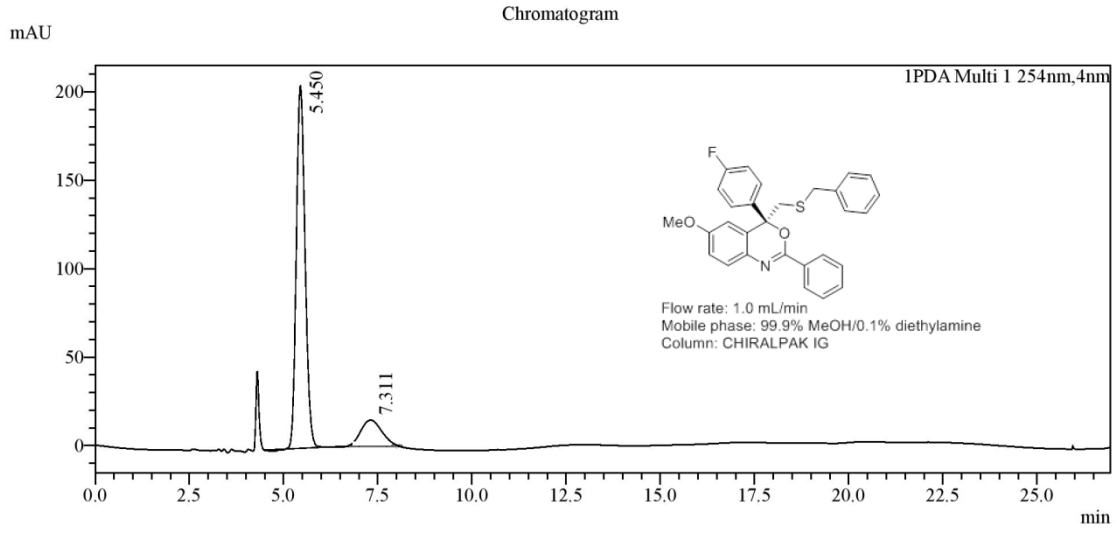
HPLC Chromatogram of compound 3ak



Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:5.442	5.442	35285125	49.744	2114700	67.832
2	RT:7.196	7.196	35648144	50.256	1002877	32.168
Total			70933270	100.000	3117577	100.000

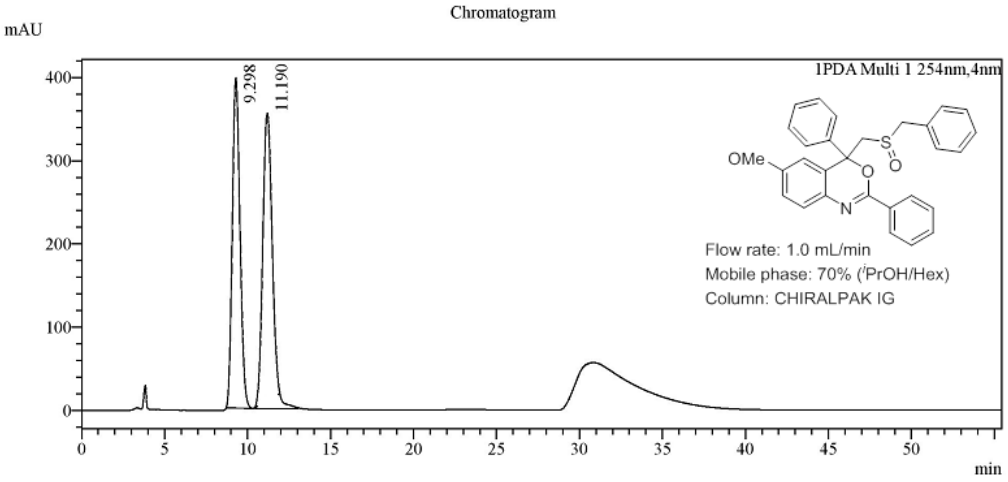


Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:5.450	5.450	3277795	87.083	204881	93.791
2	RT:7.311	7.311	486185	12.917	13562	6.209
Total			3763980	100.000	218443	100.000

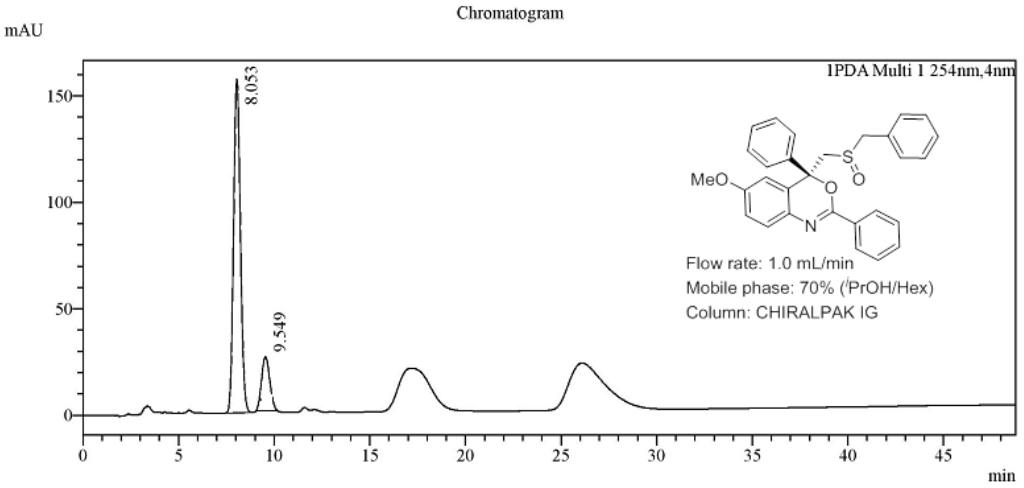
HPLC Chromatogram of compound 4:



Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:9.298	9.298	12738782	49.045	396591	53.467
2	RT:11.190	11.190	13234712	50.955	345164	46.533
Total			25973494	100.000	741755	100.000

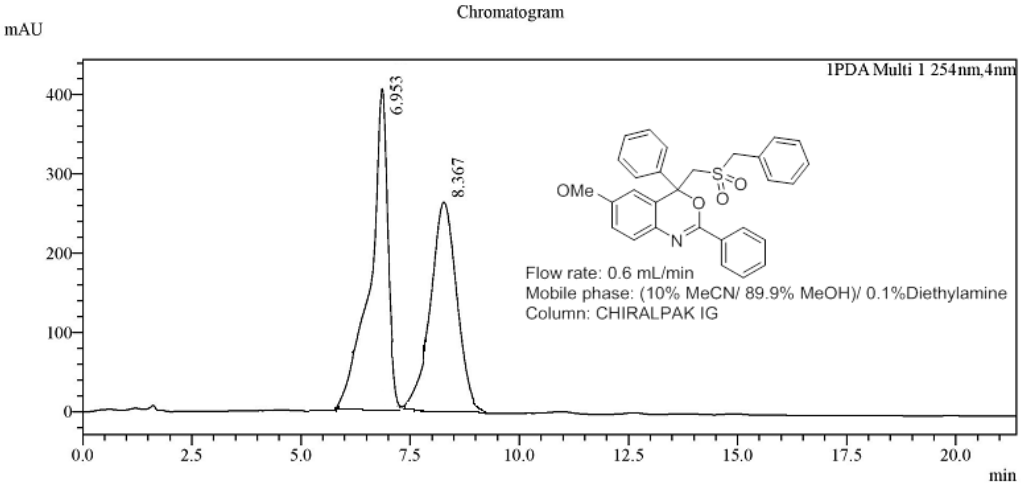


Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:8.053	8.053	3885032	89.203	156725	88.755
2	RT:9.549	9.549	470262	10.797	19856	11.245
Total			4355294	100.000	176580	100.000

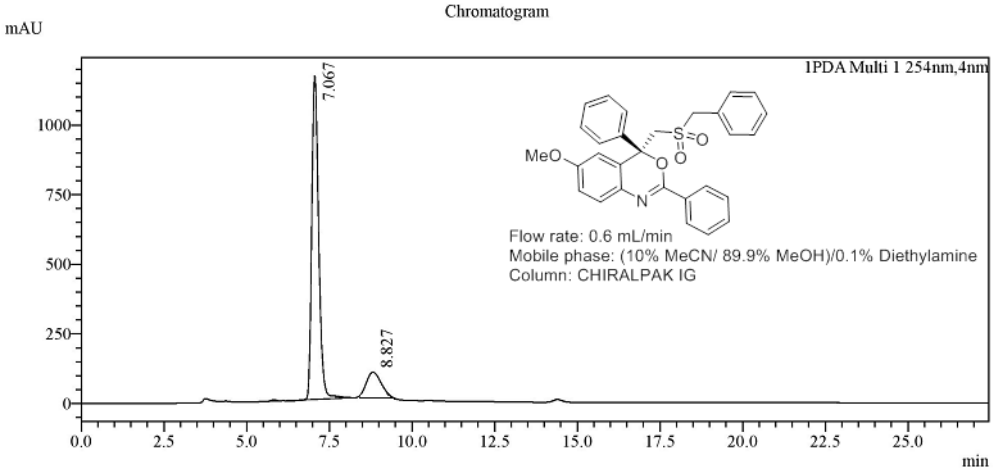
HPLC Chromatogram of compound 5:



Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:6.953	6.953	11133644	50.843	384895	60.079
2	RT:8.367	8.367	10764397	49.157	255756	39.921
Total			21898041	100.000	640651	100.000

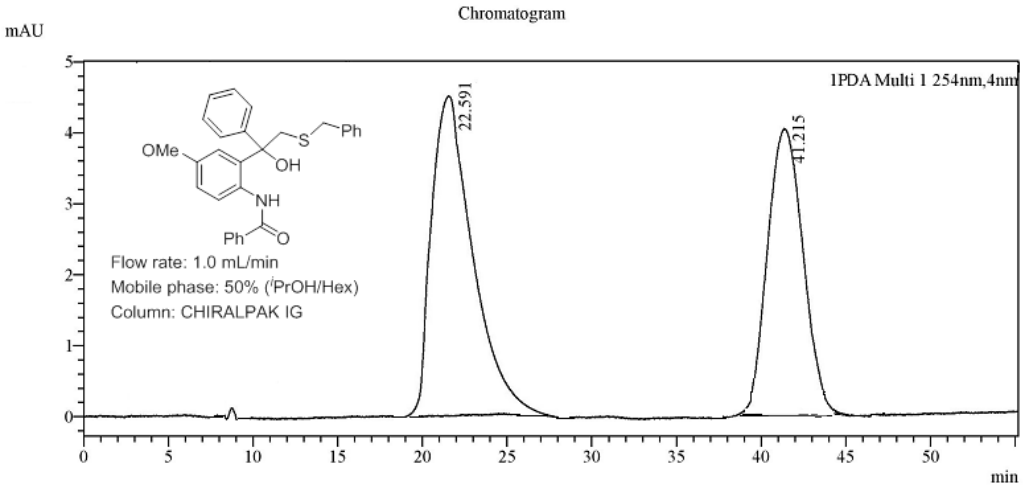


Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:7.067	7.067	16764863	87.748	1161944	93.361
2	RT:8.827	8.827	2340778	12.252	82629	6.639
Total			19105642	100.000	1244573	100.000

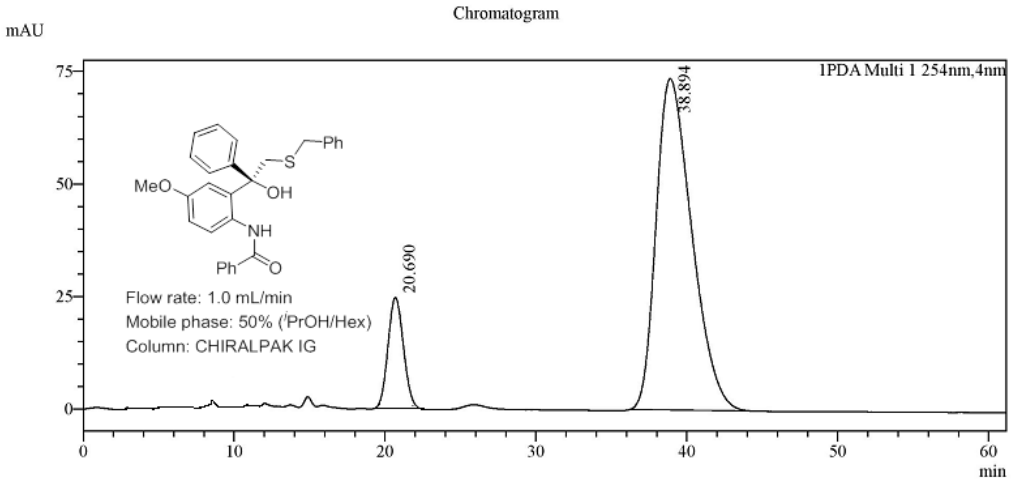
HPLC Chromatogram of compound 7:



Peak Table

PDA Ch1 254nm

Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:22.591	22.591	289325	50.515	9511	52.215
2	RT:41.215	41.215	283429	49.485	8704	47.785
Total			572754	100.000	18215	100.000



Peak Table

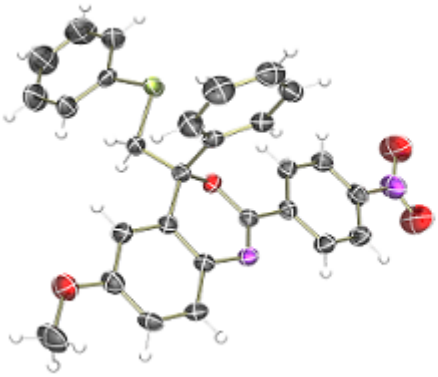
PDA Ch1 254nm

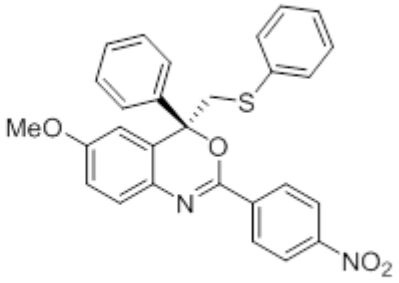
Peak#	Name	Ret. Time	Area	Area%	Height	Height%
1	RT:20.690	20.690	1653801	12.020	23976	24.578
2	RT:38.894	38.894	12104948	87.980	73577	75.422
Total			13758748	100.000	97553	100.000

16. Crystal structure of isolated compound

Crystallographic data and structure refinement for compound 3g

Recrystallization of compound **3g** from chloroform:hexane (1:4) by slow evaporation in a vial with diameter of 0.75 cm and length 5 cm at 30 °C afforded suitable size and quality crystals for X-ray diffraction





Identification code	shelx
Empirical formula	C28 H22 N2 O4 S
Formula weight	482.53
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P C
Unit cell dimensions	a = 10.2070(6) A alpha = 90 deg.
	b = 16.4841(10) A beta = 95.493(2) deg.
	c = 7.1404(4) A gamma = 90 deg.
Volume	1195.88(12) A^3
Z, Calculated density	2, 1.340 Mg/m^3
Absorption coefficient	0.173 mm^-1

F(000)	504
Crystal size	0.150 x 0.120 x 0.100 mm
Theta range for data collection	3.121 to 24.999 deg.
Limiting indices	-12<=h<=12, -19<=k<=19, -8<=l<=8
Reflections collected / unique	28518 / 4179 [R(int) = 0.0384]
Completeness to theta =	24.999 99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7471 and 0.6379
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4179 / 2 / 316
Goodness-of-fit on F^2	1.084
Final R indices [I>2sigma(I)]	R1 = 0.0401, wR2 = 0.0986
R indices (all data)	R1 = 0.0455, wR2 = 0.1023
Absolute structure parameter	0.39(3)
Extinction coefficient	n/a
Largest diff. peak and hole	0.180 and -0.170 e.A^-3