Supporting Information

Pd-Catalyzed Regio-, Diastereo-, and Enantioselective [3+2] Cycloaddition Reactions: Access to Chiral Cyclopentyl Sulfones

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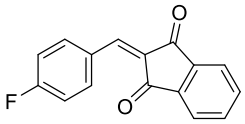
A. General Information

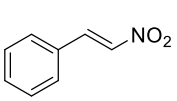
Unless otherwise noted, all reagents were purchased commercially and used as received. Anhydrous tetrahydrofuran (THF) was obtained by distillation from sodium/benzophenone and anhydrous toluene (PhMe) was obtained by distillation from sodium. Anhydrous 1.4-dioxane were purchased as such from Acros Organics in AcroSeal bottles and were used as received. When performing air-sensitive reactions, reagents and solvents were transferred using either stainless steel cannulae or plastic syringes equipped with stainless steel needles. Air-sensitive reactions were performed under a positive pressure of either nitrogen (N_2) or argon (Ar) in reaction vessels sealed with rubber septa. Analytical thin-layer chromatography (TLC) was performed on glass-backed silica-coated plates (Merck TLC Silica gel 60 F254). Visualization was typically performed using UV light and/or basic potassium permanganate ($KMnO_4$). Purification by flash column chromatography was performed on silica gel (Fisher Scientific, 230–400 mesh, grade 60) using bulk solvents. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded at 400 MHz using a Varian Mercury 400 spectrometer. All ^{1}H chemical shifts are reported in ppm relative to tetramethylsilane (0.00 ppm) or the residual solvent peak (7.264 ppm for $CDCl_3$, 5.32 ppm for CH_2Cl_2). Multiplets were assigned with the assistance of the multiplet tool in Mestrenova, and are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs = broad, app. = apparent. Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded at 101 MHz using a Varian Mercury 400 spectrometer. All ^{13}C chemical shifts are reported in ppm relative to the center of the residual solvent peak (77.16 ppm for $CDCl_3$, 53.84 ppm for CH_2Cl_2). Infrared (IR) spectra were recorded on NaCl plates using a Perkin Elmer Paragon 500 FT-IR spectrometer. Enantiomeric excess (ee) were determined by high performance liquid chromatography (HPLC) using an Agilent 1200 series HPLC system using the specified separation conditions. Optical rotations were measured on a Jasco DIP-1000 digital polarimeter using 5 cm glass cells with a Na 589 nm filter. High resolution mass spectrometry (HRMS) was performed at University of Illinois at Urbana-Champaign on a high-resolution mass spectrometer (TOF). X-Ray crystallographic analysis was performed at University of Notre Dame on a Bruker APEX-II diffractometer. For reactions that require heating, all the report reaction temperature are oil bath temperature.

B. Source of the Acceptors and Sulfone Donors

For Acceptors:



1a



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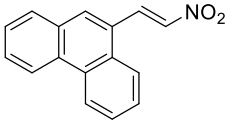

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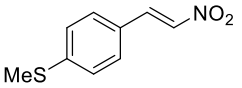

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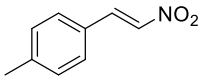

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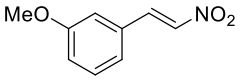

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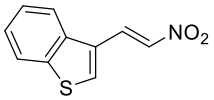
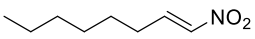
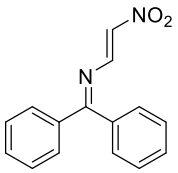


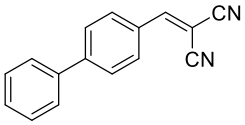
1g



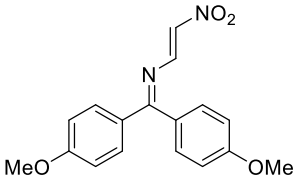
1h



1i



1j

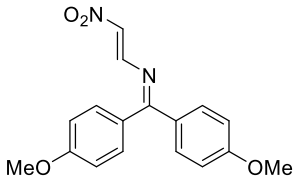


1k

Compounds **1a**,[1] **1b**,[2] **1c**,[2] **1d**,[3] **1e**,[2] **1f**, **1g**,[2] **1h**,[2] **1i**,[4] **1j**[5] were synthesized according reported literatures.

A new compound **1k** was synthesized according to the procedure for the synthesis of **1i**.[4]

(*E*)-1,1-bis(4-Methoxyphenyl)-*N*-(2-nitrovinyl)methanimine (1k)



1k

To a 100 mL round bottom flask equipped with a magnetic stir bar was dissolved bis(4-methoxyphenyl)methanone (6.05 g, 25 mmol) and ethanolamine (7.625 g, 125 mmol) in benzene (25 mL) followed by acetic acid (25 μL). The solution was equipped with a Dean-Stark trap and heated at reflux (120 °C) for 18 h. The solution was cooled to r.t. and was extracted with EtOAc (25 mL x 2) and H_2O. The organic phase was washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The clear colorless crude oil was sufficiently pure and carried on without further purification.

The bis(4-methoxyphenyl)methanone imine and Et_3N (3.03 g, 30 mmol) was dissolved in DCM (50

mL) in a 250 mL round bottom flask equipped with a magnetic stir bar. The solution was cooled to 0 °C and MsCl (3.01 g, 26.25 mmol) was added slowly. The mixture was gradually warmed up to r.t. and stirred for 30 mins. The mixture was diluted with DCM (20 mL) and quenched with H_2O (10 mL). The organic phase was extracted with H_2O (20 mL), washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo to afford the crude mesylate product, which was carried on without further purification.

To a 150 mL round bottom flask equipped with a magnetic stir bar was suspended *t*-BuOK (4.2 g, 37.5 mmol) in THF (50 mL). The solution was cooled to 0 °C with vigorous stirring. The obtained mesylate dissolved in THF (15 mL) was introduced slowly. The mixture was warmed to room temperature and stirred for 1 h. The viscous mixture was diluted with EtOAc (20 mL) and quenched with H_2O (10 mL). The organic phase was extracted, washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo to afford the crude enamine product as a yellow oil, which was carried on without further purification.

The obtained crude enamine, silver nitrite (9.23 g, 60 mmol), TEMPO (0.94 g, 6 mmol) and 4Å MS (6.1 g) was taken up in DCE (50 mL) in a sealed tube and heated to 70 °C for 18 h. The reaction mixture was then cooled to room temperature and then filtered through celite. Removal of the solvent, then purification via flash silica gel chromatography (5% diethyl ether in petroleum ether) afforded a yellow solid 2.81 g, 36% yield.

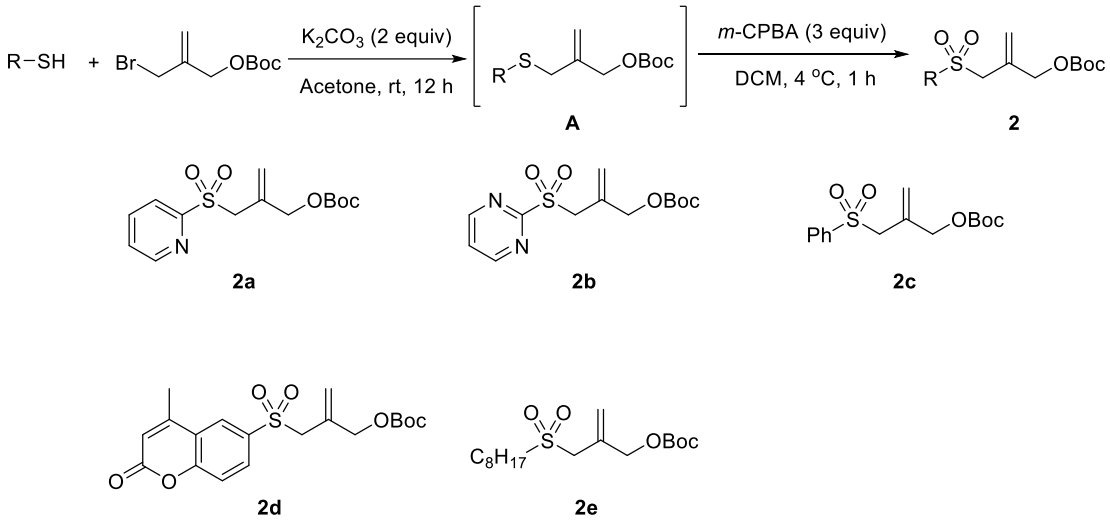
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 11.2 Hz, 1H). 7.05 (d, *J* = 8.4 Hz, 1H), 6.73-6.75 (m, 4H), 6.23-6.25 (m, 4H), 3.16 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 177.1, 161.8, 148.7, 134.7, 131.5, 113.3, 112.7, 54.8.

IR (film): 3072, 2935, 2839, 2566, 2299, 2045, 1935, 1644, 1256, 1170 cm^{-1}.

HRMS (ESI-TOF, m/z): $[M+H]^+$ Calcd. for $C_{17}H_{17}N_2O_4$, 313.1188; found, 313.1176.

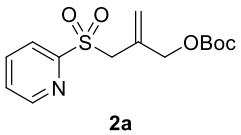
General Procedures for the Synthesis of Sulfone Donors:



To a 10 mL vial was added thiol (2 mmol, 1 equiv), K_2CO_3 (552 mg, 4 mmol), 2-(bromomethyl)allyl *tert*-butyl carbonate (504 mg, 2 mmol) and acetone (5 mL). The resulting mixture was sealed with a cap and stirred at room temperature for 12 h. Then the reaction mixture was filtered through a pad of silica gel and washed with EtOAc (20 mL). The filtrate was concentrated in vacuo to give **A**, which was used without purification.

The obtained crude of **A** was dissolved in CH_2Cl_2 (20 mL) and cooled to 4 °C. To the mixture was added 3-chlorobenzoperoxoic acid (*m*-CPBA) (1.341 g, 77% purity, 6 mmol) in two portions in 5 minutes. The resulting mixture was stirred at 4 °C for 1 h and quenched with saturated aqueous Na_2SO_3 solution (15 mL). After the layers were separated, the aqueous layer was extracted with CH_2Cl_2 (20 mL × 2), and the combined organic layers were washed with 1 M K_2CO_3 solution (20 mL × 2), H_2O (20 mL), dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure to give the crude product, which was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford sulfone donors **2**.

***tert*-Butyl (2-((pyridin-2-ylsulfonyl)methyl)allyl) carbonate (2a)**



2a

From pyridine-2-thiol (2.22 g, 20 mmol, 1 equiv) under the general procedure. The crude mixture was subjected to flash silica column chromatography (petroleum ether/EtOAc = 3:1) to yield the

title compound **2a** (4.382 g, 70% yield) as white solid.

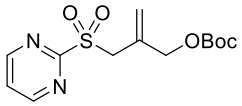
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75-8.76 (m, 1H), 8.04-8.06 (m, 1H), 7.93-7.96 (m, 1H), 7.52-7.56 (m, 1H), 5.37 (s, 1H), 5.09 (s, 1H), 4.62 (s, 2H), 4.19 (s, 2H), 1.46 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.4, 152.9, 150.2, 138.0, 131.5, 127.5, 123.6, 122.9, 82.5, 68.1, 55.2, 27.7.

IR (film): 2981, 1743, 1579, 1455, 1428, 1395, 1280 cm^{-1} .

HRMS (ESI-TOF, m/z): $[M+Na]^+$ Calcd. for $C_{14}H_{19}NO_5SNa$, 336.0882; found, 336.0868.

***tert*-Butyl (2-((pyrimidin-2-ylsulfonyl)methyl)allyl) carbonate (2b)**



2b

From pyrimidine-2-thiol (448 mg, 4 mmol, 1 equiv) under the general procedure. The crude mixture was subjected to flash silica column chromatography (petroleum ether/EtOAc = 1:1) to yield the title compound **2b** (552.6 mg, 44% yield) as clear oil.

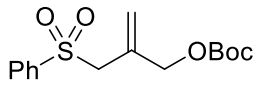
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.95 (d, *J* = 4.8 Hz, 2H), 7.56 (t, *J* = 4.8 Hz, 1H), 5.47 (s, 1H), 5.31 (s, 1H), 4.68 (s, 2H), 4.33 (s, 2H), 1.46 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6, 152.9, 131.0, 124.4, 123.8, 82.6, 68.3, 54.6, 27.7.

IR (film): 2982, 2936, 1742, 1565, 1458, 1436, 1387, 1280 cm^{-1}.

HRMS (ESI-TOF, m/z): $[M+Na]^+$ Calcd. for $C_{13}H_{18}N_2O_5SNa$, 337.0834; found, 337.0825.

***tert*-Butyl (2-((phenylsulfonyl)methyl)allyl) carbonate (2c)**



2c

From benzenethiol (220 mg, 2 mmol, 1 equiv) under the general procedure. The crude mixture was subjected to flash silica column chromatography (petroleum ether/EtOAc = 4:1) to yield the title compound **2c** (443.1 mg, 71% yield) as white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 7.2 Hz, 2H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 2H), 5.38 (s, 1H), 5.00 (s, 1H), 4.58 (s, 2H), 3.85 (s, 2H), 1.46 (s, 9H).

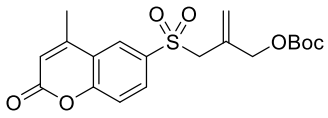
^{13}C NMR (100 MHz, $CDCl_3$): δ 152.9, 138.0, 133.9, 132.0, 129.1, 128.5, 123.3, 82.6, 68.0, 59.8,

27.7.

IR (film): 3065, 2982, 2933, 1741, 1653, 1448, 1369, 1279, 1155 cm^{-1}.

HRMS (ESI-TOF, m/z): $[M+Na]^+$ Calcd. for $C_{15}H_{20}O_5SNa$, 335.0929; found, 335.0921.

***tert*-Butyl (2-(((4-methyl-2-oxo-2*H*-chromen-6-yl)sulfonyl)methyl)allyl) carbonate (2d)**



2d

From 6-mercapto-4-methyl-2*H*-chromen-2-one (384.4 mg, 2 mmol, 1 equiv) under the general procedure. The crude mixture was subjected to flash silica column chromatography (petroleum ether/EtOAc = 3:1) to yield the title compound **2d** (591.3 mg, 75% yield) as white solid.

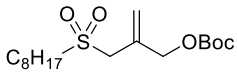
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (s, 1H), 7.74 (s, 2H), 6.41 (s, 1H), 5.38 (s, 1H), 5.01 (s, 1H), 4.59 (s, 2H), 3.89 (s, 2H), 2.46 (s, 3H), 1.43 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.1, 153.0, 152.8, 150.9, 140.5, 131.6, 125.7, 124.1, 123.7, 123.6, 118.0, 117.5, 82.7, 67.7, 59.7, 27.7, 18.7.

IR (film): 3084, 2985, 2934, 1743, 1457, 1397, 1272, 1156 cm^{-1}.

HRMS (ESI-TOF, m/z): $[M+H]^+$ Calcd. for $C_{19}H_{23}O_7S$, 395.1165; found, 395.1163.

***tert*-Butyl (2-((octylsulfonyl)methyl)allyl) carbonate (2e)**



2e

From octane-1-thiol (438.9 mg, 3 mmol, 1 equiv) under the general procedure. The crude mixture was subjected to flash silica column chromatography (petroleum ether/EtOAc = 5:1) to yield the title compound **2e** (623.4 mg, 60% yield) as white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.51 (s, 1H), 5.38 (s, 1H), 4.77 (s, 2H), 3.73 (s, 2H), 2.97 (t, *J* = 7.6 Hz, 3H), 1.76-1.83 (m, 2H), 1.44 (s, 9H), 1.37-1.41 (m, 2H), 1.20-1.27 (m, 8H), 0.83 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 152.3, 131.8, 122.1, 81.9, 67.4, 55.8, 51.1, 31.0, 28.4, 28.3, 27.9, 27.1, 21.9, 21.2, 13.4.

IR (film): 2927, 2857, 1652, 1463, 1395, 1369, 1286, 1255, 1159 cm^{-1}.

HRMS (ESI-TOF, m/z): $[M+H]^+$ Calcd. for $C_{17}H_{33}O_5S$, 349.2049; found, 349.2047.

C. References

[1] Shi, W.; Mao, B.; Xu, J.; Wang, Q.; Wang, W.; Wu, Y.; Li, X.; Guo, H. *Org. Lett.* **2020**, *22*, 2675.

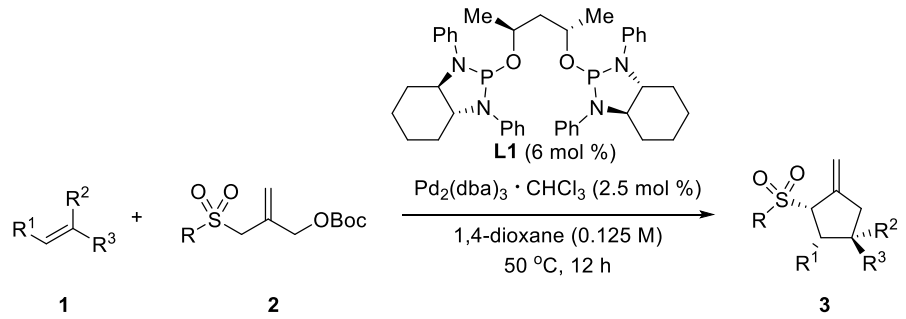
[2] Trost, B. M.; Shinde, A. H.; Wang, Y.; Zuo, Z.; Min, C. *ACS Catal.* **2020**, *10*, 1969.

[3] Zheng, C.; Huang, S.; Liu, Y.; Jiang, C.; Zhang, W.; Fang, G.; Hong, J. *Org. Lett.* **2020**, *22*, 4868.

[4] Trost, B. M.; Zhang, L.; Lam, T. M. *Org. Lett.* **2018**, *20*, 3938.

[5] Khatun, N.; Kim, M. J.; Woo, S. K. *Org. Lett.* **2018**, *20*, 6239.

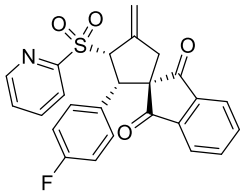
D. General Procedure for the [3+2] Cycloaddition of Sulfone-TMM Donors and Acceptors



A 5 mL thick-wall microwave vial was flame-dried (propane torch for 5 seconds under vacuum) with a magnetic stir bar inside. $Pd_2(dba)_3{\cdot}CHCl_3$ (2.6 mg, 2.5 mol %), (*R*, *R*, *S*, *S*, *R*, *R*)-diamidophosphite ligand **L1** (4.2 mg, 6 mol %), **1** (0.1 mmol, 1 equiv), and **2** (0.15 mmol, 1.5 equiv) were added and the system was placed under an atmosphere of argon (balloon). Anhydrous 1,4-dioxane (0.8 mL) was added at room temperature. The resulting mixture was stirred at room temperature for 10 minutes and heated in a 50 °C oil bath for 12 h. Filtration through a plug of Celite gave the crude reaction mixture, which was concentrated in vacuo and purified by silica gel column chromatography (petroleum ether/ethyl acetate) to give the [3+2] cycloaddition adduct **3**.

E. Analysis Data for the Obtained Products

(2*S*, 3*S*)-2-(4-Fluorophenyl)-4-methylene-3-(pyridin-2-ylsulfonyl)spiro[cyclopentane-1,2'-indene]-1',3'-dione (3a)



3a

At 0.1 mmol scale, 33.9 mg, 76% yield, dr > 15:1, 99% ee, white foam. Eluting with petroleum ether/EtOAc = 3:1 for column chromatography.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (d, *J* = 4.4 Hz, 1H), 8.00 (d, *J* = 7.2 Hz, 1H), 7.70–7.85 (m, 4H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.42–7.46 (m, 1H), 6.89–6.93 (m, 2H), 6.80 (t, *J* = 8.8 Hz, 2H), 5.89 (d, *J* = 7.6 Hz, 1H), 5.60 (d, *J* = 2.4 Hz, 1H), 5.45 (d, *J* = 2.4 Hz, 1H), 3.71 (d, *J* = 7.6 Hz, 1H), 3.33-3.38 (m, 1H), 2.83 (d, *J* = 17.6 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 201.1, 197.0, 162.4 (d, $^{1}J_{C\text{-}F}$ = 246.2 Hz), 157.9, 150.1, 142.0, 140.1 (d, $^{3}J_{C\text{-}F}$ = 5.5 Hz), 137.8, 136.1 (d, $^{2}J_{C\text{-}F}$ = 25.7 Hz), 131.5 (d, $^{3}J_{C\text{-}F}$ = 8.1 Hz), 129.1 (d, $^{4}J_{C\text{-}F}$ = 3.4 Hz), 127.2, 124.0, 123.4, 122.0, 114.6 (d, $^{2}J_{C\text{-}F}$ = 21.3 Hz), 113.5, 66.1, 61.4, 55.0, 35.8.

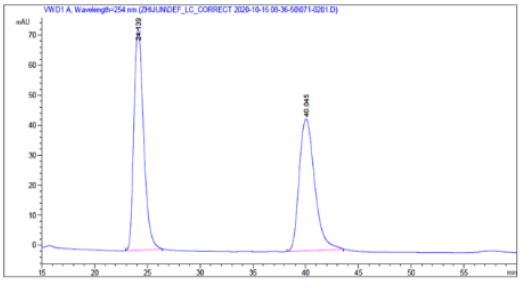
^{19}F NMR (376 MHz, $CDCl_3$): δ -113.2 – -113.3 (m, 1F).

IR (film): 2923, 1742, 1705, 1510, 1234 cm^{-1}.

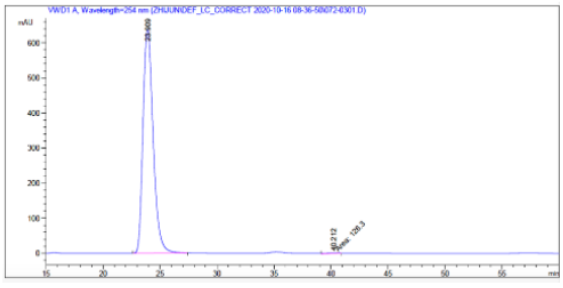
HRMS (ESI-TOF, m/z): $[M+H]^+$ Calcd. for $C_{25}H_{19}NO_4SF$, 448.1019; found, 448.1010.

Chiral HPLC: 99% ee, (Daicel CHIRALPAK IA, heptane/isopropanol = 80:20, 0.8 mL/min, λ = 254 nm, T_{major} = 23.909 min, T_{minor} = 40.212 min)

[α]$_D^{25}$: -29.92 (*c* = 1.0, $CHCl_3$).

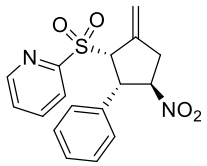


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	24.139	BB	0.9941	4715.53467	73.68591	51.2339
2	40.045	BB	1.5735	4488.39111	43.87439	48.7661



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	23.909	BB	0.9674	3.94045e4	637.28986	99.6805
2	40.212	MM	1.1653	126.30019	1.29059	0.3195

2-(((1*S*, 2*S*, 3*R*)-5-Methylene-3-nitro-2-phenylcyclopentyl)sulfonyl)pyridine (3b)



3b

At 0.1 mmol scale, 25.4 mg, 74% yield, dr > 15:1, 93% ee, clear oil. Eluting with petroleum ether/EtOAc = 3:1 for column chromatography.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (d, *J* = 4.4 Hz, 1H), 7.38–7.43 (m, 1H), 7.19–7.22 (m, 1H), 7.13 (d, *J* = 8.0 Hz, 1H), 7.00–7.02 (m, 2H), 6.87–6.92 (m, 3H), 6.07–6.14 (m, 1H), 5.72 (d, *J* = 1.2 Hz, 1H), 5.62 (d, *J* = 1.6 Hz, 1H), 5.29 (t, *J* = 7.6 Hz, 1H), 4.34–4.38 (m, 1H), 3.48–3.55 (m, 1H), 3.05–3.12 (m, 1H).

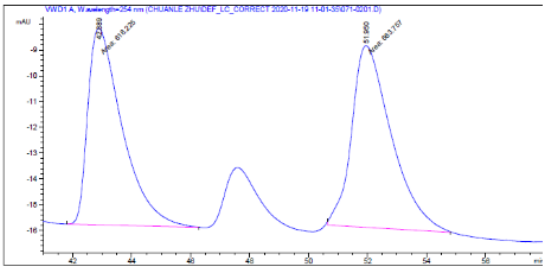
^{13}C NMR (100 MHz, $CDCl_3$): δ 156.8, 149.5, 137.6, 134.1, 131.4, 128.6, 128.1, 127.7, 126.3, 122.1, 121.1, 84.1, 67.5, 51.9, 36.9.

IR (film): 3060, 2920, 1551, 1452, 1428, 1315, 1160 cm^{-1}

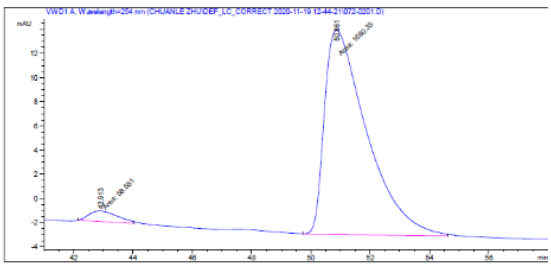
HRMS (ESI-TOF, m/z): $[M+H]^+$ Calcd. for $C_{17}H_{17}N_2O_4S$, 345.0909; found, 345.0897.

Chiral HPLC: 93% ee, (Daicel CHIRALPAK IB, heptane/isopropanol = 90:10, 0.8 mL/min, λ = 254 nm, T_{major} = 50.861 min, T_{minor} = 42.913 min)

[α]$_D^{23}$: = +9.92 (*c* = 0.5, CH_2Cl_2).

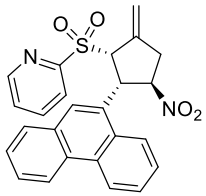


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	42.889	MM	1.3482	618.22534	7.64249	48.2242
2	51.950	MM	1.5666	663.75708	7.06141	51.7758



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	42.913	PM	1.1154	58.55099	8.74850e-1	3.3671
2	50.861	MM	1.6535	1680.35425	16.93774	96.6329

2-(((1*S*, 2*S*, 3*R*)-5-Methylene-3-nitro-2-(phenanthren-9-yl)cyclopentyl)sulfonyl)pyridine (3c)



3c

At 0.05 mmol scale, 21.1 mg, 95% yield, dr > 15:1, 99% ee, yellow solid. Eluting with petroleum ether/EtOAc = 3:1 for column chromatography.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31–8.36 (m, 2H), 7.87–7.89 (m, 1H), 7.84 (s, 1H), 7.75–7.78 (m, 1H), 7.60–7.62 (m, 2H), 7.51–7.55 (m, 3H), 6.69 (d, *J* = 7.6 Hz, 1H), 6.51–6.54 (m, 1H), 6.42–6.49 (m, 1H), 6.35–6.39 (m, 1H), 5.95 (s, 1H), 5.77 (d, *J* = 1.6 Hz, 1H), 5.60 (d, *J* = 7.6 Hz, 1H), 4.94–4.98 (m, 1H), 3.62–3.69 (m, 1H), 3.20–3.28 (m, 1H).

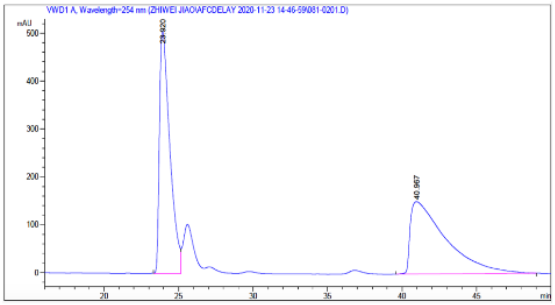
^{13}C NMR (100 MHz, $CDCl_3$): δ 155.2, 148.2, 135.6, 133.5, 130.4, 130.1, 130.0, 129.7, 129.1, 127.6, 127.1, 127.1, 126.7, 126.6, 125.7, 125.1, 123.4, 122.8, 121.8, 121.5, 121.2, 83.7, 65.9, 48.4, 36.7.

IR (film): 3064, 2921, 1557, 1451, 1372, 1314, 1164 cm^{-1} .

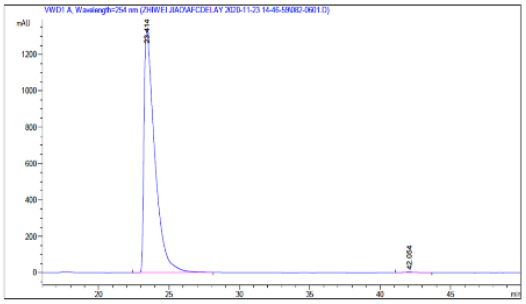
HRMS (ESI-TOF, m/z): $[M+H]^+$ Calcd. for $C_{25}H_{21}N_2O_4S$, 445.1222; found, 445.1217.

Chiral HPLC: 99% ee, ((Daicel CHIRALPAK IB, heptane/ethyl acetate = 80:20, 0.8 mL/min, λ = 254 nm, T_{major} = 23.414 min, T_{minor} = 42.054 min)

[α]$_D^{23}$: = -21.67 (*c* =1.0, CH_2Cl_2).

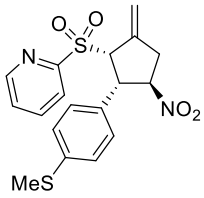


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	23.920	BV	0.7244	2.45402e4	506.07626	49.3647
2	40.967	BB	2.2329	2.51719e4	151.35538	50.6353



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	23.414	BB	0.7755	7.06977e4	1327.87976	99.7719
2	42.054	BB	0.7235	161.63367	2.67645	0.2281

2-(((1*S*, 2*S*, 3*R*)-5-Methylene-2-(4-(methylthio)phenyl)-3-nitrocyclopentyl)sulfonyl)pyridine (3d)



3d

At 0.1 mmol scale, 35.5 mg, 91% yield, dr > 15:1, 99% ee, clear oil. Eluting with petroleum ether/EtOAc = 3:1 for column chromatography.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49–8.51 (m, 1H), 7.48–7.52 (m, 1H), 7.26–7.29 (m, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 2H), 6.72 (d, *J* = 8.4 Hz, 2H), 6.02–6.09 (m, 1H), 5.74 (d, *J* = 1.2 Hz, 1H), 5.63 (d, *J* = 1.2 Hz, 1H), 5.27 (d, *J* = 7.6 Hz, 1H), 4.28–4.33 (m, 1H), 3.48–3.54 (m, 1H), 3.06–3.14 (m, 1H), 2.35 (m, 3H).

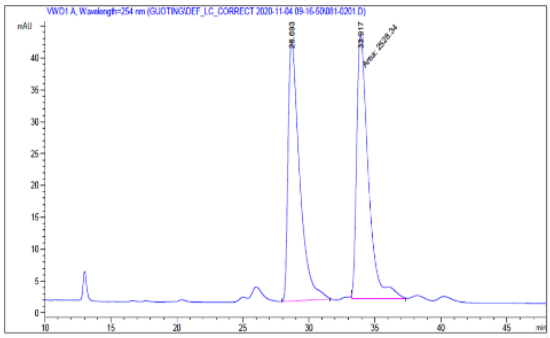
^{13}C NMR (100 MHz, $CDCl_3$): δ 156.8, 149.5, 138.5, 137.7, 134.0, 129.0, 127.9, 126.1, 125.6, 122.0, 121.1, 84.0, 67.8, 51.5, 36.9, 15.2.

IR (film): 2924, 1552, 1497, 1314, 1161 cm^{-1}.

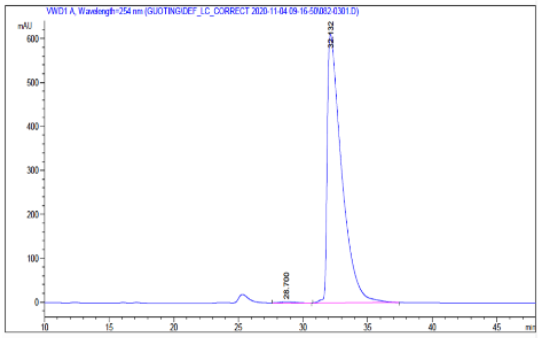
HRMS (ESI-TOF, m/z): $[M+H]^+$ Calcd. for $C_{18}H_{19}N_2O_4S_2$, 391.0786; found, 391.0776.

Chiral HPLC: 99% ee, (Daicel CHIRALPAK IB, heptane/isopropanol = 80:20, 0.8 mL/min, λ = 254 nm, T_{major} = 32.132 min, T_{minor} = 28.700 min)

$[\alpha]_D^{23}$: = +21.98 (*c* =1.0, $CHCl_3$).

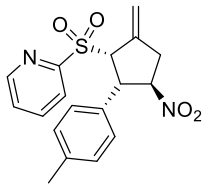


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	28.693	BB	0.8949	2477.30249	40.78974	49.4902
2	33.917	MM	1.0187	2528.33813	41.36705	50.5098



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	28.700	BB	0.9362	183.35193	2.35070	0.3873
2	32.132	BB	1.1207	4.71517e4	610.65179	99.6127

2-(((1*S*, 2*S*, 3*R*)-5-Methylene-3-nitro-2-(*p*-tolyl)cyclopentyl)sulfonyl)pyridine (3e)



3e

At 0.1 mmol scale, 27.9 mg, 78% yield, dr > 15:1, 99% ee, white solid. Eluting with petroleum ether/EtOAc = 3:1 for column chromatography.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49–8.50 (m, 1H), 7.40–7.44 (m, 1H), 7.23–7.26 (m, 1H), 7.13 (d, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 7.6 Hz, 2H), 6.68 (d, *J* = 8.0 Hz, 2H), 6.05–6.12 (m, 1H), 5.73 (d, *J* = 1.2 Hz, 1H), 5.62 (d, *J* = 1.2 Hz, 1H), 5.26 (d, *J* = 7.6 Hz, 1H), 4.31–4.36 (m, 1H), 3.48–3.55 (m, 1H), 3.05–3.13 (m, 1H), 2.12 (s, 3H).

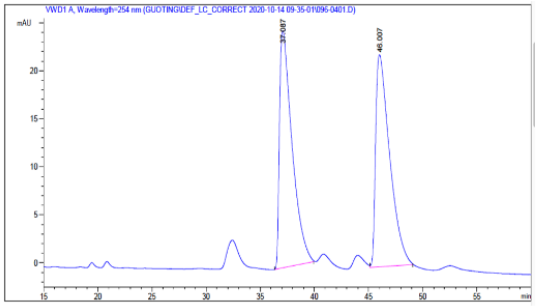
^{13}C NMR (100 MHz, $CDCl_3$): δ 156.9, 149.5, 137.4, 137.2, 134.2, 128.8, 128.4, 128.3, 125.9, 122.1, 121.0, 84.1, 67.9, 51.6, 36.9, 20.8.

IR (film): 360, 2922, 2854, 1553, 1317, 1109 cm^{-1} .

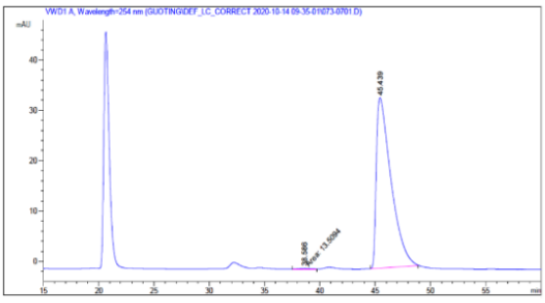
HRMS (ESI-TOF, m/z): $[M+H]^+$ Calcd. for $C_{18}H_{19}N_2O_4S$, 359.1066; found, 359.1057.

Chiral HPLC: 99% ee, (Daicel CHIRALPAK IB, heptane/isopropanol = 90:10, 0.8 mL/min, λ = 254 nm, T_{major} = 45.439 min, T_{minor} = 35.586 min)

[α]$_D^{23}$: +19.48 (*c* = 1.0, $CHCl_3$).

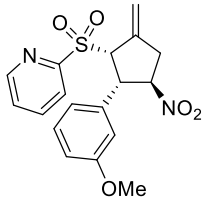


Peak #	RetTime [min]	Type	Width [min]	Area mAU	*s	Height [mAU]	Area %
1	37.087	BB	1.1509	1994.08630		24.67951	50.0230
2	46.007	VB	1.2619	1992.25159		22.08986	49.9770



Peak #	RetTime [min]	Type	Width [min]	Area mAU	*s	Height [mAU]	Area %
1	38.586	MM	1.3389	13.50945		1.68163e-1	0.4291
2	45.439	BB	1.3236	3135.10620		33.85292	99.5709

2-(((1*S*, 2*S*, 3*R*)-2-(3-Methoxyphenyl)-5-methylene-3-nitrocyclopentyl)sulfonyl)pyridine (3f)



3f

At 0.1 mmol scale, 28.8 mg, 77% yield, dr > 15:1, 99% ee, clear oil. Eluting with petroleum ether/EtOAc = 2:1 for column chromatography.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53–8.54 (m, 1H), 7.46–7.50 (m, 1H), 7.23–7.27 (m, 2H), 6.88 (t, *J* = 7.6 Hz, 1H), 6.69 (d, *J* = 7.6 Hz, 1H), 6.47–6.49 (m, 2H), 6.06–6.14 (m, 1H), 5.78 (s, 1H), 5.66 (s, 1H), 5.29 (d, *J* = 7.6 Hz, 1H), 4.33–4.38 (m, 1H), 3.63 (s, 3H), 3.51–3.57 (m, 1H), 3.07–3.14 (m, 1H).

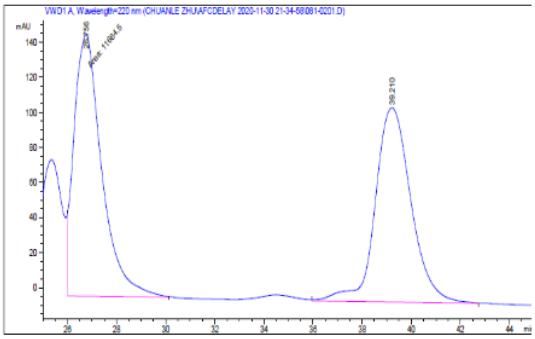
^{13}C NMR (100 MHz, $CDCl_3$): δ 156.4, 154.4, 146.8, 134.8, 131.4, 130.4, 126.6, 123.6, 119.5, 118.6, 118.0, 111.7, 111.0, 81.5, 65.0, 52.3, 49.2, 34.3.

IR (film): 2932, 2844, 1551, 1430, 1315, 1160 cm^{-1} .

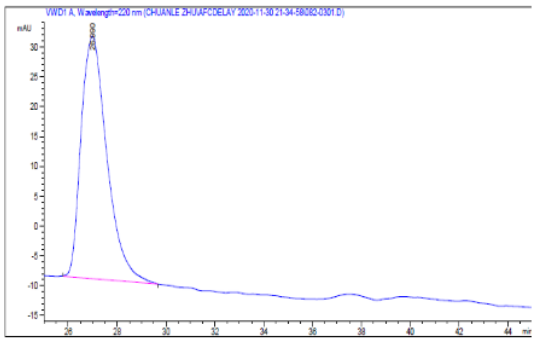
HRMS (ESI-TOF, m/z): $[M+H]^+$ Calcd. for $C_{18}H_{19}N_2O_5S$, 375.1015; found, 375.1014.

Chiral HPLC: 99% ee, (Daicel CHIRALPAK IA, heptane/isopropanol = 85:15, 0.8 mL/min, λ = 220 nm, T_{major} = 26.990 min)

$[\alpha]_D^{23}$: -9.06 (*c* = 0.5, CH_2Cl_2).

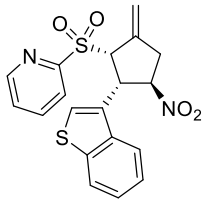


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	26.756	MM	1.3044	1.16645e4	149.03995	51.0748
2	39.210	VB	1.5324	1.11736e4	110.60650	48.9252



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	26.990	BB	1.1328	2984.40356	40.59871	100.0000

2-(((1*S*, 2*S*, 3*R*)-2-(Benzo[*b*]thiophen-3-yl)-5-methylene-3-nitrocyclopentyl)sulfonyl)pyridine (3g)



3g,

At 0.05 mmol scale, 14.0 mg, 70% yield, dr > 15:1, 99% ee, clear oil. Eluting with petroleum ether/EtOAc = 3:1 for column chromatography.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 3.6 Hz, 1H), 7.37–7.44 (m, 3H), 7.24–7.34 (m, 1H), 7.15–7.23 (m, 3H), 6.65–6.68 (m, 1H), 6.12–6.19 (m, 1H), 5.91 (s, 1H), 5.57 (s, 1H), 5.50 (d, *J* = 8.0 Hz, 1H), 4.49–4.54 (m, 1H), 3.54–3.56 (m, 1H), 3.15–3.21 (m, 1H).

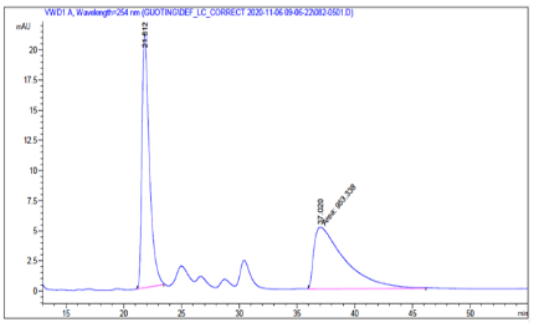
^{13}C NMR (100 MHz, $CDCl_3$): δ 155.1, 148.6, 139.5, 137.4, 136.4, 133.6, 127.2, 125.3, 124.6, 123.9, 122.2, 121.5, 120.7, 85.1, 65.7, 46.5, 36.5.

IR (film): 2930, 1553, 1428, 1314, 1162 cm^{-1}.

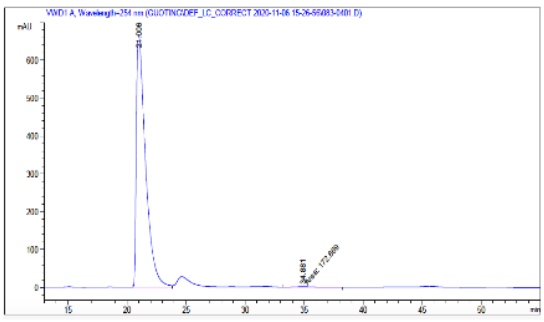
HRMS (ESI-TOF, m/z): $[M+H]^+$ Calcd. for $C_{19}H_{17}N_2O_4S_2$, 401.0630; found, 401.0622.

Chiral HPLC: 99% ee, (Daicel CHIRALPAK IB, heptane/isopropanol = 80:20, 0.8 mL/min, λ = 254 nm, T_{major} = 21.006 min, T_{minor} = 34.881 min).

$[\alpha]_D^{23}$: = -21.36 (*c* = 1.0, $CHCl_3$).

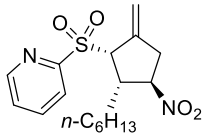


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	21.812	BB	0.6732	940.65747	20.97555	49.6652
2	37.020	MM	3.0999	953.33826	5.12562	50.3348



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	21.006	BB	0.8103	3.63120e4	666.53723	99.5262
2	34.881	MM	1.9206	172.86945	1.50012	0.4738

2-(((1*S*, 2*S*, 3*R*)-2-Hexyl-5-methylene-3-nitrocyclopentyl)sulfonyl)pyridine (3h)



3h

At 0.05 mmol scale, 9.1 mg, 51% yield, dr > 15:1, 99% ee, clear oil. Eluting with petroleum ether/EtOAc = 3:1 for column chromatography.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.79 (d, *J* = 4.4 Hz, 1H), 7.90–7.99 (m, 2H), 7.53–7.56 (m, 1H), 5.31–5.37 (m, 1H), 5.00 (s, 1H), 4.80 (d, *J* = 7.2 Hz, 1H), 4.56 (s, 1H), 3.28–3.33 (m, 1H), 3.09–3.12 (m, 1H), 2.78–2.83 (m, 1H), 2.02–2.12 (m, 1H), 1.67–1.73 (m, 1H), 1.35–1.50 (m, 1H), 1.20–1.29 (m, 7H), 0.84 (t, *J* = 7.0 Hz, 3H).

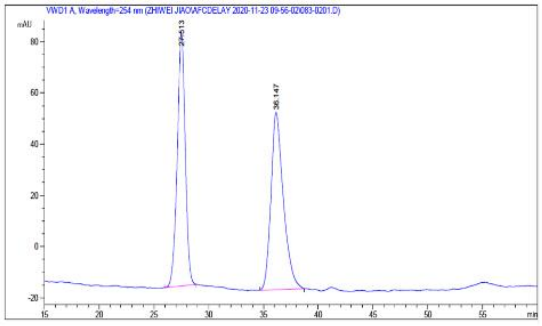
^{13}C NMR (400 MHz, $CDCl_3$): δ 156.6, 150.2, 138.9, 137.8, 127.5, 123.2, 117.9, 88.6, 67.8, 49.7, 36.7, 31.4, 29.1, 28.4, 27.9, 22.5, 14.0.

IR (film): 3038, 2929, 1551, 1315, 1160 cm^{-1}.

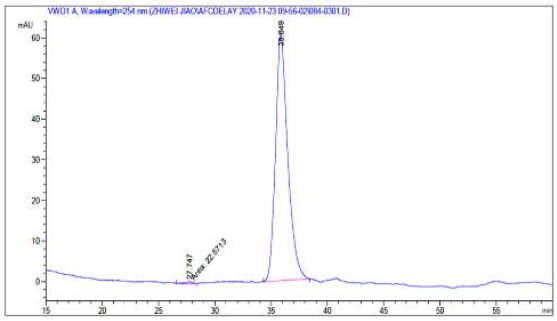
HRMS (ESI-TOF, m/z): $[M+H]^+$ Calcd. for $C_{17}H_{25}N_2O_4S$, 353.1535; found, 353.1524.

Chiral HPLC: 99% ee, (Daicel CHIRALPAK IC, heptane/isopropanol = 90:10, 0.8 mL/min, λ = 254 nm, T_{minor} = 27.747 min, T_{major} = 35.849 min).

$[\alpha]_D^{23}$: +0.33 (*c* = 0.5, $CHCl_3$).

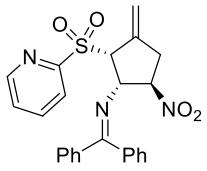


Peak #	RetTime [min]	Type	Width [min]	Area mAU	*s	Height [mAU]	Area %
1	27.513	BB	0.7671	5006.25586		98.83785	47.9028
2	36.147	BB	1.1311	5444.61279		69.26588	52.0972



Peak #	RetTime [min]	Type	Width [min]	Area mAU	*s	Height [mAU]	Area %
1	27.747	MM	0.8198	22.57133		4.58872e-1	0.4907
2	35.849	BB	1.1001	4577.53857		60.97091	99.5093

***N*-((1*S*, 2*R*, 5*R*)-3-Methylene-5-nitro-2-(pyridin-2-ylsulfonyl)cyclopentyl)-1,1-diphenylmethanimine (3i)**



3i

At 0.1 mmol scale, 26.8 mg, 60% yield, dr > 15:1, 99% ee, clear oil. Eluting with petroleum ether/EtOAc = 3:1 for column chromatography.

^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.40–8.41 (m, 1H), 7.94 (d, *J* = 7.6 Hz, 1H), 7.47–7.49 (m, 3H), 7.29–7.37 (m, 2H), 7.10–7.21 (m, 6H), 6.82–6.85 (m, 1H), 5.81 (q, *J* = 9.2 Hz, 1H), 5.67 (d, *J* = 1.2 Hz, 1H), 5.53 (d, *J* = 1.2 Hz, 1H), 5.02 (d, *J* = 7.6 Hz, 1H), 4.49–4.54 (m, 1H), 3.42–3.49 (m, 1H), 2.89–2.97 (m, 1H).

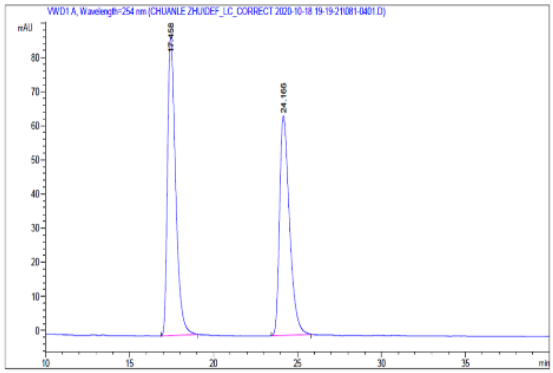
^{13}C NMR (100 MHz, CD_2Cl_2): δ 172.4, 158.9, 148.9, 137.9, 137.5, 135.1, 134.1, 130.9, 129.1, 128.7, 127.5, 127.2, 125.8, 121.3, 120.1, 87.8, 68.5, 67.4, 35.3.

IR (film): 3361, 2927, 1551, 1316, 1112 cm^{-1}.

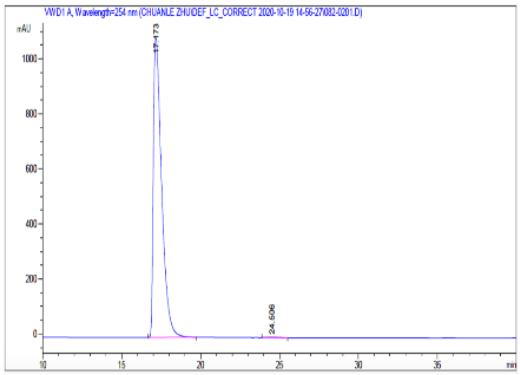
HRMS (ESI-TOF, m/z): $[M+H]^+$ Calcd. for $C_{24}H_{22}N_3O_4S$, 448.1331; found, 448.1328.

Chiral HPLC: 99% ee, (Daicel CHIRALPAK IA, heptane/isopropanol = 90:10, 0.8 mL/min, λ = 254 nm, T_{minor} = 24.506 min, T_{major} = 17.173 min).

[α]$_D^{23}$: -61.59 (c = 0.5 CH_2Cl_2).

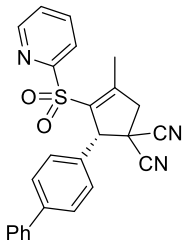


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.458	BB	0.5153	2930.67896	87.33562	52.6143
2	24.166	BB	0.6289	2639.43872	64.29652	47.3857



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.173	BB	0.5516	3.95938e4	1087.17139	99.7759
2	24.506	BB	0.5778	88.92953	2.29261	0.2241

(*S*)-2-([1,1'-Biphenyl]-4-yl)-4-methyl-3-(pyridin-2-ylsulfonyl)cyclopent-3-ene-1,1-dicarbonitrile (3j')



3j'

At 0.05 mmol scale, 15.8 mg, 74% yield, 97% ee, clear oil. Eluting with petroleum ether/EtOAc = 3:1 for column chromatography.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.65 (d, *J* = 4.8 Hz, 1H), 7.53–7.58 (m, 2H), 7.24–7.48 (m, 8H), 7.01 (d, *J* = 7.6 Hz, 2H), 4.98 (s, 1H), 3.53 (d, *J* = 17.6 Hz, 1H), 3.39 (d, *J* = 18.0 Hz, 1H), 2.52 (s, 3H).

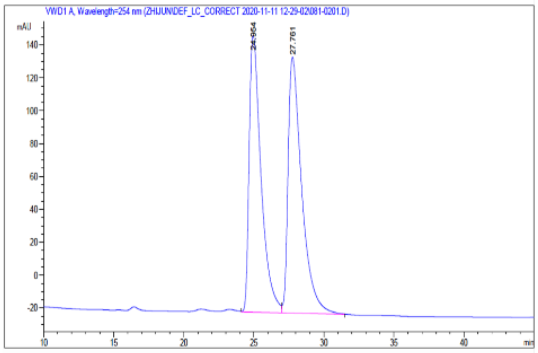
^{13}C NMR (100 MHz, $CDCl_3$): δ 158.0, 153.8, 150.2, 142.2, 139.8, 137.6, 134.8, 131.4, 128.9, 128.8, 127.8, 127.6, 127.1, 127.0, 122.2, 116.1, 112.8, 61.7, 49.6, 38.2, 15.9.

IR (film): 3031, 2924, 1638, 1325, 1166 cm^{-1}.

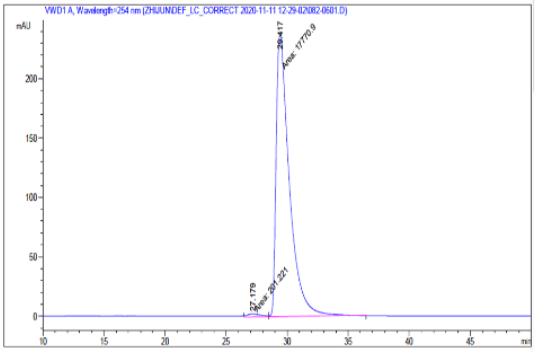
HRMS (ESI-TOF, m/z): $[M+H]^+$ Calcd. for $C_{25}H_{20}N_3O_2S$, 426.1276; found, 426.1266.

Chiral HPLC: 97% ee, (Daicel CHIRALPAK IB, heptane/isopropanol = 80:20, 0.8 mL/min, λ = 254 nm, T_{minor} = 27.179 min, T_{major} = 29.417 min).

[α]$_D^{23}$: -133.26 (*c* = 1.0, $CHCl_3$).

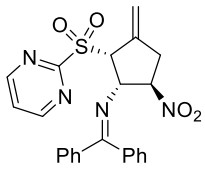


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	24.954	VV	0.8846	9916.60059	168.14011	48.5371
2	27.761	VB	1.0085	1.05144e4	155.54721	51.4629



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	27.179	MF	1.3473	201.22096	2.48911	1.1196
2	29.417	FM	1.2486	1.77709e4	237.21649	98.8804

***N*-((1*S*, 2*R*, 5*R*)-3-Methylene-5-nitro-2-(pyrimidin-2-ylsulfonyl)cyclopentyl)-1,1-diphenylmethanimine (3k)**



3k

At 0.1 mmol scale, 42.1 mg, 94% yield, dr > 15:1, 99% ee, clear oil. Eluting with petroleum ether/EtOAc = 1:1 for column chromatography.

^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.47 (d, *J* = 5.2 Hz, 2H), 7.50–7.51 (m, 3H), 7.34–7.38 (m, 1H), 7.12–7.21 (m, 6H), 6.68 (t, *J* = 6.8 Hz, 1H), 5.72–5.81 (m, 2H), 5.57 (d, *J* = 1.2 Hz, 1H), 5.11 (d, *J* = 7.6 Hz, 1H), 4.60–4.64 (m, 1H), 3.44–3.51 (m, 1H), 2.92–3.00 (m, 1H).

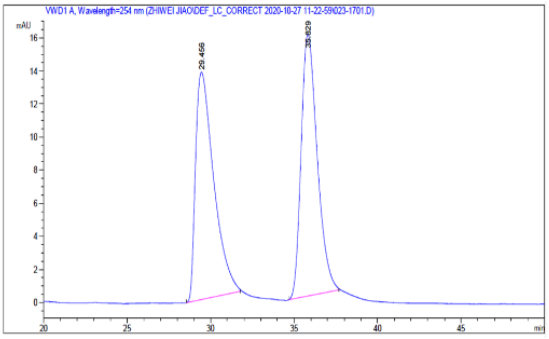
^{13}C NMR (100 MHz, CD_2Cl_2): δ 172.5, 166.6, 157.8, 137.6, 134.8, 133.7, 131.2, 129.2, 128.9, 128.7, 127.7, 127.1, 121.8, 120.3, 87.5, 68.4, 67.5, 35.2.

IR (film): 3361, 2927, 1551, 1316, 1112 cm^{-1}.

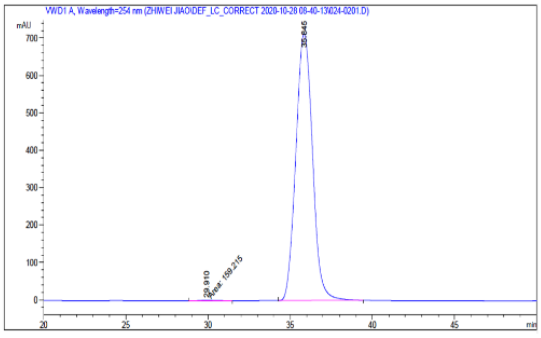
HRMS (ESI-TOF, m/z): $[M+H]^+$ Calcd. for $C_{23}H_{21}N_4O_4S$, 449.1284; found, 449.1289.

Chiral HPLC: 99% ee, (Daicel CHIRALPAK IB, heptane/isopropanol = 80:20, 0.8 mL/min, λ = 254 nm, T_{minor} = 29.910 min, T_{major} = 35.845 min).

[α]$_D^{23}$: -92.99 (*c* = 1.0, CH_2Cl_2).

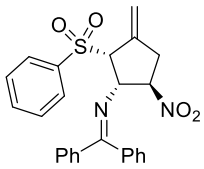


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	29.456	BB	1.1042	1040.14514	13.74439	49.5372
2	35.829	BB	1.0170	1059.58020	15.82546	50.4628



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	29.910	MM	1.4558	159.21518	1.82276	0.3161
2	35.845	BB	1.1166	5.02094e4	712.23151	99.6839

***N*-((1*S*, 2*R*, 5*R*)-3-Methylene-5-nitro-2-(phenylsulfonyl)cyclopentyl)-1,1-diphenylmethanimine (3l)**



3l

At 0.05 mmol scale, 21.0 mg, 94% yield, dr > 15:1, 98% ee, clear oil. Eluting with petroleum ether/EtOAc = 4:1 for column chromatography.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84–7.87 (m, 2H), 7.39–7.43 (m, 7H), 7.26–7.31 (m, 3H), 7.15–7.17 (m, 2H), 6.85–6.86 (m, 1H), 5.68–5.75 (m, 1H), 5.36–5.38 (m, 2H), 4.52–4.56 (m, 1H), 3.96–3.98 (m, 1H), 3.34–3.41 (m, 1H), 2.81–2.87 (m, 1H).

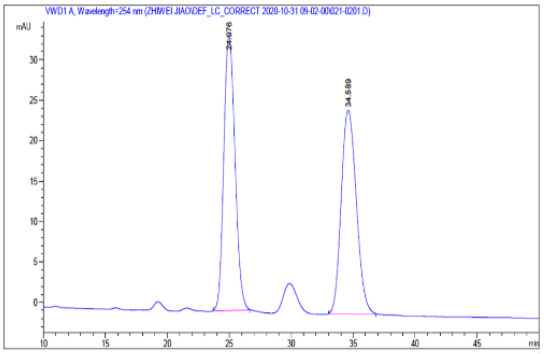
^{13}C NMR (100 MHz, $CDCl_3$): δ 139.7, 138.0, 135.8, 135.5, 133.1, 130.9, 129.3, 129.2, 129.0, 128.8, 128.4, 127.8, 126.8, 120.1, 88.3, 72.8, 67.7, 35.1.

IR (film): 3030, 2921, 1550, 1446, 1308, 1145 cm^{-1}.

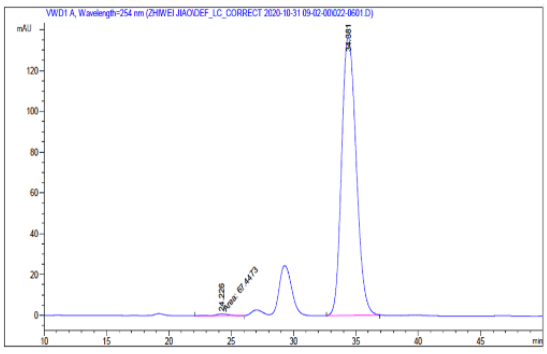
HRMS (ESI-TOF, m/z): $[M+H]^+$ Calcd. for $C_{25}H_{23}N_2O_4S$, 447.1379; found, 447.1370.

Chiral HPLC: 98% ee, (Daicel CHIRALPAK IA, heptane/isopropanol = 85:15, 0.8 mL/min, λ = 254 nm, T_{minor} = 24.226 min, T_{major} = 34.381 min).

$[\alpha]_D^{23}$: -43.69 (*c* = 1.0, $CHCl_3$)

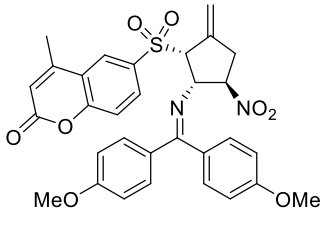


Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	24.976	BB	0.9832	2139.34570		33.99603	50.0378
2	34.589	BB	1.3090	2136.11426		25.20753	49.9622



Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	24.226	MM	1.2300	67.44730	9.13932e-1		0.6045
2	34.381	BB	1.2730	1.10900e4		136.43614	99.3955

6-(((1*R*, 2*S*, 3*R*)-2-((bis(4-Methoxyphenyl)methylene)amino)-5-methylene-3-nitrocyclopentyl)sulfonyl)-4-methyl-2*H*-chromen-2-one (3m)



3m

At 0.1 mmol scale, 42.9 mg, 73% yield, dr > 15:1, 98% ee, clear oil. Eluting with petroleum ether/EtOAc = 1:1 for column chromatography.

^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.77–7.78 (m, 1H), 7.67–7.69 (m, 1H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.15 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 6.67 (d, *J* = 8.8 Hz, 2H), 6.19 (s, 1H), 5.71 (q, *J* = 8.0 Hz, 1H), 5.61 (s, 1H), 5.51 (s, 1H), 4.52–4.56 (m, 1H), 4.26 (d, *J* = 7.6 Hz, 1H), 3.83 (s, 3H), 3.79 (s, 3H), 3.40–3.46 (m, 1H), 2.86–2.94 (m, 1H), 2.21 (s, 3H).

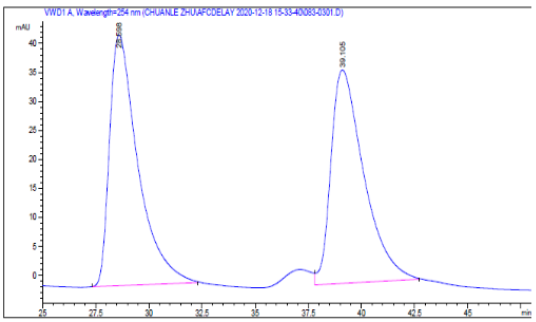
^{13}C NMR (100 MHz, CD_2Cl_2): δ 171.9, 161.8, 160.1, 159.0, 152.7, 150.8, 143.5, 135.0, 130.7, 130.7, 128.2, 125.2, 122.9, 122.8, 120.0, 117.1, 114.1, 112.8, 88.1, 72.9, 67.4, 55.3, 55.2, 35.2, 18.1.

IR (film): 3073, 2962, 1730, 1602, 1550, 1509, 1312, 1251, 1138cm^{-1};

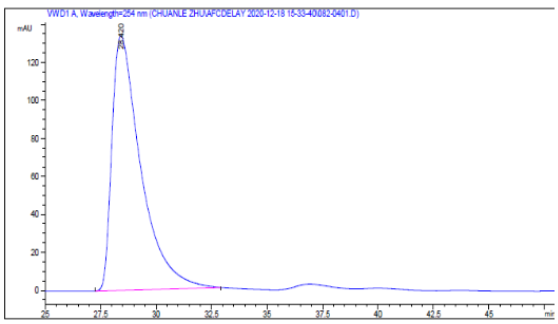
HRMS (ESI-TOF, m/z): $[M+H]^+$ Calcd. for $C_{31}H_{29}N_2O_8S$, 589.1645; found, 589.1650.

Chiral HPLC: 99% ee, (Daicel CHIRALPAK IB, heptane/isopropanol = 70:30, 0.8 mL/min, λ = 254 nm, T_{major} = 28.420 min).

[α]$_D^{23}$: -232.75 (*c* = 2.0, CH_2Cl_2)



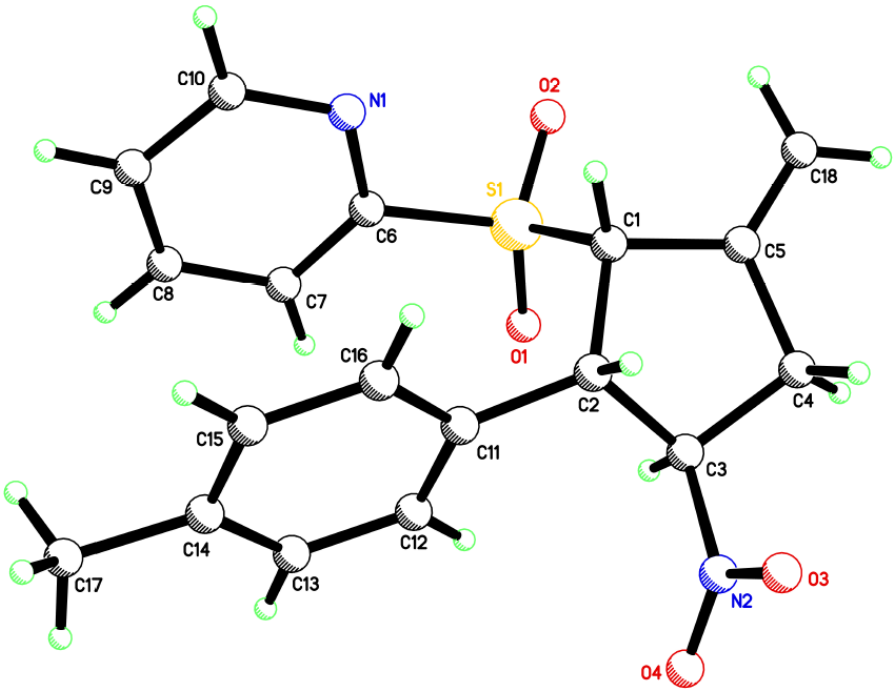
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	28.598	BB	1.3611	4027.43213	43.32834	50.3666
2	39.105	VB	1.5689	3968.80908	36.86852	49.6334



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	28.420	BB	1.3341	1.21467e4	133.83191	100.0000

F. X-Ray Crystallographic Data

The obtained compound **3e** (20 mg, 99% ee) was dissolved in CH_2Cl_2 (0.2 mL) in a 20 mL vial, then petroleum ether (15 mL) was added slowly. The resulted two-phase mixture allowed to open to air to volatilize the solvent via a needle hole on the cap. Then the colorless crystal of **3e** was formed. The X-ray crystallographic structures for **3e**. ORTEP representation with 50% probability thermal ellipsoids. Solvent are omitted for clarity. Crystal data have been deposited to CCDC, number 2056297.

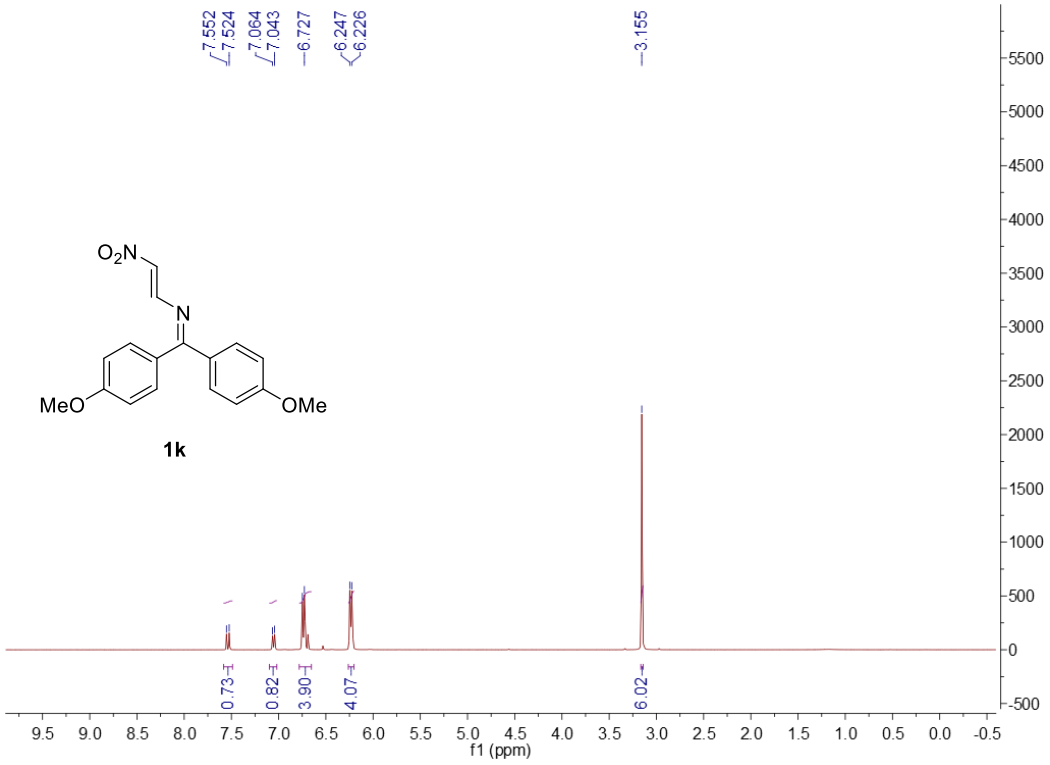


Empirical formula	$C_{18}H_{18}N_2O_4S$	
Formula weight	358.40	
Temperature	120 (2) K	
Wavelength	1.54178 Å	
Crystal system, space group	Monoclinic; $P2_1$	
Unit cell dimensions	a = 8.8478(6) Å b = 10.5745(7) Å c = 8.9386(6) Å	alpha = 90 deg. beta = 96.515(2) deg. gamma = 90 deg.
Volume	830.90(10) $Å^3$	
Z, Calculated density	2, 1.433 $g.cm^{-3}$	

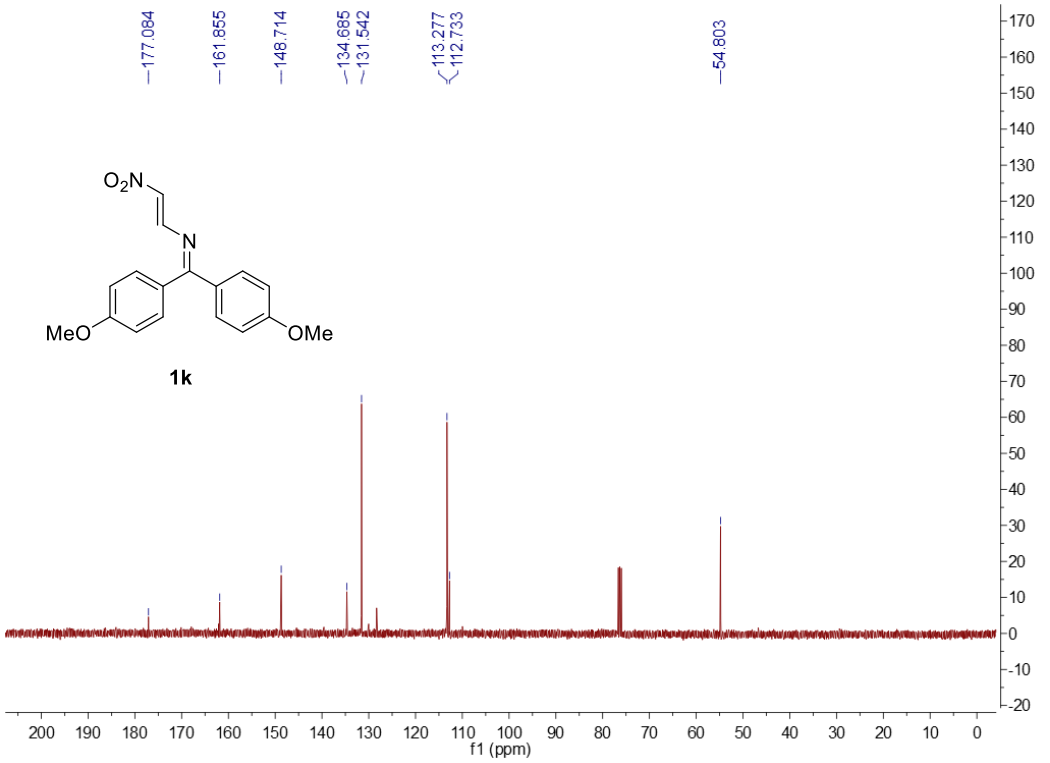
Absorption coefficient	1.965 mm^{-1}
F(000)	376
Crystal size	0.201 × 0.141 × 0.068 mm^3
Theta range for data collection	4.980 to 70.394°
Limiting indices	$-10 \leq h \leq 10$, $-12 \leq k \leq 12$, $-10 \leq l \leq 10$
Reflections collected / unique	16968 / 3139 [R_{int} = 0.0365]
Completeness to theta = 67.679°	100.0 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3139 / 1 / 227
Goodness-of-fit on F^2	1.063
Final R indices [I>2sigma(I)]	R_1 = 0.0260, wR_2 = 0.0664
R indices (all data)	R_1 = 0.0261, wR_2 = 0.0665
Absolute structure parameter	0.067(6)
Largest diff. peak and hole	0.181 and -0.305 $e^-.Å^{-3}$

G. NMR Spectra of New Compounds

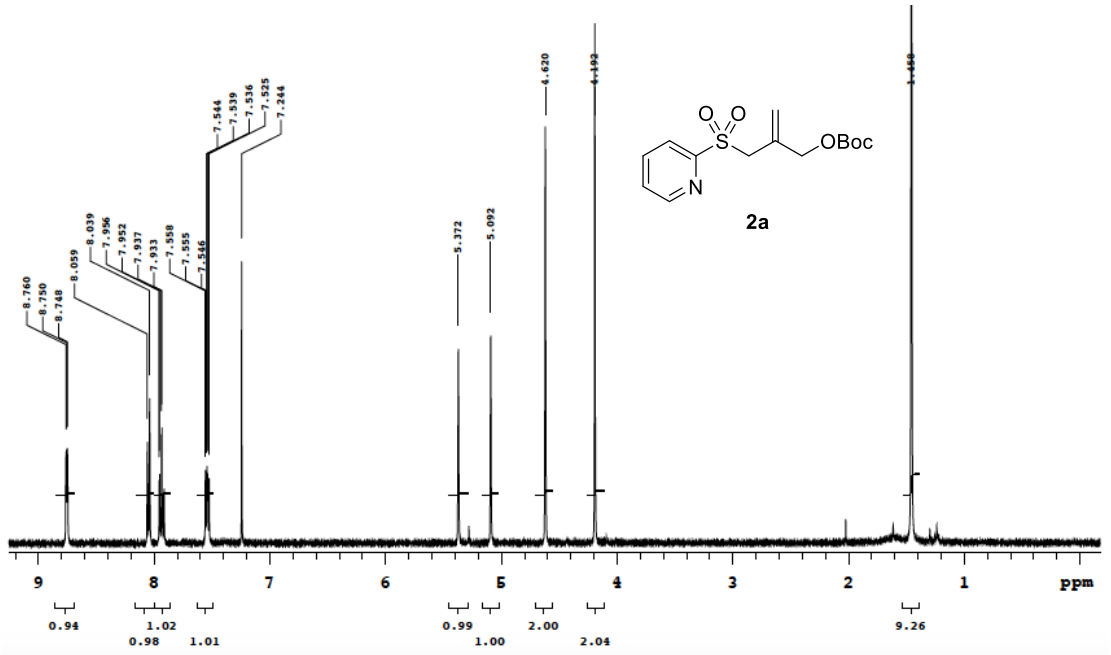
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 1k



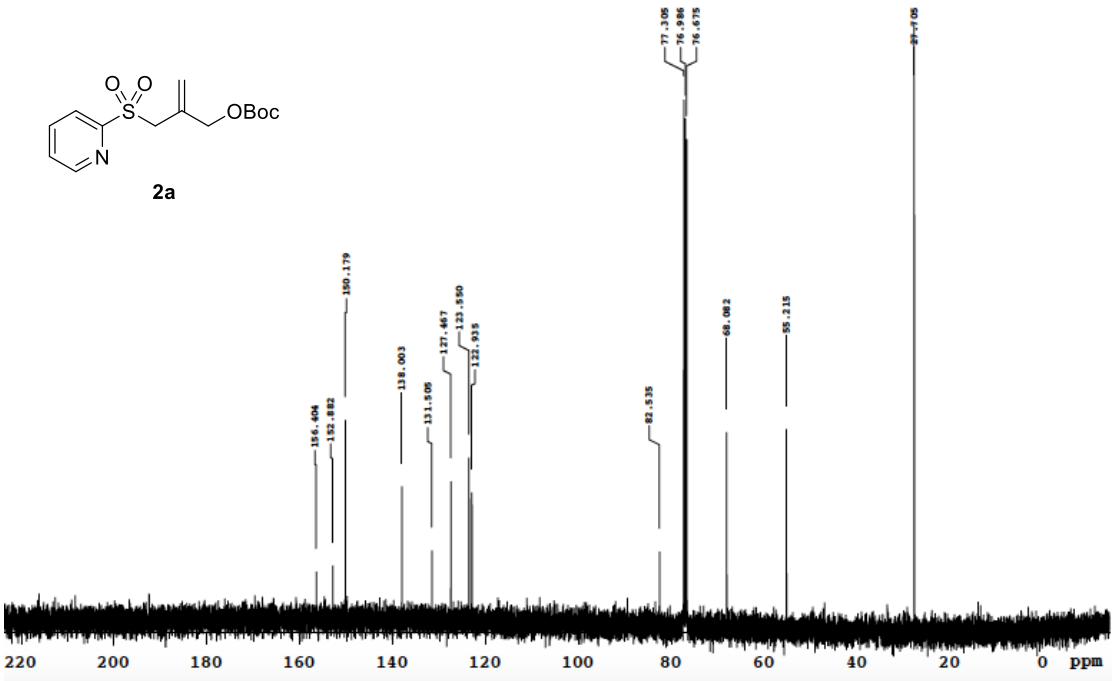
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 1k



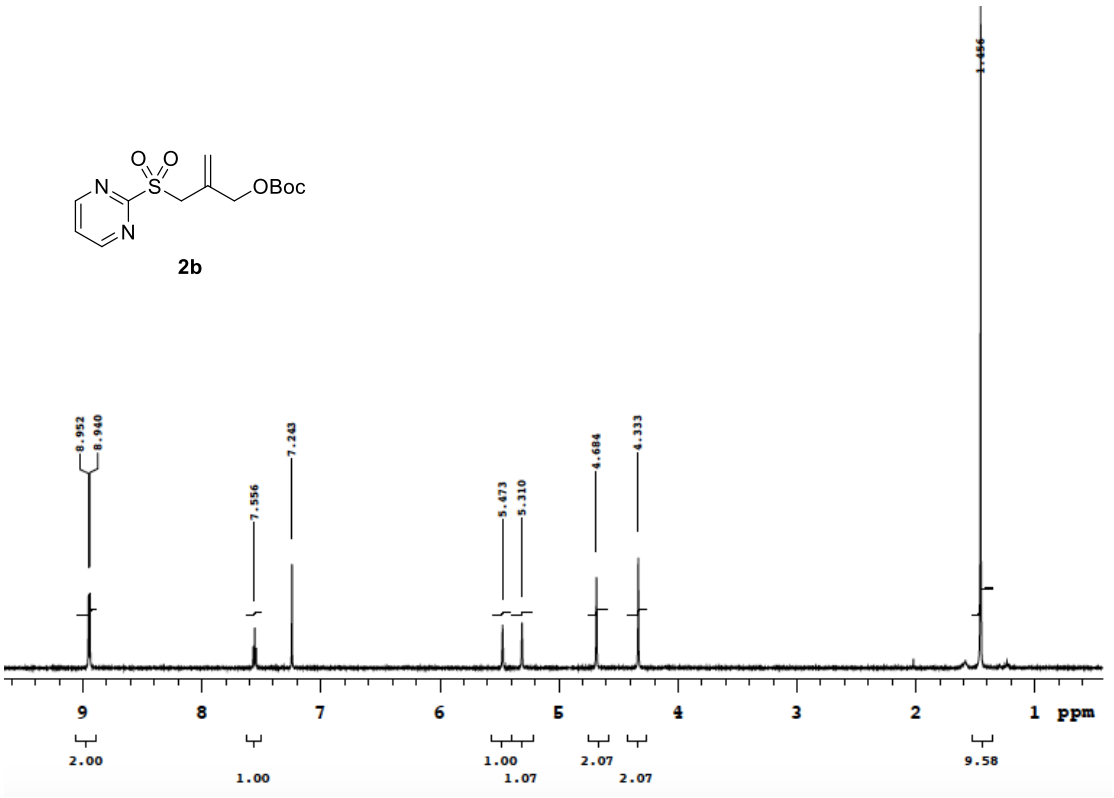
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 2a



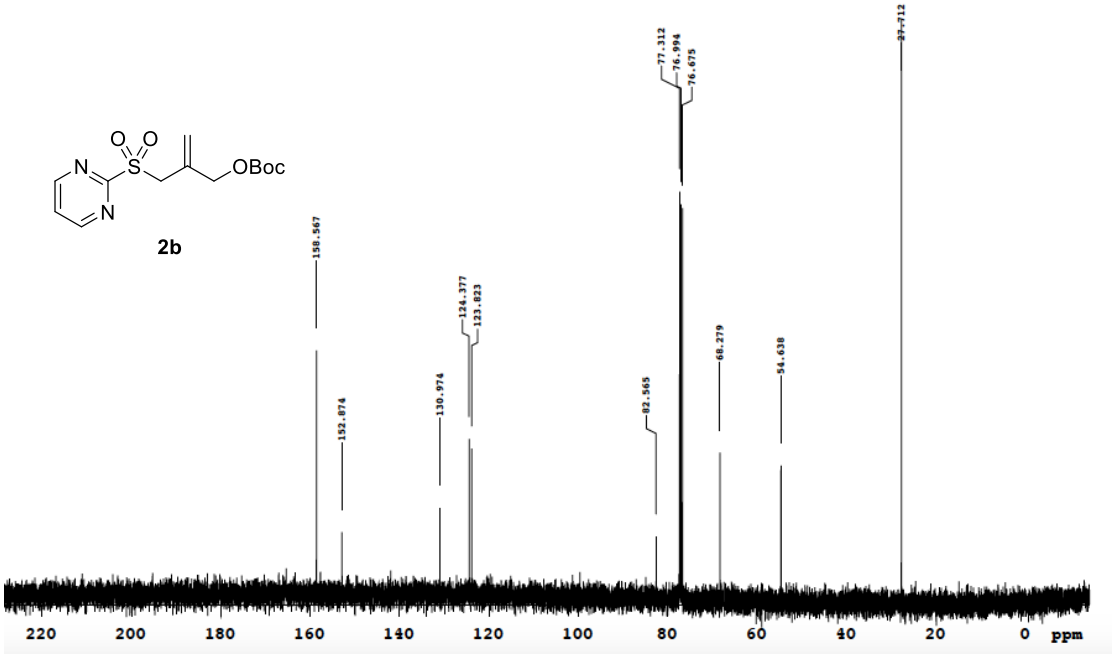
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 2a



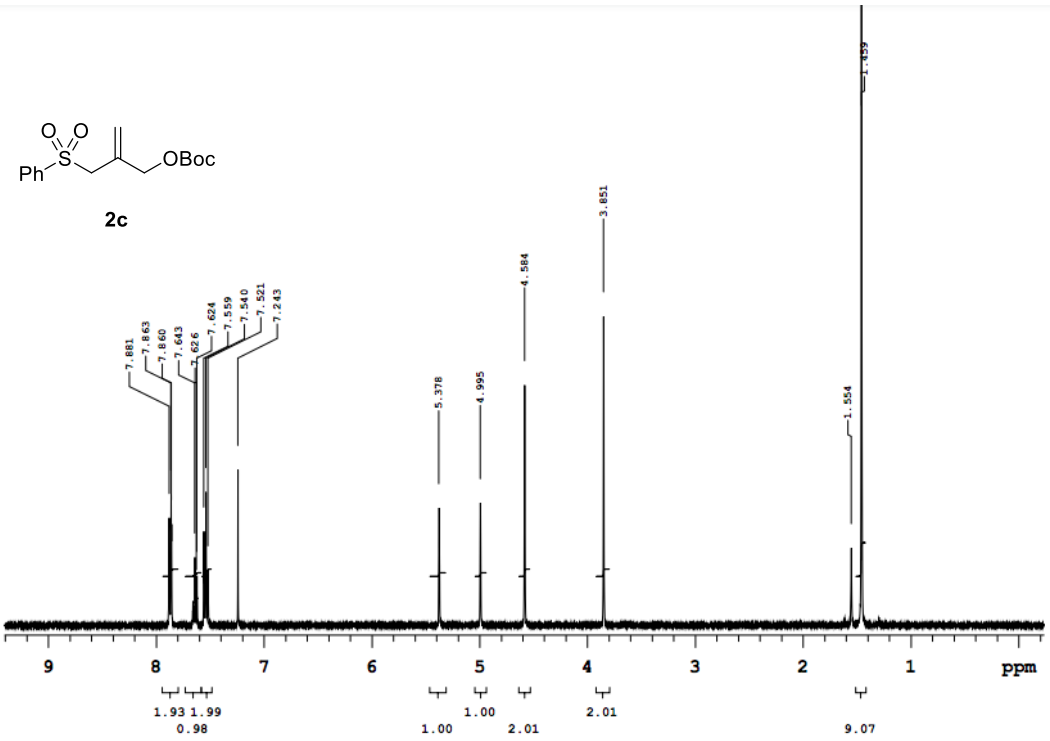
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 2b



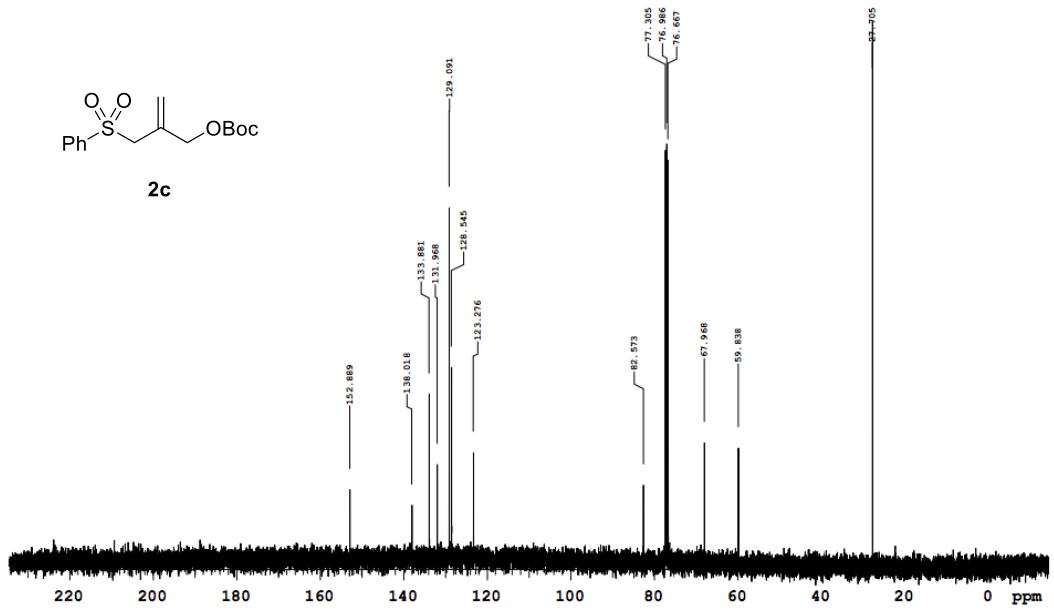
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 2b



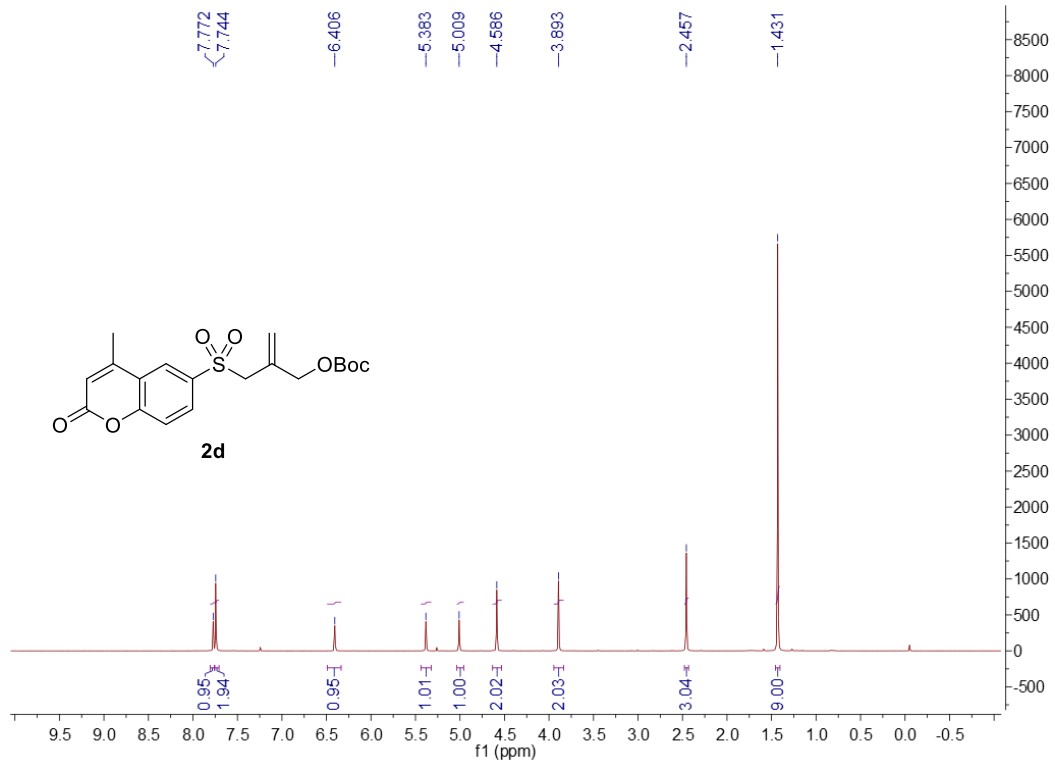
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 2c



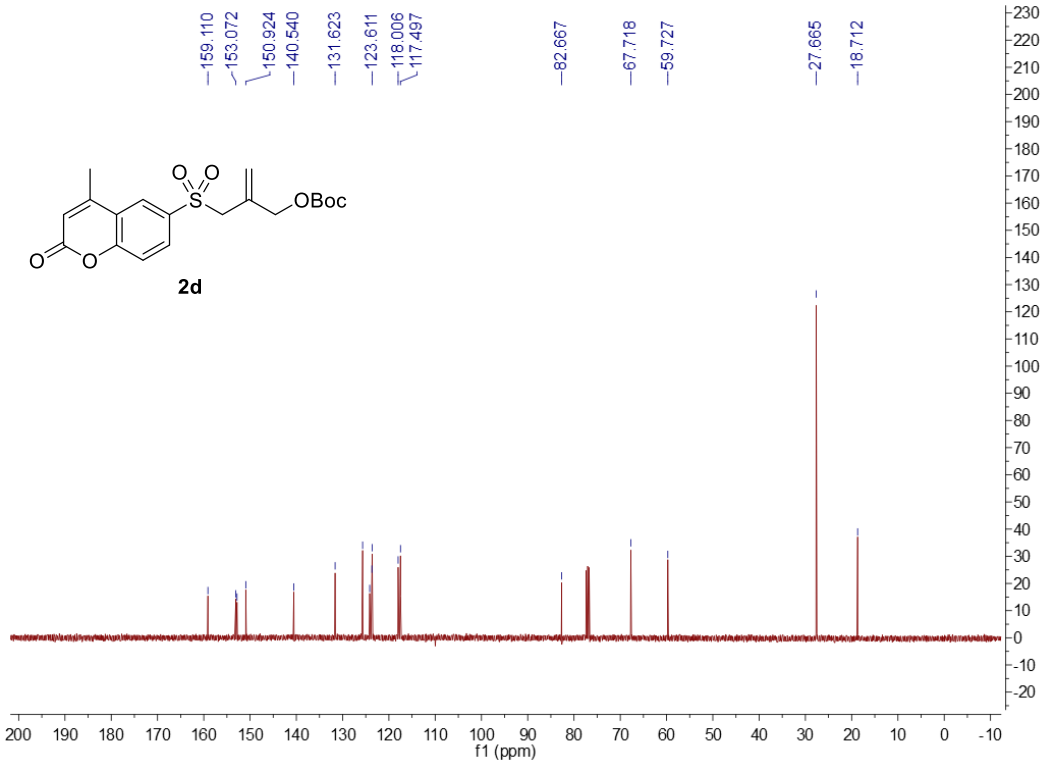
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 2c



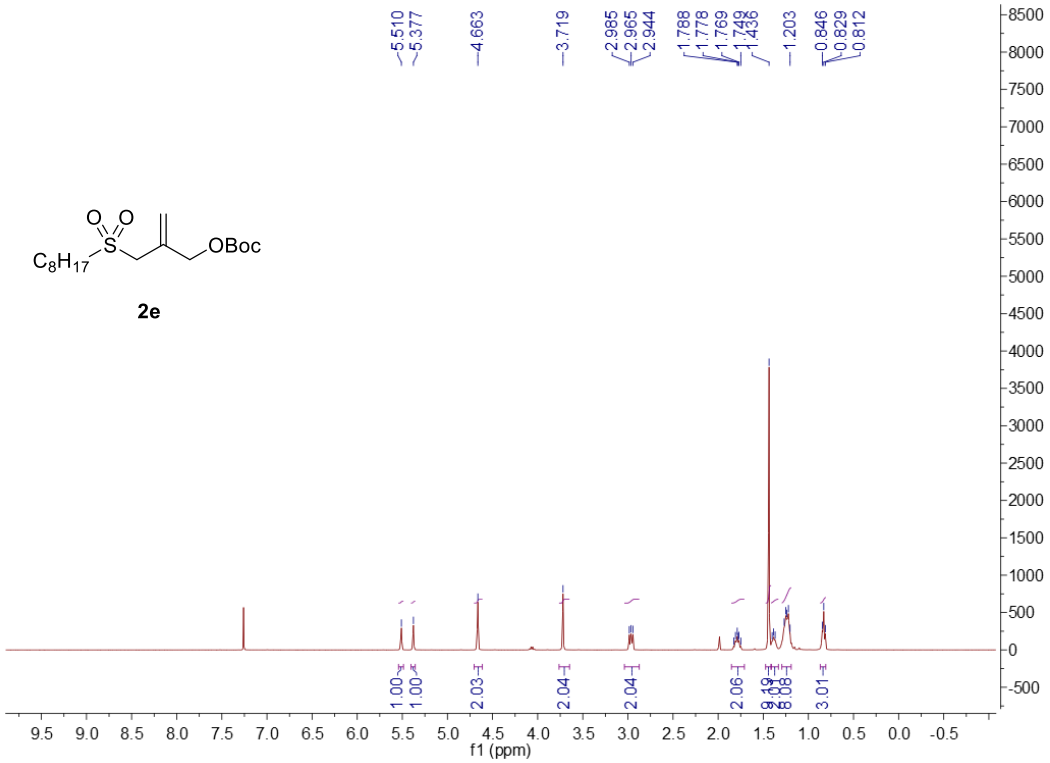
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 2d



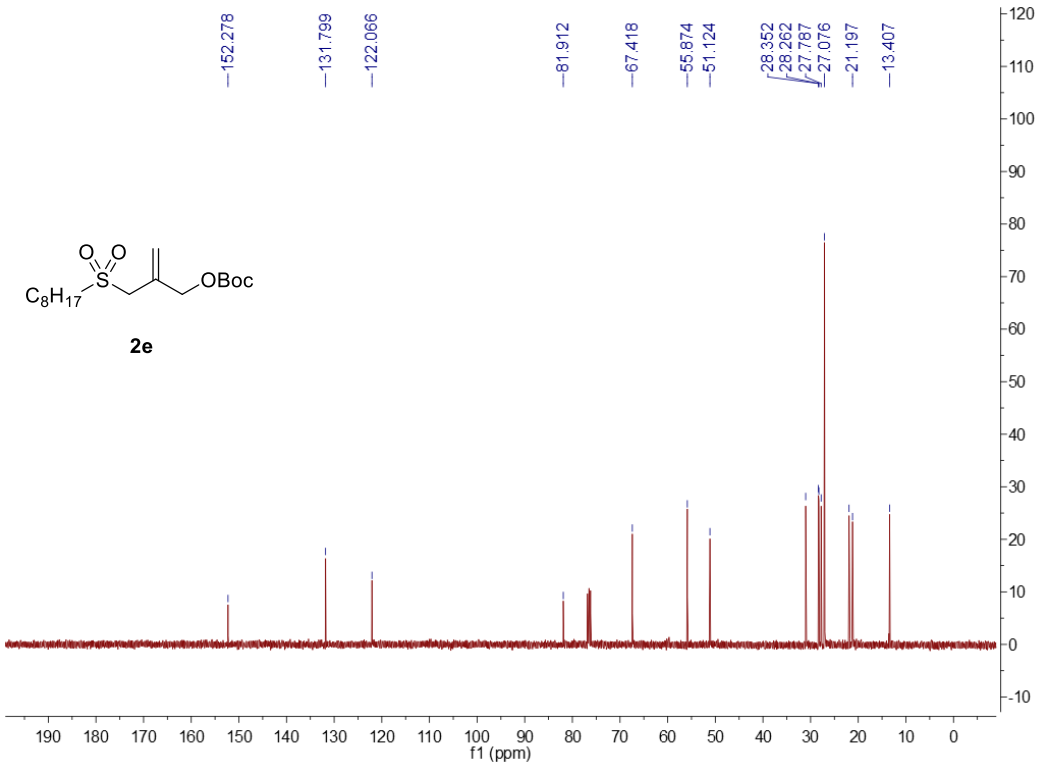
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 2d



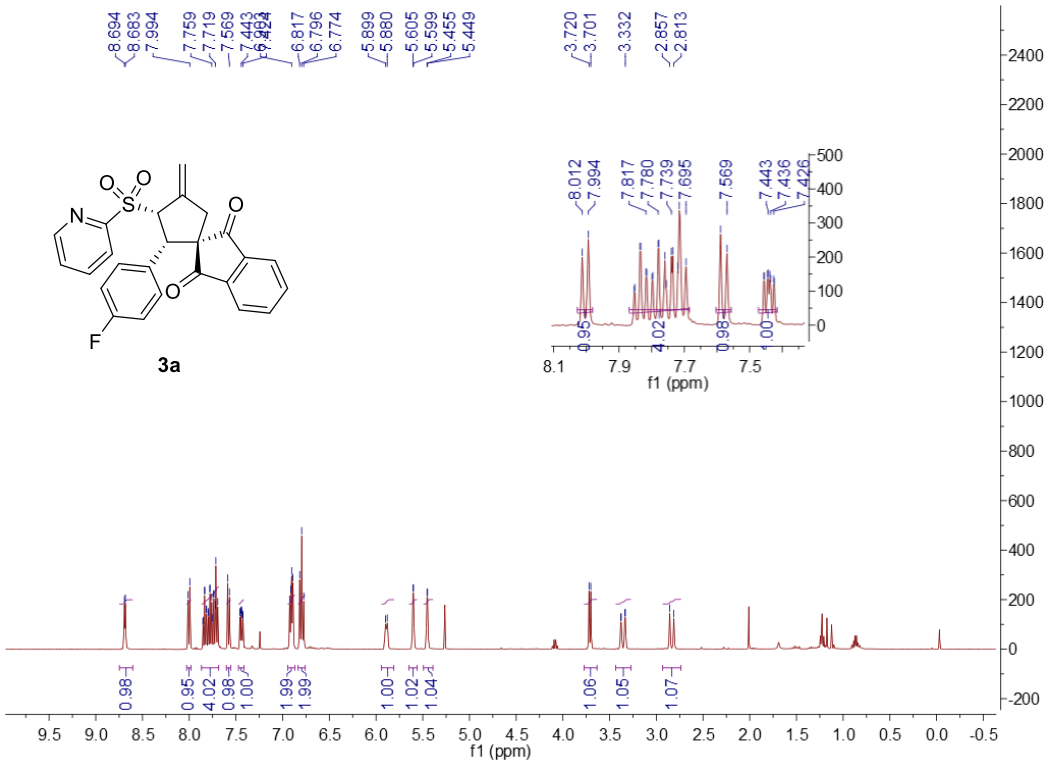
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 2e



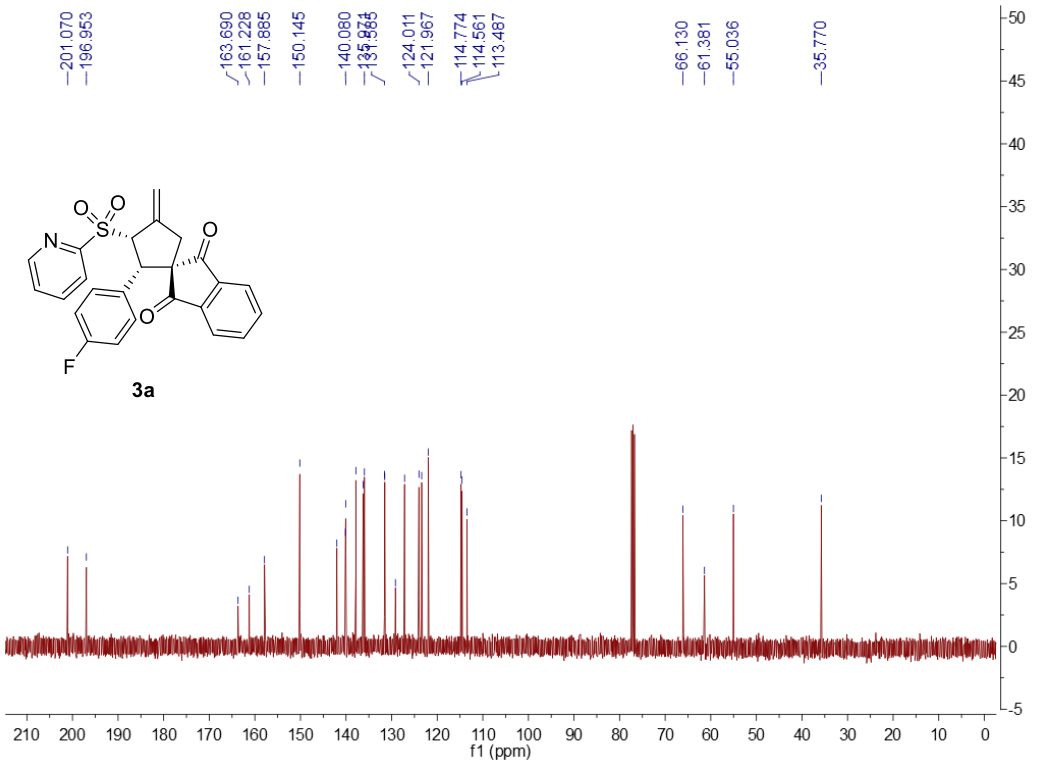
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 2e



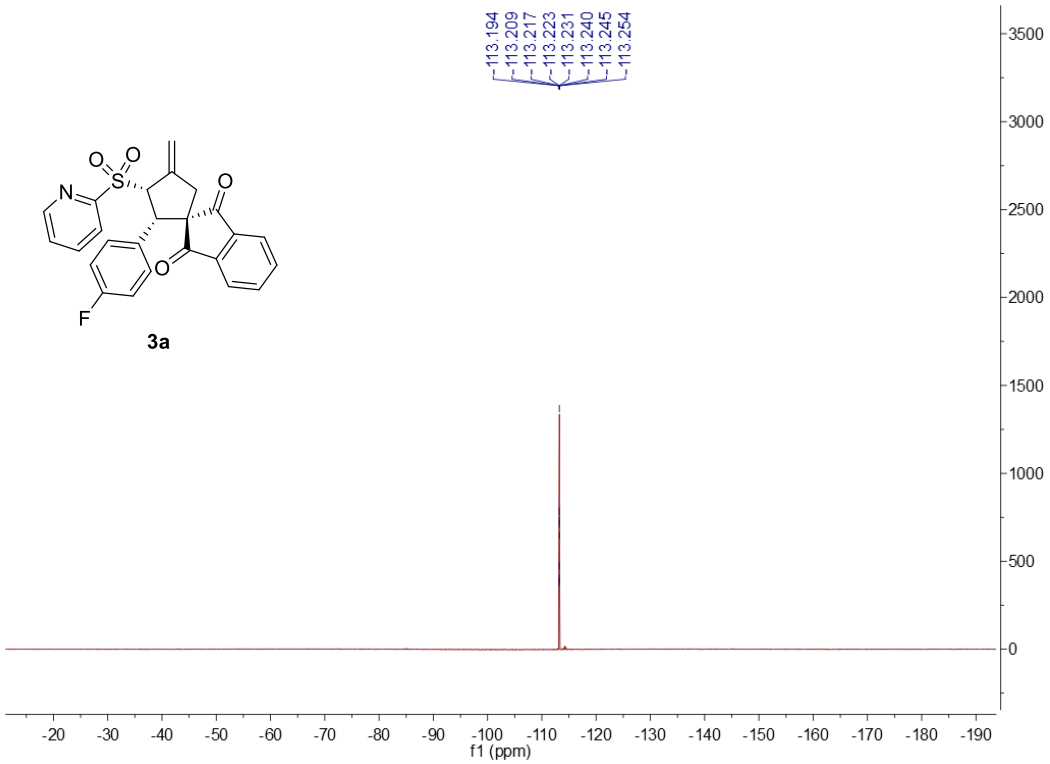
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3a



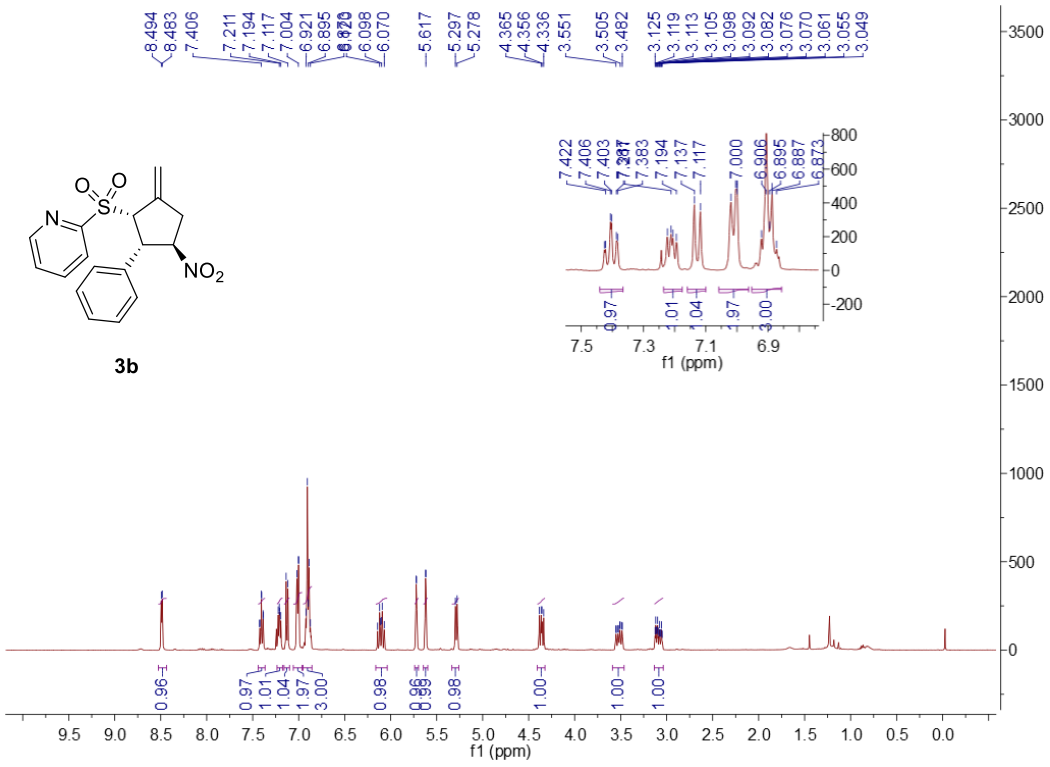
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 3a



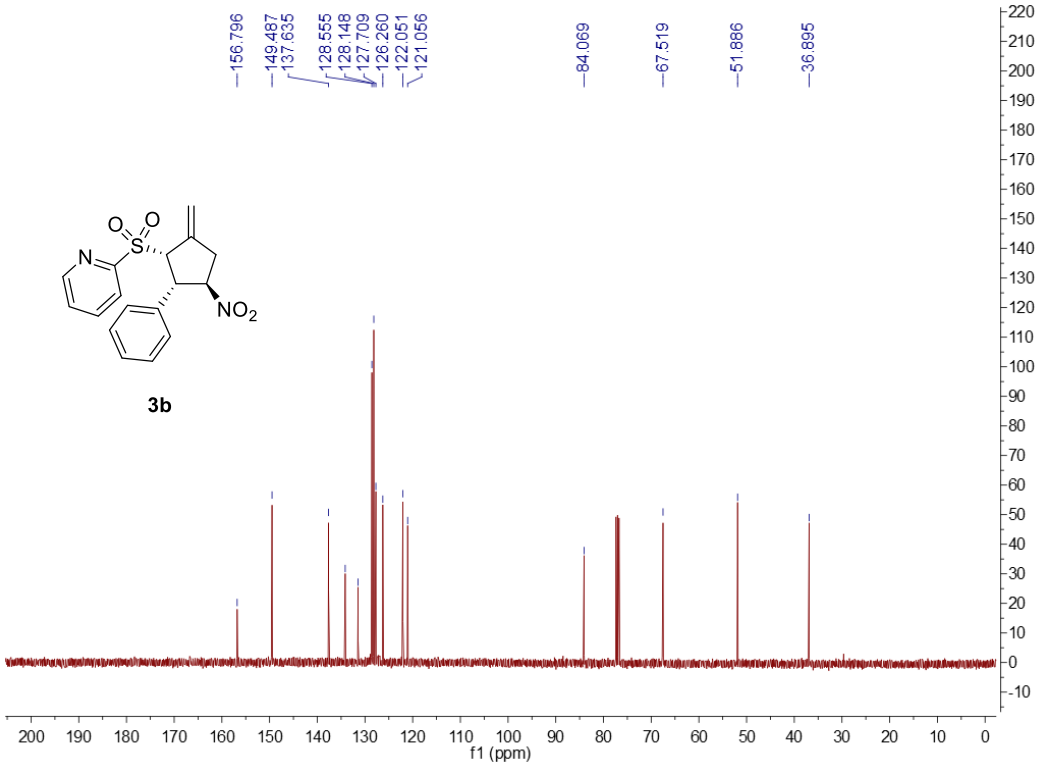
^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 3a



^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3b

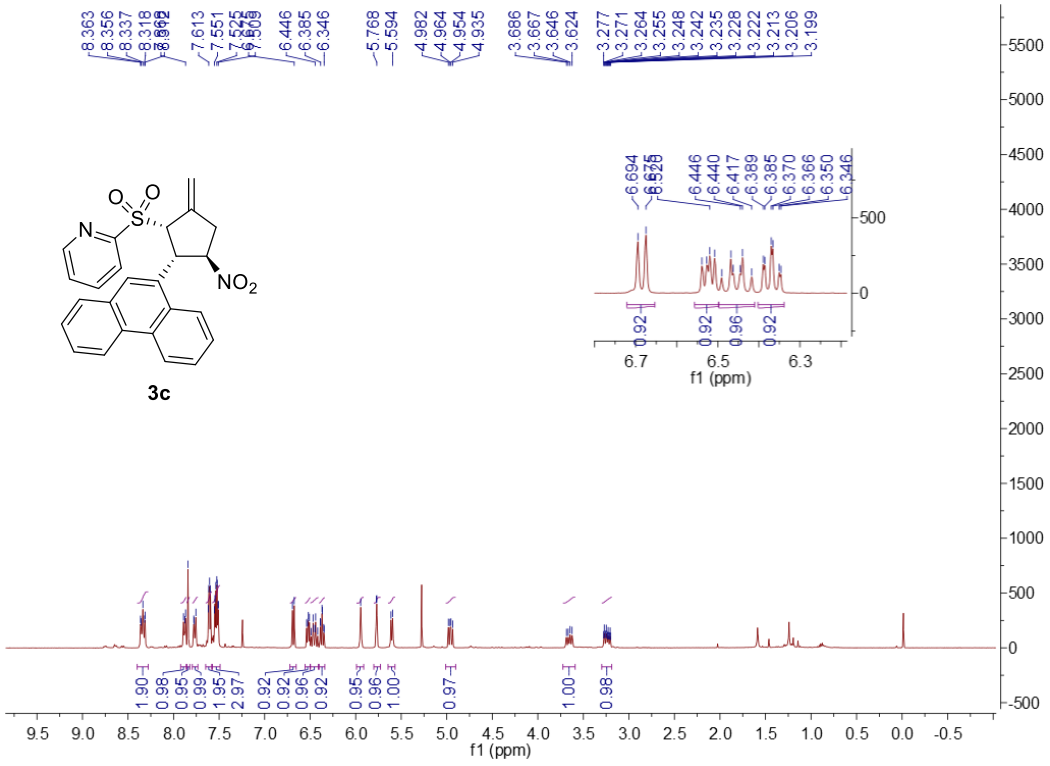


^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 3b



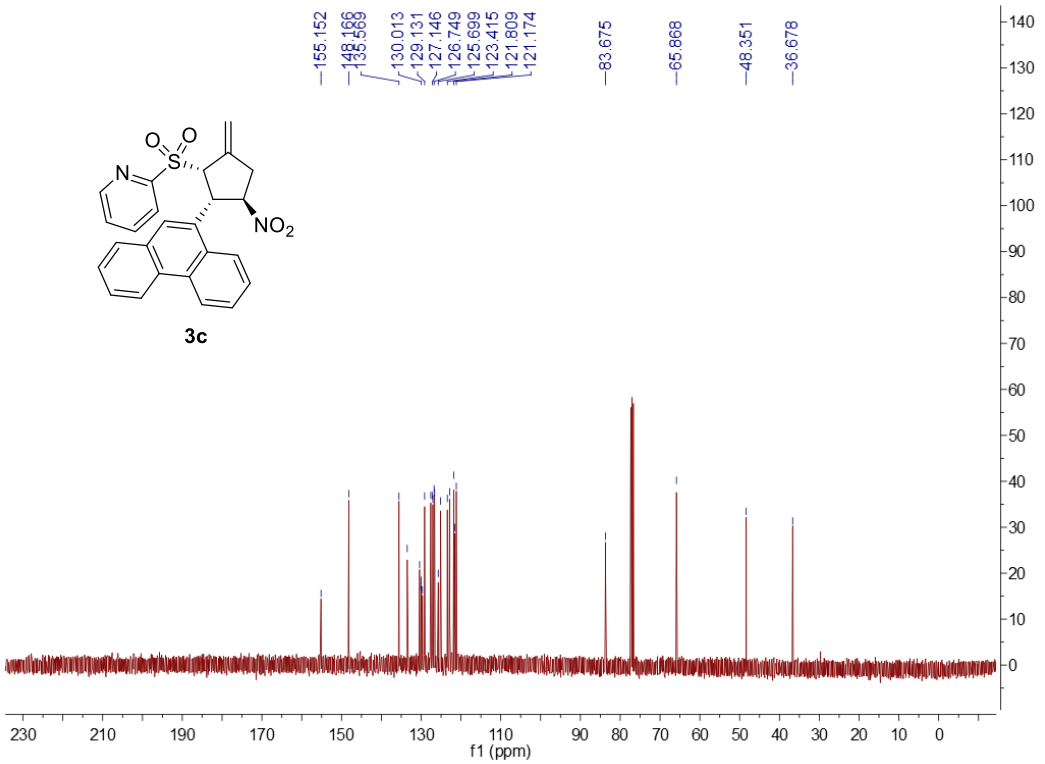
3b

^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3c

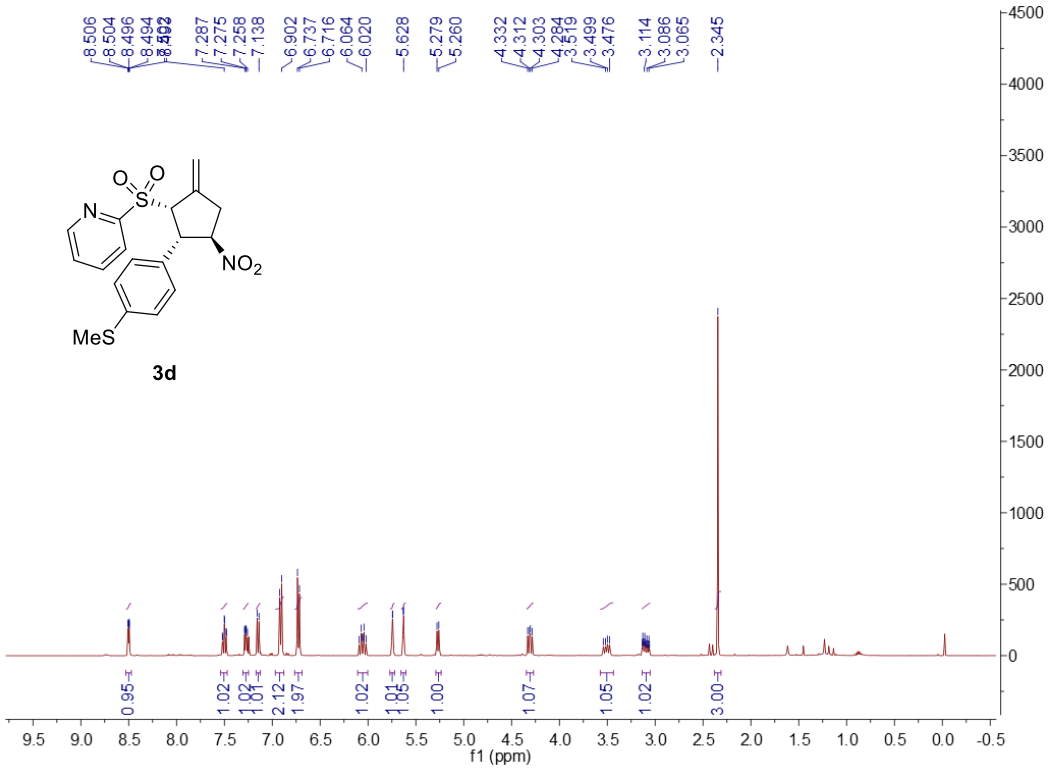


3c

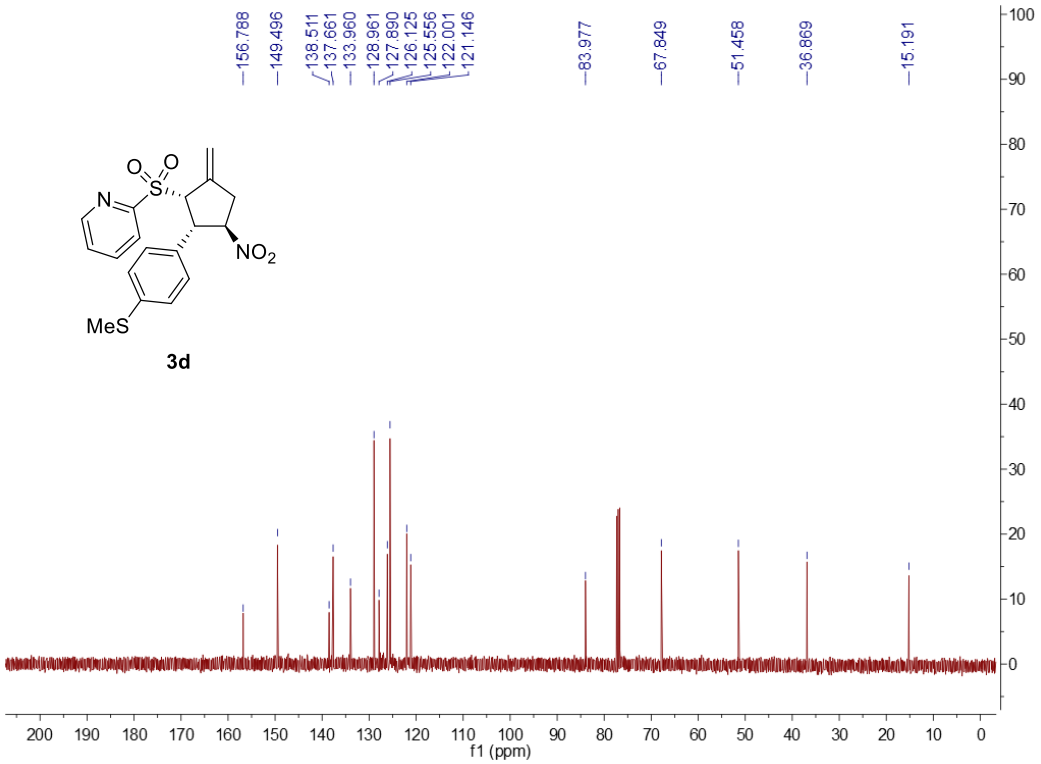
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 3c



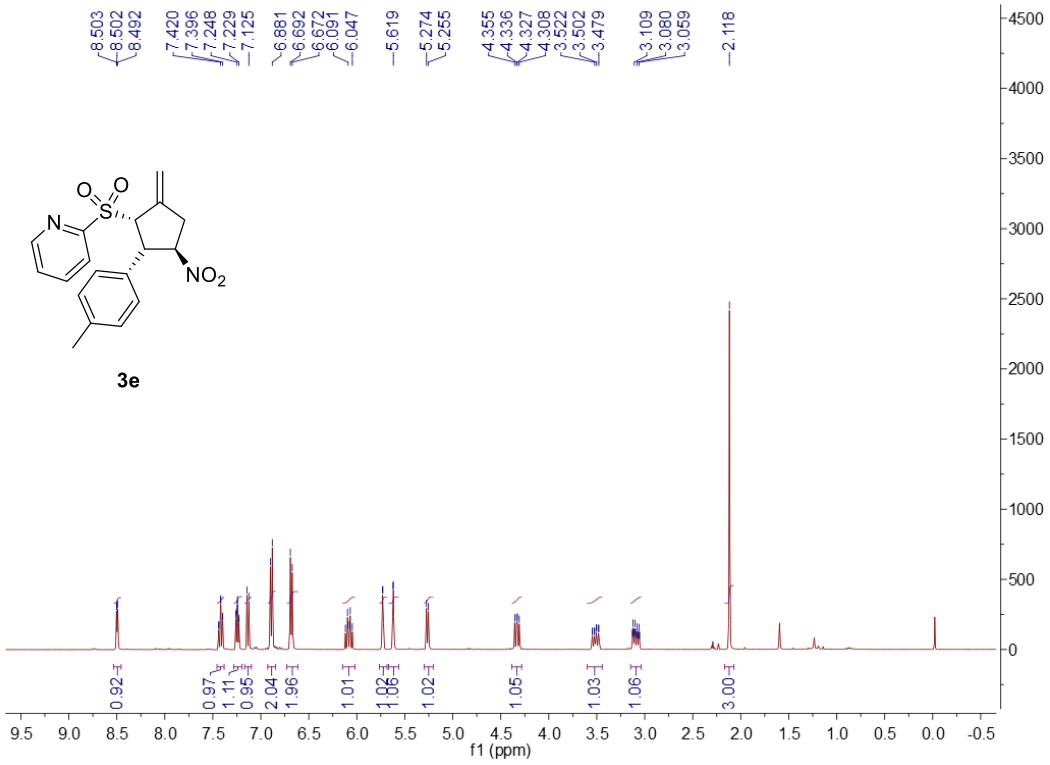
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3d



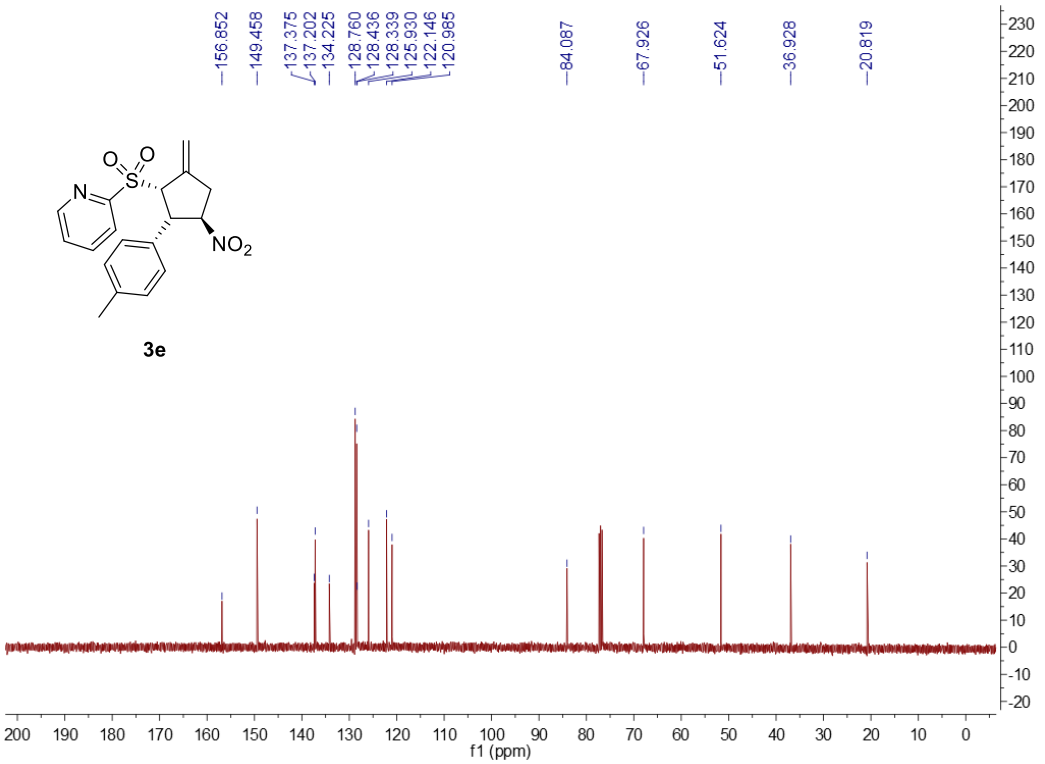
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 3d



^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3e

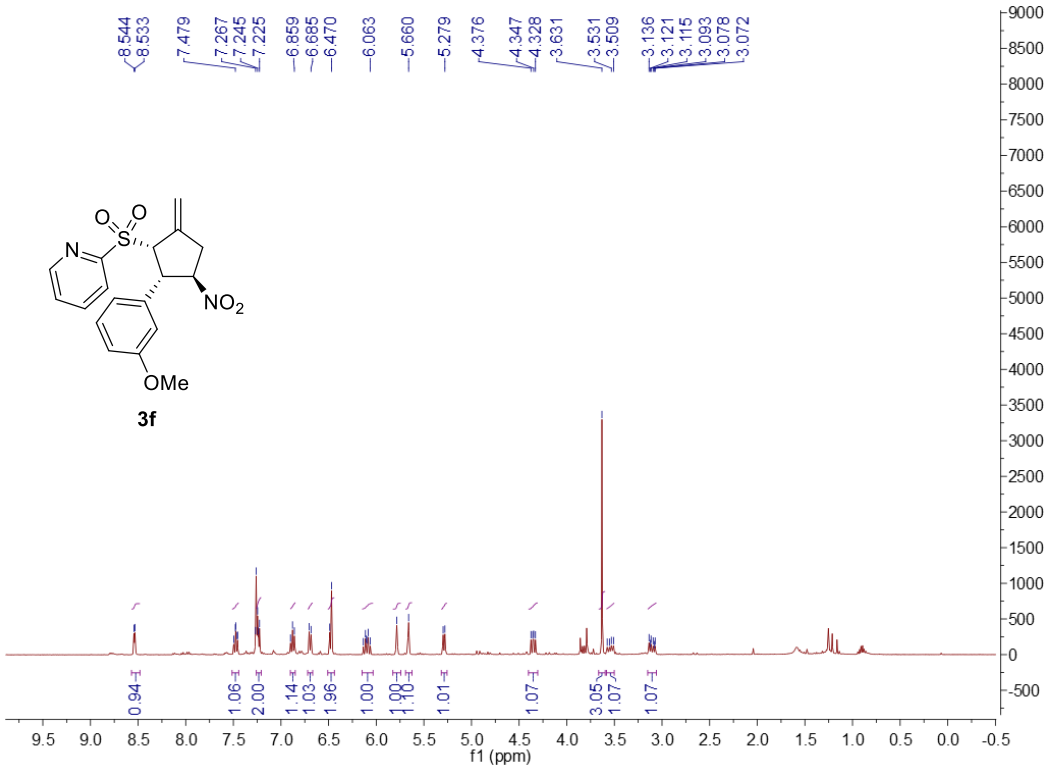


^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 3e



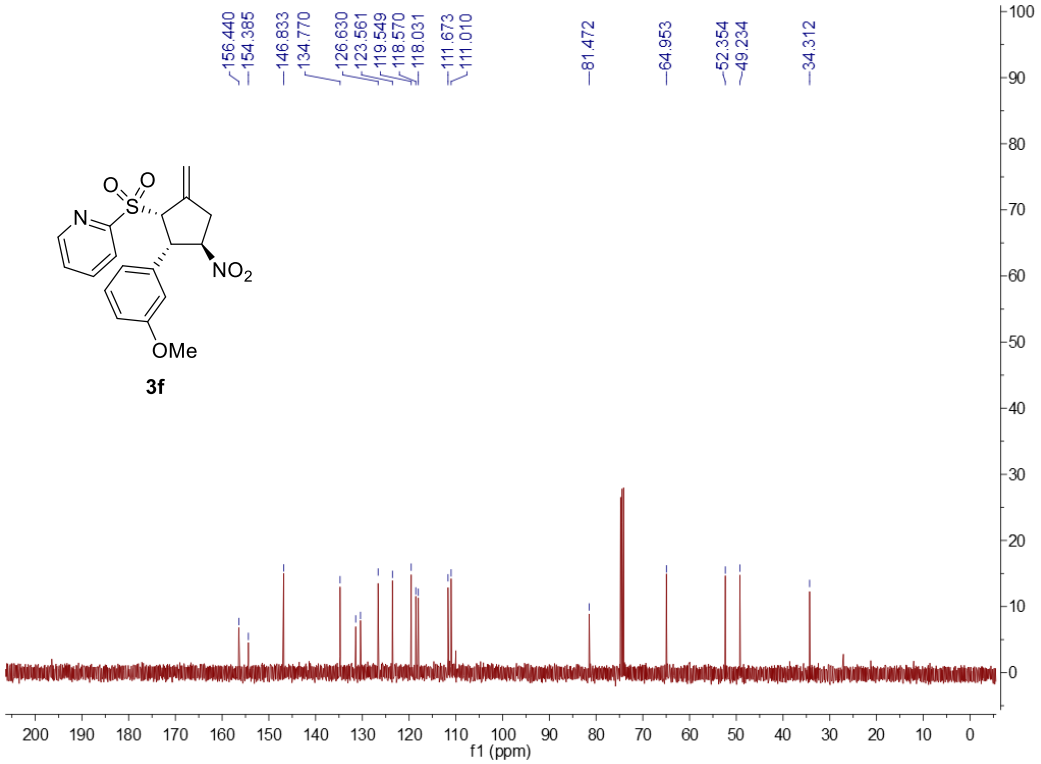
3e

^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3f

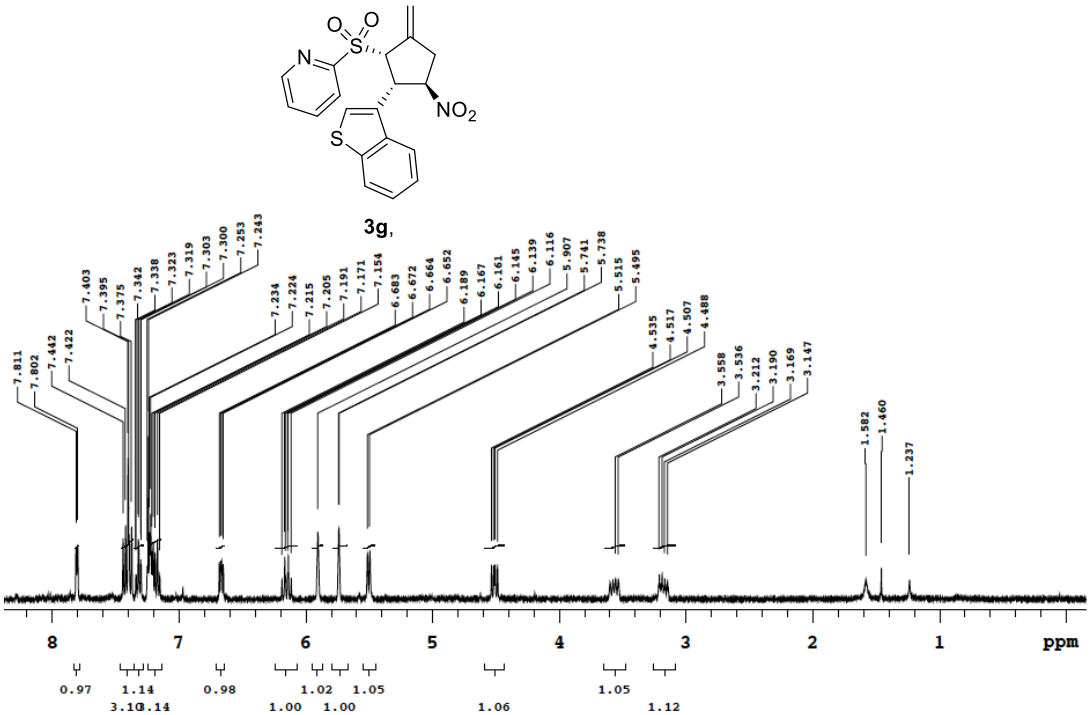


3f

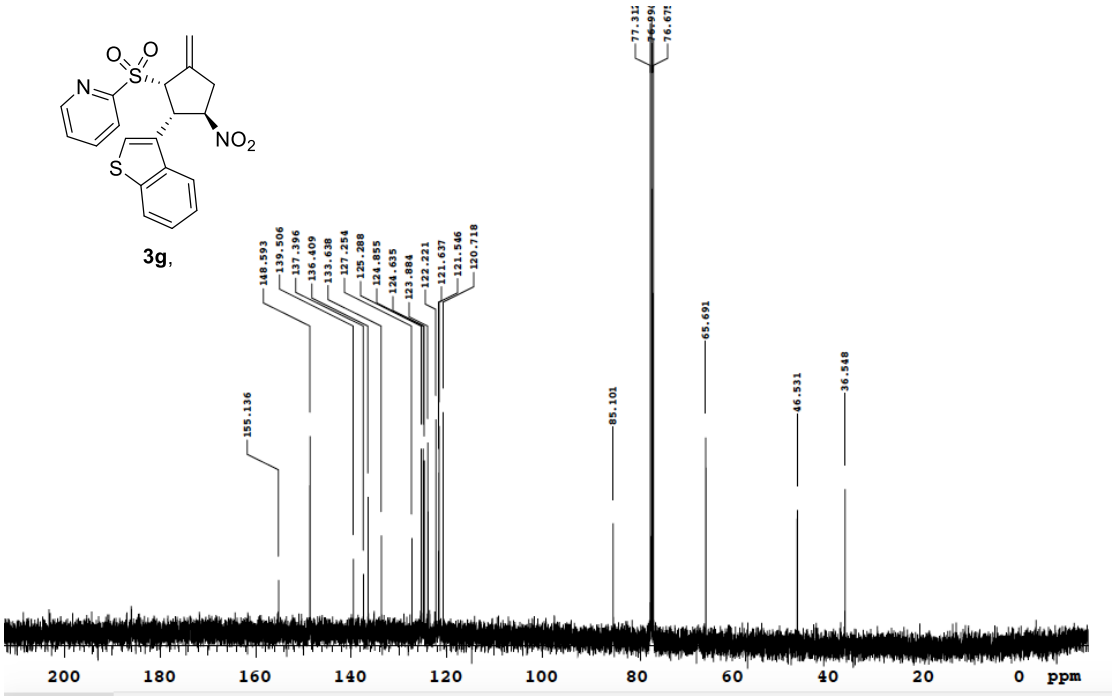
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 3f



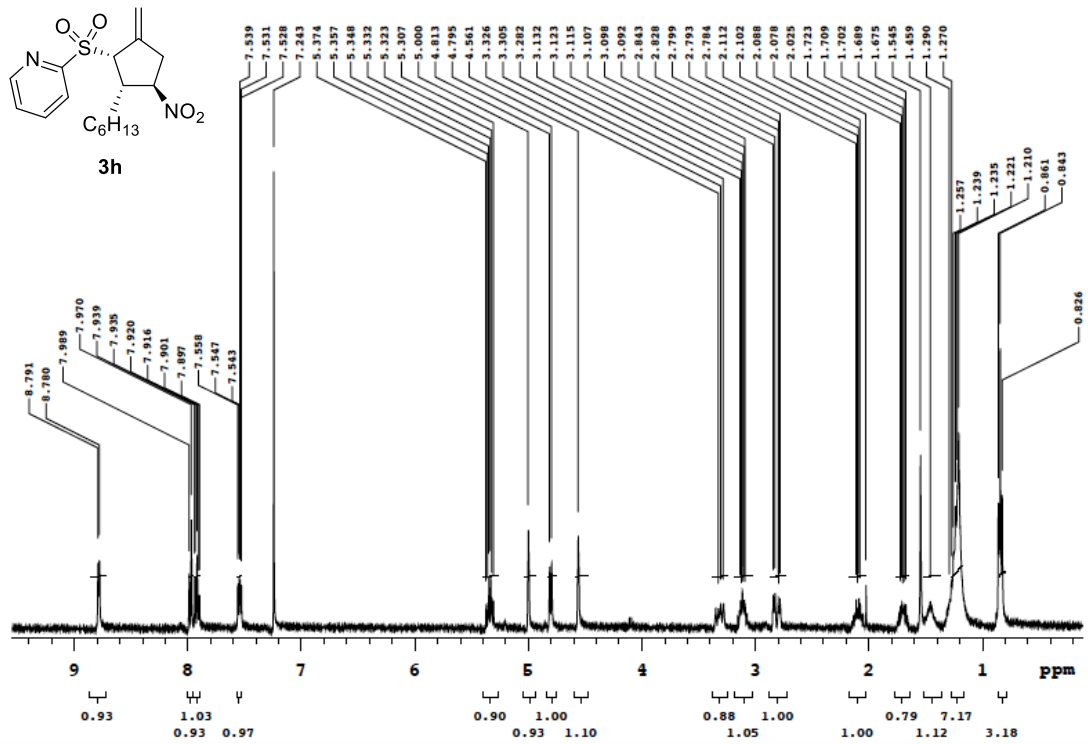
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3g



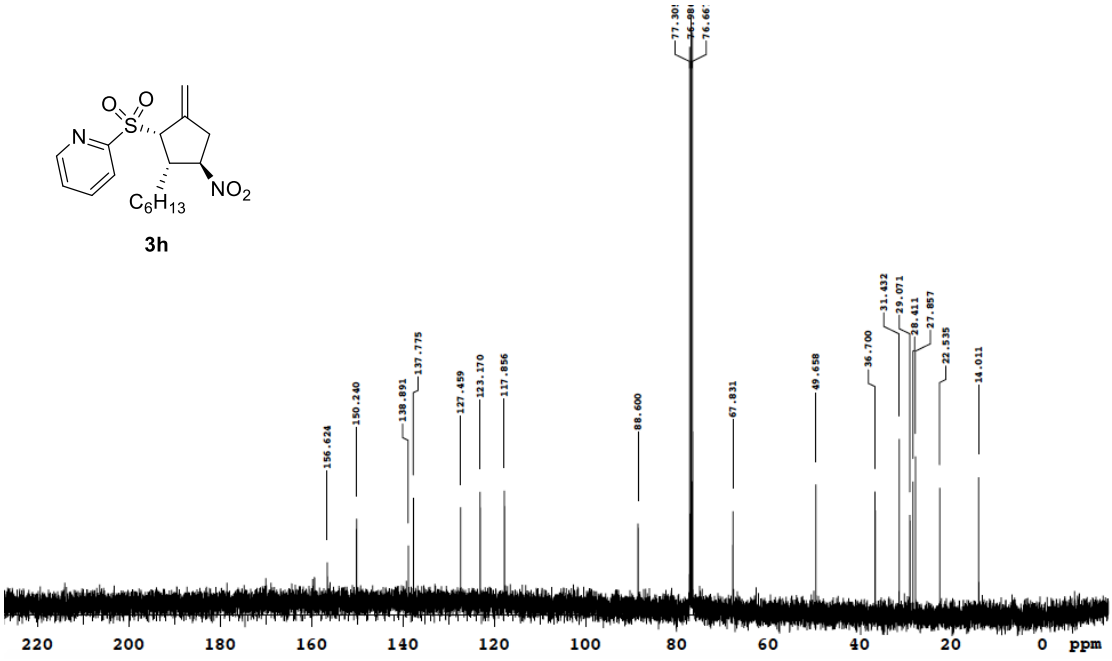
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 3g



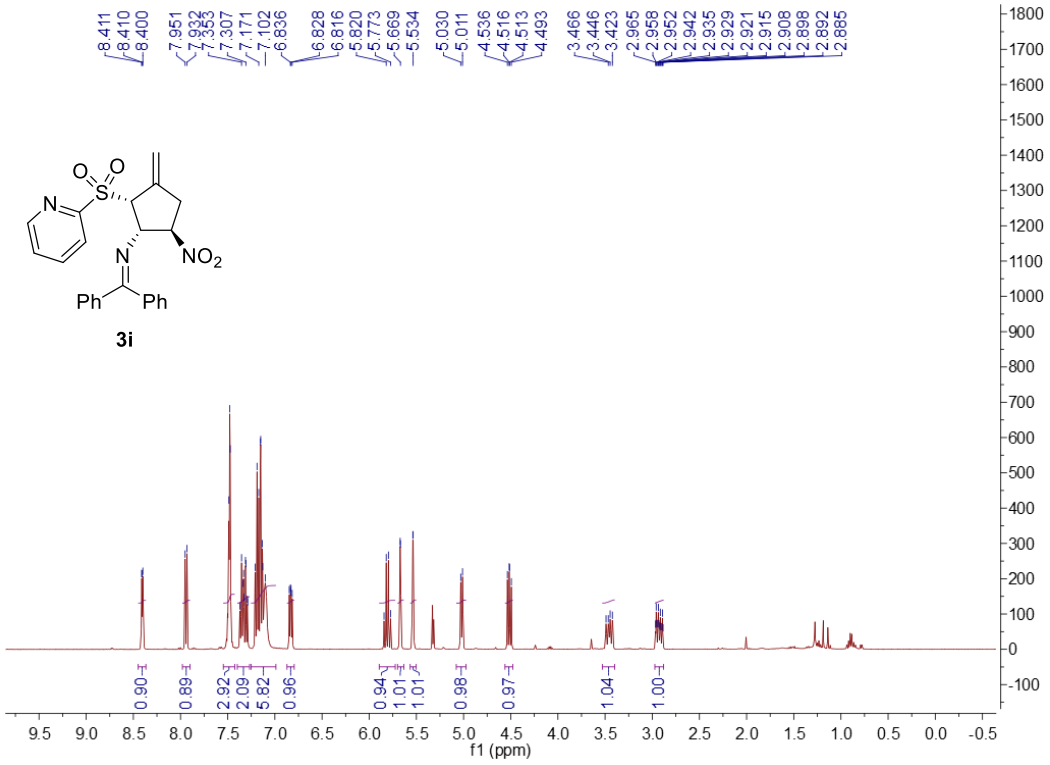
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3h



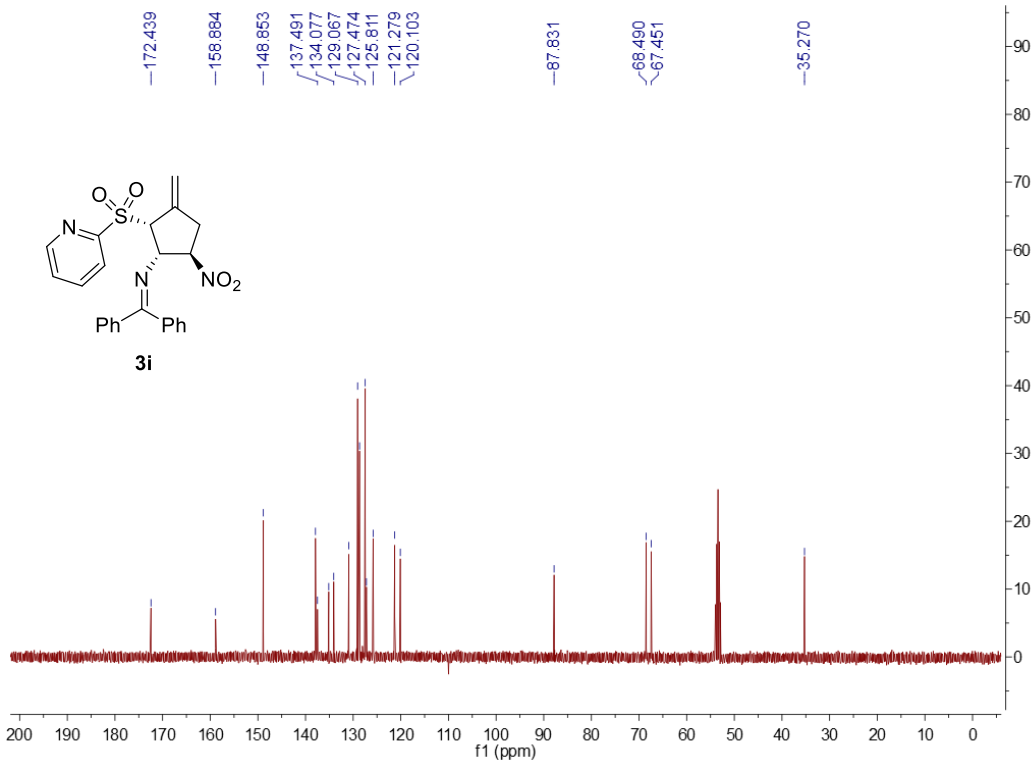
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 3h



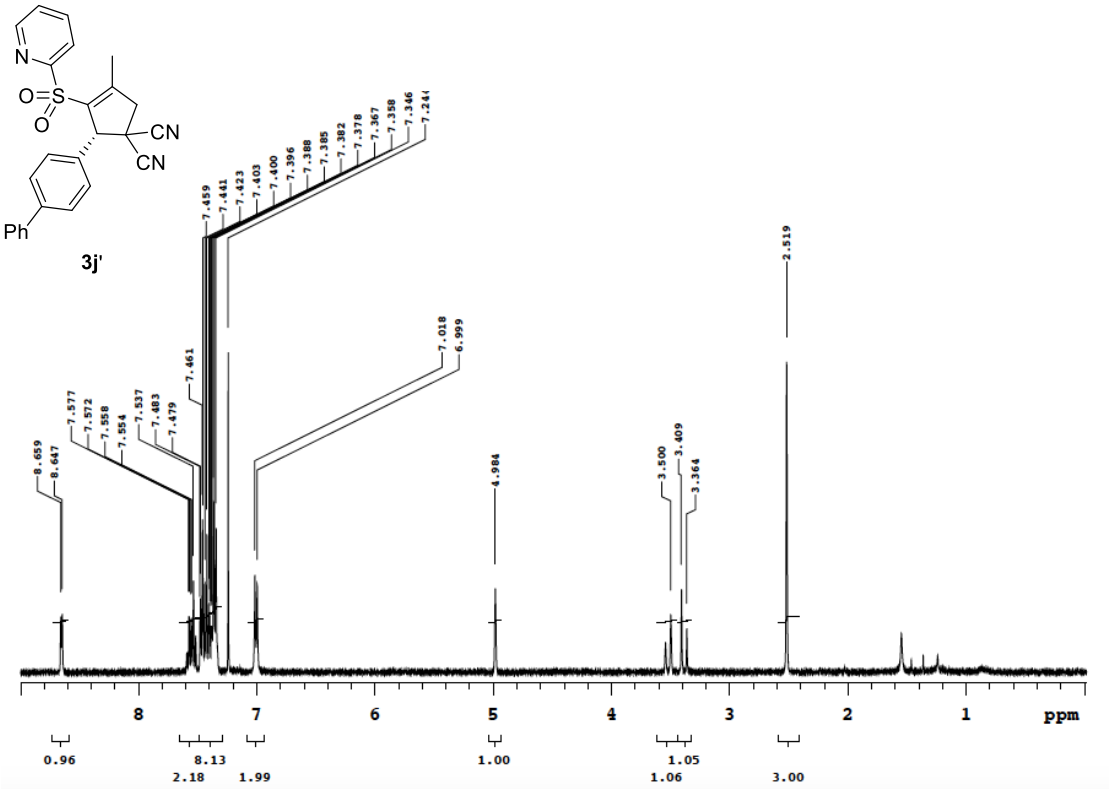
^{1}H NMR (400 MHz, CD_2Cl_2) spectrum for 3i



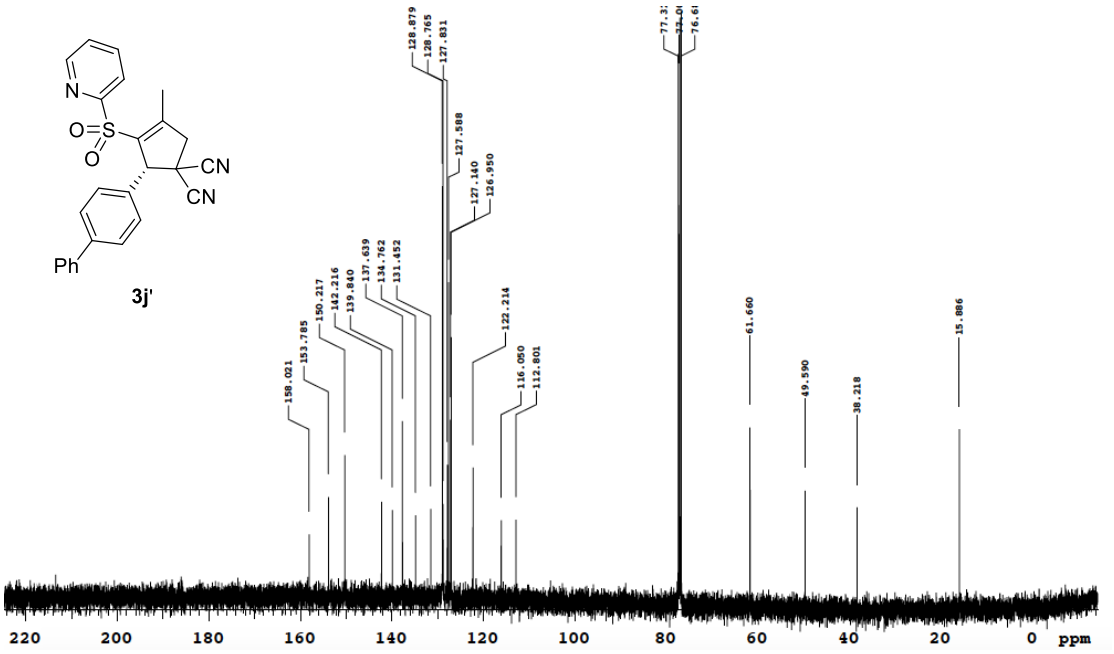
^{13}C NMR (100 MHz, CD_2Cl_2) spectrum for 3i



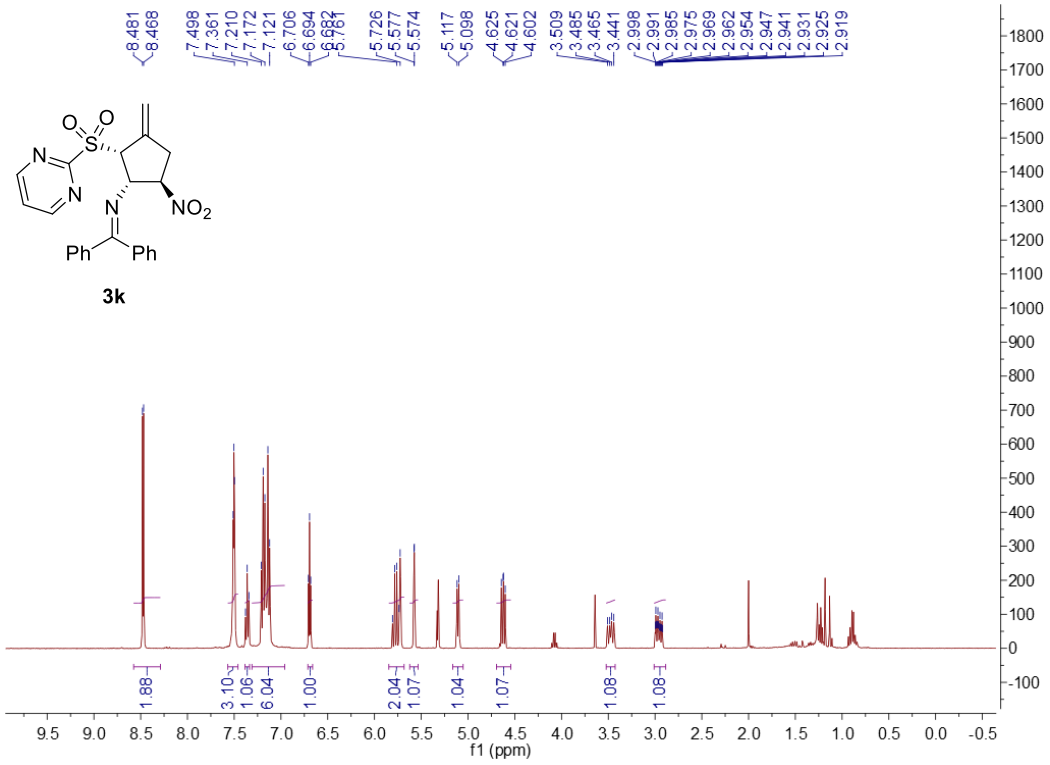
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3j'



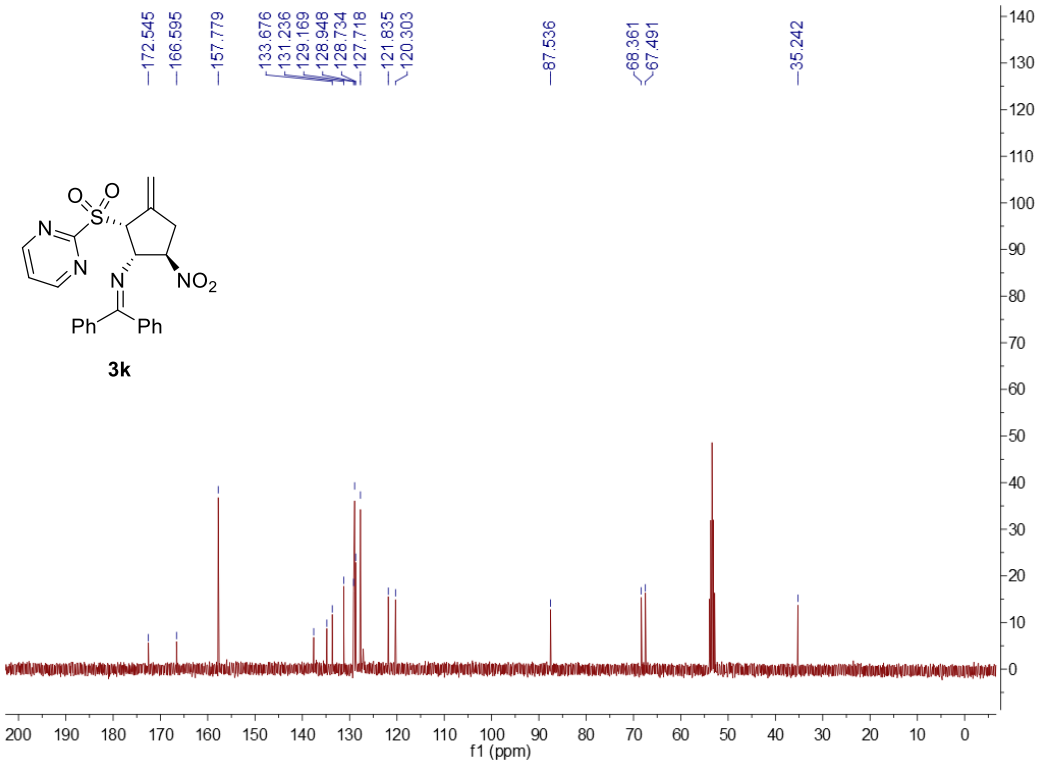
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 3j'



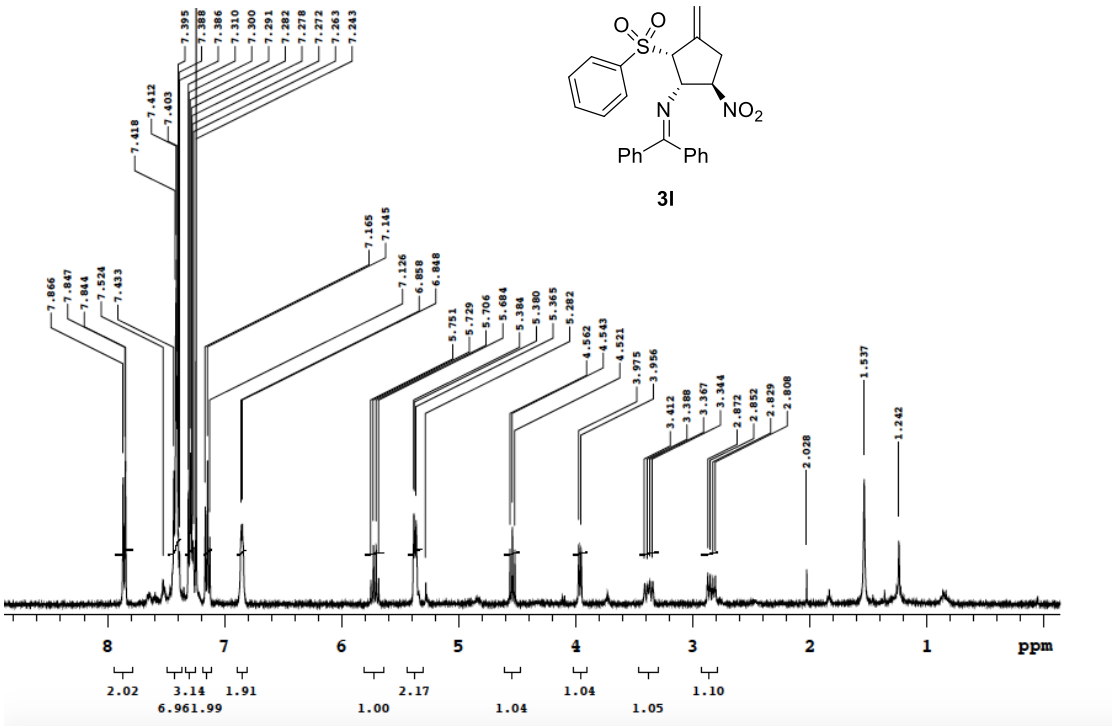
^{1}H NMR (400 MHz, CD_2Cl_2) spectrum for 3k



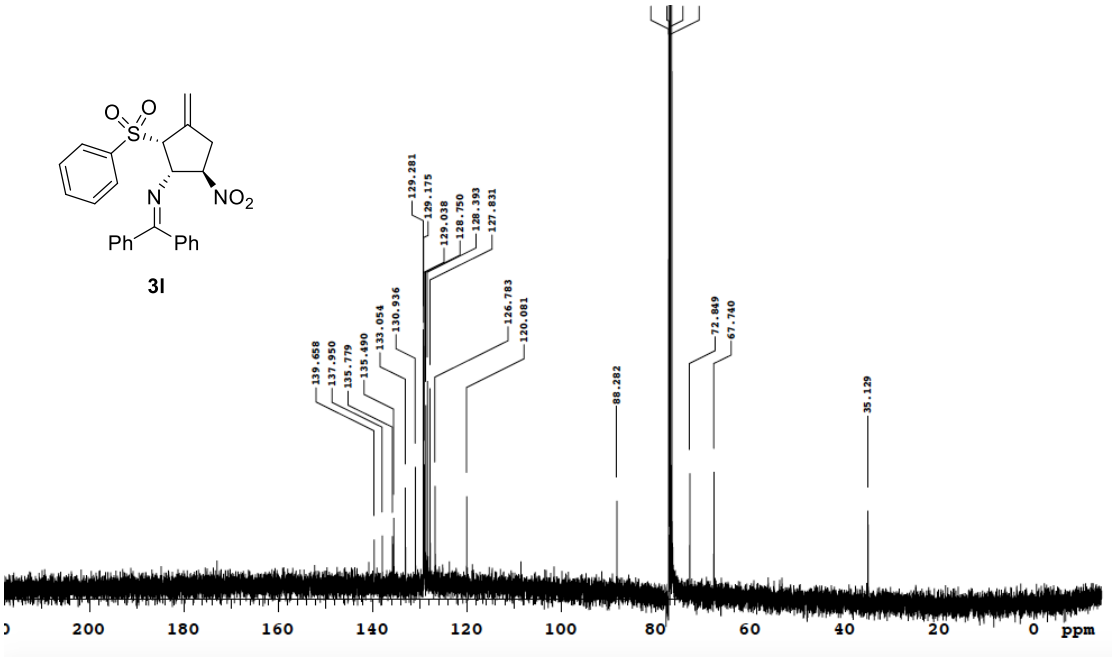
^{13}C NMR (100 MHz, CD_2Cl_2) spectrum for 3k



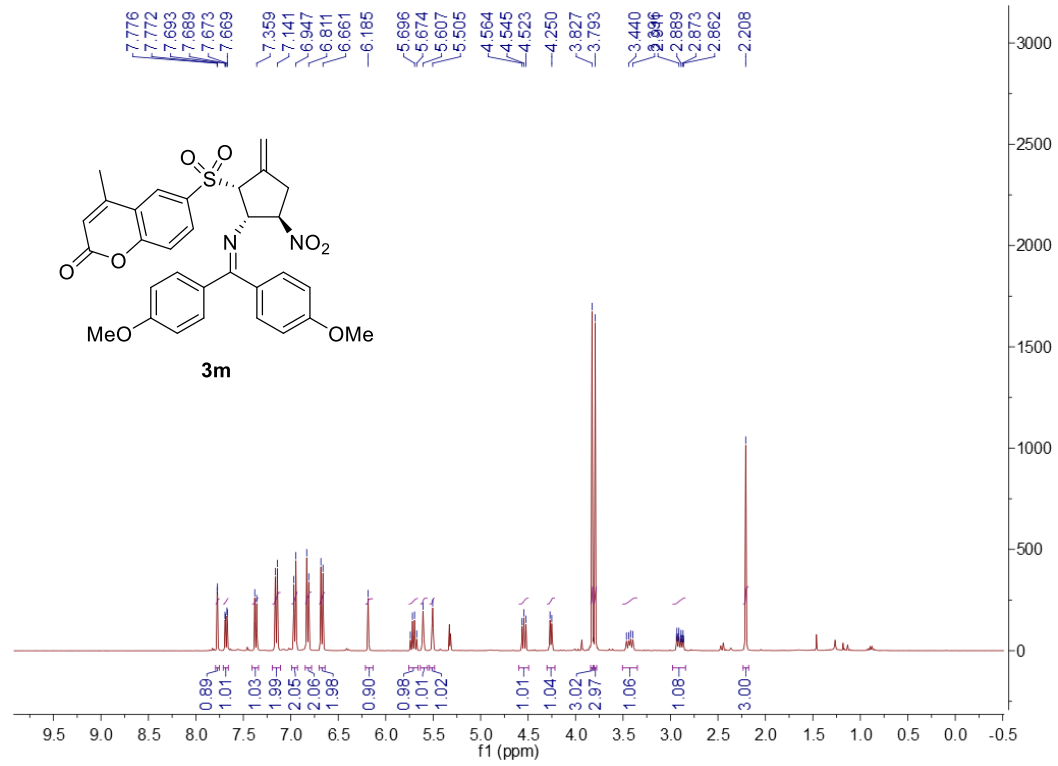
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3l



^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 3l



^{1}H NMR (400 MHz, CD_2Cl_2) spectrum for 3m



^{13}C NMR (100 MHz, CD_2Cl_2) spectrum for 3m