

Electronic Supplementary Information

Copper-Catalyzed Regioselective 1,2-Thioamidation of Alkenes

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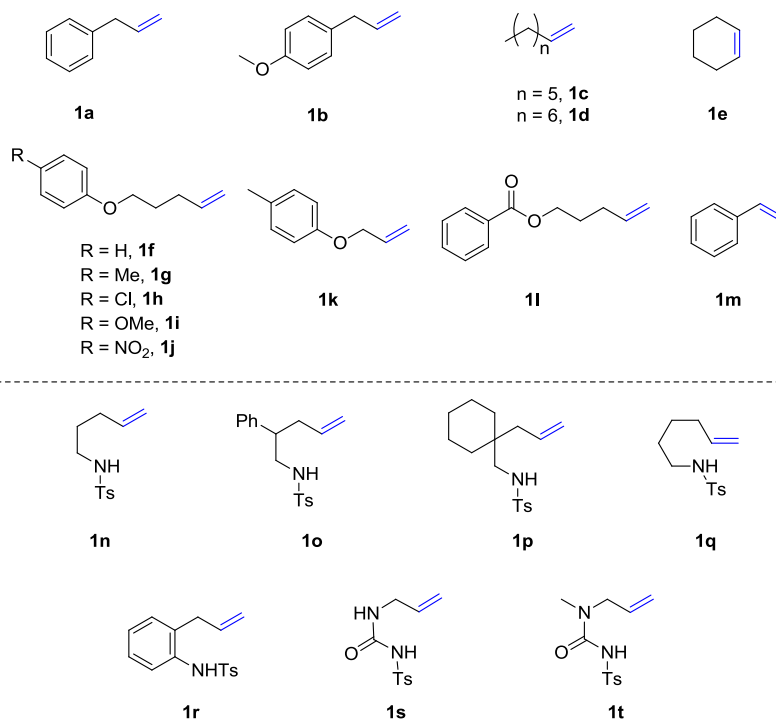
I. General Information

All the solvents and commercially available reagents were purchased from commercial suppliers. ^1H NMR, ^{13}C NMR spectra were recorded on a 400 MHz or/and 500 MHz Bruker FT-NMR spectrometers. All chemical shifts are given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, J , are reported in Hertz (Hz). High Resolution Mass (MS) analysis was obtained using on a LC/MSD TOF spectrometer system with Electrospray Ionization (ESI). Melting points were measured on a Mel-Temp apparatus and are uncorrected. Reactions were monitored by thin-layer chromatography (TLC) carried out on commercial silica gel plates (GF254) under UV light. Flash chromatography was performed on silica gel 60 (200–300 mesh).

II. Preparation of Starting Materials

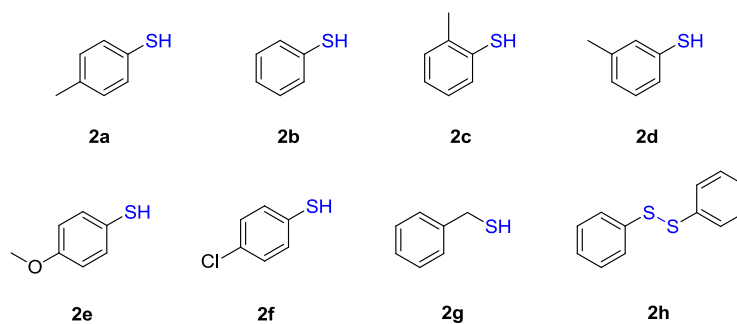
2.1 Preparation of alkene substrates

Alkenes **1a–1e**, and **1m** were purchased from commercial sources and used as received, **1f–1l**,¹ **1n**, **1q**,² **1o**, **1p** and **1r**,³ **1s–1t**⁴ were prepared according to literature procedures.



2.2. Preparation of thiol substrates

Thiols **2a–2g** and disulfide **2h** in the reaction were obtained from commercial sources and used without further purification.



III. Optimization of the Reaction Conditions and the General Procedure

3.1 Optimization of the reaction conditions

In Ar atmosphere, allylbenzene (**1a**, 1.0 equiv, 0.2 mmol) was added to a solution of 4-methylbenzenethiol (**2a**, 1.5 equiv, 0.3 mmol), NFSI (1.5 equiv, 0.3 mmol), catalyst (20 mol%) and additive (20 mol%) in CH₃CN (1.5 mL) in an oven-dried 10 mL Schlenk tube. The mixture was heated at 45 °C for 12–20 h (monitored by TLC). After the reaction was completed, the resulting solution was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1, R_f = 0.2) to give the desired product *N*-(3-phenyl-2-(*p*-tolylthio)propyl)-*N*-(phenylsulfonyl)benzenesulfonamide (**3a**) as a colourless oil.

Table S1. Optimization of the reaction conditions^a

Entry	Catalyst (mol%)	Additive (mol%)	Solvent	T (°C) / Time (h)	Yield (%) ^b
1	CuCl (10)	--	CH ₃ CN	45 / 18	44
2	CuCl (10)	--	CH ₃ CN	80 / 18	38
3	CuCl (10)	--	CH ₃ CN	r.t. / 20	40
4	CuI (10)	--	CH ₃ CN	45 / 18	36
5	CuBr (10)	--	CH ₃ CN	45 / 16	27
6	Cu(OAc) ₂ (10)	--	CH ₃ CN	45 / 20	30

7	Cu(OTf) ₂ (10)	--	CH ₃ CN	45 / 16	24
8	CuCl ₂ (10)	--	CH ₃ CN	45 / 16	45
9	AgNO ₃ (10)	--	CH ₃ CN	45 / 16	N.R.
10	FeCl ₃ (10)	--	CH ₃ CN	45 / 16	trace
11	Pd(OAc) ₂ (10)	--	CH ₃ CN	45 / 16	N.R.
12	--	--	CH ₃ CN	45 / 20	N.R.
13	CuCl (20)	--	CH ₃ CN	45 / 16	47
14	CuCl ₂ (20)	--	CH ₃ CN	45 / 16	49
15	CuCl (10)	phen (10)	CH ₃ CN	45 / 12	15
16	CuCl (10)	L-proline(10)	CH ₃ CN	45 / 12	< 10
17	CuCl (10)	Bipy (10)	CH ₃ CN	45 / 12	< 10
18	CuCl (10)	B ₂ Pin ₂ (10)	CH ₃ CN	45 / 16	30
19	CuCl (20)	B₂Pin₂ (20)	CH₃CN	45 / 15	61
20	CuCl ₂ (20)	B ₂ Pin ₂ (20)	CH ₃ CN	45 / 15	56
21	CuCl (20)	B ₂ Pin ₂ (10)	CH ₃ CN	45 / 12	48
22	CuCl (20)	B ₂ Pin ₂ (50)	CH ₃ CN	45 / 12	32
23	CuCl (30)	B ₂ Pin ₂ (30)	CH ₃ CN	45 / 12	43
24	CuCl (12)	B ₂ Pin ₂ (12)	CH ₃ CN	45 / 15	45
25	CuCl (15)	B ₂ Pin ₂ (15)	CH ₃ CN	45 / 15	47
26	CuCl (20)	B ₂ Pin ₂ (20)	CH ₃ CN	45 / 15	30 ^c
27	CuCl (20)	B ₂ Pin ₂ (20)	CH ₃ CN	45 / 15	17 ^d
28	CuCl (20)	B ₂ Pin ₂ (20)	CH ₃ CN	45 / 15	26 ^e
29	CuCl (20)	B ₂ Pin ₂ (20)	CH ₃ CN	45 / 15	54 ^f

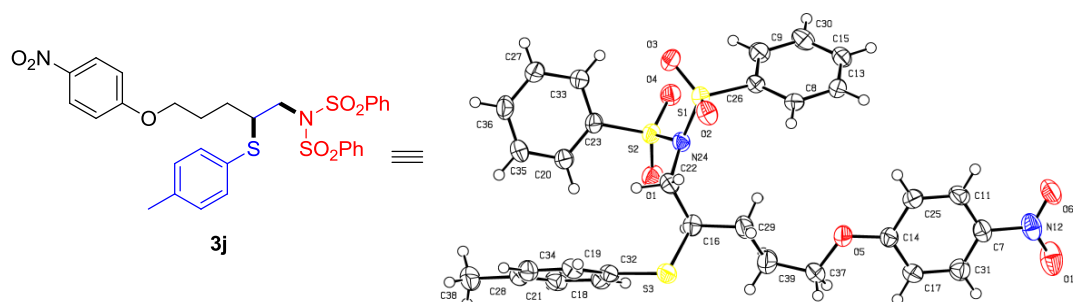
30	CuCl (20)	B ₂ Pin ₂ (20)	CH ₃ CN	45 / 15	54 ^g
31	CuCl (20)	B ₂ Pin ₂ (20) /TFA (20)	CH ₃ CN	45 / 12	22
32	CuCl (20)	B ₂ Pin ₂ (20) /TfOH (20)	CH ₃ CN	45 / 12	26
33	CuCl (20)	B ₂ Pin ₂ (20) /K ₂ CO ₃ (20)	CH ₃ CN	45 / 12	23
34	CuCl (20)	B ₂ Pin ₂ (20)	toluene	45 / 15	< 10
35	CuCl (20)	B ₂ Pin ₂ (20)	DMF	45 / 15	N.R.
36	CuCl (20)	B ₂ Pin ₂ (20)	DMSO	45 / 15	N.R.
37	CuCl (20)	B ₂ Pin ₂ (20)	THF	45 / 15	N.R.
38	CuCl (20)	B ₂ Pin ₂ (20)	dioxane	45 / 15	N.R.
39	CuCl (20)	B ₂ Pin ₂ (20)	DCE	45 / 15	N.R.

^a Reaction conditions: In Ar atmosphere, **1a** (1.0 equiv, 0.2 mmol), **2a** (1.5 equiv, 0.3 mmol), NFSI (1.5 equiv, 0.3 mmol), catalyst (0–30 mol%), additive (0–50 mol%) in solvent (1.5 mL). ^b Isolated yield. ^c **2a** (1.2 equiv, 0.24 mmol) and NFSI (1.2 equiv, 0.24 mmol) were used. ^d **2a** (1.2 equiv, 0.24 mmol) was used. ^e NFSI (1.2 equiv, 0.24 mmol) was used. ^f **2a** (2.0 equiv, 0.4 mmol) was used. ^g NFSI (2.0 equiv, 0.4 mmol) was used. Unless otherwise noted, B₂Pin₂ = Bis(pinacolato)diboron; phen = 1,10-phenanthroline; Bipy=2,2'-Bipyridine.

3.2 General procedure

In a dry 10 mL Schlenk tube, alkenes **1** (1.0 equiv, 0.2 mmol) and thiols **2** (1.5 equiv, 0.3 mmol), NFSI (1.5 equiv, 0.3 mmol), CuCl (20 mol%), B₂Pin₂ (20 mol%) were mixed in CH₃CN (1.5 mL) in Ar. Then the mixture was heated at 45 °C for 15 h (monitored by TLC). After the reaction was completed, it was cooled to room temperature and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to give the desired products **3** or **4**.

IV X-ray Crystallography of 3j



Crystallographic data for compound **3j** (CCDC- 1525419) has been deposited with the Cambridge Crystallographic Data Centre, Copies of the data can be obtained, free of charge, on application to CCDC (Email:deposit@ccdc.cam.ac.uk).

Bond precision: C-C = 0.0039 Å Wavelength=1.54184
 Cell: a=8.86824 (15) b=10.25459 (19) c=16.1386 (3)
 alpha=89.3079 (16) beta=81.4110 (16) gamma=84.4246 (14)
 Temperature: 116 K

	Calculated	Reported
Volume	1444.32 (5)	1444.32 (5)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C30 H30 N2 O7 S3	C30 H30 N2 O7 S3
Sum formula	C30 H30 N2 O7 S3	C30 H30 N2 O7 S3
Mr	626.74	626.74
Dx, g cm ⁻³	1.441	1.441
Z	2	2
Mu (mm ⁻¹)	2.783	2.783
F000	656.0	656.0
F000'	659.83	
h,k,lmax	10,11,18	10,11,18
Nref	4600	4598
Tmin,Tmax	0.499,0.573	0.816,1.000
Tmin'	0.377	

Correction method= # Reported T Limits: Tmin=0.816 Tmax=1.000
 AbsCorr = MULTI-SCAN

Data completeness= 1.000 Theta(max)= 62.380

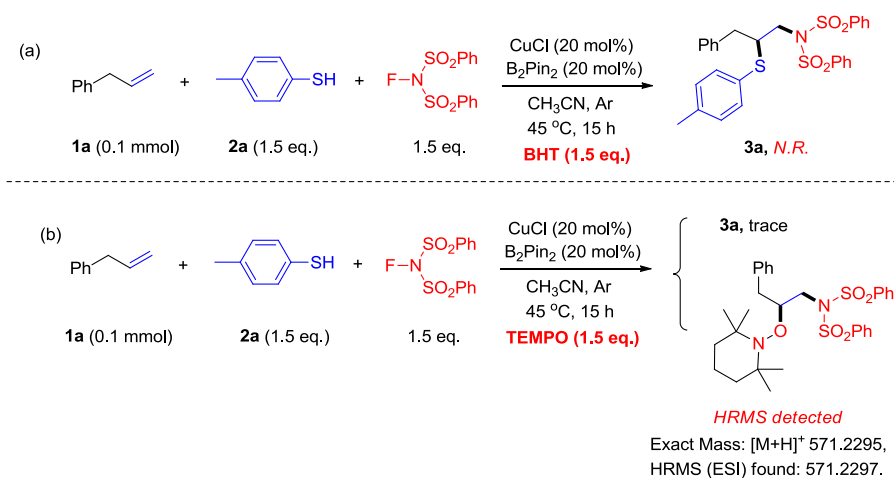
R(reflections)= 0.0409(4069) wR2(reflections)= 0.1087(4598)

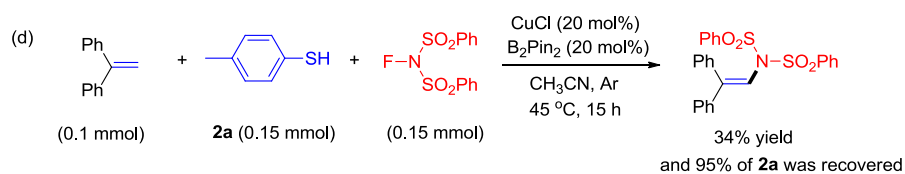
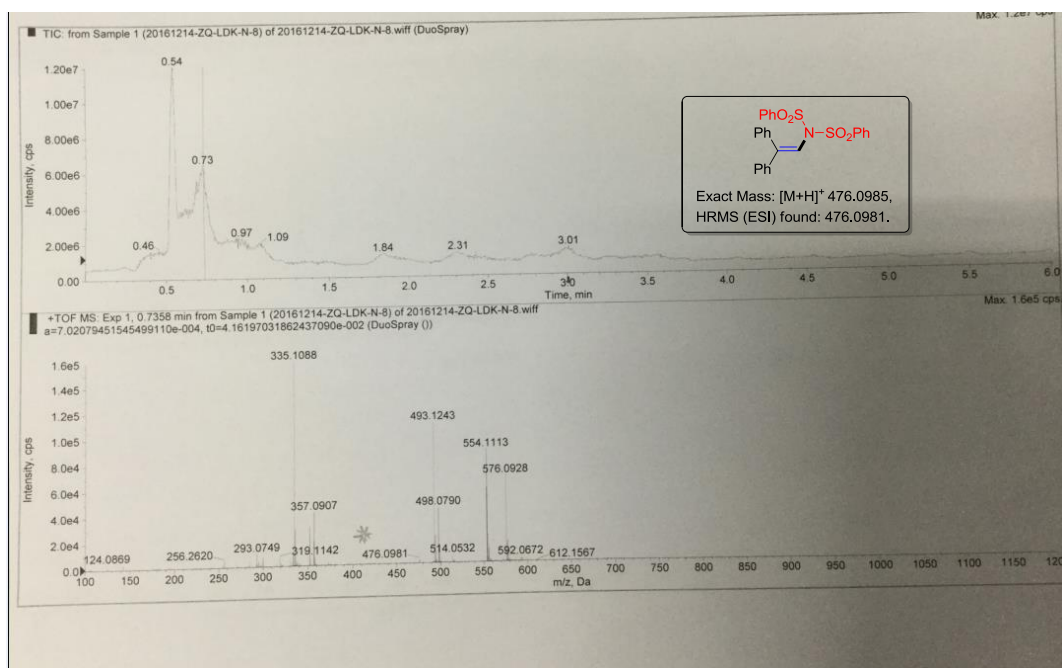
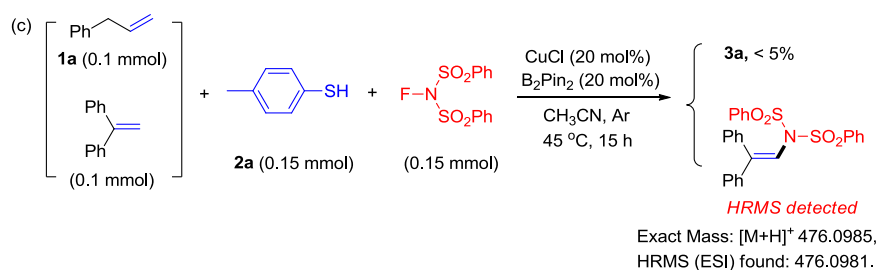
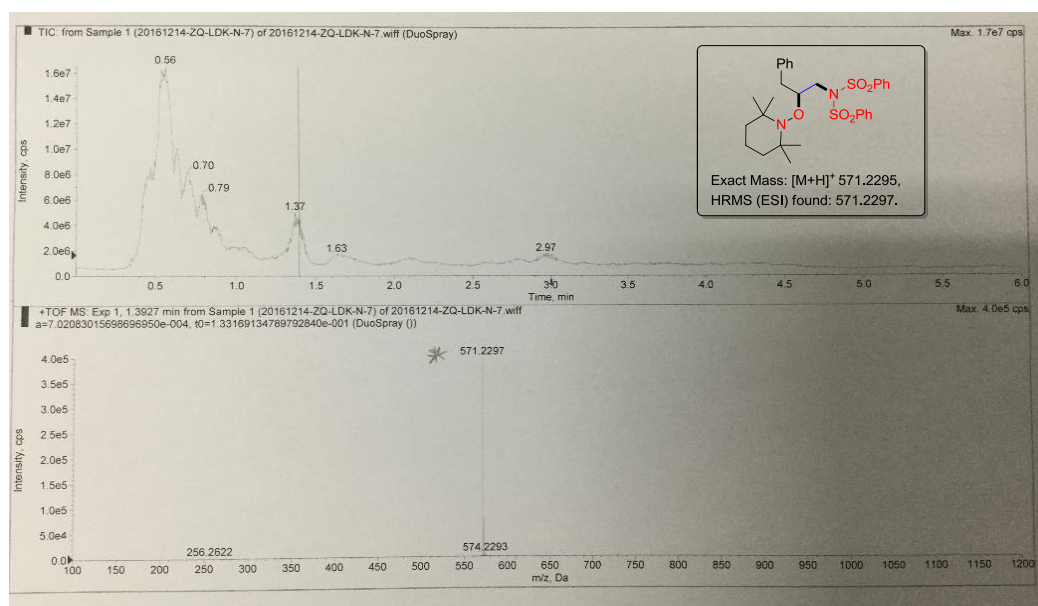
S = 1.038 Npar= 380

V. Mechanistic Studies

5.1 General procedure for the control experiments of 3a

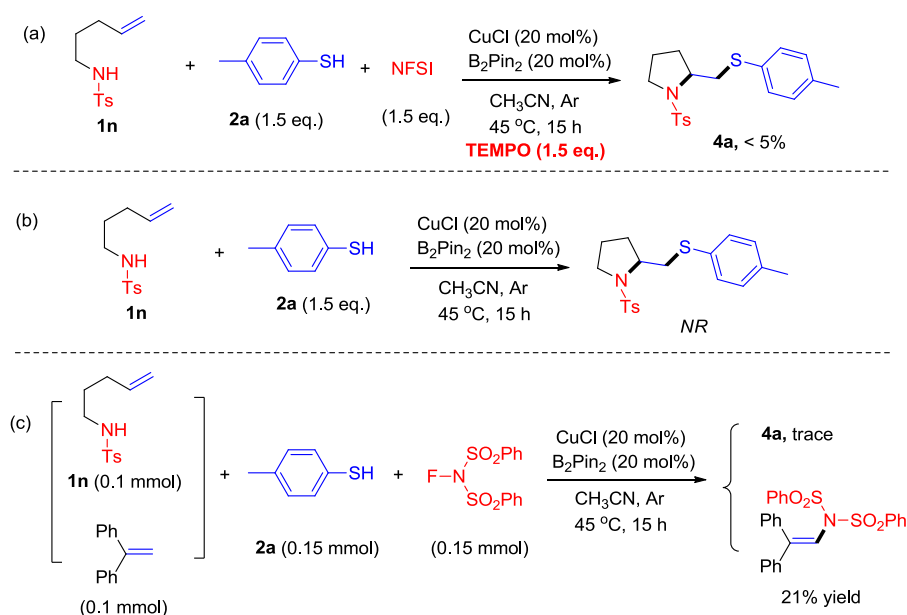
In a dry 10 mL Schlenk tube, allylbenzene (**1a**, 1.0 equiv, 0.1 mmol) was added to a solution of 4-methylbenzenethiol (**2a**, 1.5 equiv, 0.15 mmol), NFSI (1.5 equiv, 0.15 mmol), CuCl (20 mol%), B₂Pin₂ (20 mol%) and a radical scavenger, such as, butylated hydroxytoluene (BHT, 1.5 equiv, 0.15 mmol), or 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 1.5 equiv, 0.15 mmol), or 1,1-diphenylethylene (1.0 equiv, 0.1 mmol) in CH₃CN (1.5 mL) in Ar. Then the mixture was heated at 45 °C for 15 h. After completion of the reaction, it was cooled to room temperature. The residue was detected on High Resolution Mass (MS) analysis using a LC/MSD TOF spectrometer system with Electrospray Ionization (ESI).



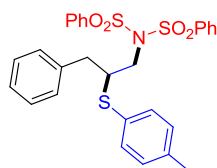


5.2 General procedure for the control experiments of 4a

In a dry 10 mL Schlenk tube, alkene substrate (**1n**, 1.0 equiv, 0.1 mmol) was added to a solution of 4-methylbenzenethiol (**2a**, 1.5 equiv, 0.15 mmol), NFSI (1.5 equiv, 0.15 mmol), CuCl (20 mol%), B₂Pin₂ (20 mol%) and a radical scavenger, such as, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 1.5 equiv, 0.15 mmol), or 1,1-diphenylethylene (1.0 equiv, 0.1 mmol) in CH₃CN (1.5 mL) in Ar. Then the mixture was heated at 45 °C for 15 h. After completion of the reaction, it was cooled to room temperature. The residue was detected on High Resolution Mass (MS) analysis using a LC/MSD TOF spectrometer system with Electrospray Ionization (ESI) or monitored by TLC.

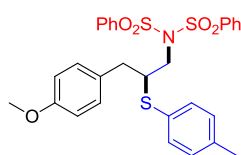


VI. Characterization Data



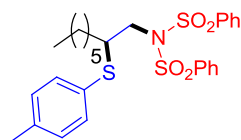
***N*-(3-phenyl-2-(*p*-tolylthio)propyl)-*N*-(phenylsulfonyl)benzenesulfonamide (3a)**

Colourless oil (66.0 mg, 61% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.86-7.84 (m, 4H), 7.63-7.59 (m, 2H), 7.47-7.43 (m, 4H), 7.30-7.23 (m, 5H), 7.11-7.10 (m, 2H), 7.05-7.03 (m, 2H), 3.94-3.89 (m, 1H), 3.86-3.80 (m, 1H), 3.77-3.70 (m, 1H), 3.02 (dd, $J = 14.0$ Hz, 5.6 Hz, 1H), 2.67 (dd, $J = 15.0$ Hz, 9.2 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): 139.06, 138.48, 137.61, 133.87, 132.95, 129.93, 129.76, 129.13, 128.97, 128.57, 128.32, 126.49, 52.13, 49.76, 38.25, 21.09; HRMS (ESI) calcd for $\text{C}_{28}\text{H}_{28}\text{NO}_4\text{S}_3^+ [\text{M}+\text{H}]^+$ 538.1175, found 538.1178.



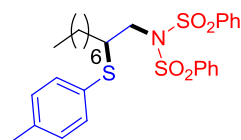
***N*-(3-(4-methoxyphenyl)-2-(*p*-tolylthio)propyl)-*N*-(phenylsulfonyl)benzenesulfonamide (3b)**

Colourless oil (67.0 mg, 59% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.87-7.85 (m, 4H), 7.64-7.60 (m, 2H), 7.48-7.44 (m, 4H), 7.25-7.23 (m, 2H), 7.11-7.09 (m, 2H), 6.97-6.95 (m, 2H), 6.83-6.81 (m, 2H), 3.92-3.86 (m, 1H), 3.85-3.78 (m, 1H), 3.80 (s, 3H), 3.73-3.66 (m, 1H), 2.95 (dd, $J = 14.4$ Hz, 5.6 Hz, 1H), 2.62 (dd, $J = 14.4$ Hz, 9.6 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): 158.29, 139.10, 137.55, 133.87, 132.90, 130.50, 130.11, 130.02, 129.75, 128.97, 128.59, 113.74, 55.24, 52.13, 49.95, 37.38, 21.10; HRMS (ESI) calcd for $\text{C}_{29}\text{H}_{30}\text{NO}_5\text{S}_3^+ [\text{M}+\text{H}]^+$ 568.1281, found 568.1290.



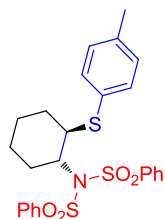
***N*-(phenylsulfonyl)-*N*-(2-(*p*-tolylthio)octyl)benzenesulfonamide (3c)**

Colourless oil (70.0 mg, 66% yield). ^1H NMR (500 MHz, CDCl_3): δ 7.89-7.88 (m, 4H), 7.64-7.62 (m, 2H), 7.51-7.48 (m, 4H), 7.34-7.33 (m, 2H), 7.16-7.14 (m, 2H), 3.87 (dd, $J = 15.0$ Hz, 11.0 Hz, 1H), 3.77 (dd, $J = 15.0$ Hz, 4.5 Hz, 1H), 3.45-3.40 (m, 1H), 2.37 (s, 3H), 1.65-1.63 (m, 2H), 1.29-1.16 (m, 8H), 0.89 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3): 139.40, 137.42, 133.83, 132.68, 130.06, 129.77, 128.96, 128.37, 53.12, 47.75, 31.65, 30.77, 28.95, 26.90, 22.55, 21.10, 14.04; HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{34}\text{NO}_4\text{S}_3^+$ $[\text{M}+\text{H}]^+$ 532.1644, found 532.1648.



***N*-(phenylsulfonyl)-*N*-(2-(*p*-tolylthio)nonyl)benzenesulfonamide (3d)**

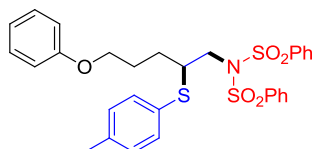
Colourless oil (69.0 mg, 63% yield). ^1H NMR (500 MHz, CDCl_3): δ 7.90-7.88 (m, 4H), 7.64-7.61 (m, 2H), 7.50-7.47 (m, 4H), 7.35-7.33 (m, 2H), 7.16-7.15 (m, 2H), 3.88 (dd, $J = 15.0$ Hz, 10.5 Hz, 1H), 3.78 (dd, $J = 15.0$ Hz, 5.0 Hz, 1H), 3.46-3.39 (m, 1H), 2.37 (s, 3H), 1.68-1.61 (m, 2H), 1.32-1.16 (m, 10H), 0.91 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3): 139.36, 137.39, 133.81, 132.66, 130.03, 129.75, 128.93, 128.33, 53.08, 47.73, 31.73, 30.75, 29.22, 29.10, 26.92, 22.58, 21.07, 14.06; HRMS (ESI) calcd for $\text{C}_{28}\text{H}_{36}\text{NO}_4\text{S}_3^+$ $[\text{M}+\text{H}]^+$ 546.1801, found 546.1809.



Phenylsulfonyl-*N*-2-(*p*-tolylthio)cyclohexylbenzenesulfonamide (3e)

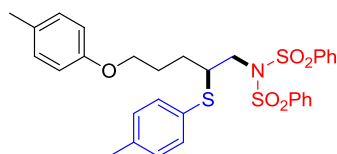
White solid (25.0 mg, 25% yield) mp 171-173 $^\circ\text{C}$. ^1H NMR (500 MHz, CDCl_3): δ 8.30 (br, s, 2H), 7.97 (br, s, 2H), 7.63 (br, s, 2H), 7.52 (br, s, 4H), 7.32-7.30 (m, 2H),

7.11-7.09 (m, 2H), 4.05-4.00 (m, 1H), 3.89-3.84 (m, 1H), 2.32 (s, 3H), 2.30-2.20 (m, 1H), 2.06-2.03 (m, 1H), 1.72-1.71 (m, 2H), 1.60-1.56 (m, 1H), 1.30-1.26 (m, 1H), 1.19-1.15 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3): 137.03, 134.08, 133.47, 132.59, 130.65, 129.67, 128.90, 128.52, 67.29, 49.97, 35.84, 32.82, 26.55, 25.53, 21.04; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{28}\text{NO}_4\text{S}_3^+$ $[\text{M}+\text{H}]^+$ 502.1175, found 502.1164.



***N*-(5-phenoxy-2-(*p*-tolylthio)pentyl)-*N*-(phenylsulfonyl)benzenesulfonamide (3f)**

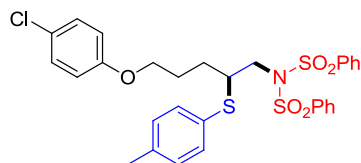
Colourless oil (61.0 mg, 52% yield). ^1H NMR (500 MHz, CDCl_3): δ 7.90-7.88 (m, 4H), 7.60-7.57 (m, 2H), 7.46-7.43 (m, 4H), 7.38-7.36 (m, 2H), 7.32-7.29 (m, 2H), 7.18-7.16 (m, 2H), 6.98-6.95 (m, 1H), 6.89-6.87 (m, 2H), 3.94-3.89 (m, 1H), 3.88-3.85 (m, 2H), 3.84-3.80 (m, 1H), 3.55-3.49 (m, 1H), 2.38 (s, 3H), 2.21-2.13 (m, 1H), 1.92-1.85 (m, 1H), 1.78-1.70 (m, 1H), 1.50-1.42 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3): 158.92, 139.18, 137.70, 133.88, 133.03, 129.82, 129.53, 129.38, 128.97, 128.36, 120.58, 114.54, 67.37, 52.90, 47.79, 27.58, 26.76, 21.11; HRMS (ESI) calcd for $\text{C}_{30}\text{H}_{32}\text{NO}_5\text{S}_3^+$ $[\text{M}+\text{H}]^+$ 582.1437, found 582.1404.



***N*-(phenylsulfonyl)-*N*-(5-(*p*-tolyloxy)-2-(*p*-tolylthio)pentyl)benzenesulfonamide (3g)**

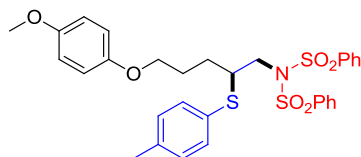
Colourless oil (64.0 mg, 54% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.89-7.87 (m, 4H), 7.61-7.57 (m, 2H), 7.47-7.43 (m, 4H), 7.36-7.34 (m, 2H), 7.17-7.15 (m, 2H), 7.10-7.08 (m, 2H), 6.78-6.76 (m, 2H), 3.92-3.86 (m, 1H), 3.84-3.77 (m, 3H), 3.54-3.46 (m, 1H), 2.37 (s, 3H), 2.30 (s, 3H), 2.20-2.09 (m, 1H), 1.90-1.81 (m, 1H), 1.76-1.66 (m, 1H), 1.49-1.39 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3): 156.84, 139.23, 137.69, 133.89, 133.04, 129.83, 129.77, 129.59, 128.99, 128.40, 114.45, 67.58, 52.92, 47.82, 27.60, 26.82, 21.12, 20.45; HRMS (ESI) calcd for $\text{C}_{31}\text{H}_{34}\text{NO}_5\text{S}_3^+$ $[\text{M}+\text{H}]^+$

596.1594, found 596.1563.



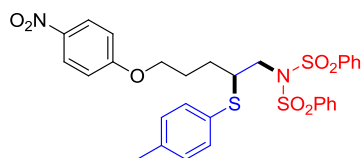
***N*-(5-(4-chlorophenoxy)-2-(*p*-tolylthio)pentyl)-*N*-(phenylsulfonyl)benzenesulfonamide (3h)**

Colourless oil (71.0 mg, 58% yield). ^1H NMR (500 MHz, CDCl_3): δ 7.87-7.85 (m, 4H), 7.61-7.58 (m, 2H), 7.46-7.43 (m, 4H), 7.36-7.35 (m, 2H), 7.26-7.23 (m, 2H), 7.17-7.16 (m, 2H), 6.80-6.78 (m, 2H), 3.90 (dd, $J = 15.0$ Hz, 10.5 Hz, 1H), 3.85-3.78 (m, 3H), 3.54-3.48 (m, 1H), 2.38 (s, 3H), 2.19-2.11 (m, 1H), 1.91-1.84 (m, 1H), 1.76-1.68 (m, 1H), 1.49-1.41 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3): 157.52, 139.15, 137.75, 133.89, 133.00, 129.84, 129.49, 129.23, 128.97, 128.36, 125.42, 115.83, 67.80, 52.87, 47.75, 27.45, 26.61, 21.10; HRMS (ESI) calcd for $\text{C}_{30}\text{H}_{30}\text{ClNNaO}_5\text{S}_3^+$ $[\text{M}+\text{Na}]^+$ 638.0867, found 638.0868.



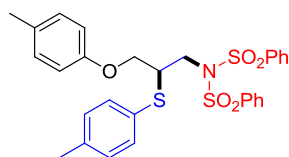
***N*-(5-(4-methoxyphenoxy)-2-(*p*-tolylthio)pentyl)-*N*-(phenylsulfonyl)benzenesulfonamide (3i)**

Colourless oil (76.0 mg, 62% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.88-7.86 (m, 4H), 7.61-7.57 (m, 2H), 7.46-7.42 (m, 4H), 7.36-7.34 (m, 2H), 7.17-7.15 (m, 2H), 6.86-6.83 (m, 2H), 6.82-6.79 (m, 2H), 3.89 (dd, $J = 15.0$ Hz, 10.5 Hz, 1H), 3.83-3.76 (m, 3H), 3.78 (s, 3H), 3.55-3.50 (m, 1H), 2.37 (s, 3H), 2.18-2.08 (m, 1H), 1.91-1.82 (m, 1H), 1.75-1.65 (m, 1H), 1.49-1.39 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3): 153.79, 153.15, 139.22, 137.70, 133.89, 133.03, 129.84, 129.61, 128.99, 128.41, 115.55, 114.64, 68.20, 55.75, 52.91, 47.82, 27.60, 26.86, 21.12; HRMS (ESI) calcd for $\text{C}_{31}\text{H}_{33}\text{NNaO}_6\text{S}_3^+$ $[\text{M}+\text{Na}]^+$ 634.1362, found 634.1354.



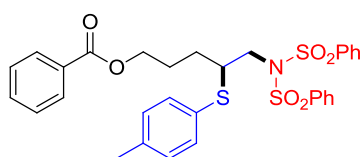
***N*-(5-(4-nitrophenoxy)-2-(*p*-tolylthio)pentyl)-*N*-(phenylsulfonyl)benzenesulfonamide (3j)**

White solid (73.0 mg, 58% yield) mp 119-121 °C. ¹H NMR (500 MHz, CDCl₃): δ 8.21-8.20 (m, 2H), 7.81-7.80 (m, 4H), 7.62-7.59 (m, 2H), 7.46-7.43 (m, 4H), 7.36-7.35 (m, 2H), 7.18-7.16 (m, 2H), 6.92-6.90 (m, 2H), 3.99-3.96 (m, 2H), 3.90 (dd, *J* = 15.0 Hz, 11.0 Hz, 1H), 3.77 (dd, *J* = 15.0 Hz, 4.5 Hz, 1H), 3.55-3.49 (m, 1H), 2.38 (s, 3H), 2.23-2.17 (m, 1H), 1.96-1.89 (m, 1H), 1.82-1.73 (m, 1H), 1.52-1.42 (m, 1H); ¹³C NMR (125 MHz, CDCl₃): 163.94, 141.38, 138.97, 137.89, 133.95, 132.98, 129.91, 129.33, 128.99, 128.35, 125.88, 114.43, 68.31, 52.77, 47.62, 27.18, 26.37, 21.14; HRMS (ESI) calcd for C₃₀H₃₀N₂NaO₇S₃⁺ [M+Na]⁺ 649.1107, found 649.1082.



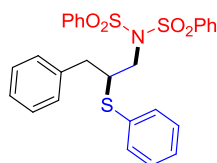
***N*-(phenylsulfonyl)-*N*-(3-(*p*-tolylloxy)-2-(*p*-tolylthio)propyl)benzenesulfonamide (3k)**

Colourless oil (51.0 mg, 45% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.93-7.91 (m, 4H), 7.62-7.58 (m, 2H), 7.46-7.42 (m, 4H), 7.38-7.36 (m, 2H), 7.17-7.15 (m, 2H), 7.09-7.07 (m, 2H), 6.75-6.73 (m, 2H), 4.26-4.20 (m, 1H), 4.09-4.05 (m, 1H), 4.02-3.92 (m, 2H), 3.89-3.83 (m, 1H), 2.38 (s, 3H), 2.31 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): 156.17, 138.90, 137.99, 133.87, 133.32, 130.32, 129.85, 129.81, 129.36, 128.94, 128.50, 114.53, 67.44, 49.32, 47.73, 21.10, 20.45; HRMS (ESI) calcd for C₂₉H₂₉NNaO₅S₃⁺ [M+Na]⁺ 590.1100, found 590.1093.



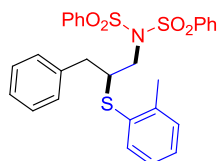
5-(*N*-(phenylsulfonyl)phenylsulfonamido)-4-(*p*-tolylthio)pentylbenzoate (3l)

Colourless oil (76.0 mg, 62% yield). ^1H NMR (400 MHz, CDCl_3): δ 8.03-8.01 (m, 2H), 7.88-7.86 (m, 4H), 7.60-7.55 (m, 3H), 7.46-7.42 (m, 6H), 7.35-7.33 (m, 2H), 7.15-7.13 (m, 2H), 4.24-4.15 (m, 2H), 3.93-3.80 (m, 2H), 3.49-3.41 (m, 1H), 2.36 (s, 3H), 2.22-2.10 (m, 1H), 1.90-1.82 (m, 1H), 1.70-1.62 (m, 1H), 1.46-1.38 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3): 166.50, 139.29, 137.82, 133.93, 133.05, 132.84, 130.33, 129.88, 129.63, 129.35, 129.01, 128.35, 128.31, 64.43, 52.97, 47.53, 27.41, 26.27, 21.11; HRMS (ESI) calcd for $\text{C}_{31}\text{H}_{31}\text{NNaO}_6\text{S}_3^+$ $[\text{M}+\text{Na}]^+$ 632.1206, found 632.1218.



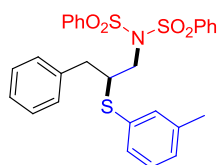
***N*-(3-phenyl-2-(phenylthio)propyl)-*N*-(phenylsulfonyl)benzenesulfonamide (3m)**

Colourless oil (64.0 mg, 61% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.91-7.89 (m, 4H), 7.66-7.63 (m, 2H), 7.51-7.47 (m, 4H), 7.39-7.36 (m, 2H), 7.34-7.28 (m, 6H), 7.09-7.07 (m, 2H), 4.00-3.88 (m, 2H), 3.87-3.81 (m, 1H), 3.10-3.05 (m, 1H), 2.76-2.70 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3): 139.04, 138.35, 133.90, 132.19, 129.12, 129.00, 128.55, 128.35, 127.33, 126.55, 52.13, 49.49, 38.28; HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{25}\text{NNaO}_4\text{S}_3^+$ $[\text{M}+\text{Na}]^+$ 546.0838, found 546.0858.



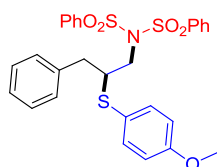
***N*-(3-phenyl-2-(o-tolylthio)propyl)-*N*-(phenylsulfonyl)benzenesulfonamide (3n)**

Colourless oil (42.0 mg, 39% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.84-7.81 (m, 4H), 7.63-7.59 (m, 2H), 7.47-7.43 (m, 4H), 7.39-7.37 (m, 1H), 7.32-7.21 (m, 3H), 7.19-7.13 (m, 3H), 7.09-7.04 (m, 2H), 3.95-3.82 (m, 2H), 3.80-3.71 (m, 1H), 3.10 (dd, $J = 14.5$ Hz, 5.0 Hz, 1H), 2.67 (dd, $J = 14.4$ Hz, 10.0 Hz, 1H), 2.22 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): 140.37, 138.96, 138.42, 133.88, 133.14, 132.72, 130.48, 129.15, 128.99, 128.54, 128.28, 127.51, 126.51, 126.45, 52.08, 49.05, 38.29, 20.58; HRMS (ESI) calcd for $\text{C}_{28}\text{H}_{27}\text{NNaO}_4\text{S}_3^+$ $[\text{M}+\text{Na}]^+$ 560.0994, found 560.0986.



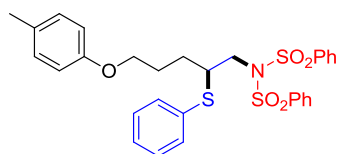
***N*-(3-phenyl-2-(*m*-tolylthio)propyl)-*N*-(phenylsulfonyl)benzenesulfonamide (3o)**

Colourless oil (45.0 mg, 42% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.88-7.86 (m, 4H), 7.63-7.60 (m, 2H), 7.48-7.44 (m, 4H), 7.30-7.25 (m, 3H), 7.20-7.14 (m, 3H), 7.07-7.03 (m, 3H), 3.97-3.92 (m, 1H), 3.88-3.78 (m, 2H), 3.04 (dd, $J = 14.4$ Hz, 5.0 Hz, 1H), 2.68 (dd, $J = 14.4$ Hz, 9.2 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): 139.07, 138.78, 138.39, 133.89, 133.59, 132.51, 129.13, 128.99, 128.94, 128.81, 128.55, 128.32, 128.07, 126.52, 52.23, 49.17, 38.22, 21.24; HRMS (ESI) calcd for $\text{C}_{28}\text{H}_{27}\text{NNaO}_4\text{S}_3^+$ $[\text{M}+\text{Na}]^+$ 560.0994, found 560.0991.



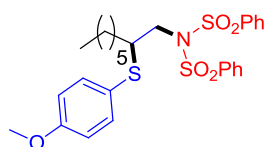
***N*-(2-((4-methoxyphenyl)thio)-3-phenylpropyl)-*N*-(phenylsulfonyl)benzenesulfonamide (3p)**

Colourless oil (67.0 mg, 60% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.86-7.84 (m, 4H), 7.64-7.60 (m, 2H), 7.48-7.44 (m, 4H), 7.31-7.24 (m, 5H), 7.05-7.03 (m, 2H), 6.84-6.82 (m, 2H), 3.90 (dd, $J = 15.0$ Hz, 6.4 Hz, 1H), 3.86-3.78 (m, 1H), 3.81 (s, 3H), 3.67-3.60 (m, 1H), 2.97 (dd, $J = 14.4$ Hz, 5.6 Hz, 1H), 2.66 (dd, $J = 14.4$ Hz, 9.6 Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3): 159.75, 139.07, 138.59, 135.66, 133.87, 129.16, 128.97, 128.60, 128.33, 126.48, 123.73, 114.58, 55.33, 52.11, 50.52, 38.29; HRMS (ESI) calcd for $\text{C}_{28}\text{H}_{27}\text{NNaO}_5\text{S}_3^+$ $[\text{M}+\text{Na}]^+$ 576.0944, found 576.0931.



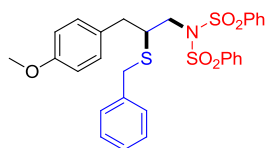
***N*-(phenylsulfonyl)-*N*-(2-(phenylthio)-5-(*p*-tolylloxy)pentyl)benzenesulfonamide (3q)**

Colourless oil (58.0 mg, 50% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.90-7.89 (m, 4H), 7.61-7.57 (m, 2H), 7.47-7.43 (m, 6H), 7.37-7.29 (m, 3H), 7.11-7.09 (m, 2H), 6.79-6.76 (m, 2H), 3.92 (dd, $J = 15.2$ Hz, 10.4 Hz, 1H), 3.85-3.77 (m, 3H), 3.63-3.56 (m, 1H), 2.31 (s, 3H), 2.20-2.09 (m, 1H), 1.93-1.85 (m, 1H), 1.77-1.67 (m, 1H), 1.53-1.43 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3): 156.80, 139.16, 133.91, 133.61, 132.19, 129.82, 129.78, 129.07, 129.00, 128.37, 127.36, 114.42, 67.52, 52.87, 47.47, 27.67, 26.80, 20.44; HRMS (ESI) calcd for $\text{C}_{30}\text{H}_{31}\text{NNaO}_5\text{S}_3^+$ $[\text{M}+\text{Na}]^+$ 604.1257, found 604.1261.



***N*-(2-((4-methoxyphenyl)thio)octyl)-*N*-(phenylsulfonyl)benzenesulfonamide (3r)**

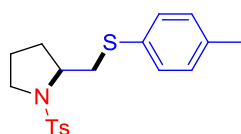
Colourless oil (44.0 mg, 40% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.87-7.85 (m, 4H), 7.65-7.61 (m, 2H), 7.51-7.47 (m, 4H), 7.39-7.36 (m, 2H), 6.89-6.87 (m, 2H), 3.88-3.83 (m, 1H), 3.83 (s, 3H), 3.77-3.72 (m, 1H), 3.33-3.27 (m, 1H), 1.62-1.60 (m, 2H), 1.27-1.17 (m, 8H), 0.88 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3): 159.68, 139.38, 135.50, 133.84, 128.97, 128.39, 123.69, 114.60, 55.36, 53.08, 48.50, 31.67, 30.73, 28.96, 26.88, 22.57, 14.06; HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{33}\text{NNaO}_5\text{S}_3^+$ $[\text{M}+\text{Na}]^+$ 570.1413, found 570.1414.



***N*-(2-(benzylthio)-3-(4-methoxyphenyl)propyl)-*N*-(phenylsulfonyl)benzenesulfonamide (3t)**

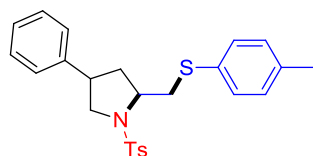
Colourless oil (31.0 mg, 27% yield). colourless oil. ^1H NMR (400 MHz, CDCl_3): δ 7.91-7.89 (m, 4H), 7.65-7.61 (m, 2H), 7.50-7.46 (m, 4H), 7.27-7.26 (m, 3H), 7.19-7.17 (m, 2H), 6.75-6.73 (m, 2H), 6.68-6.66 (m, 2H), 4.05 (dd, $J = 15.2$ Hz, 6.0 Hz, 1H), 3.81 (s, 3H), 3.80-3.72 (m, 1H), 3.67-3.64 (m, 1H), 3.50-3.47 (m, 1H),

3.06-2.99 (m, 1H), 2.84 (dd, $J = 14.4$ Hz, 5.2 Hz, 1H), 2.51 (dd, $J = 14.4$ Hz, 10.0 Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3): 158.15, 139.61, 137.88, 133.80, 130.58, 130.15, 129.02, 128.45, 128.41, 126.94, 113.50, 55.26, 52.80, 45.24, 37.66, 35.44; HRMS (ESI) calcd for $\text{C}_{29}\text{H}_{29}\text{NNaO}_5\text{S}_3^+$ $[\text{M}+\text{Na}]^+$ 590.1100, found 590.1107.



2-((*p*-tolylthio)methyl)-1-tosylpyrrolidine (4a)

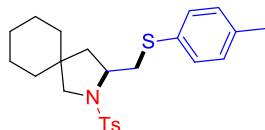
Colourless oil (62.0 mg, 86% yield). ^1H NMR (500 MHz, CDCl_3): δ 7.52 (d, $J = 8.0$ Hz, 2H), 7.36 (d, $J = 8.0$ Hz, 2H), 7.22 (d, $J = 8.0$ Hz, 2H), 7.16 (d, $J = 8.0$ Hz, 2H), 3.65-3.57 (m, 2H), 3.49-3.45 (m, 1H), 3.11-3.06 (m, 1H), 2.74 (dd, $J = 13.0$ Hz, 10.5 Hz, 1H), 2.39 (s, 3H), 2.36 (s, 3H), 1.89-1.82 (m, 1H), 1.81-1.74 (m, 1H), 1.65-1.58 (m, 1H), 1.53-1.47 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3): 143.30, 135.99, 133.75, 131.44, 129.64, 129.60, 129.49, 127.34, 58.89, 49.59, 38.91, 30.10, 23.61, 21.35, 20.88; HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{23}\text{NNaO}_2\text{S}_2^+$ $[\text{M}+\text{Na}]^+$ 384.1062, found 384.1067.



4-Phenyl-2-((*p*-tolylthio)methyl)-1-tosylpyrrolidine (4b)

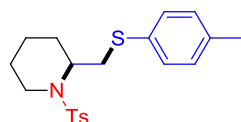
Colourless oil (72.0 mg, 82% yield, *d.r.* = 1.7 : 1). ^1H NMR (400 MHz, CDCl_3): δ 7.60-7.58 (m, 1.3H), 7.52-7.50 (m, 2.1H), 7.40-7.38 (m, 2.1H), 7.37-7.35 (m, 1.3H), 7.27-7.19 (m, 9.7H), 7.16-7.14 (m, 2.3H), 7.07-7.05 (m, 1.3H), 7.02-7.01 (m, 2.1H), 3.91-3.87 (m, 1.1H), 3.85-3.80 (m, 1.4H), 3.78-3.67 (m, 2.8H), 3.51-3.44 (m, 1.0H), 3.43-3.37 (m, 0.7H), 2.96-2.88 (m, 2.1H), 2.86-2.82 (m, 0.8H), 2.57-2.44 (m, 1.5H), 2.41 (s, 1.8H), 2.39 (s, 3H), 2.36 (s, 3.2H), 2.35 (s, 1.9H), 1.92-1.83 (m, 0.7H), 1.67-1.60 (m, 1.0H); ^{13}C NMR (125 MHz, CDCl_3): 143.56, 143.51, 139.14, 136.23, 134.45, 133.19, 131.55, 131.21, 130.01, 129.87, 129.75, 129.72, 129.70, 129.58, 128.52, 127.51, 127.40, 126.97, 126.84, 126.80, 59.83, 58.83, 55.45, 55.37, 42.74,

41.13, 40.16, 39.32, 38.89, 36.00, 21.44, 21.42, 20.94; HRMS (ESI) calcd for $C_{25}H_{27}NNaO_2S_2^+$ $[M+Na]^+$ 460.1375, found 460.1378.



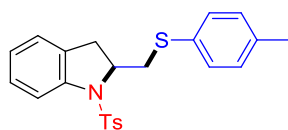
3-((*p*-tolylthio)methyl)-2-tosyl-2-azaspiro[4.5]decane (4c)

Colourless oil (80.0 mg, 93% yield). 1H NMR (500 MHz, $CDCl_3$): δ 7.51 (d, J = 7.5 Hz, 2H), 7.36 (d, J = 7.5 Hz, 2H), 7.20 (d, J = 7.5 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 3.88 (dd, J = 13.5 Hz, 2.0 Hz, 1H), 3.56-3.52 (m, 1H), 3.19 (s, 2H), 2.83 (dd, J = 12.5 Hz, 11.0 Hz, 1H), 2.39 (s, 3H), 2.36 (s, 3H), 1.92-1.88 (m, 1H), 1.59-1.55 (m, 1H), 1.42-1.32 (m, 4H), 1.25-1.07 (m, 4H), 0.74-0.70 (m, 1 H), 0.56-0.53 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): 143.28, 136.21, 134.14, 131.74, 130.14, 129.71, 129.42, 127.47, 59.03, 58.36, 44.17, 41.15, 40.51, 36.24, 34.24, 25.74, 23.53, 22.84, 21.43, 20.97; HRMS (ESI) calcd for $C_{24}H_{31}NNaO_2S_2^+$ $[M+Na]^+$ 452.1688, found 452.1698.



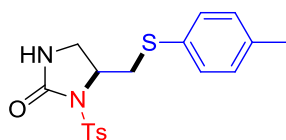
2-((*p*-tolylthio)methyl)-1-tosylpiperidine (4d)

Colourless oil (24.0 mg, 32% yield). 1H NMR (500 MHz, $CDCl_3$): δ 7.62 (d, J = 8.5 Hz, 2H), 7.26-7.23 (m, 4H), 7.11 (d, J = 8.0 Hz, 2H), 4.12-4.10 (m, 1H), 3.79-3.77 (m, 1H), 3.06-2.92 (m, 3H), 2.41 (s, 3H), 2.33 (s, 3H), 1.98-1.97 (m, 1H), 1.54-1.51 (m, 2H), 1.44-1.39 (m, 2H), 1.37-1.27 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): 142.94, 138.18, 136.51, 131.43, 130.32, 129.73, 129.56, 126.96, 51.73, 40.92, 33.61, 25.25, 24.55, 21.45, 20.99, 18.05; HRMS (ESI) calcd for $C_{20}H_{25}NNaO_2S_2^+$ $[M+Na]^+$ 398.1219, found 398.1232.



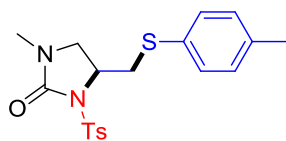
2-((*p*-tolylthio)methyl)-1-tosylindoline (4e)

White solid (32.0 mg, 39% yield) mp 113-115 °C. ^1H NMR (500 MHz, CDCl_3): δ 7.65 (d, J = 8.0 Hz, 1H), 7.40 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.22-7.19 (m, 1H), 7.18-7.17 (m, 2H), 7.09 (d, J = 8.0 Hz, 2H), 7.05-7.01 (m, 2H), 4.26-4.20 (m, 1H), 3.66 (dd, J = 13.6 Hz, 3.4 Hz, 1H), 2.92-2.80 (m, 3H), 2.37 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): 143.90, 141.25, 136.34, 134.63, 131.04, 129.85, 129.69, 129.54, 127.79, 126.98, 125.25, 124.70, 116.99, 60.82, 39.14, 33.23, 21.48, 21.02; HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{23}\text{NNaO}_2\text{S}_2^+$ $[\text{M}+\text{Na}]^+$ 432.1062, found 432.1069.



5-((*p*-tolylthio)methyl)-1-tosylimidazolidin-2-one (4f)

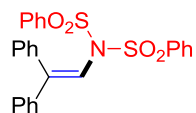
White solid (43.0 mg, 57% yield) mp 104-105 °C. ^1H NMR (500 MHz, CDCl_3): δ 7.80-7.78 (m, 2H), 7.72 (br, s, 1H), 7.28-7.24 (m, 4H), 7.10-7.09 (m, 2H), 4.76-4.70 (m, 1H), 3.84 (t, J = 10.0 Hz, 1H), 3.57 (dd, J = 10.0 Hz, 7.0 Hz, 1H), 3.27 (dd, J = 14.0 Hz, 4.5 Hz, 1H), 2.95 (dd, J = 14.0 Hz, 9.0 Hz, 1H), 2.39 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): 161.13, 142.80, 139.24, 137.92, 131.57, 130.10, 129.53, 129.24, 126.34, 46.88, 37.73, 21.43, 20.99; HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{20}\text{N}_2\text{NaO}_3\text{S}_2^+$ $[\text{M}+\text{Na}]^+$ 399.0808, found 399.0821.



1-Methyl-4-((*p*-tolylthio)methyl)-3-tosylimidazolidin-2-one (4g)

White solid (31.0 mg, 40% yield) mp 133-134 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.86-7.84 (m, 2H), 7.28-7.22 (m, 4H), 7.14-7.12 (m, 2H), 4.76-4.69 (m, 1H), 3.67 (t, J = 9.2 Hz, 1H), 3.39 (dd, J = 9.6 Hz, 6.4 Hz, 1H), 3.24 (dd, J = 14.0 Hz, 4.4 Hz, 1H), 2.90 (s, 3H), 2.82 (dd, J = 14.0 Hz, 9.6 Hz, 1H), 2.39 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): 157.57, 142.18, 140.02, 138.04, 131.52, 130.16, 129.37, 128.91,

127.05, 51.67, 37.57, 31.77, 21.43, 21.01; HRMS (ESI) calcd for $C_{19}H_{22}N_2NaO_3S_2^+$ $[M+Na]^+$ 413.0964, found 413.0974.



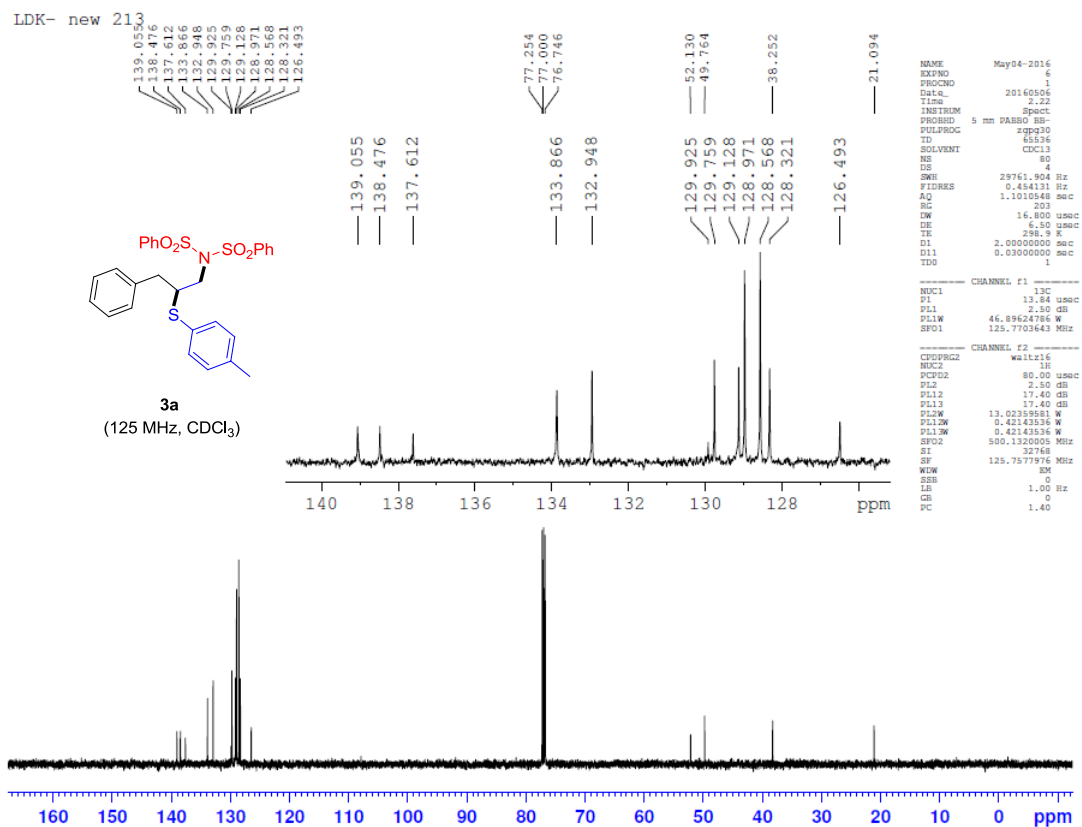
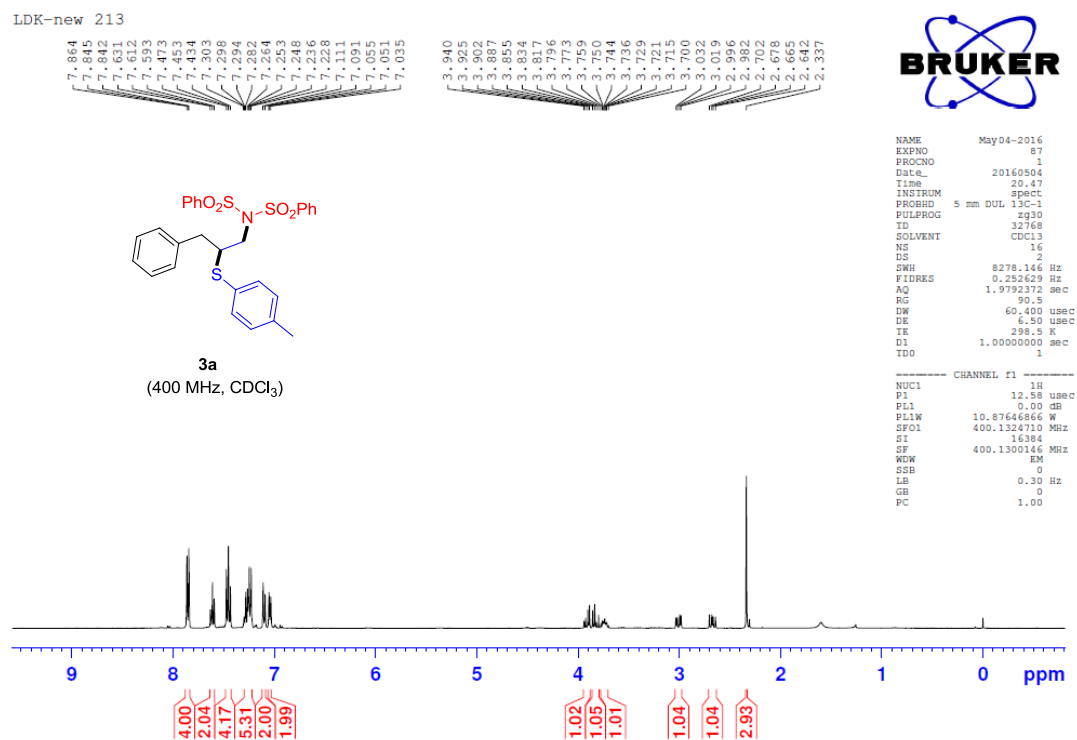
***N*-(2,2-diphenylvinyl)-*N*-(phenylsulfonyl)benzenesulfonamide⁵**

White solid. 1H NMR (400 MHz, $CDCl_3$): δ 7.71-7.68 (m, 4H), 7.57-7.54 (m, 2H), 7.40-7.35 (m, 4H), 7.34-7.31 (m, 3H), 7.29-7.17 (m, 7H), 6.13 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): 152.22, 139.85, 138.80, 136.75, 133.73, 129.86, 129.03, 128.74, 128.63, 128.35, 128.20, 128.08, 116.40.

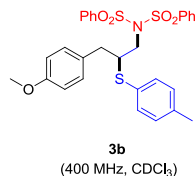
VII. References

1. J. Xu, Y. Fu, D.-F. Luo, Y.-Y. Jiang, B. Xiao, Z.-J. Liu, T.-J. Gong, L. Liu, *J. Am. Chem. Soc.* 2011, **133**, 15300.
2. W. E. Brenzovich, Jr., D. Benitez, A. D. Lackner, H. P. Shunatona, E. Tkatchouk, W. A. Goddard, 3rd, F. D. Toste, *Angew. Chem., Int. Ed.* 2010, **49**, 5519.
3. M. T. Bovino, S. R. Chemler, *Angew. Chem., Int. Ed.* 2012, **51**, 3923.
4. S. Nicolai, C. Piemontesi, J. Waser, *Angew. Chem., Int. Ed.* 2011, **50**, 4680.
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VIII. Copies of ^1H and ^{13}C NMR Spectra

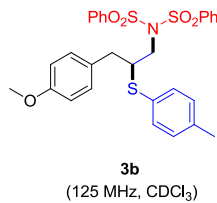


LDK- new 223



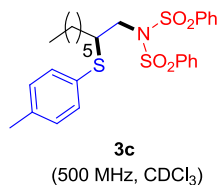
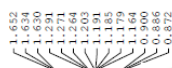
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 PULPROG zg30
 ID 22768
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 8278.146 Hz
 FIDRES 0.252629 Hz
 AQ 1.9792372 sec
 RG 114
 DW 60.400 usec
 DE 6.50 usec
 TE 298.6 K
 D1 1.00000000 sec
 TDO 1
 CHANNEL f1
 NUC1 13C
 P1 12.58 usec
 PL1 0.00 dB
 PL1W 10.8764686 W
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 SI 16384
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 PC 1.00

LDK- new 223



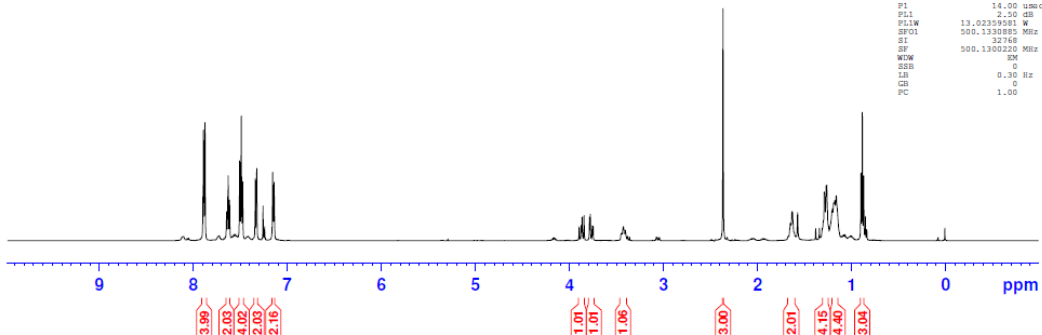
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 Time 12.09
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 ID 6534
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 NS 120
 DS 4
 SWH 29761.904 Hz
 FIDRES 0.484131 Hz
 AQ 1.1010548 sec
 RG 203
 DW 16.800 usec
 DE 6.50 usec
 TE 298.5 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TDO 1
 CHANNEL f1
 NUC1 13C
 P1 13.84 usec
 PL1 2.50 dB
 PL1W 46.89624786 W
 SFO1 125.7703443 MHz
 CHANNEL f2
 NUC2 1H
 P2 80.00 usec
 PL2 2.50 dB
 PL2W 17.40 dB
 PL13 17.40 dB
 PL1W 13.02359881 W
 PL12W 0.42143536 W
 PL13W 0.42143536 W
 SFO2 500.1320000 MHz
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 SSB 0
 LB 1.00 Hz
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 PC 1.40

LDK-239 NEW

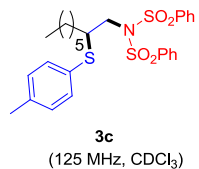


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 PROCNO 1
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 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 10330.578 Hz
 FIDRES 0.127632 Hz
 AQ 3.1719923 sec
 RG 90.5
 WC 49.400 umsec
 DE 6.50 umsec
 TE 298.1 K
 D1 1.00000000 sec
 TDO 1

----- CHANNEL f1 -----
 NUC1 1H
 P1 14.00 umsec
 PL1 2.50 dB
 PL1W 13.02359581 W
 SFO1 500.1300200 MHz
 SI 32768
 SF 500.1300200 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



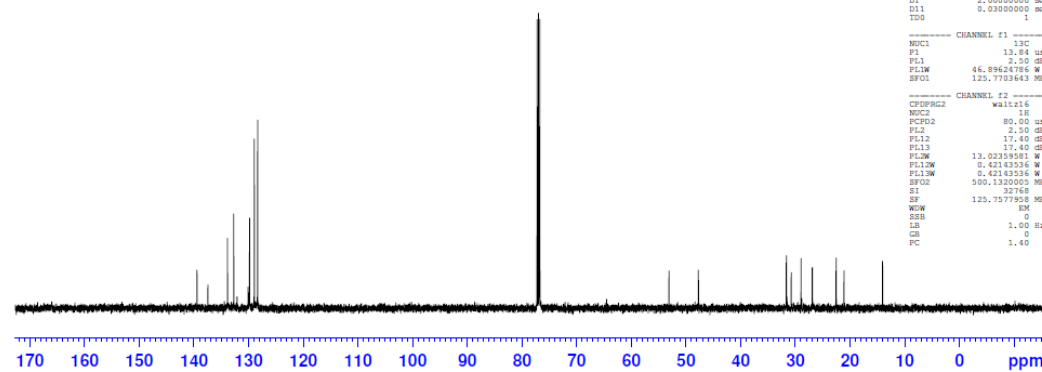
LDK-239 NEW



NAME sn500c
 EXPNO 57
 PROCNO 1
 DATE_ 20160225
 TIME 1.08
 INSTRUM spect
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 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 100
 DS 1
 SWH 29761.904 Hz
 FIDRES 0.434131 Hz
 AQ 1.1010548 sec
 RG 203
 WC 16.800 umsec
 DE 6.50 umsec
 TE 298.2 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TDO 1

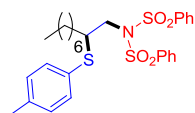
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 P1 13.86 umsec
 PL1 2.50 dB
 PL1W 46.89626785 W
 SFO1 125.7703643 MHz

----- CHANNEL f2 -----
 CFPFREQ waltz16
 NUC2 1H
 PCPD2 80.00 umsec
 PL2 2.50 dB
 PL12 17.40 dB
 PL13 17.40 dB
 PL1W 13.02359581 W
 PL12W 0.42143536 W
 PL13W 0.42143536 W
 SFO2 500.1300200 MHz
 SI 32768
 SF 125.7577568 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

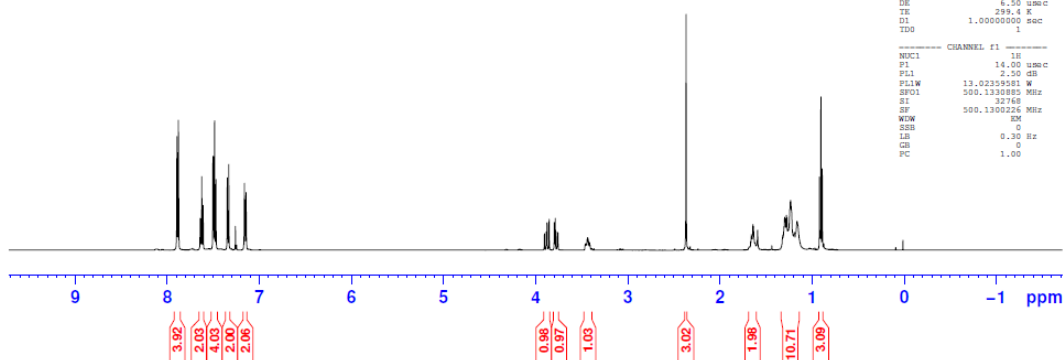


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1990	23.0
1995	24.5
2000	26.0
2005	27.5
2010	29.0

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3.5161
3.5161
3.5150
3.5150
3.5140
3.5140



3d
(500 MHz, CDCl₃)



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NAME                               sm500h
EXPNO                               4
PROCNO                              1
DATE_                                20111111
TIME                               7.50
INSTRUM                             LUNO
PROBHD 5 mm F4BBO-BB              zgpg
PULPROG                             zg30
PCPDPRG                             zgpg36
TD                                65536
SOLVENT                             CDCl3
DS                                  16
NS                                   2
DSH                                  0
AQW                                  10330.575 Hz
AQWRES                              0.1767475 Hz
RG                                  3.7119923 sec
RG                                  6.50
DE                                  40.400 usec
DE                                  58.8
TE                                  299.4 K
D1                                  1.00000000 sec
TD0                                  1
===== CHANNEL f1 =====
NUC1                                P1
P1                                  14.00 usec
P2                                  P11
P11                                2.50 dB
P12                                13.02200000 MHz
SF01                                500.1303085 MHz
SI                                  32768
SF                                  500.13030225 MHz
NUW                                MW
SLSB                                0.0
SSB                                  0.30 Hz
GB                                  1.00
GB                                  0.00
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137.389
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132.660
130.031
129.749
128.934
128.330

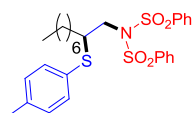
77.255
77.000
76.746

— 53.080

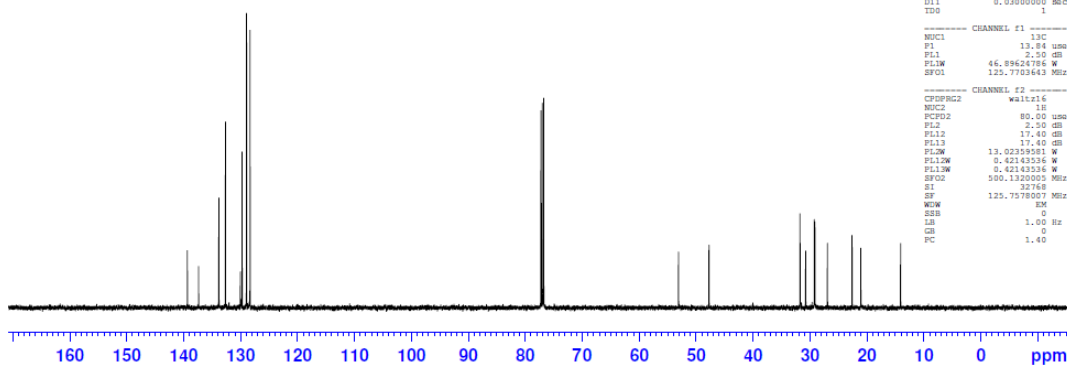
— 47.727

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31.729	30.748	29.222	29.099	26.915	22.581	21.070

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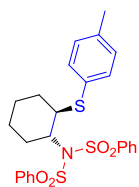
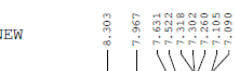


3d
(125 MHz, CDCl₃)



NAME	sm500c
EXPNO	1
PROCNO	59
Date_	20160121
Time	12.56
INSTRUM	Spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	128
DS	4
SWH	29761.904 Hz
FIDRES	0.454131 Hz
AQ	1.1010548 sec
RG	203
DE	16.800 usec
DW	6.50 usec
TE	298.5 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1

LDK-240 NEW

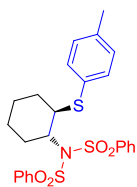


3e
(500 MHz, CDCl₃)



NAME sn500h
EXPNO 510
PROCNO 1
DATE_ 20160225
TIME 4.41
INSTRUM spect
PROBHD 5 mm PABBO BB
PULPROG zgpg30
TD 65536
SOLVENT CDCl₃
NS 16
DS 10330.278 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 101
DM 48.400 umsc
DE 6.50 umsc
TE 298.0 K
D1 1.00000000 sec
TDO 1
----- CHANNEL f1 -----
NUC1 1H
P1 14.00 umsc
PL1 0.00 dB
PL1W 13.02359581 W
SFO1 500.1330989 MHz
SI 32768
SF 500.1330989 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

LDK-240 NEW

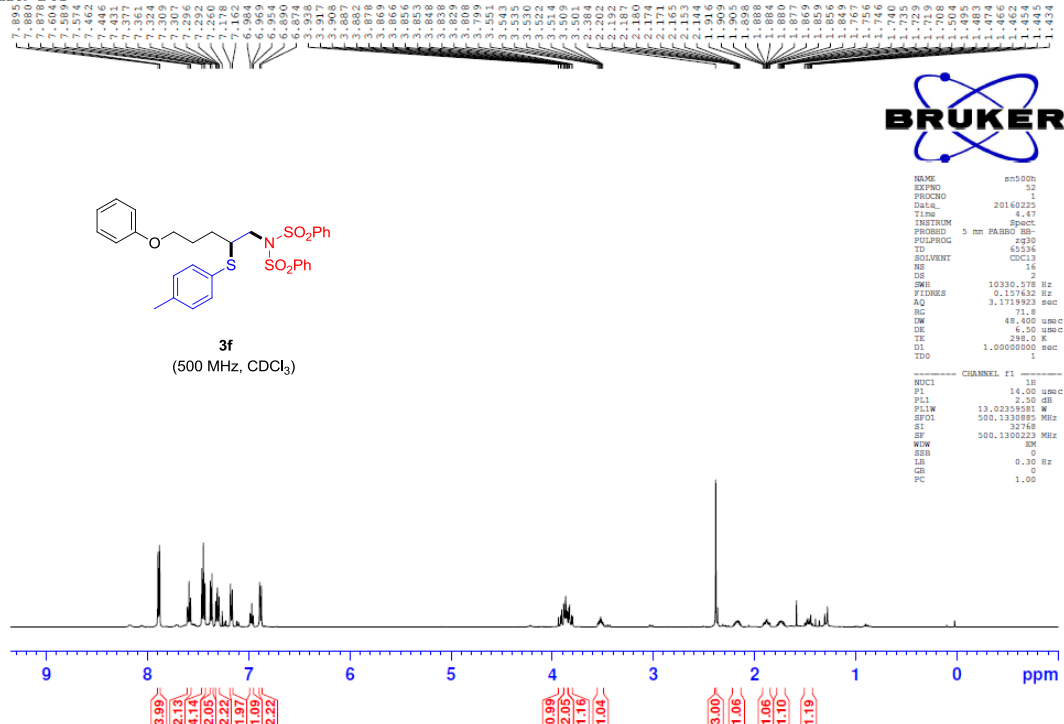


3e
(125 MHz, CDCl₃)

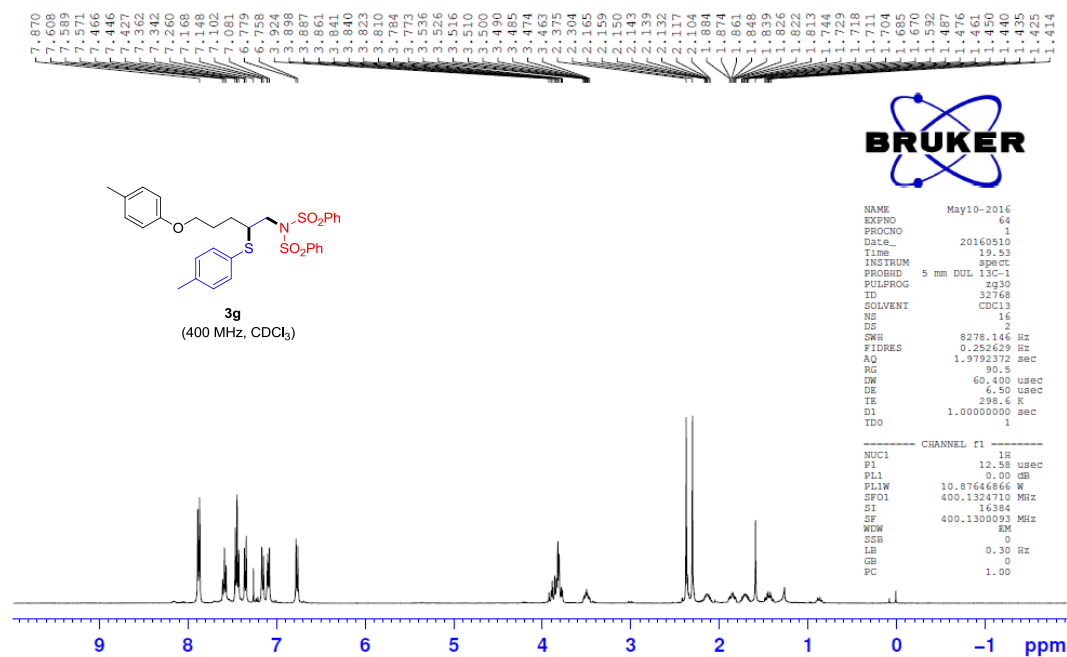


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EXPNO 58
PROCNO 1
DATE_ 20160225
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INSTRUM spect
PROBHD 5 mm PABBO BB
PULPROG zgpg30
TD 65536
SOLVENT CDCl₃
NS 128
DS 4
SWH 29761.904 Hz
FIDRES 0.454121 Hz
AQ 1.1010548 sec
RG 203
DM 16.800 umsc
DE 6.50 umsc
TE 298.0 K
D1 2.00000000 sec
D11 0.00000000 sec
TDO 1
----- CHANNEL f1 -----
NUC1 13C
P1 13.84 umsc
PL1 2.50 dB
PL1W 46.89624788 W
SFO1 125.7703643 MHz
----- CHANNEL f2 -----
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 umsc
PL2 2.50 dB
PL2W 17.40 dB
PL2 17.40 dB
PL2W 13.02359581 W
SFO2 500.1330989 MHz
PL1W 0.42143336 W
SFO2 500.1330989 MHz
SI 32768
SF 125.757948 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

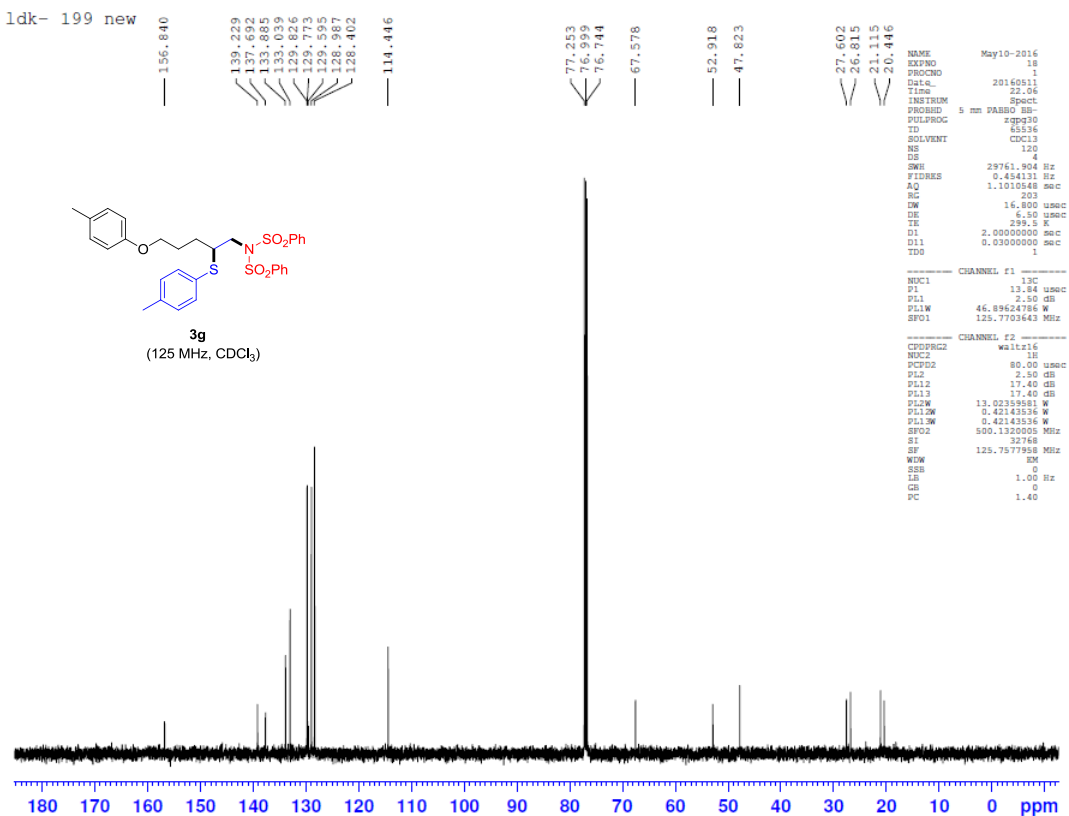
LDK-241



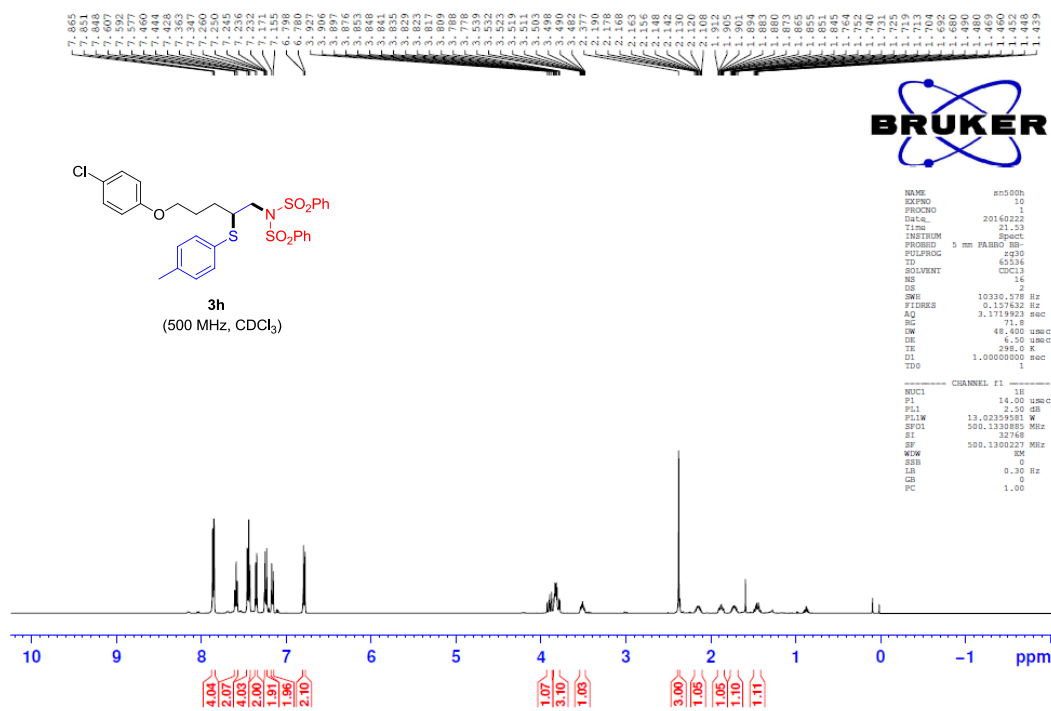
LDK-199 new



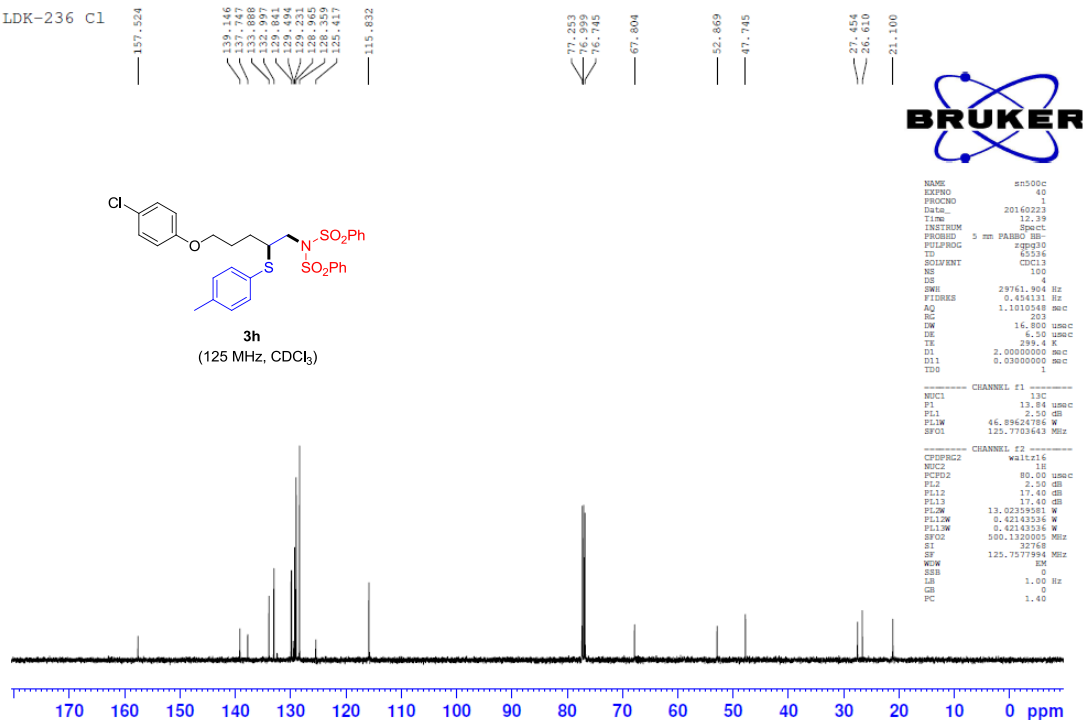
ldk- 199 new



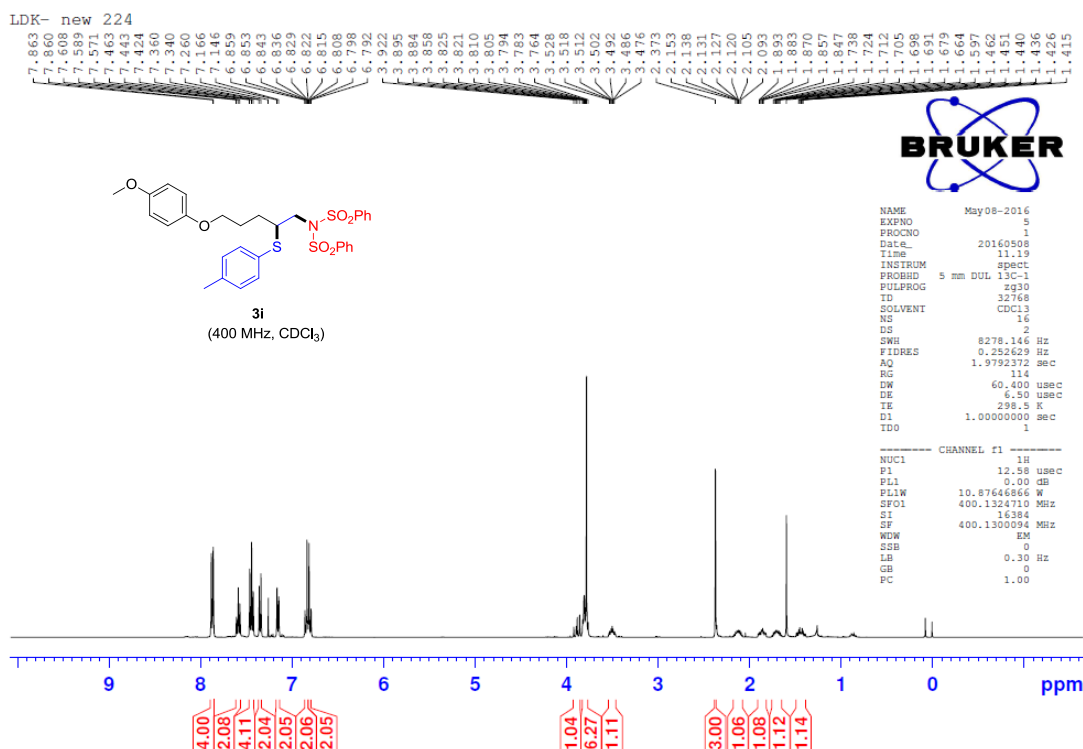
ldk-236 c1



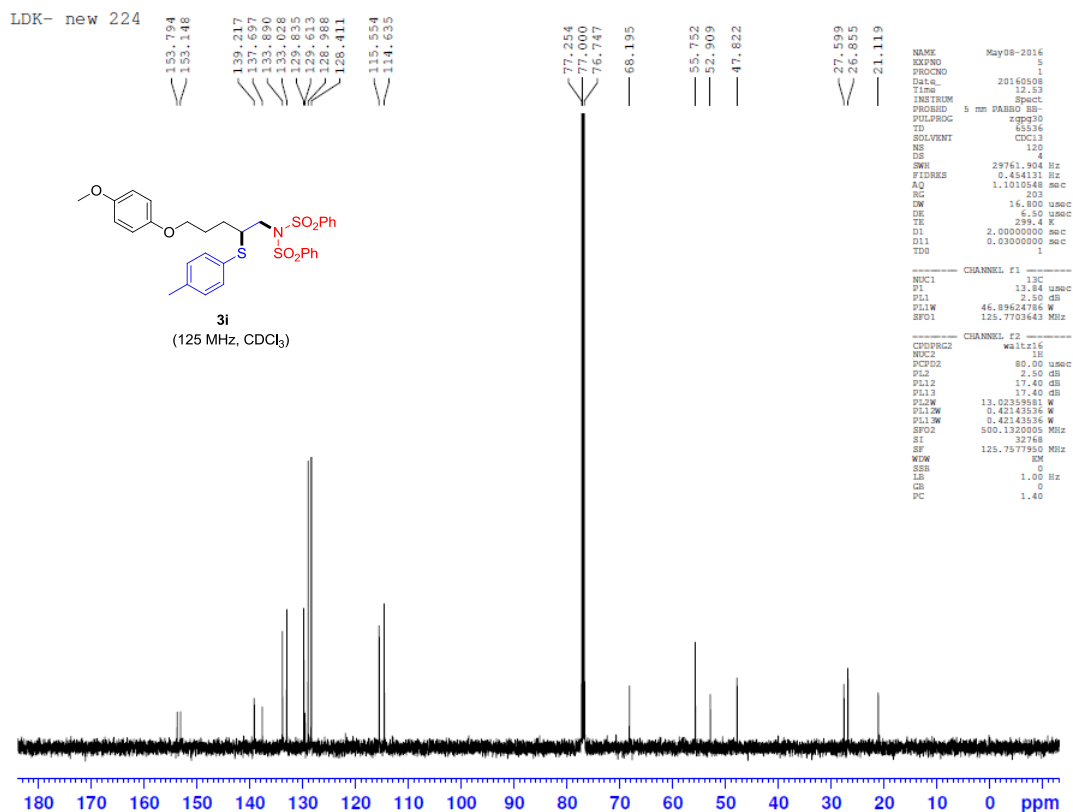
LDK-236 C1



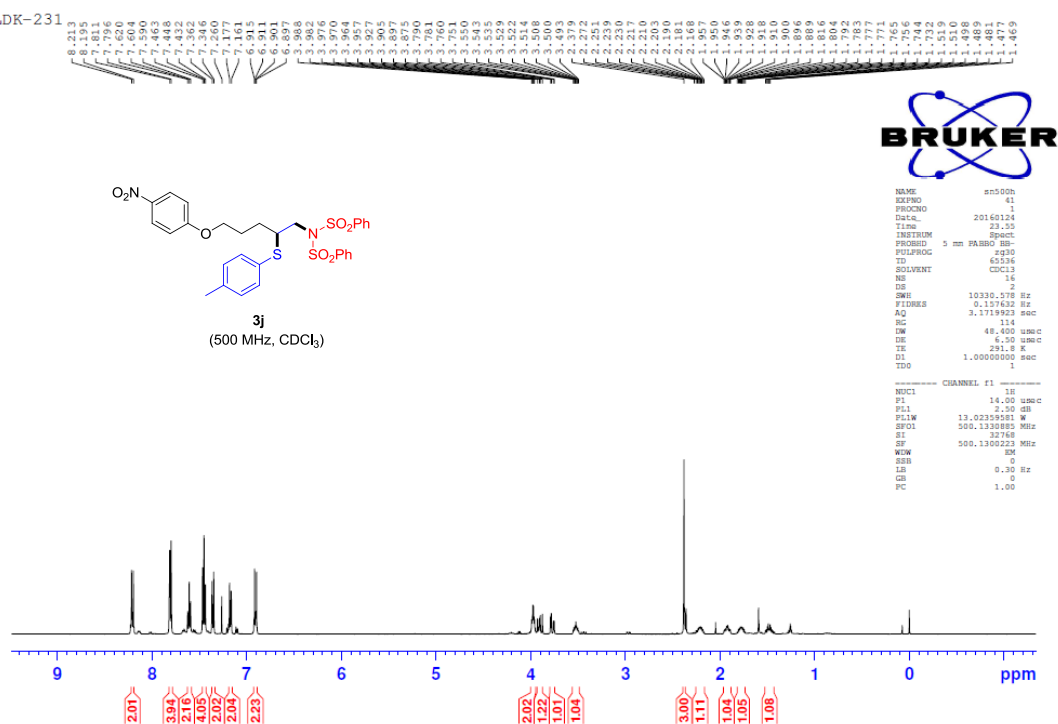
LDK- new 224



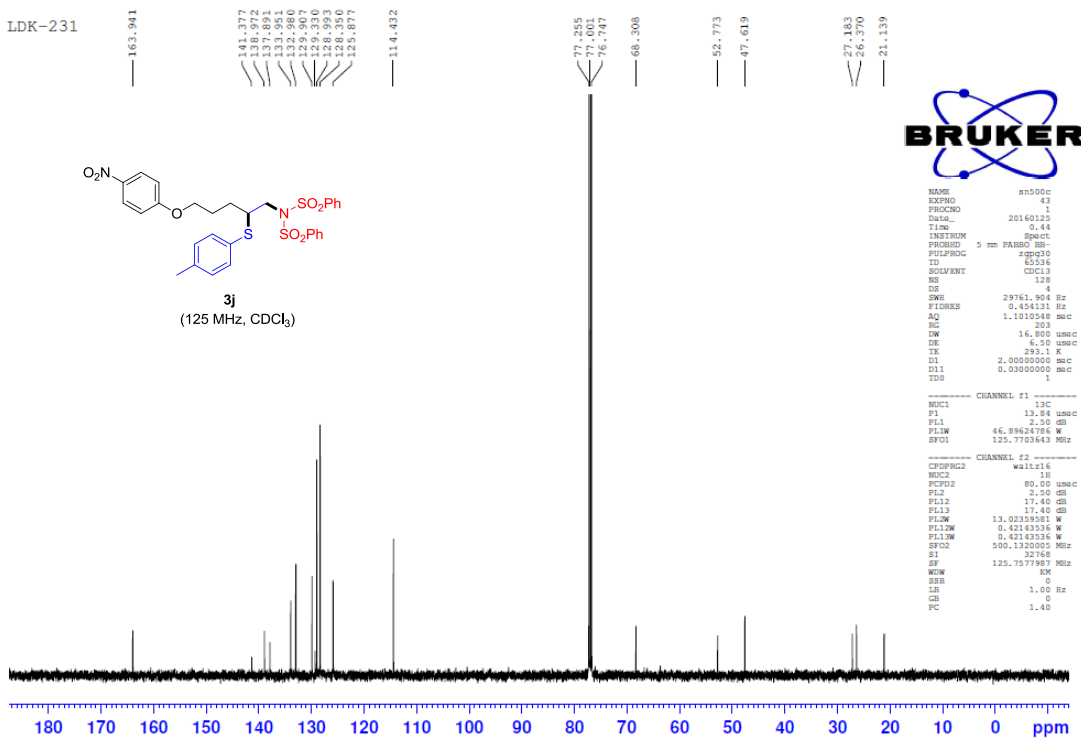
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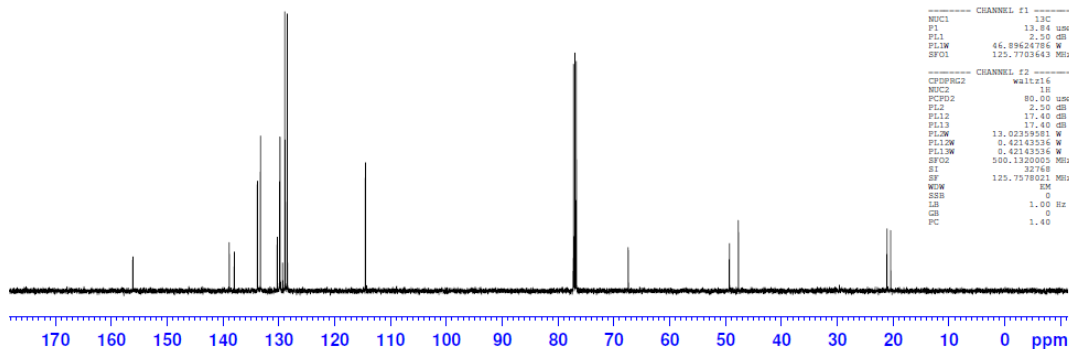
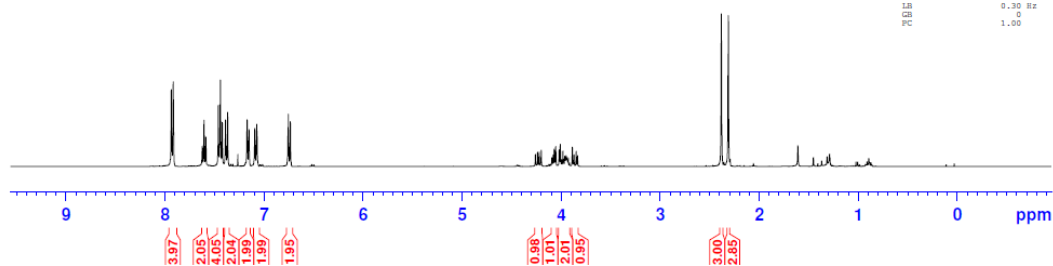


LDK-231

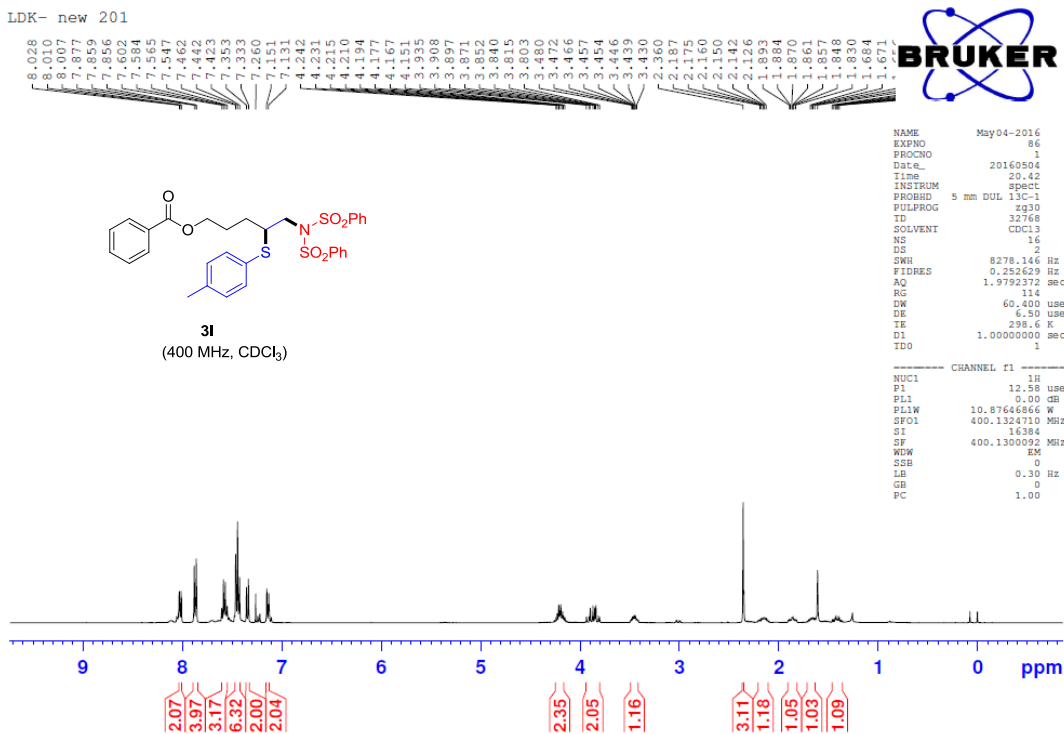


LDK-231

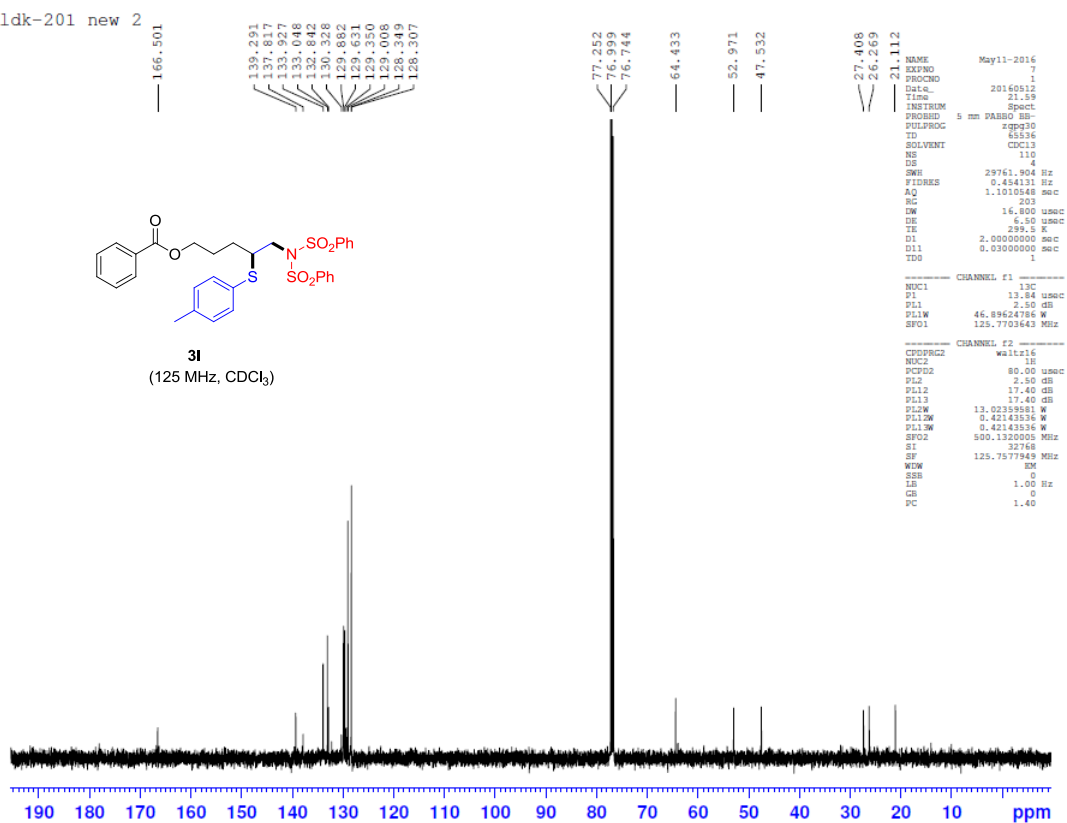


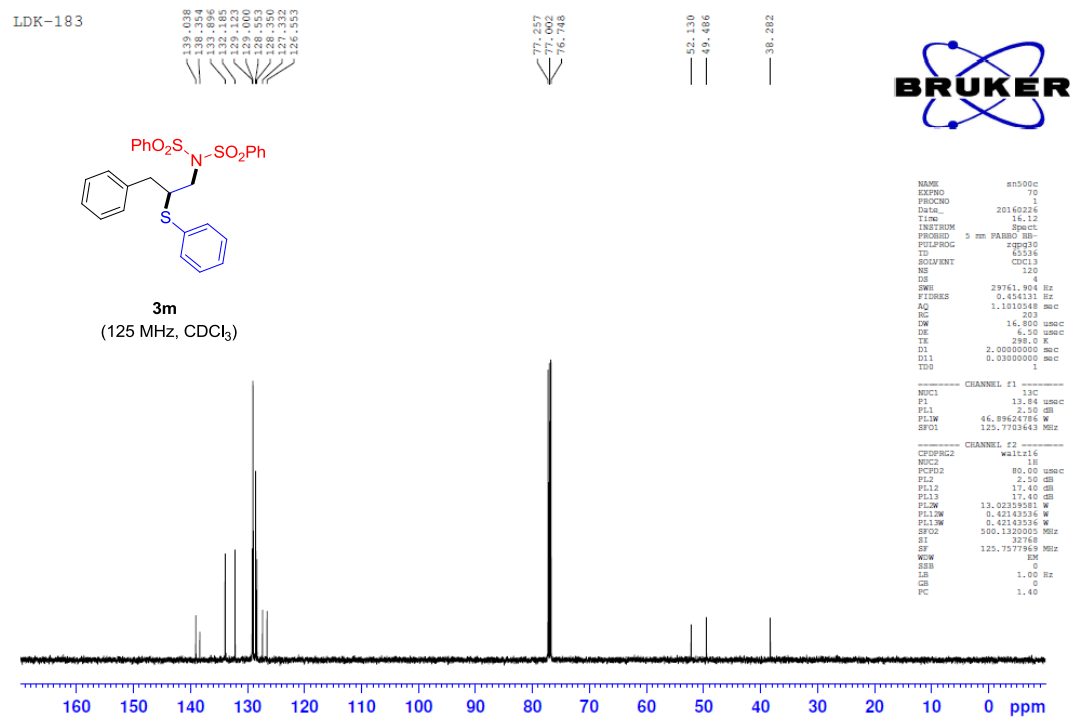
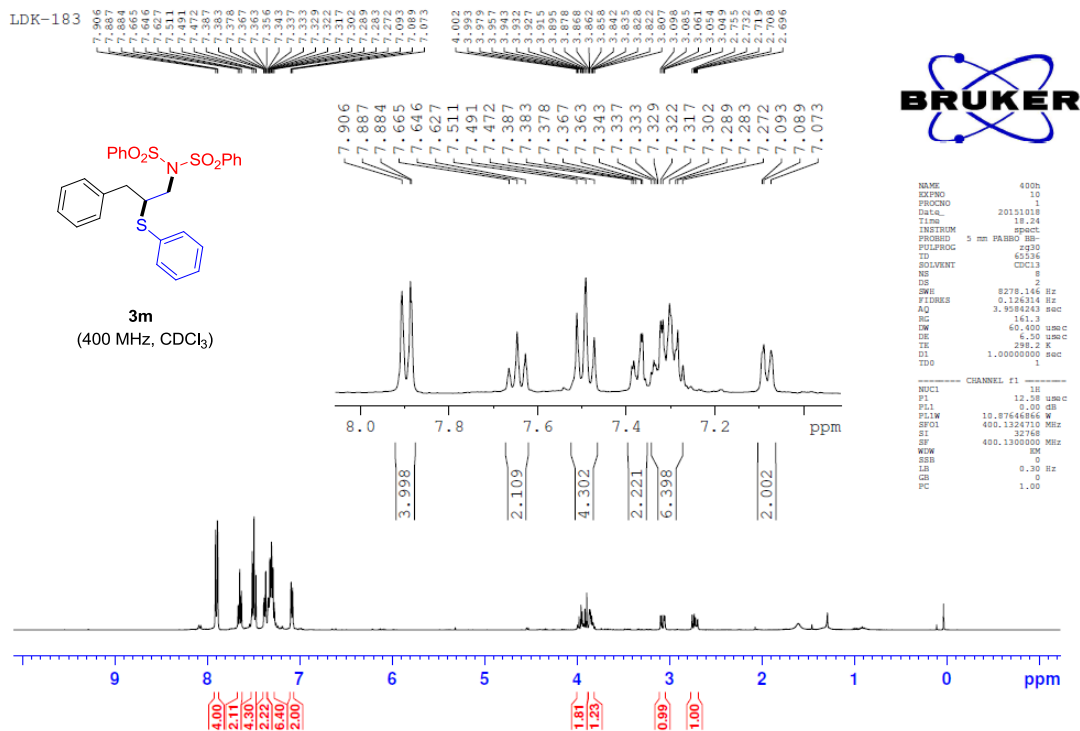


LDK- new 201

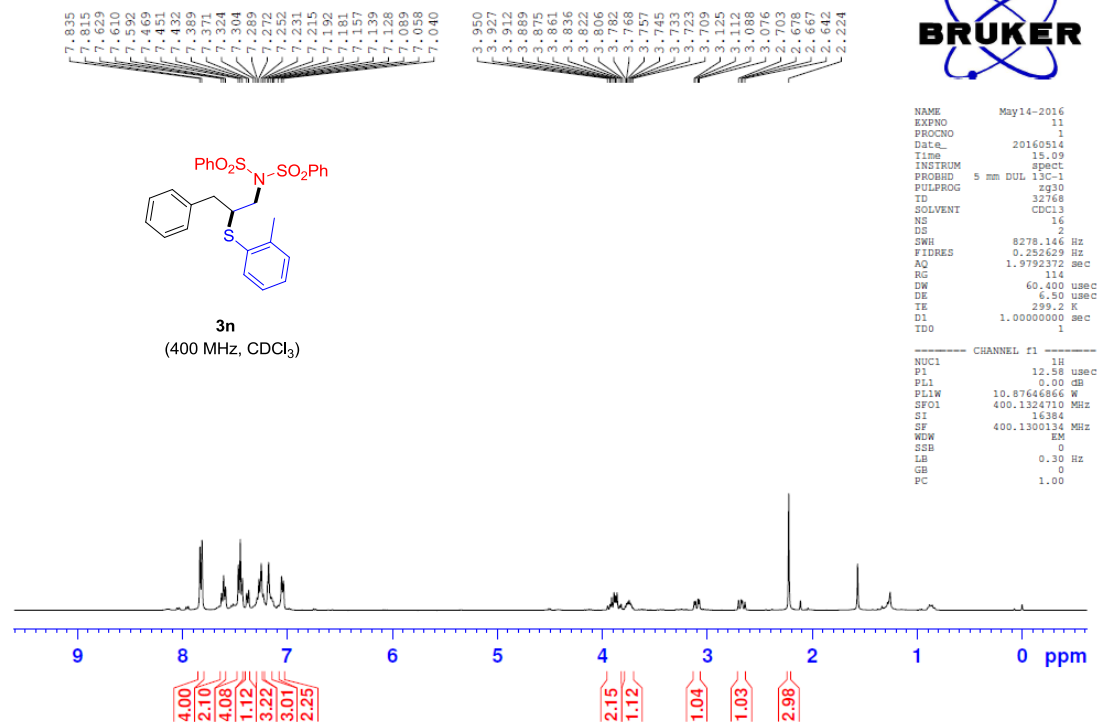


ldk-201 new 2

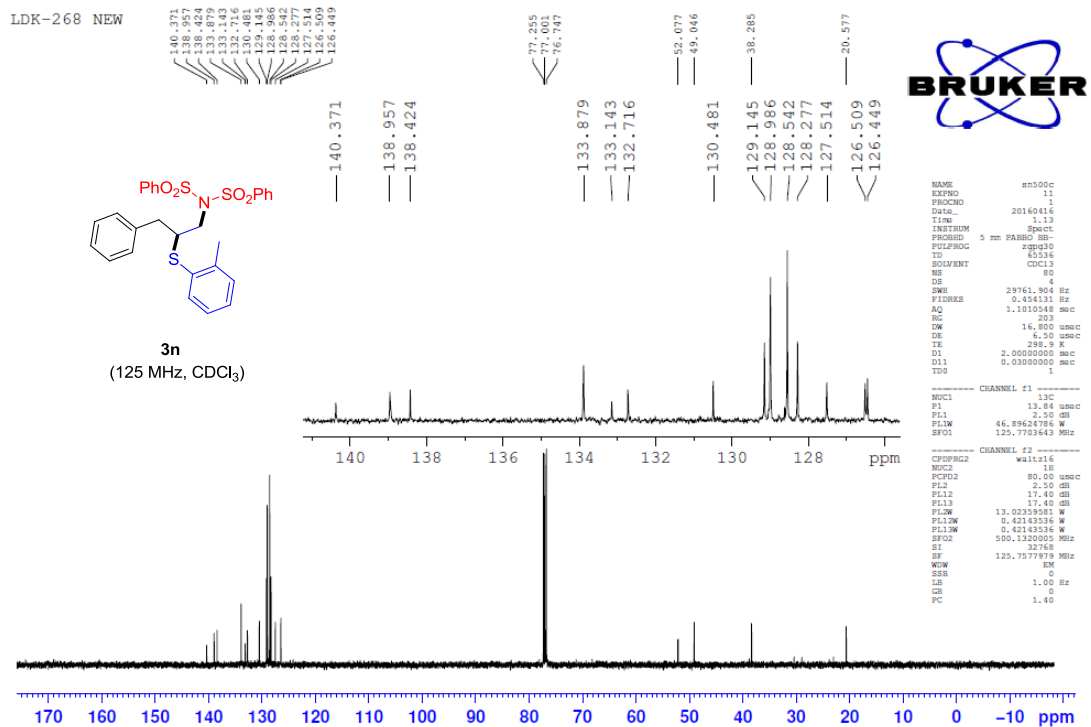




LDK- 268 h



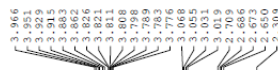
LDK-268 NEW



LDK-260



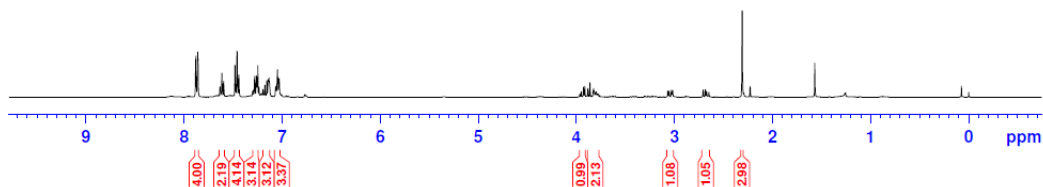
3o
(400 MHz, CDCl₃)



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PROCNO    1
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TD         65536
SOLVENT   CDCl3
NS         16
DS         2
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FIDRES     0.232629 Hz
AQ         1.9792372 sec
RG         90.5
DW         60.400 usec
DE         6.50 usec
TE         296.6 K
D1         1.00000000 sec
TDO        1
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NUC1       13C
P1         12.58 usec
PL1        0.00 dB
PL1W       10.87648844 W
SFO1       400.1324710 MHz
SI         132864
SF         400.1300137 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00

```



ldk-260



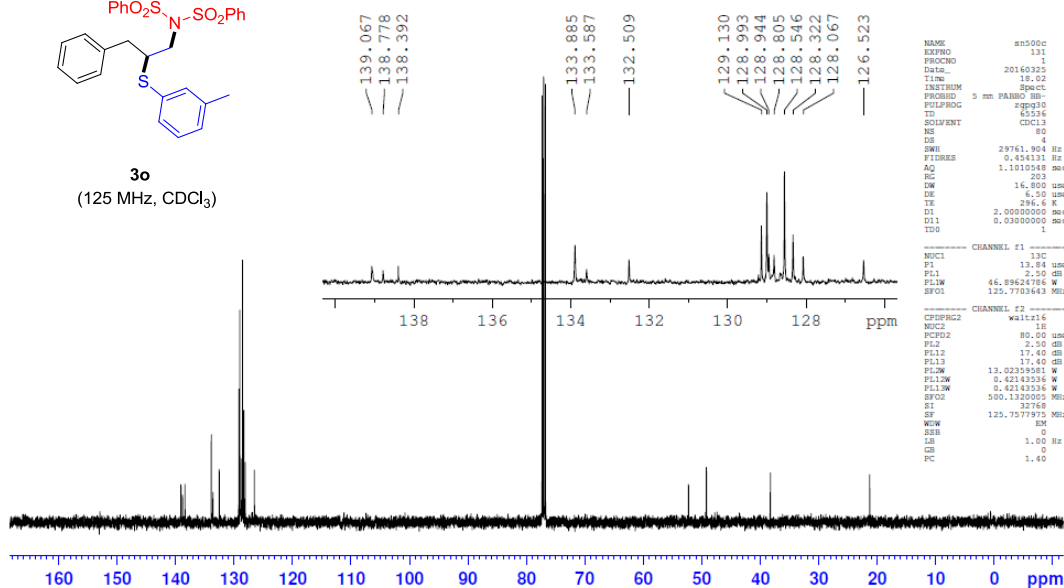
3o
(125 MHz, CDCl₃)



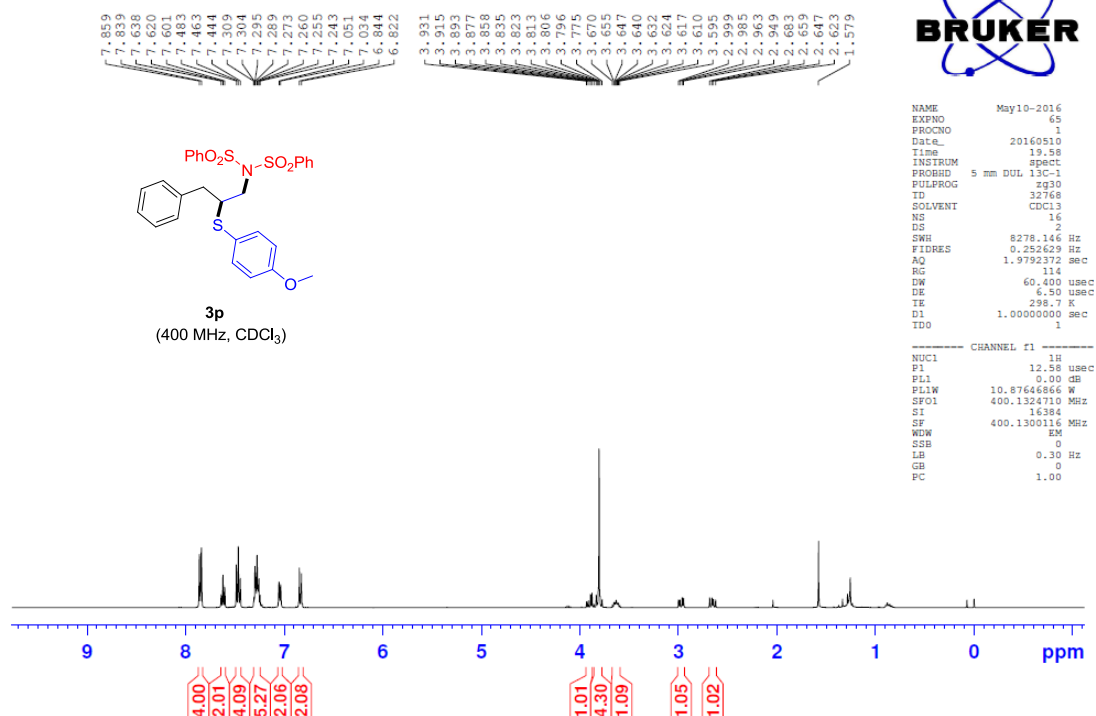
```

NAME      sn500c
EXPNO     131
PROCNO    1
Date_     20160325
Time      15.02
INSTRUM   spect
PROBHD    5 mm PABBO 13C
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         80
DS         4
SWH        29761.904 Hz
FIDRES     0.454133 Hz
AQ         1.1010348 sec
RG         203
DW         16.800 usec
DE         16.50 usec
TE         296.6 K
D1         2.00000000 sec
D11        0.02000000 sec
TDO        1
----- CHANNEL f1 -----
NUC1       13C
P1         13.84 usec
PL1        2.50 dB
PL1W       46.89624786 W
SFO1       125.7703643 MHz
----- CHANNEL f2 -----
CPDPRG2   waltz16
NUC2       1H
PCPD2     80.00 usec
PL2        2.50 dB
PL2W      17.40 dB
PL12       17.40 dB
PL13       17.40 dB
PL1W      13.02335981 W
PL12W     0.42143336 W
PL13W     0.42143336 W
SFO2      500.1324995 MHz
SI         32768
SF        125.7577973 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40

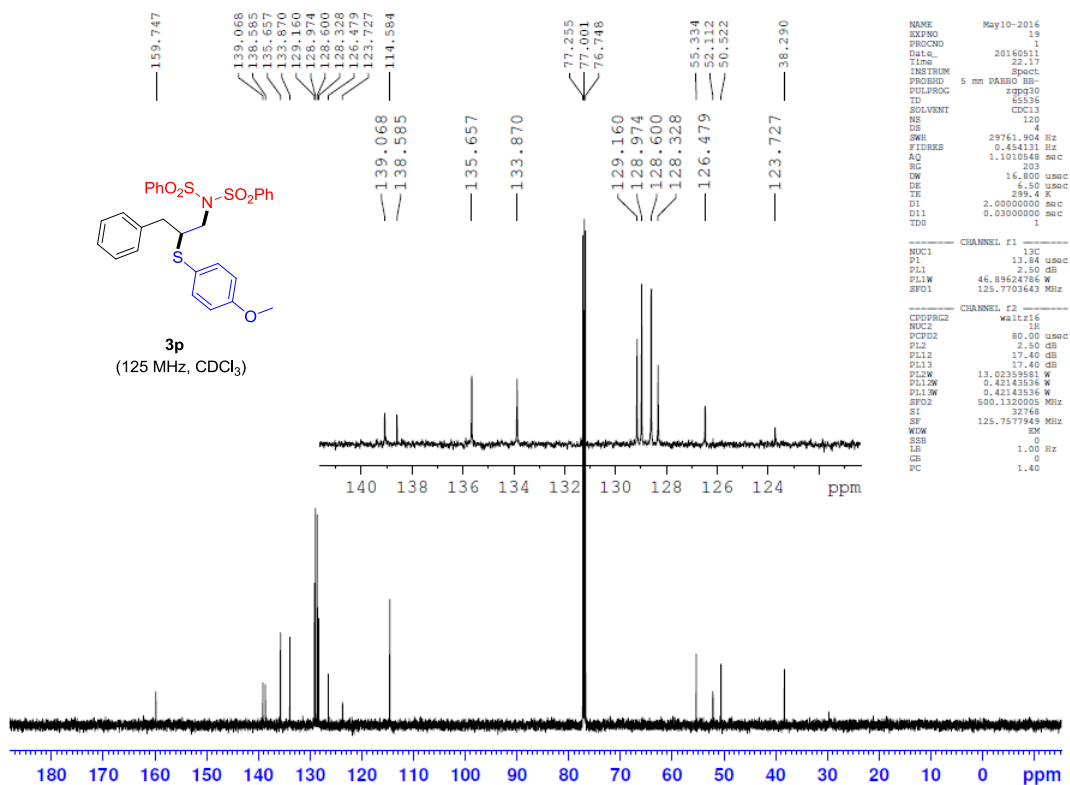
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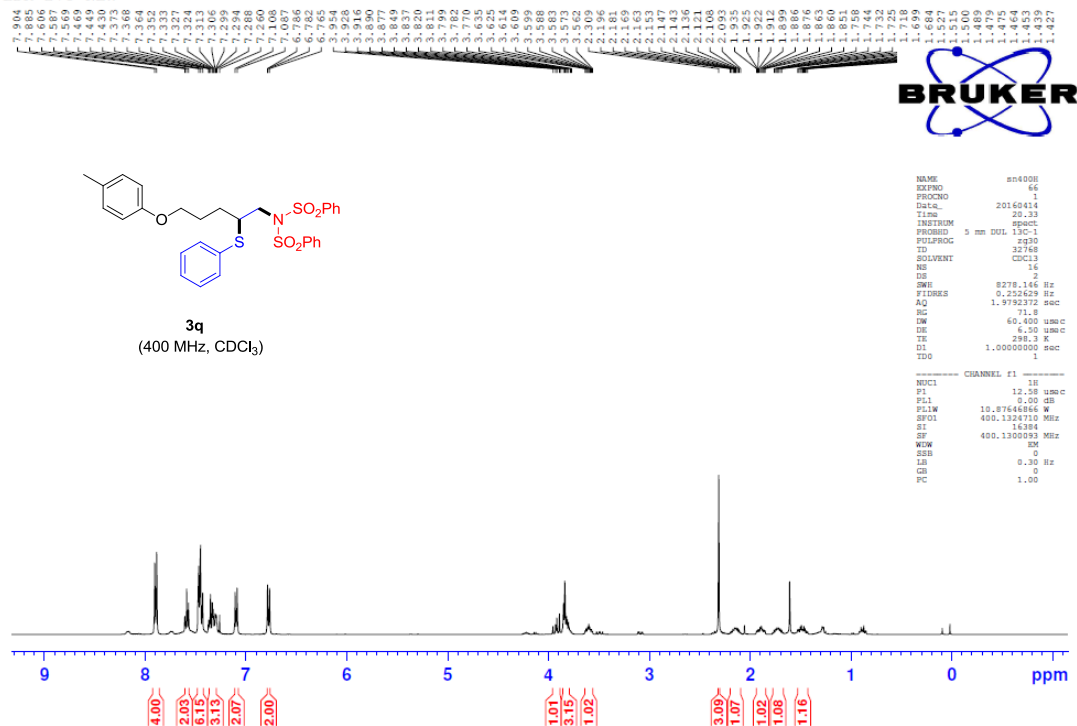
LDK-262 new 2



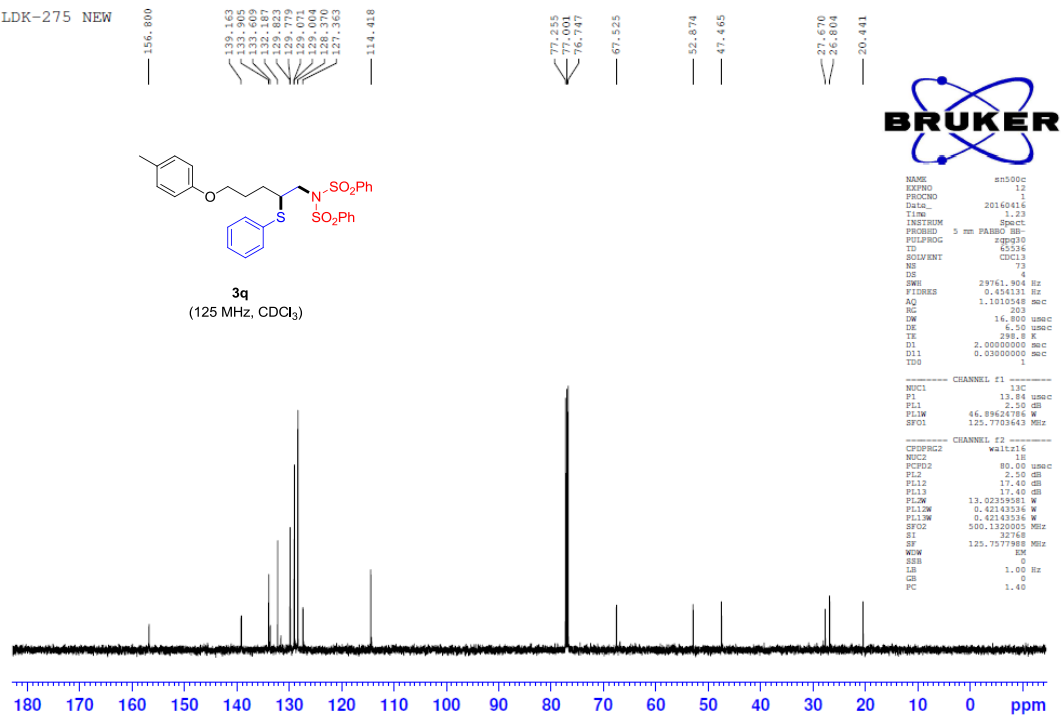
ldk - 262 new 2



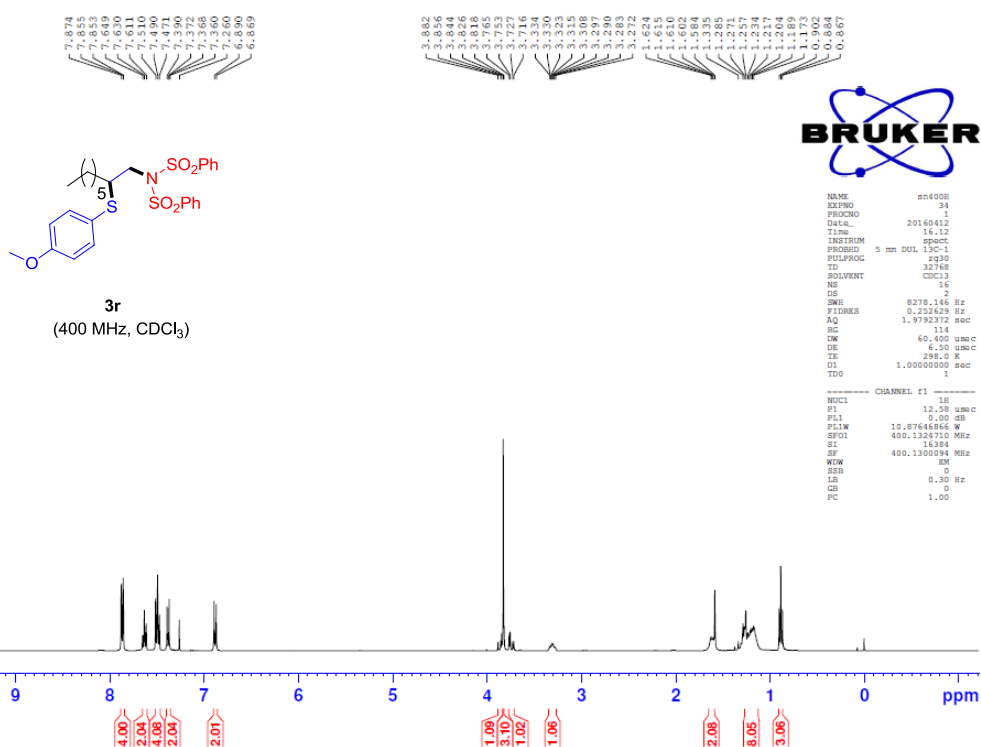
LDK-275 NEW



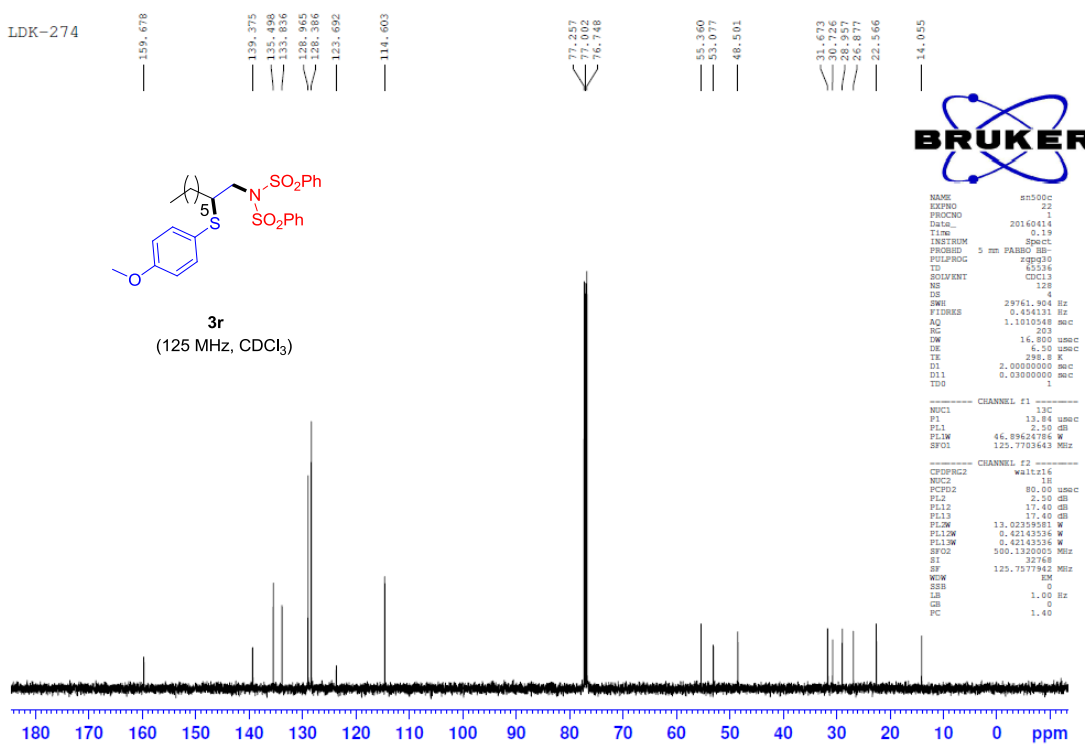
LDK-275 NEW

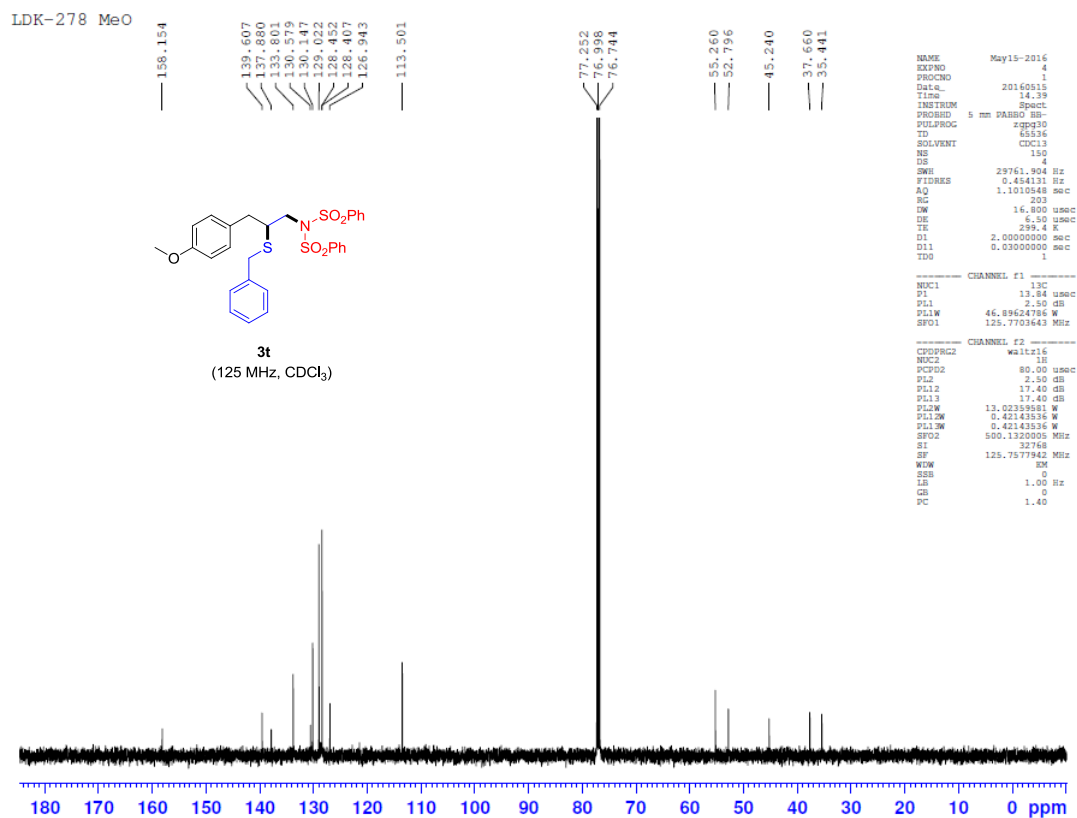
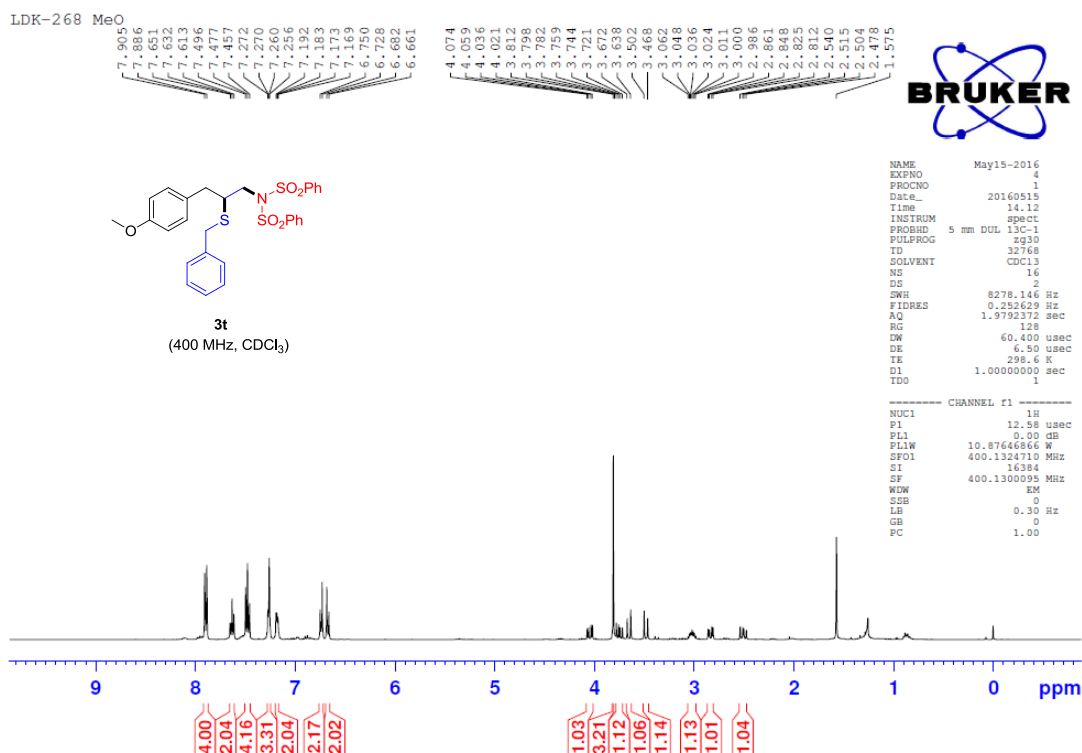


ldk-274

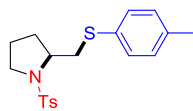


LDK-274



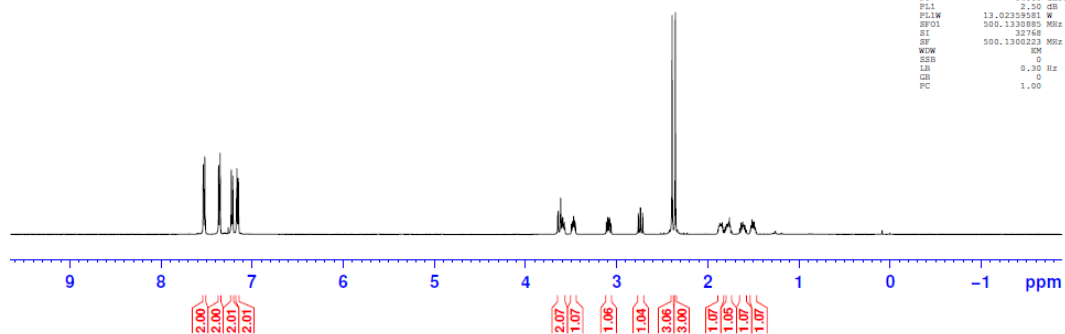


LDK-252

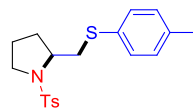
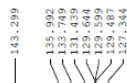
(500 MHz, CDCl₃)

NAME m500h
EXPNO 34
PROCNO 1
Date_ 20160315
Time 22.18
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 16
DS 4
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719821 sec
RG 25.4
DW 48.400 usec
DE 6.50 usec
TE 295.2 K
D1 1.00000000 sec
TD0 1

----- CHANNEL f1 -----
NUC1 1H
P1 14.00 usec
PL1 2.50 dB
PL1W 13.02359581 W
SFO1 500.1330023 MHz
SI 32768
SF 500.1330023 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



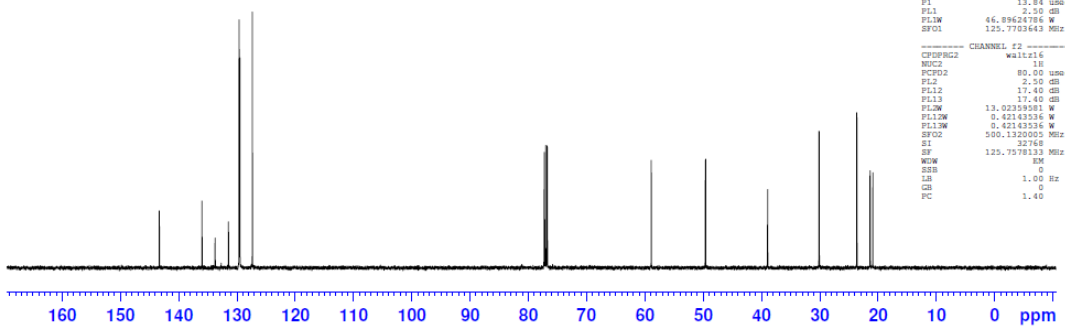
ldk-252

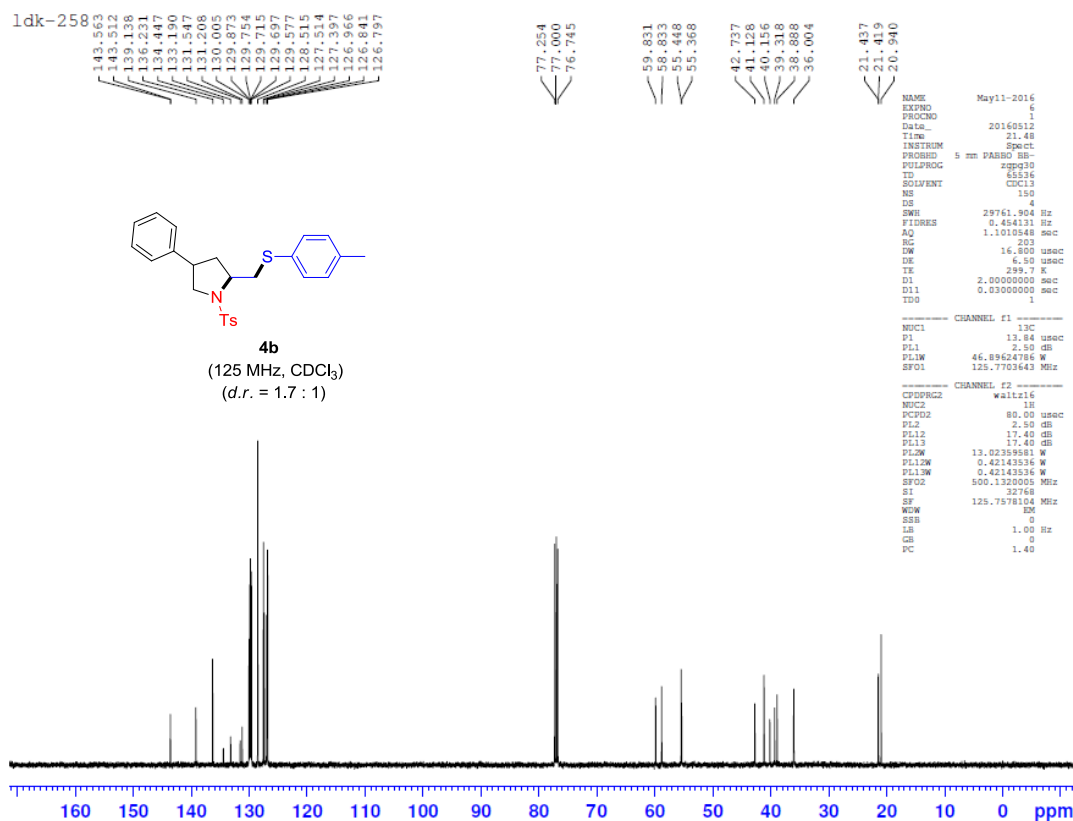
(125 MHz, CDCl₃)

NAME m500c
EXPNO 140
PROCNO 1
Date_ 20160317
Time 13.22
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 100
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 203
DW 16.800 usec
DE 6.50 usec
TE 297.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

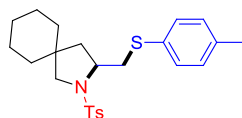
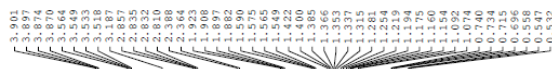
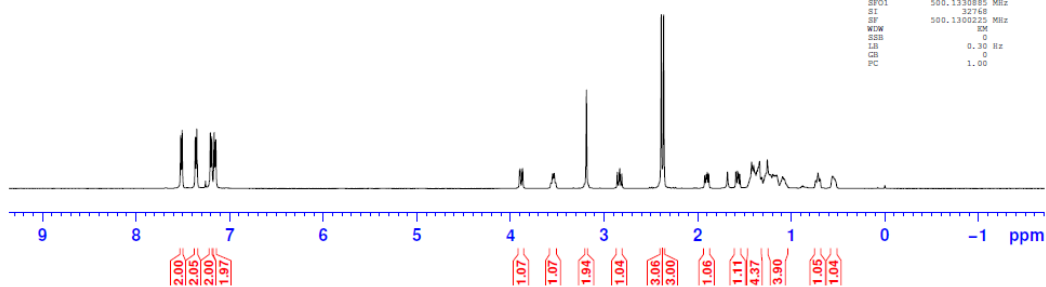
----- CHANNEL f1 -----
NUC1 13C
P1 13.84 usec
PL1 2.50 dB
PL1W 46.89624786 W
SFO1 125.7703643 MHz

----- CHANNEL f2 -----
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 2.50 dB
PL12 17.40 dB
PL13 17.40 dB
PL2W 13.02359581 W
SFO2 500.1330023 MHz
SI 32768
SF 125.7578133 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40





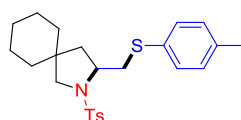
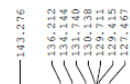
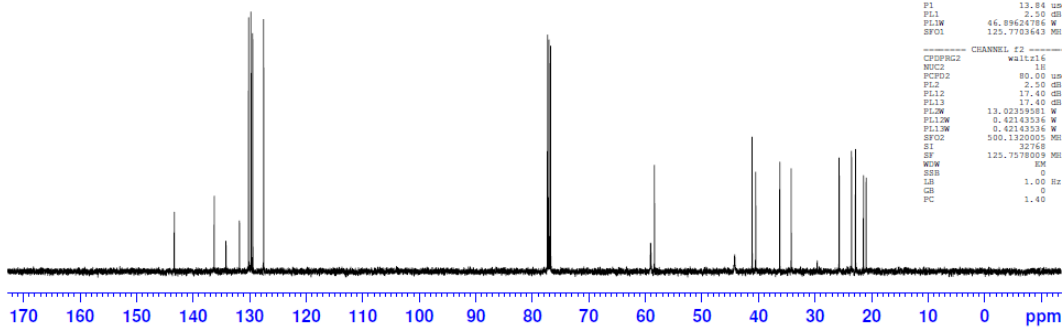
LDK-244

(500 MHz, CDCl₃)

NAME sn500h
EXPNO 18
PROCNO 1
Date_ 20160309
Time 22.19
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.17632 Hz
AQ 3.1719923 sec
RG 50.8
DW 48.400 usec
DE 6.50 usec
TE 295.0 K
D1 1.00000000 sec
TD0 1

----- CHANNEL f1 -----
NUC1 13C
P1 14.00 usec
PL1 2.50 dB
PL1W 13.02359581 W
SFO1 500.1330885 MHz
SI 32768
SF 500.1300225 MHz
WDW DM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

ldk-244

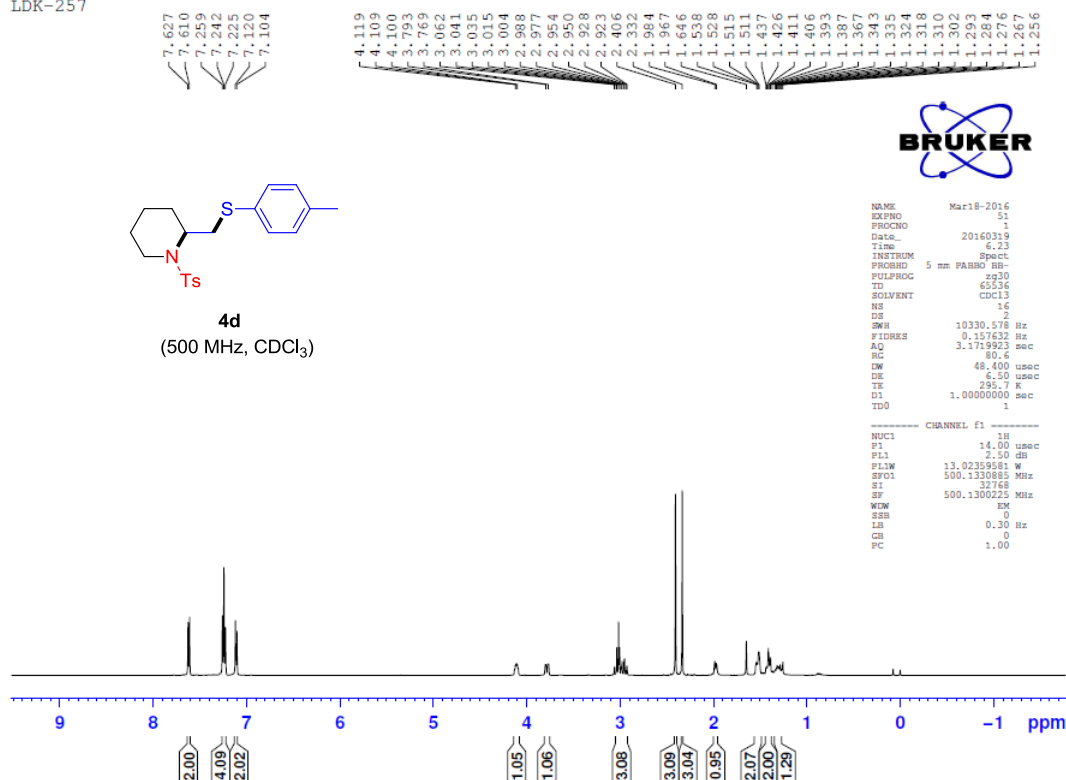
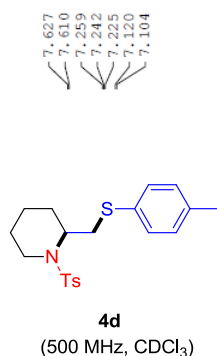
(125 MHz, CDCl₃)

NAME sn500c
EXPNO 54
PROCNO 1
Date_ 20160310
Time 12.40
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 128
DS 8
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 203
DW 16.800 usec
DE 6.50 usec
TE 299.7 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

----- CHANNEL f1 -----
NUC1 13C
P1 13.84 usec
PL1 2.50 dB
PL1W 46.89624788 W
SFO1 125.7703643 MHz

----- CHANNEL f2 -----
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 2.50 dB
PL12 17.40 dB
PL13 17.40 dB
PL1W 13.02359581 W
PL12W 0.42143536 W
PL13W 0.42143536 W
SFO2 500.1320000 MHz
SI 32768
SF 125.7578009 MHz
WDW DM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

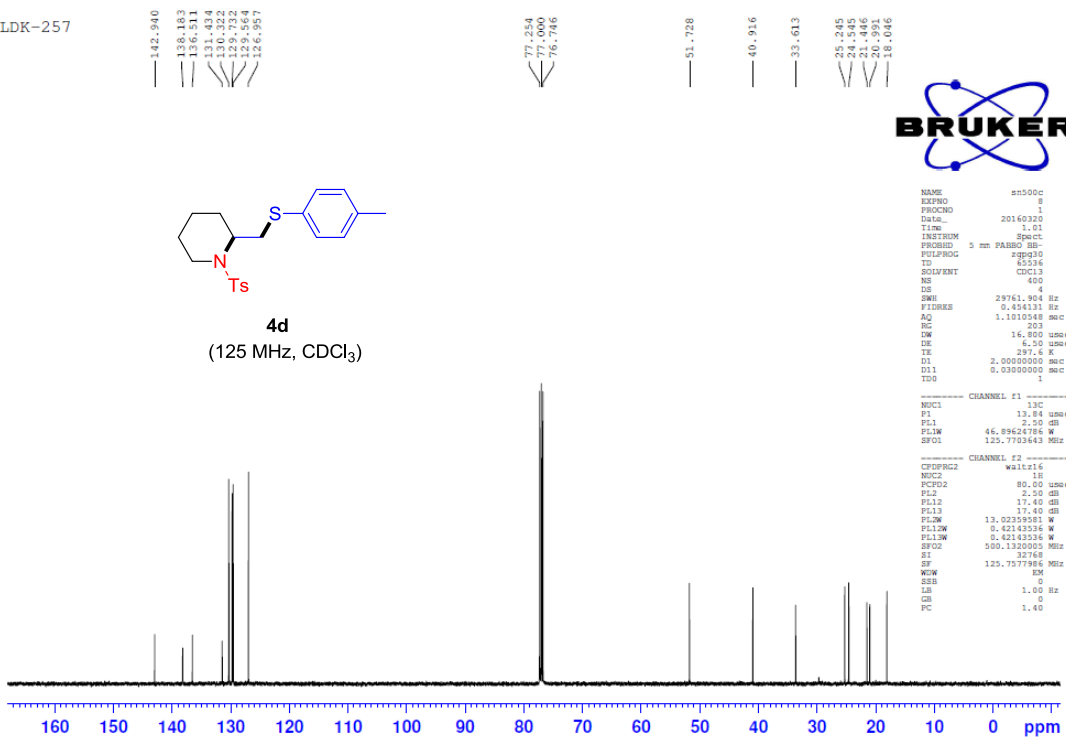
LDK-257



NAME Mar18-2016
 EXPRO 51
 PROCNO 1
 Date_ 20160319
 Time 6.23
 INSTRUM Spect
 PROBH0 5 mm PABBO BB-
 PULPROG zgpg30
 TO 65.516
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 10330.578 Hz
 FIDRES 0.157632 Hz
 AQ 3.1719923 sec
 RG 80.6
 DW 48.400 usec
 DE 6.50 usec
 TE 295.7 K
 D1 1.00000000 sec
 TD0 1

CHANNEL F1
 NUC1 1H
 P1 14.00 usec
 PL1 2.50 dB
 PL1W 13.02359581 W
 SFO1 500.1330885 MHz
 SI 32768
 SF 500.1300225 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

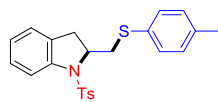
LDK-257



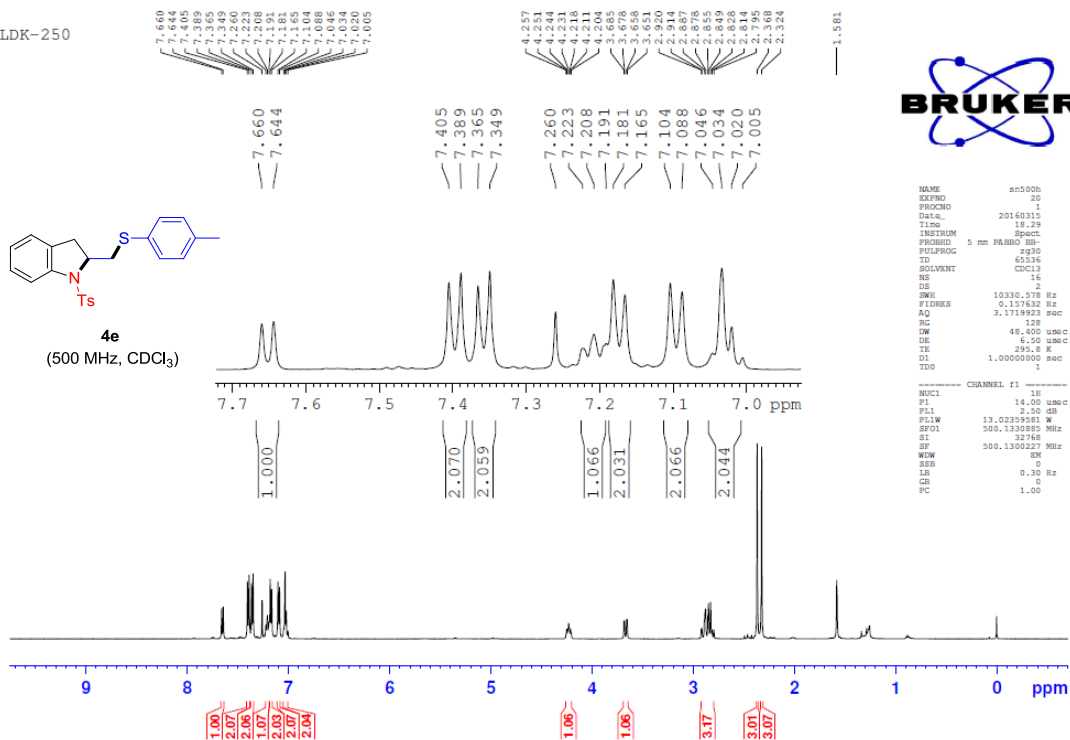
NAME sm500c
 EXPRO 8
 PROCNO 20160320
 Date_ 1.01
 INSTRUM Spect
 PROBH0 5 mm PABBO BB-
 PULPROG zgpg30
 TO 65.516
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 29761.904 Hz
 FIDRES 0.454131 Hz
 AQ 3.1030548 sec
 RG 203
 DW 16.800 usec
 DE 6.50 usec
 TE 291.6 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1

CHANNEL F1
 NUC1 13C
 P1 13.84 usec
 PL1 2.50 dB
 PL1W 46.89624768 W
 SFO1 125.7703643 MHz
 CHANNEL F2
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PL2 2.50 dB
 PL12 17.40 dB
 PL13 17.40 dB
 PL1W 13.02359581 W
 SFO2 0.42143536 W
 SFO3 0.42143536 W
 SI 32768
 SF 500.1300225 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.60

LDK-250



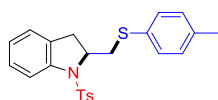
4e
(500 MHz, CDCl₃)



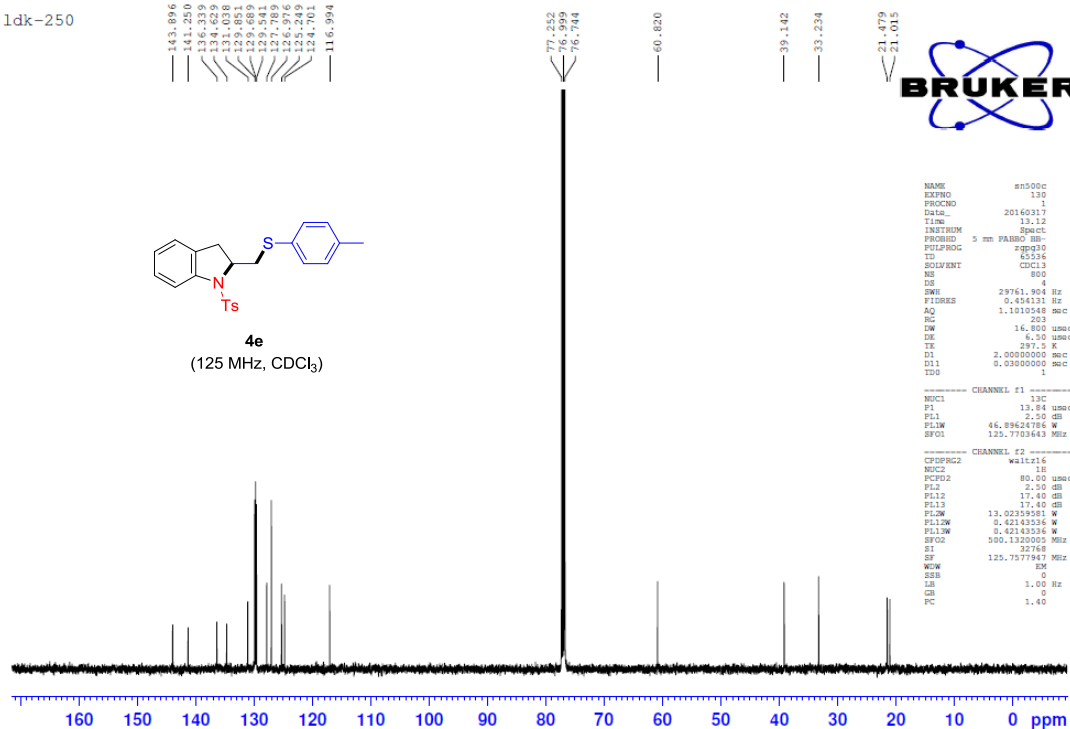
NAME sn500h
EXPNO 20
PROCNO 1
Date_ 20160315
Time 18.29
INSTRUM spect
PROBHD 5 mm WALTBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157832 Hz
AQ 3.1719923 sec
RG 328
DM 48.400 umsec
DE 6.50 umsec
TE 295.2 K
D1 1.00000000 sec
TD0 1

----- CHANNEL f1 -----
NUC1 1H
P1 14.00 umsec
PL1 2.50 dB
PL1W 13.02359581 W
SFO1 500.130207 MHz
SI 32768
SF 500.130207 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 1.00
PC 1.00

1dk-250



4e
(125 MHz, CDCl₃)



NAME sn500c
EXPNO 130
PROCNO 1
Date_ 20160317
Time 13.12
INSTRUM spect
PROBHD 5 mm WALTBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 800
DS 2
SWH 29761.904 Hz
FIDRES 0.456131 Hz
AQ 1.1010549 sec
RG 203
DM 16.800 umsec
DE 6.50 umsec
TE 297.5 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

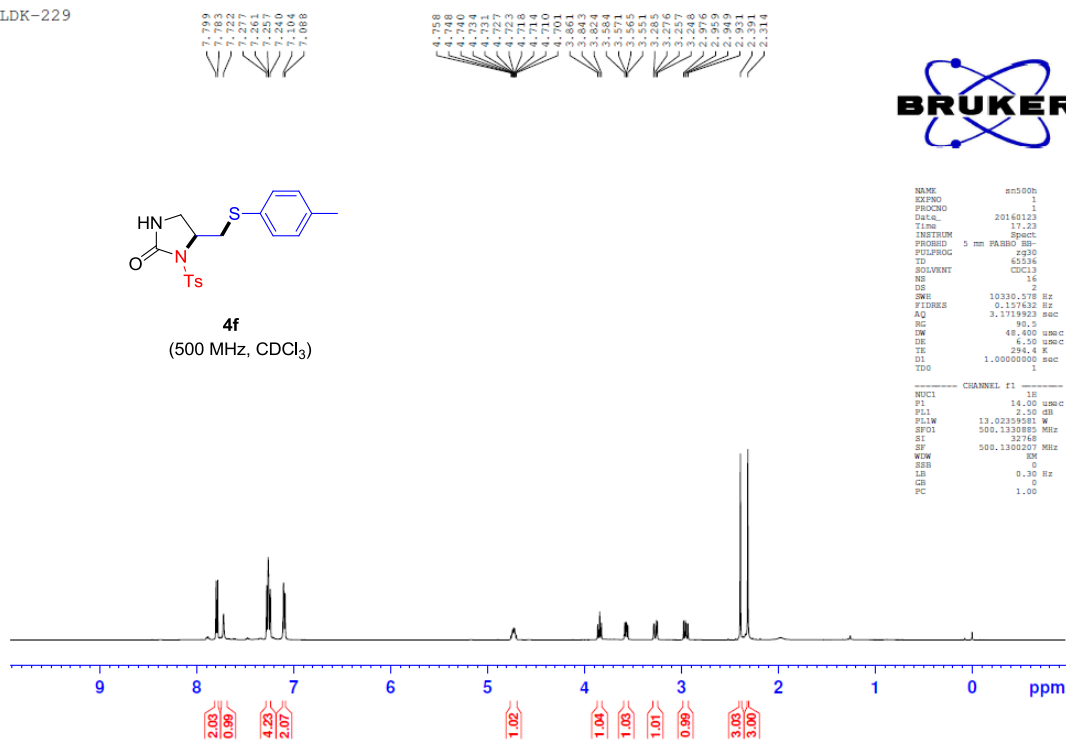
----- CHANNEL f1 -----
NUC1 13C
P1 13.00 umsec
PL1 2.50 dB
PL1W 13.02359581 W
SFO1 125.7577947 MHz

----- CHANNEL f2 -----
waitz16
NUC2 1H
PCPD2 80.00 umsec
PL2 2.50 dB
PL12 17.40 dB
PL13 17.40 dB
PL1W 13.02359581 W
PL12W 0.42143536 W
PL13W 0.42143536 W
SFO2 500.130207 MHz
SI 32768
SF 125.7577947 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 1.00
PC 1.40

LDK-229



4f
(500 MHz, CDCl₃)

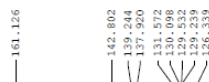


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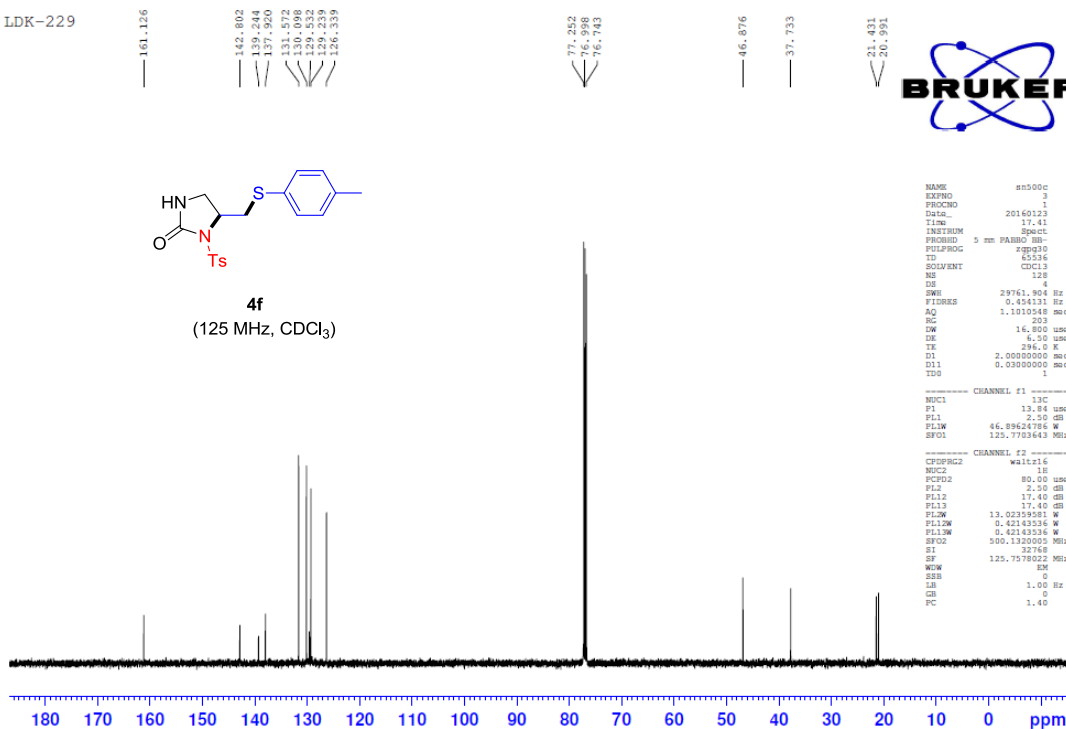
NAME          an500h
EXPNO         1
PROCNO        1
DATA_         20160123
Time          17.23
INSTRUM       spect
PROBHD        5 mm PABBO BB-
PULPROG       zg30
TD            65536
SOLVENT       CDCl3
NS            16
DS            2
SWH           10330.518 Hz
FIDRES        0.157632 Hz
AQ            3.1719823 sec
RG            90.5
DW            48.400 usec
DE            6.50 usec
TE            294.4 K
D1            1.0000000 sec
TD0           1

===== CHANNEL f1 =====
NUC1           1H
P1            14.00 usec
PL1           2.50 dB
PL1W          13.02359581 W
SFO1          500.1300885 MHz
SI            32758
SF            500.1300207 MHz
WDW           EM
SSB           0
LB            0.30 Hz
GB            0
PC            1.00
  
```

LDK-229



4f
(125 MHz, CDCl₃)



```

NAME          an500c
EXPNO         3
PROCNO        1
DATA_         20160123
Time          17.41
INSTRUM       spect
PROBHD        5 mm PABBO BB-
PULPROG       zgpg30
TD            65536
SOLVENT       CDCl3
NS            16
DS            4
SWH           29761.904 Hz
FIDRES        0.454131 Hz
AQ            1.1010540 sec
RG            203
DW            16.800 usec
DE            6.50 usec
TE            296.0 K
D1            2.0000000 sec
D11           0.0300000 sec
TD0           1

===== CHANNEL f1 =====
NUC1           13C
P1            13.04 usec
PL1           2.50 dB
PL1W          13.02359581 W
SFO1          125.7703443 MHz

===== CHANNEL f2 =====
CPDPRG2       waltz16
NUC2           1H
PCPD2         80.00 usec
PL2           2.50 dB
PL2W          17.40 dB
PL12          17.40 dB
PL13          17.40 dB
PL2W          13.02359581 W
PL12W         0.42143533 W
PL13W         0.42143533 W
SFO2          500.1300885 MHz
SI            32760
SF            125.7578022 MHz
WDW           EM
SSB           0
LB            1.00 Hz
GB            0
PC            1.40
  
```

