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Supporting Information

Cobalt-catalyzed amination of aziridines and azetidines toward 1,2- and 1,3-diamines

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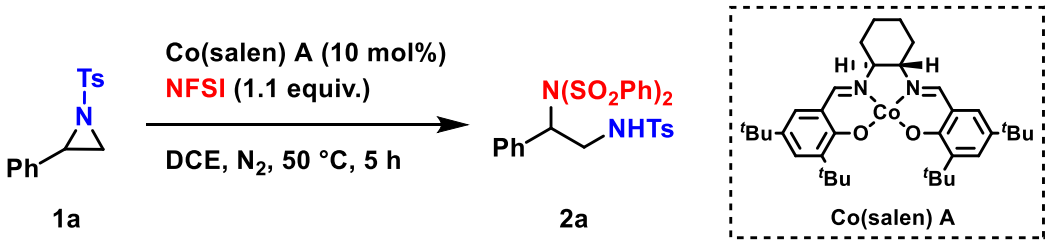
1. General Information

All reactions were performed under an atmosphere of nitrogen using standard Schlenk techniques, unless otherwise indicated. All commercial reagents were used without further purification, unless otherwise noted. Reactions were monitored by thin layer chromatography (TLC) analysis. TLC plates were viewed under UV light and stained with phosphomolybdic Acid. Yields refer to products isolated after purification by column chromatography, unless otherwise stated. Proton nuclear magnetic resonance (^{1}H NMR) spectra, carbon nuclear magnetic resonance (^{13}C NMR) spectra, fluorine nuclear magnetic resonance (^{19}F NMR) spectra were recorded on Bruker AV-400 (400 MHz), JEOL-500 (500 MHz) and JEOL-600 (600 MHz) spectrometers. NMR samples were dissolved in $CDCl_3$ (unless specified otherwise) and chemical shifts are reported in ppm referenced to residual nondeuterated solvent. IR spectra were obtained from Thermo Scientific NICOLET 380 FT-IR (KCl card). HRMS were obtained on an Exactive Plus LC-MS (ESI) mass spectrometer with the use of quadrupole analyzer. Co(salen) complexes[1] were synthesized according to literature precedent.

2. Optimizations of Reaction Conditions

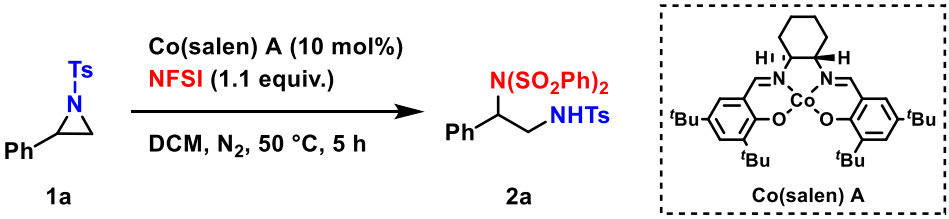
Screening of solvents



Entry[a]	Deviation from standard conditions	2[b]
1	None	77%
2	DCM	87%[c]
3	EA	86%
4	MeCN	24%
5	THF	60%
6	Toluene	trace
7	1,4-dioxane	81%[c]
8	DMSO	n.d.
9	DMF	n.d.

[a] Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), Co(salen) **A** (0.02 mmol, 10 mol%) were added to Solvent (c 0.1 M) under N_2 at 50 °C for 5 h. [b] ^{1}HMR yield, internal standard: CH_2Br_2. [c] Isolated yield.

Screening of temperature



Entry[a]	Deviation from standard conditions	2[b]
1	None	87%
2	r.t.	64%
3	60°C	81%
4	80°C	72%

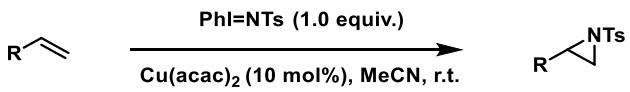
[a] Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), Co(salen) **A** (0.02 mmol, 10 mol%) were added to DCM (c 0.1 M) under N_2 at the corresponding temperature for 5 h. [b] Isolated yield.

3. Preparation of Aziridines

General Procedure A

Procedure for synthesizing PhI=NTs[2]: To a flame-dried 250 ml flask was subsequently added $TsNH_2$ (6.80 g, 40.0 mmol, 1.0 equiv.), KOH (5.60 g, 100.0 mmol, 2.5 equiv.), and MeOH (60 ml) under nitrogen. After the reaction was allowed to stir for 10 min, it was cooled to 0 °C. $PhI(OAc)_2$ (14.2 g, 44.0 mmol, 1.1 equiv.) was then added portionwise over 10 min. The reaction was stirred for 1 h at 0 ℃ and another1 h at room temperature. After the reaction was cooled to 0 ℃ again, 150 ml cold water was added slowly under stirring. The mixture was kept at 0 ℃ for 1 h to maximize the amount of the precipitates. The reaction was then filtered, subsequently washed with cold water (100 ml), MeOH (100 ml), and Et_2O (100 ml), and dried under high vacuum for 12 h. The product was obtained in 86% yield (12.8 g, 34.4 mmol).

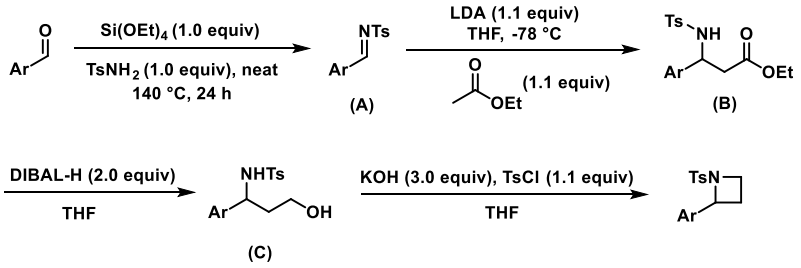
General Procedure B



Following the procedure described in the literature[3], to a flame-dried flask equipped with a stir bar was added PhI=NTs (1.0 equiv.), MeCN (0.25 M), and alkenes (5.0 equiv.). After the mixture was degassed for 10 min, $Cu(acac)_2$ (10 mol%) was added quickly under Argon. The reaction was stirred for 1 h at room temperature. After the reaction was complete as monitored by TLC, the crude mixture was concentrated and purified via flash column chromatography with a gradient of appropriate eluent on silica gel.

4. Preparation of Azetidines

General Procedure C



Synthesis of *N*-Tosyl imines A: Follow a procedure described in the literature[4]. To the solution of the corresponding aldehyde (30 mmol) in $Si(OEt)_4$ (7.0 mL, 31.5 mmol, 1.05 equiv.) was added $TsNH_2$ (5.14 g, 30 mmol, 1.0 equiv.). The mixture was stirred at 140 °C using a Dean-Stark apparatus for 24 h. The solution was cooled to room temperature and recrystallized from EtOAc/Hexanes. The product was used for the next step without further purification

Synthesis of *β*-amino ester B: To a flame-dried flask was added THF (10 ml), followed by a solution of LDA 1.0 M in THF (5.5 ml, 1.1 equiv.) at -78 °C. Dried ethyl acetate (0.55 ml, 5.5 mmol, 1.1 equiv.) was then added dropwise. After the reaction was allowed to stir at -78 °C for 1 h, a solution of N-tosyl imine (5 mmol, 1.0 equiv.) in THF (15 ml) was added dropwise. The reaction was stirred at that temperature until the reaction completion as monitored by TLC. The reaction was quenched with saturated aqueous NH_4Cl solution and allowed to warm to room temperature. The reaction mixture was then extracted with EtOAc, washed with saturated brine, dried over Na_2SO_4, concentrated under reduced pressure, and purified by flash column chromatography with a gradient of 10 - 25% ethyl acetate in hexanes as eluent.

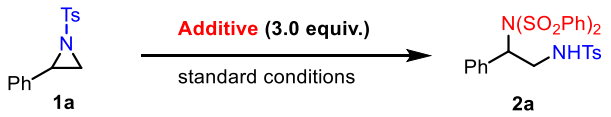
Synthesis of *γ*-amino alcohol C: To a flame-dried flask containing β-amino esters B of the previous step was added THF (10 ml) under Argon. After the reaction was cooled to 0 °C, a solution of DIBAL-H 1.0 M in PhMe (10 ml, 2.0 equiv.) was then added dropwise. The reaction was then allowed to stir at room temperature for 5 h. After the reaction completion as monitored by TLC, water (10 ml) and then 15% aqueous NaOH solution (5 ml) were added at 0 °C. The reaction mixture was stirred for 15 min, extracted with EtOAc, washed with saturated brine, dried over Na_2SO_4, concentrated, and passed through a short silica gel plug (5 cm) to give the crude product. It was used as starting material for the next step without any further purification.

Synthesis of *N*-sulfonylazetidines: To a flame-dried flask equipped with a stir bar was added KOH (841 mg, 15 mmol, 3.0 equiv.), followed by THF (10 ml). A solution of alcohol C (1 equiv.) in THF (15 ml) was then added dropwise at room temperature. After that, TsCl (1.1 g, 5.5 mmol, 1.1 equiv.) was added portionwise and the reaction mixture was refluxed for 2 h. After the reaction was complete as monitored by TLC, cold water (10 ml) was added, extracted with EtOAc, washed with brine, dried over Na_2SO_4, concentrated, and purified via flash column chromatography with a gradient of 10 - 20% ethyl acetate in hexanes as eluent.

5. Mechanistic Experiments

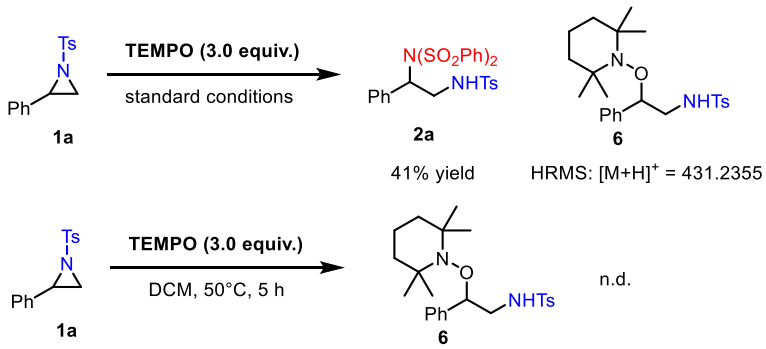
Radical Probe Experiments

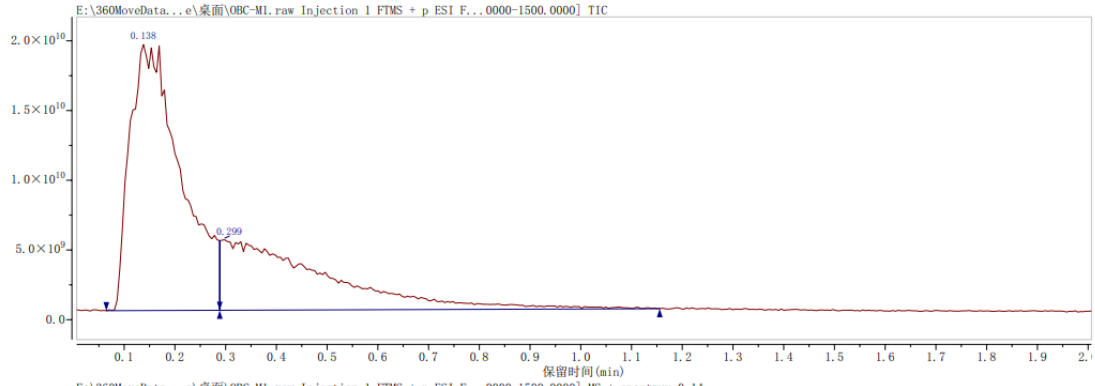
To a flame-dried Schlenk tube with a stir bar was added Co(salen) complex **A** (10 mol%), N-Fluorobenzenesulfonimide (0.22 mmol), aziridines (0.2 mmol) and 2,2,6,6-Tetra-methylpiperidinooxy (TEMPO) or Butylated Hydroxytoluene (BHT) (0.6 mmol). The contents were evacuated and backfilled three times with nitrogen. Then anhydrous dichloromethane (0.1 M) was added. The reaction mixture was kept stirring at 50 °C. When the reaction was complete as suggested by TLC, the reaction mixture was directly concentrated by rotary evaporation. The products were isolated by silica column chromatography (typically 20% of ethyl acetate in petroleum ether).

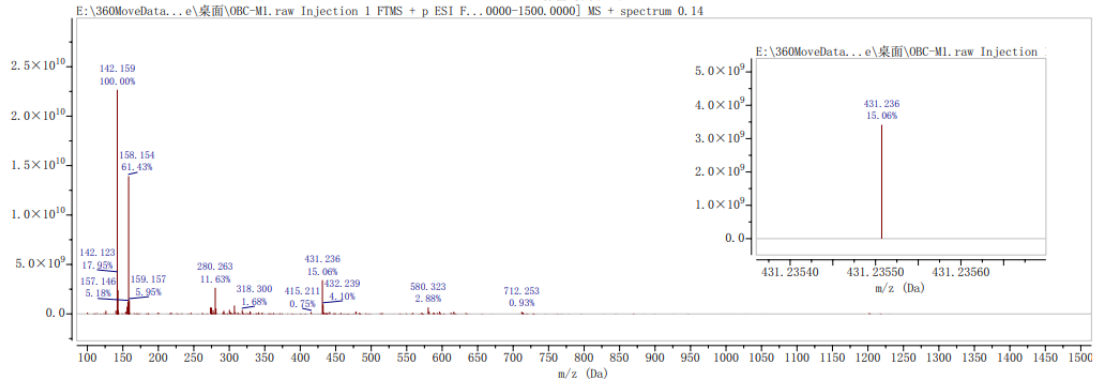


Entry	Additive	Yield (**2a**)
1	TEMPO	41%
2	BHT	26%

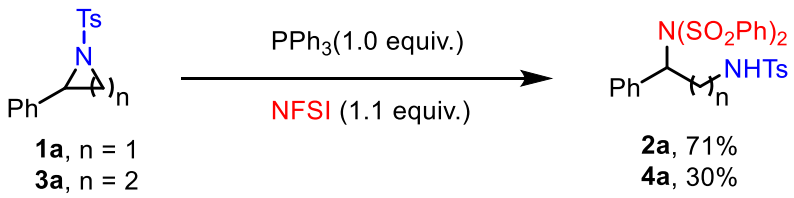
To a flame-dried Schlenk tube with a stir bar was added Co(salen) complex **A** (10 mol%), N-Fluorobenzenesulfonimide (0.22 mmol), aziridines (0.2 mmol) and 2,2,6,6-Tetra-methylpiperidinooxy (TEMPO). The contents were evacuated and backfilled three times with nitrogen. Then anhydrous dichloromethane (0.1 M) was added. The reaction mixture was kept stirring at 50 °C. HRMS experiment was performed after the reaction was completed.







Nucleophilic Attack Experiments

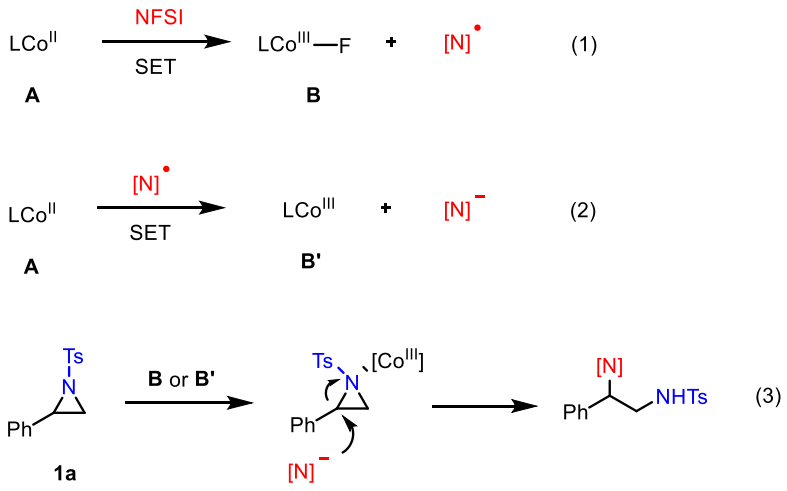


1a, n = 1
3a, n = 2

2a, 71%
4a, 30%

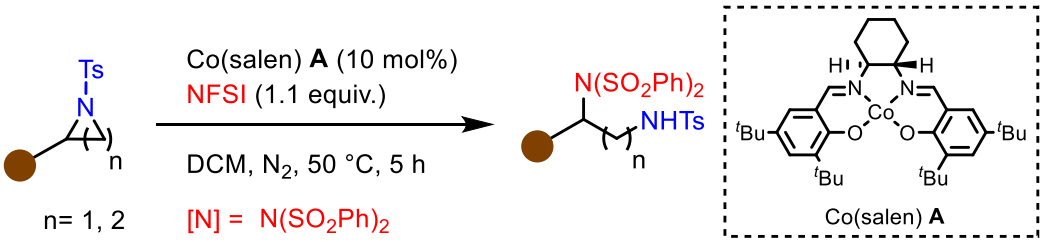
To a flame-dried Schlenk tube with a stir bar was added PPh_3 (0.2 mmol), N-Fluorobenzenesulfonimide (0.22 mmol), aziridines (0.2 mmol) and. The contents were evacuated and backfilled three times with nitrogen. Then anhydrous dichloromethane (0.1 M) was added. The reaction mixture was kept stirring at 50 ^{o}C. When the reaction was complete as suggested by TLC, the reaction mixture was directly concentrated by rotary evaporation. The products were isolated by silica column chromatography (typically 20% of ethyl acetate in petroleum ether).

Proposed mechanism

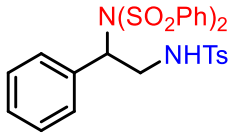


6. Cobalt-catalyzed Amination of Aziridines and Azetidines toward 1,2- and 1,3-Diamines

General Procedure D

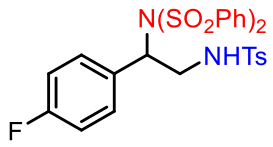


To a flame-dried Schlenk tube with a stir bar was added Co(salen) complex **A** (10 mol%). The contents were evacuated and backfilled three times with nitrogen. N-Fluorobenzenesulfonimide (0.22 mmol) and aziridines or azetidines (0.2 mmol) were added and dissolved in anhydrous dichloromethane (0.1 M). The reaction mixture was kept stirring at 50 ºC or 80 ºC. When the reaction was complete as suggested by TLC, the reaction mixture was directly concentrated by rotary evaporation. The products were isolated by silica column chromatography (typically 20% of ethyl acetate in petroleum ether).



2a, N-(2-((4-Methylphenyl)sulfonamido)-1-phenylethyl)-N-(phenylsulfonyl)benzenesulfonamide Synthesized according to **General Procedure D**. Purification via column chromatography (petroleum ether/ethyl acetate = 5:1) afforded 99.2 mg (87% yield) of the desired product as a white solid.

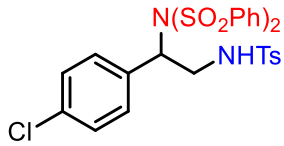
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 - 7.51 (m, 6H), 7.40 (s, 4H), 7.32 - 7.26 (m, 4H), 7.26 - 7.20 (m, 5H), 5.71 (dd, *J* = 9.5, 5.9 Hz, 1H), 4.71 (t, *J* = 6.8 Hz, 1H), 4.00 (m, 1H), 3.37 (m, 1H), 2.42 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.8, 140.1, 136.8, 133.8, 133.4, 129.9, 129.6, 128.9, 128.9, 128.7, 128.5, 127.0, 63.5, 44.0, 21.6. **IR** (neat, cm^{-1}): 3252 (w), 1447 (w), 1335 (m), 1161(s), 884(m), 684 (m), 545 (s). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{27}H_{27}N_2O_6S_3^+$: 571.1026; Found: 571.1026.



2b, N-(1-(4-Fluorophenyl)-2-((4-methylphenyl)sulfonamido)ethyl)-N-(phenylsulfonyl) benzene sulfonamide

Synthesized according to **General Procedure D**. Purification via column chromatography (petroleum ether/ethyl acetate = 5:1) afforded 48.2 mg (41% yield) of the desired product as a yellow solid.

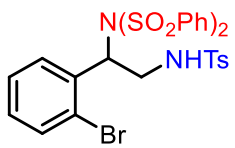
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 - 7.53 (m, 7H), 7.45 (s, 4H), 7.31 - 7.25 (m, 5H), 6.92 (t, *J* = 8.6 Hz, 2H), 5.70 (dd, *J* = 9.3, 6.1 Hz, 1H), 4.58 (t, *J* = 6.8 Hz, 1H), 3.95 (m, 1H), 3.44 - 3.37 (m, 1H), 2.44 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 163.7, 162.1, 143.9, 134.0, 136.7, 134.0, 131.5 (d, *J* = 8.3 Hz), 130.0, 129.0, 128.5, 127.1, 115.6 (d, *J* = 21.6 Hz), 62.9, 44.2, 21.7. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -112.19 (t, *J* = 7.0 Hz). **IR** (neat, cm^{-1}): 3288 (br), 2923 (m), 1512 (m), 1379 (m), 1164 (s), 1085 (m), 834 (m), 730 (m), 582 (s), 551(s). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{27}H_{26}FN_2O_6S_3^+$: 589.0923; Found: 589.0929.



2c, N-(1-(4-Chlorophenyl)-2-((4-methylphenyl)sulfonamido)ethyl)-N-(phenylsulfonyl) benzene sulfonamide

Synthesized according to **General Procedure D**. Purification via column chromatography (petroleum ether/ethyl acetate = 5:1) afforded 99.1 mg (82% yield) of the desired product as a yellow solid.

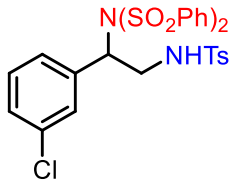
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 - 7.53 (m, 4H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.47 - 7.30 (m, 5H), 7.23 - 7.11 (m, 7H), 5.66 (dd, *J* = 9.6, 5.7 Hz, 1H), 4.94 (t, *J* = 6.7 Hz, 1H), 3.99 - 3.92 (m, 1H), 3.32 - 3.24 (m, 1H), 2.42 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.9, 139.9, 136.6, 134.9, 134.0, 132.1, 131.0, 129.9, 129.0, 128.7, 128.5, 127.0, 62.7, 43.9, 21.7. **IR** (neat, cm^{-1}): 3266 (w), 1447 (w), 1381 (m), 1160 (s), 1090 (m), 905 (m), 816 (m), 685 (m), 547 (s). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{27}H_{26}ClN_2O_6S_3^+$: 605.0636; Found: 605.0635.



2d, N-(1-(2-Bromophenyl)-2-((4-methylphenyl)sulfonamido)ethyl)-N-(phenylsulfonyl) benzene sulfonamide

Synthesized according to **General Procedure D**. Purification via column chromatography (petroleum ether/ethyl acetate = 5:1) afforded 88.1 mg (68% yield) of the desired product as a yellow solid.

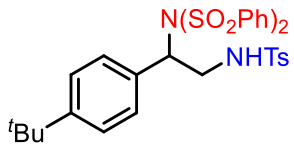
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 - 7.70 (m, 3H), 7.65 (t, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 7.6 Hz, 2H), 7.47 (d, *J* = 7.9 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 4H), 7.27 - 7.23 (m, 4H), 6.97 (dd, *J* = 7.2, 1.7 Hz, 2H), 5.86 (dd, *J* = 10.4, 5.0 Hz, 1H), 4.95 (dd, *J* = 7.5, 5.7 Hz, 1H), 4.05 - 3.97 (m, 1H), 3.76 - 3.70 (m, 1H), 2.42 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.8, 140.1, 136.9, 133.6, 133.5, 132.0, 130.5, 130.4, 130.0, 128.7, 128.4, 127.7, 127.3, 127.0, 61.9, 44.0, 21.7. **IR** (neat, cm^{-1}): 3286 (br), 2923 (w), 1447 (w), 1376 (m), 1159 (s), 896 (m), 718 (m), 548 (s). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{27}H_{26}BrN_2O_6S_3^+$: 649.0131; Found: 649.0129.



2e, N-(1-(3-Chlorophenyl)-2-((4-methylphenyl)sulfonamido)ethyl)-N-(phenylsulfonyl) benzene sulfonamide

Synthesized according to **General Procedure D**. Purification via column chromatography (petroleum ether/ethyl acetate = 5:1) afforded 89.4 mg (74% yield) of the desired product as a yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 - 7.56 (m, 4H), 7.54 (d, *J* = 8.3 Hz, 2H), 7.51 - 7.27 (m, 5H), 7.30 - 7.19 (m, 5H), 7.17 - 7.10 (m, 2H), 5.65 (dd, *J* = 9.5, 5.7 Hz, 1H), 4.87 (t, *J* = 6.7 Hz, 1H), 3.96 (m, 1H), 3.34 (m, 1H), 2.42 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.9, 139.8, 136.6, 135.5, 134.6, 134.0, 129.9, 129.9, 129.8, 129.0, 128.9, 128.5, 127.6, 127.0, 62.6, 43.9, 21.7. **IR** (neat, cm^{-1}): 3272 (w), 1447(w), 1377 (m), 1150 (s), 885(m), 683 (m), 545 (s). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{27}H_{26}ClN_2O_6S_3^+$: 605.0636; Found: 605.0634.

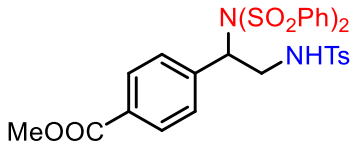


2f, N-(1-(4-(tert-butyl)phenyl)-2-((4-methylphenyl)sulfonamido)ethyl)-N-(phenylsulfonyl)benze nesulfonamide

Synthesized according to **General Procedure D**. Purification via column chromatography (petroleum ether/ethyl acetate = 5:1) afforded 107.7 mg (86% yield) of the desired product as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 - 7.50 (m, 5H), 7.46 - 7.32 (m, 4H), 7.30 - 7.21 (m, 9H), 5.72 (dd, *J* = 9.5, 5.9 Hz, 1H), 4.69 - 4.63 (m, 1H), 4.00 - 3.94 (m, 1H), 3.40 - 3.34 (m, 1H), 2.42 (s, 3H), 1.32 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 152.1, 143.7, 140.2, 136.8, 133.8, 130.3, 129.9, 129.4, 128.9, 128.6, 127.1, 125.6, 63.3, 44.0, 34.7, 31.5, 21.6. **IR** (neat, cm^{-1}): 3275 (w), 2960 (w),

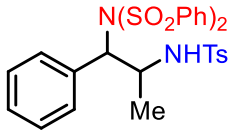
1448(w), 1378 (m), 1161 (s), 1086 (m), 905 (m), 830 (m), 719 (m), 561 (s). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{31}H_{34}N_2O_6S_3^+$: 627.1652; Found: 627.1656.



2g, Methyl 4-(2-((4-methylphenyl)sulfonamido)-1-(N-(phenylsulfonyl)phenylsulfonamido)ethyl) benzoate

Synthesized according to **General Procedure D**. Purification via column chromatography (petroleum ether/ethyl acetate = 3:1) afforded 77.9 mg (62% yield) of the desired product as a yellow solid.

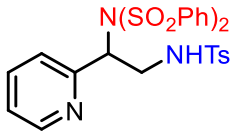
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 - 7.74 (m, 4H), 7.73 - 7.49 (m, 6H), 7.34 (m, 6H), 7.22 (d, *J* = 7.7 Hz, 2H), 5.70 (dd, *J* = 9.4, 5.7 Hz, 1H), 4.90 (t, *J* = 6.7 Hz, 1H), 4.04 - 3.98 (m, 1H), 3.94 (s, 3H), 3.37 - 3.31 (m, 1H), 2.41 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.6, 143.9, 139.8, 138.5, 136.6, 134.0, 130.3, 129.9, 129.7, 129.6, 129.0, 128.5, 127.0, 62.8, 52.5, 43.9, 21.6. **IR** (neat, cm^{-1}): 3279 (br), 1720 (m), 1378 (m), 1282 (s), 1160 (s), 735 (m), 548 (s). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{29}H_{29}N_2O_8S_3^+$: 629.1081; Found: 629.1079.



2h, N-(2-((4-Methylphenyl)sulfonamido)-1-phenylpropyl)-N-(phenylsulfonyl) benzenesulfona mide

Synthesized according to **General Procedure D**. Purification via column chromatography (petroleum ether/ethyl acetate = 5:1) afforded 79.4 mg (68% yield, 4:1 d.r.) of the desired product as a yellow solid.

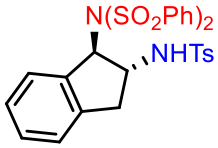
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.43 - 7.55 (m, 8H), 7.29 - 7.22 (m, 2H), 7.05 - 7.21(m, 8H), 5.06 (d, *J* = 10.5 Hz, 1H), 4.92 (d, *J* = 8.3 Hz, 1H), 4.74 - 4.66 (m, 1H), 2.40 (s, 3H), 0.68 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.4, 137.8, 134.3, 130.5, 129.7, 129.3, 128.6, 128.5, 127.1, 68.4, 51.4, 21.6, 18.8. **IR** (neat, cm^{-1}): 3264 (br), 3063 (w), 1448(w), 1367 (m), 1164 (s), 1085 (m), 684 (m), 546 (s). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{28}H_{29}N_2O_6S_3^+$: 585.1182; Found: 585.1184.



2i, N-(2-((4-Methylphenyl)sulfonamido)-1-(pyridin-2-yl)ethyl)-N-(phenylsulfonyl) benzene sulfonamide

Synthesized according to **General Procedure D**. Purification via column chromatography (petroleum ether/ethyl acetate = 3:1) afforded 90.2 mg (79% yield) of the desired product as a gray solid.

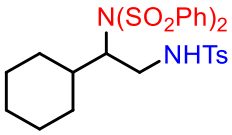
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (dt, *J* = 4.7, 1.4 Hz, 1H), 7.88 - 7.83 (m, 4H), 7.64 - 7.60 (m, 2H), 7.54 - 7.45 (m, 6H), 7.38 (m, 1H), 7.11 - 7.02 (m, 3H), 6.92 (d, *J* = 7.8 Hz, 1H), 6.14 (d, *J* = 8.4 Hz, 1H), 4.96 (q, *J* = 7.5 Hz, 1H), 4.00 - 3.88 (m, 2H), 2.29 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.5, 149.7, 143.2, 138.5, 137.2, 136.6, 134.2, 129.4, 129.2, 128.8, 127.2, 123.5, 123.2, 57.0, 52.6, 21.5. **IR** (neat, cm^{-1}): 3314 (br), 3064 (w), 1447(w), 1374 (m), 1161 (s), 1084 (m), 735 (s), 545(s). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{26}H_{26}N_3O_6S_3^+$: 572.0978; Found: 572.0976.



2j, N-(2-((4-Methylphenyl)sulfonamido)-2,3-dihydro-1H-inden-1-yl)-N-(phenylsulfonyl) benzene sulfonamide

Synthesized according to **General Procedure D**. Purification via column chromatography (petroleum ether/ethyl acetate = 5:1) afforded 87.8 mg (76% yield, 10:1 d.r.) of the desired product as a white solid.

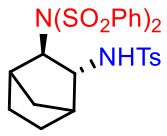
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.26 (dd, *J* = 7.7, 1.8 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 3H), 7.68 (dd, *J* = 8.4, 6.8 Hz, 2H), 7.42 (m, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.25 - 7.22 (m, 2H), 7.20 - 7.14 (m, 3H), 7.05 (d, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 7.7 Hz, 1H), 6.78 (t, *J* = 7.5 Hz, 1H), 6.22 (d, *J* = 9.6 Hz, 1H), 5.26 (d, *J* = 11.2 Hz, 1H), 4.47 - 4.39 (m, 1H), 2.85 (dd, *J* = 16.1, 8.6 Hz, 1H), 2.52 (dd, *J* = 16.1, 9.0 Hz, 1H), 2.46 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.7, 141.7, 140.2, 139.6, 138.5, 134.9, 134.2, 133.3, 130.0, 129.6, 129.4, 129.1, 128.4, 128.3, 127.3, 127.0, 126.7, 124.9, 66.4, 53.2, 38.0, 21.7. **IR** (neat, cm^{-1}): 3350 (br), 2925 (w), 1448 (w), 1346 (m), 1162 (s), 926 (m), 752 (m), 548 (s). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{28}H_{27}N_2O_6S_3^+$: 583.1026; Found: 583.1024.



2k, N-(1-Cyclohexyl-2-((4-methylphenyl)sulfonamido)ethyl)-N-(phenylsulfonyl) benzenesulfona mide

Synthesized according to **General Procedure D**. Purification via column chromatography (petroleum ether/ethyl acetate = 5:1) afforded 69.1 mg (60% yield) of the desired product as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 - 7.94 (m, 4H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.66 - 7.63 (m, 2H), 7.54 - 7.50 (m, 4H), 7.27 (d, *J* = 8.0 Hz, 2H), 4.89 (d, *J* = 6.8 Hz, 1H), 3.89 (dd, *J* = 14.3, 7.0 Hz, 1H), 3.68 - 3.57 (m, 2H), 2.42 (s, 3H), 1.76 - 1.67 (m, 2H), 1.59 - 1.50 (m, 2H), 1.46 (m, 1H), 1.09 (m, 1H), 1.04 - 0.95 (m, 2H), 0.89 - 0.79 (m, 2H), 0.73 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.5, 138.9, 137.6, 134.2, 129.7, 129.2, 128.7, 127.5, 57.1, 48.9, 38.1, 26.7, 26.3, 26.1, 21.7. **IR** (neat, cm^{-1}): 3293 (br), 2927 (m), 1447 (m), 1374 (m), 1163 (s), 1088 (m), 812 (m), 738 (m), 549 (s). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{27}H_{33}N_2O_6S_3^+$: 577.1495; Found: 577.1491.



2l, N-(3-((4-Methylphenyl)sulfonamido)bicyclo[2.2.1]heptan-2-yl)-N-(phenylsulfonyl)benzene sulfonamide

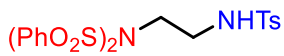
Synthesized according to **General Procedure D**. Purification via column chromatography (petroleum ether/ethyl acetate = 5:1) afforded 67.2 mg (62% yield, >20:1 d.r.) of the desired product as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 7.7, 1.8 Hz, 4H), 7.76 (d, *J* = 8.1 Hz, 2H), 7.69 - 7.64 (m, 2H), 7.58 (t, *J* = 7.8 Hz, 4H), 7.29 (m, 2H), 6.51 (d, *J* = 6.7 Hz, 1H), 3.98 (t, *J* = 7.6 Hz, 1H), 3.25 (d, *J* = 6.7 Hz, 1H), 2.63 - 2.60 (m, 1H), 2.52 (m, 1H), 2.44 (s, 3H), 2.19 - 2.14 (m, 1H), 1.65 (m, 1H), 1.59 - 1.47 (m, 2H), 1.13 - 1.01 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.2, 140.6, 138.1, 134.1, 129.8, 129.5, 128.0, 127.2, 65.1, 61.1, 45.6, 39.9, 36.5, 27.8, 24.9, 21.7. **IR** (neat, cm^{-1}): 3290 (br), 2962 (w), 1448 (m), 1363 (m), 1158 (s), 827 (m), 753 (m), 666 (m), 549 (s). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{26}H_{29}N_2O_6S_3^+$: 561.1182; Found: 561.1185.

2m, N-(3,3-Dimethyl-1-((4-methylphenyl)sulfonamido)butan-2-yl)-N-(phenylsulfonyl)benzene sulfonamide

Synthesized according to **General Procedure D**. Purification via column chromatography (petroleum ether/ethyl acetate = 5:1) afforded 73.7 mg (67% yield) of the desired product as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 - 8.01 (m, 4H), 7.68 - 7.64 (m, 2H), 7.57 - 7.53 (m, 6H), 7.17 - 7.14 (m, 2H), 4.78 (d, *J* = 8.1 Hz, 1H), 4.02 (dd, *J* = 15.4, 3.2 Hz, 1H), 3.83 (m, 1H), 3.52 (dd, *J* = 15.4, 10.7 Hz, 1H), 2.37 (s, 3H), 0.89 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 142.9, 139.0, 138.7, 134.3, 129.4, 129.2, 127.1, 61.6, 49.0, 35.3, 26.7, 21.6. **IR** (neat, cm^{-1}): 3311 (br), 2963 (w), 1448 (w), 1372 (m), 1159 (s), 1086 (m), 737 (m), 549 (s). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{25}H_{31}N_2O_6S_3^+$: 551.1339; Found:551.1337.



2n, N-(2-((4-Methylphenyl)sulfonamido)ethyl)-N-(phenylsulfonyl)benzenesulfonamide

Synthesized according to **General Procedure D**. Purification via column chromatography (petroleum ether/ethyl acetate = 5:1) afforded 63.2 mg (64% yield) of the desired product as a yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 8.4, 1.5 Hz, 4H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.67 - 7.62 (m, 2H), 7.52 (t, *J* = 7.8 Hz, 4H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.09 (t, *J* = 6.1 Hz, 1H), 3.79 (t, *J* = 6.8 Hz, 2H), 3.21 (q, *J* = 6.6 Hz, 2H), 2.43 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.8, 139.0, 136.6, 134.3, 129.9, 129.4, 128.4, 127.3, 47.8, 42.6, 21.7. **IR** (neat, cm^{-1}): 3306 (br), 1448 (m), 1372 (m), 1162 (s), 1085 (m), 735 (m), 548 (s). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{21}H_{23}N_2O_6S_3^+$: 495.0713; Found: 495.0713.

2o, N-(1-((4-Methylphenyl)sulfonamido)-3-phenoxypropan-2-yl)-N-(phenylsulfonyl)benzene sulfonamide

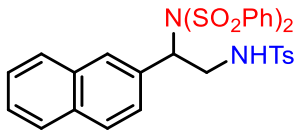
Synthesized according to **General Procedure D**. Purification via column chromatography (petroleum ether/ethyl acetate = 5:1) afforded 61.2 mg (51% yield) of the desired product as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.9 Hz, 4H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 2H), 7.44 (t, *J* = 7.8 Hz, 4H), 7.24 (t, *J* = 9.0 Hz, 4H), 6.97 (t, *J* = 7.4 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 2H), 5.32 (d, *J* = 6.5 Hz, 1H), 4.15 - 4.06 (m, 2H), 3.82 (dd, *J* = 9.7, 3.4 Hz, 2H), 3.71 (dd, *J* = 10.2, 3.6 Hz, 1H), 2.38 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 157.7, 143.8, 138.3, 137.1, 134.3, 129.8, 129.6, 129.2, 128.7, 127.3, 121.6, 114.5, 65.9, 52.3, 48.9, 21.6. **IR** (neat, cm^{-1}): 3296 (br), 3065 (w), 1598 (w), 1374 (m), 1161 (s), 1085(m), 736 (s), 547(s). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{28}H_{29}N_2O_7S_3^+$: 601.1131; Found: 601.1133.

2p, N-(1-((4-Methylphenyl)sulfonamido)-4-phenylbutan-2-yl)-N-(phenylsulfonyl)benzenesulfonamide

Synthesized according to **General Procedure D**. Purification via column chromatography (petroleum ether/ethyl acetate = 5:1) afforded 93.3 mg (78% yield) of the desired product as yellowish solid.

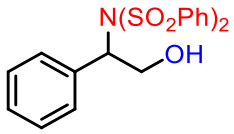
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.1 Hz, 4H), 7.81 (d, *J* = 8.1 Hz, 2H), 7.62 (t, *J* = 7.5 Hz, 2H), 7.47 (t, *J* = 7.9 Hz, 4H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.21 (t, *J* = 7.1 Hz, 2H), 7.16 (t, *J* = 7.2 Hz, 1H), 6.88 (d, *J* = 6.8 Hz, 2H), 5.09 (d, *J* = 6.5 Hz, 1H), 3.81 - 3.72 (m, 3H), 2.47 - 2.39 (m, 4H), 2.16 - 2.09 (m, 1H), 1.82 - 1.74 (m, 1H), 1.56 - 1.51 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.7, 140.8, 138.6, 137.5, 134.3, 129.9, 129.2, 128.7, 128.5, 128.4, 127.5, 126.1, 53.1, 51.9, 33.9, 31.3, 21.7. **IR** (neat, cm^{-1}): 3289 (br), 2923 (w), 1448 (w), 1374 (m), 1161 (s), 1085 (m), 736 (s), 549 (s). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{29}H_{31}N_2O_6S_3^+$: 599.1339; Found: 599.1336.



2q, N-(2-((4-Methylphenyl)sulfonamido)-1-(naphthalen-2-yl)ethyl)-N-(phenylsulfonyl)benzene sulfonamide

Synthesized according to **General Procedure D**. Purification via column chromatography (petroleum ether/ethyl acetate = 5:1) afforded 110.4 mg (89% yield) of the desired product as a white solid.

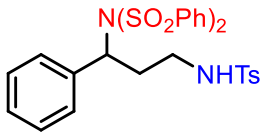
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 - 7.88 (m, 1H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.71 - 7.64 (m, 3H), 7.59 (dd, *J* = 8.5, 6.8 Hz, 4H), 7.55 - 7.40 (m, 6H), 7.35 (dd, *J* = 8.6, 1.9 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 3H), 5.93 - 5.87 (m, 1H), 4.68 (t, *J* = 6.8 Hz, 1H), 4.15 - 4.08 (m, 1H), 3.60 - 3.51 (m, 1H), 2.41 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.8, 140.0, 136.9, 133.7, 133.2, 132.8, 130.6, 129.9, 128.8, 128.6, 128.5, 128.4, 127.6, 127.1, 126.9, 126.6, 63.5, 44.1, 21.7. **IR** (neat, cm^{-1}): 3229 (w), 2918 (w), 1352 (m), 1155(m), 816 (m), 684 (m), 584 (s), 546(s). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{31}H_{29}N_2O_6S_3^+$: 621.1182; Found: 621.1182.



5, N-(2-Hydroxy-1-phenylethyl)-N-(phenylsulfonyl)benzenesulfonamide

Synthesized according to **General Procedure D**. Purification via column chromatography (petroleum ether/ethyl acetate = 3:1) afforded 53.4 mg (64% yield) of the desired product as a white solid.

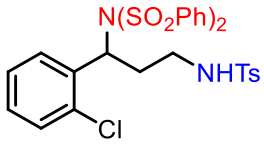
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 - 7.68 (m, 3H), 7.58 (t, *J* = 7.5 Hz, 2H), 7.50 - 7.36 (m, 6H), 7.29 (dd, *J* = 10.5, 3.2 Hz, 4H), 5.69 (t, *J* = 7.3 Hz, 1H), 4.45 (dd, *J* = 11.5, 7.2 Hz, 1H), 4.24 (dd, *J* = 11.5, 7.5 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 140.4, 134.3, 133.7, 129.4, 128.8, 128.6, 128.6, 65.6, 62.7. **IR** (neat, cm^{-1}): 3229 (w), 2918 (w), 1352 (m), 1155(m), 816 (m), 684 (m), 584 (s), 546(s). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{20}H_{20}NO_5S_2^+$: 418.0777; Found: 418.0775.



4a, N-(3-((4-Methylphenyl)sulfonamido)-1-phenylpropyl)-N-(phenylsulfonyl)benzenesulfonamide

Synthesized according to **General Procedure D**. Purification via column chromatography (petroleum ether/ethyl acetate = 5:1) afforded 78.3 mg (67% yield) of the desired product as white solid.

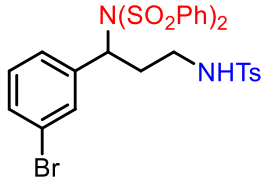
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 - 7.53 (m, *J* = 10.4 Hz, 6H), 7.53 - 7.37 (m, 4H), 7.32 (d, *J* = 6.2 Hz, 4H), 7.30 - 7.22 (m, 5H), 5.44 (dd, *J* = 9.8, 4.7 Hz, 1H), 4.39 - 4.31 (m, 1H), 2.99 - 2.85 (m, 2H), 2.83 - 2.70 (m, 1H), 2.43 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.7, 136.7, 134.8, 129.9, 129.6, 129.0, 128.6, 128.5, 127.1, 61.7, 40.5, 33.1, 21.7. **IR** (neat, cm^{-1}): 3287 (br), 1449 (m), 1369 (m), 1165 (s), 1085 (m), 721 (m), 578 (s), 548 (s). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{28}H_{28}ClN_2O_6S_3^+$: 585.1182; Found: 585.1185.



4b, N-(1-(2-Chlorophenyl)-3-((4-methylphenyl)sulfonamido)propyl)-N-(phenylsulfonyl)benzene sulfonamide

Synthesized according to **General Procedure D**. Purification via column chromatography (petroleum ether/ethyl acetate = 5:1) afforded 64.2 mg (52% yield) of the desired product as a yellow oil.

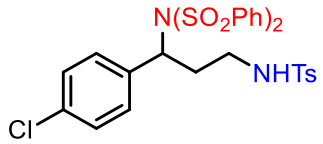
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.8 Hz, 1H), 7.81 - 7.70 (m, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.63 - 7.57 (m, 1H), 7.52 - 7.44 (m, 3H), 7.39 - 7.27 (m, 4H), 7.24 - 7.15 (m, 3H), 7.04 (t, *J* = 7.8 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 5.95 (dd, *J* = 10.5, 4.1 Hz, 1H), 5.03 - 4.97 (m, 1H), 3.02 – 2.75 (m, 3H), 2.47 - 2.39 (m, 1H), 2.37 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.6, 140.2, 139.6, 136.7, 136.5, 133.9, 133.4, 131.5, 130.3, 129.9, 129.8, 129.2, 128.6, 128.2, 127.8, 127.1, 126.6, 58.6, 40.2, 33.7, 21.6. **IR** (neat, cm^{-1}): 3284 (w), 1378 (w), 1166 (w), 902 (s), 722 (s), 649 (m), 549 (s). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{28}H_{28}ClN_2O_6S_3^+$:619.0793; Found: 619.0801.



4c, N-(1-(3-Bromophenyl)-3-((4-methylphenyl)sulfonamido)propyl)-N-(phenylsulfonyl)benzene sulfonamide

Synthesized according to **General Procedure D**. Purification via column chromatography (petroleum ether/ethyl acetate = 5:1) afforded 79.4 mg (60% yield) of the desired product as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 - 7.53 (m, 7H), 7.52 - 7.36 (m, 5H), 7.28 - 7.21 (m, 4H), 7.19 - 7.17 (m, 1H), 7.11 (t, *J* = 7.9 Hz, 1H), 5.35 (dd, *J* = 9.3, 5.0 Hz, 1H), 4.50 (dd, *J* = 7.5, 5.3 Hz, 1H), 2.89 (dt, *J* = 13.5, 5.5 Hz, 1H), 2.85 - 2.73 (m, 2H), 2.40 (s, 3H), 2.03 -1.96 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.8, 137.4, 136.6, 134.2, 132.4, 131.6, 123.0, 129.9, 129.2, 128.4, 127.9, 127.1, 122.5, 60.8, 40.2, 33.1, 21.7. **IR** (neat, cm^{-1}): 3267 (w), 1447 (m), 1370 (m), 1165 (s), 1081 (m), 727 (m), 578 (s), 548 (s). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{28}H_{28}BrN_2O_6S_3^+$: 663.0287; Found: 663.0281.



4d, N-(1-(4-Chlorophenyl)-3-((4-methylphenyl)sulfonamido)propyl)-N-(phenylsulfonyl)benzene sulfonamide

Synthesized according to **General Procedure D**. Purification via column chromatography (petroleum ether/ethyl acetate = 5:1) afforded 87.8 mg (71% yield) of the desired product as a white solid.

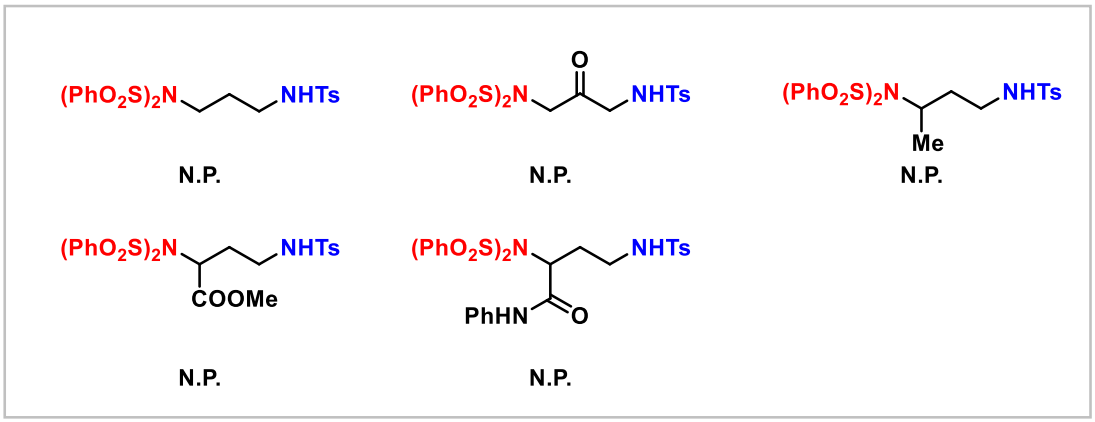
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 - 7.27 (m, 10H), 7.25 - 7.11 (m, 8H), 5.39 (dd, *J* = 10.0, 4.8 Hz, 1H), 4.60 (dd, *J* = 7.7, 5.0 Hz, 1H), 2.86 - 2.77 (m, 2H), 2.72 - 2.64 (m, 1H), 2.39 (s, 3H), 1.96 - 1.89 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.7, 136.6, 134.5, 134.0, 133.5, 131.0, 129.9, 129.1, 128.5, 128.4, 127.1, 60.9, 40.3, 33.1, 21.6. **IR** (neat, cm^{-1}): 3294 (br), 3065 (w), 1448(w), 1369(m), 1157(s), 1084 (m), 823 (m), 720 (m), 547 (s). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{28}H_{28}ClN_2O_6S_3^+$: 619.0793; Found: 619.0793.

4e, N-(3-((4-methylphenyl)sulfonamido)-1-(naphthalen-2-yl)propyl)-N-(phenylsulfonyl)benzene sulfonamide

Synthesized according to **General Procedure D**. Purification via column chromatography (petroleum ether/ethyl acetate = 5:1) afforded 83.7 mg (66% yield) of the desired product as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.9 Hz, 2H), 7.74 - 7.56 (m, 7H), 7.55 - 7.41 (m, 5H), 7.41 - 7.24 (m, 4H), 7.17 (d, *J* = 8.0 Hz, 3H), 5.61 (dd, *J* = 10.0, 4.7 Hz, 1H), 4.53 (t, *J* = 6.4 Hz, 1H), 3.09 - 2.90 (m, 2H), 2.88 - 2.75 (m, 1H), 2.33 (s, 3H), 2.14 - 2.02 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.6, 140.1, 136.7, 133.8, 133.1, 132.9, 132.1, 129.8, 128.9, 128.7, 128.4, 128.4, 128.1, 127.5, 127.1, 127.1, 126.8, 126.4, 61.8, 40.6, 33.2, 21.6. **IR** (neat, cm^{-1}): 3297 (br), 3062 (w), 1448 (w), 1370 (m), 1158 (s), 1084 (m), 857 (m), 720 (m), 547 (s). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{28}H_{28}ClN_2O_6S_3^+$: 639.1339; Found: 639.1334.

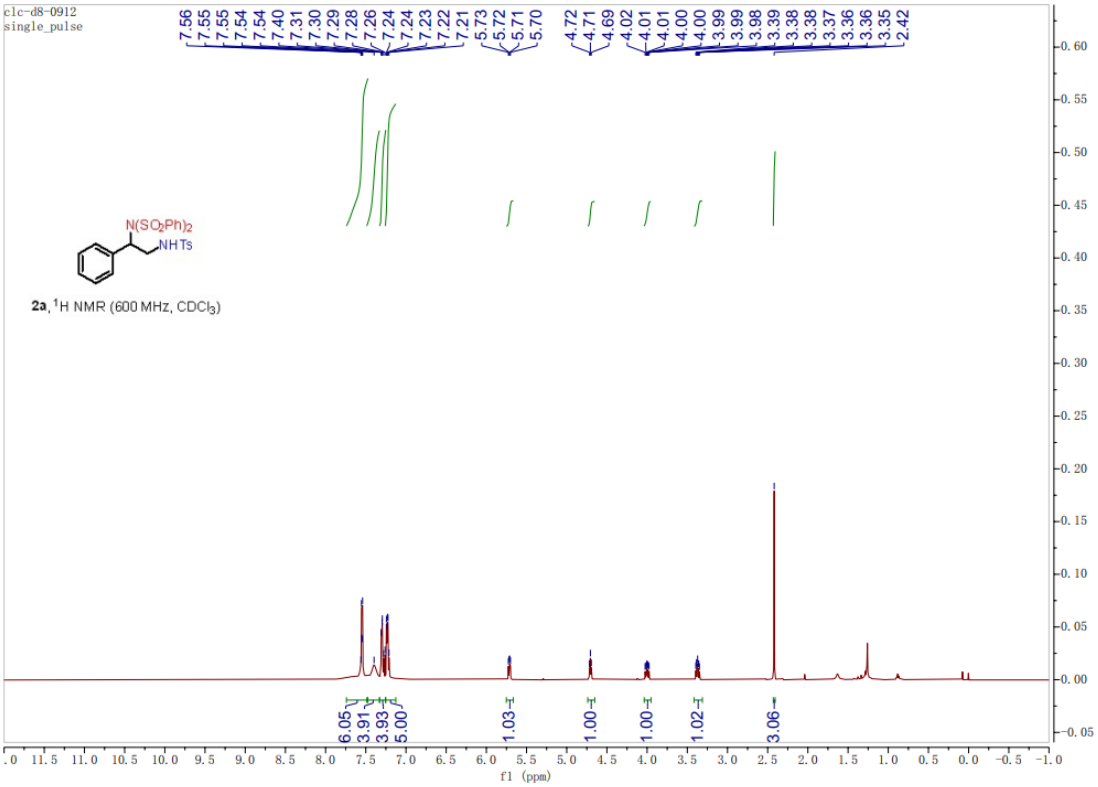
7. Unsuccessful substrate scope

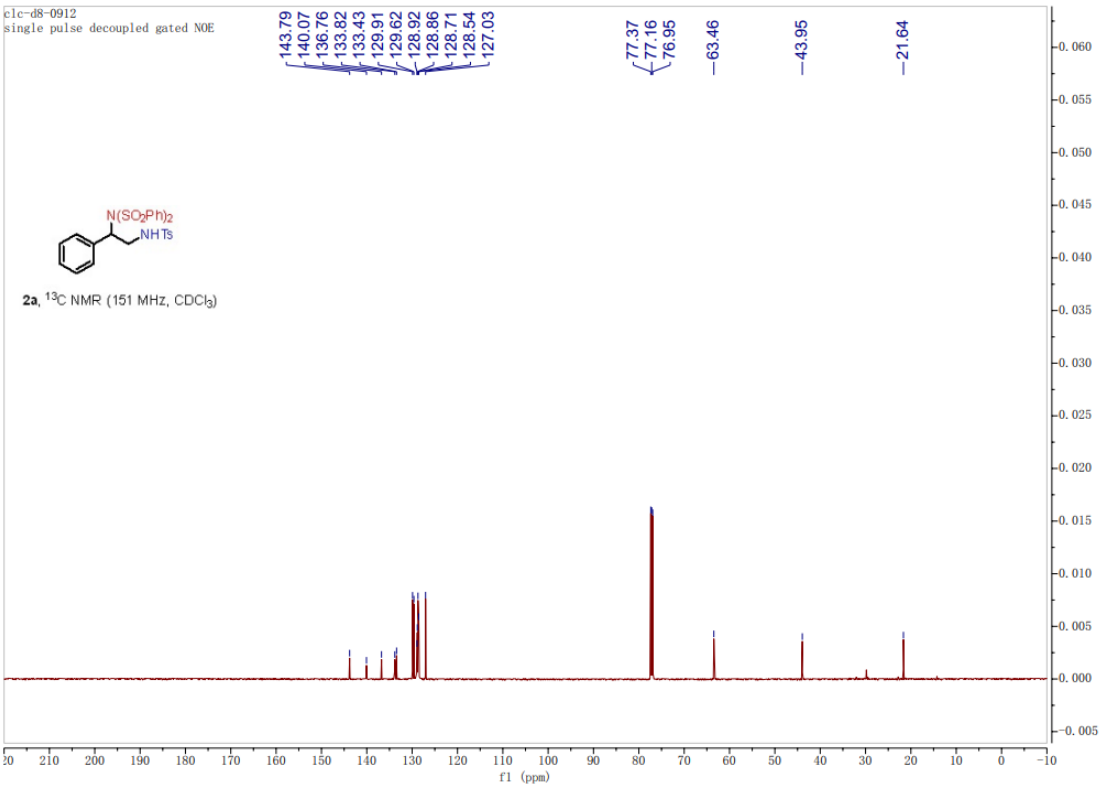


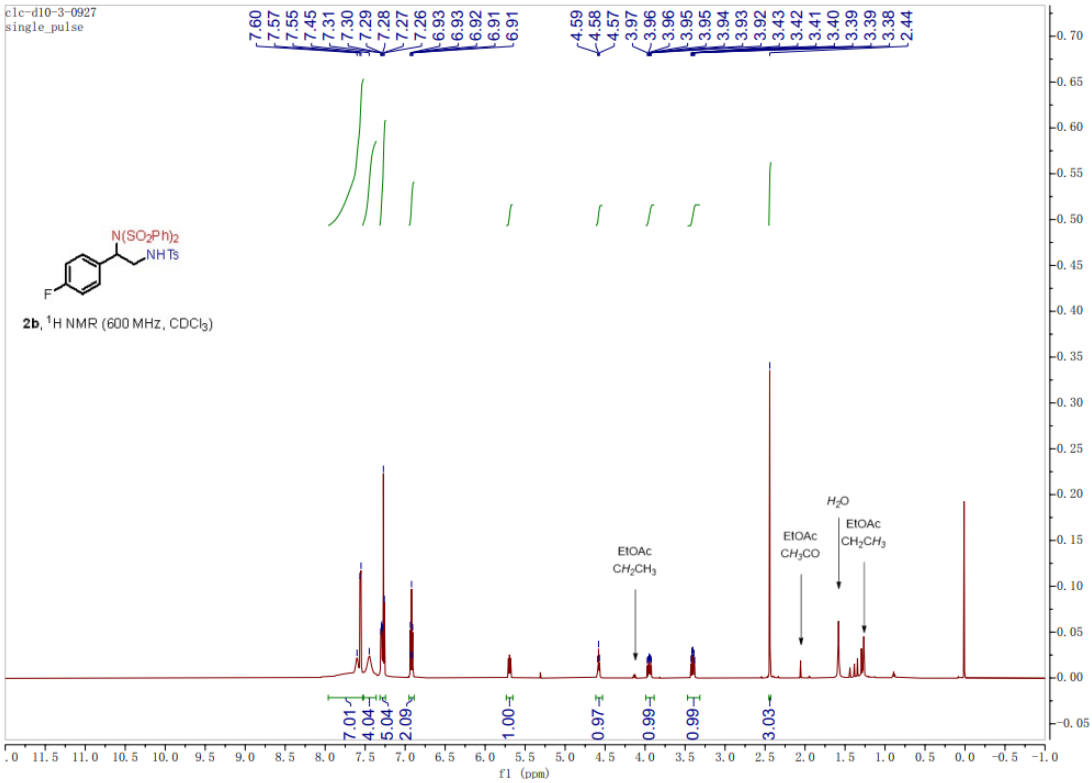
8. References

1. K. B. Hansen, J. L. Leighton, E. N. Jacobsen, *J. Am. Chem. Soc.* **1996**, 118, 10924-10925.
2. Q. Wu, J. Hu, X. Ren, J. Zhou, *Chemistry* **2011**, 17, 11553-11558.
3. D. A. Evans, M. M. Paul, M. T. Bilodeau, *J. Am. Chem. Soc.* **1994**, 116, 2742–2753.
4. M. K. Ghorai, S. Das, K. Das, A. Kumar, *Org. Biomol. Chem.* **2015**, 13, 9042–9049.

9. NMR Spectra



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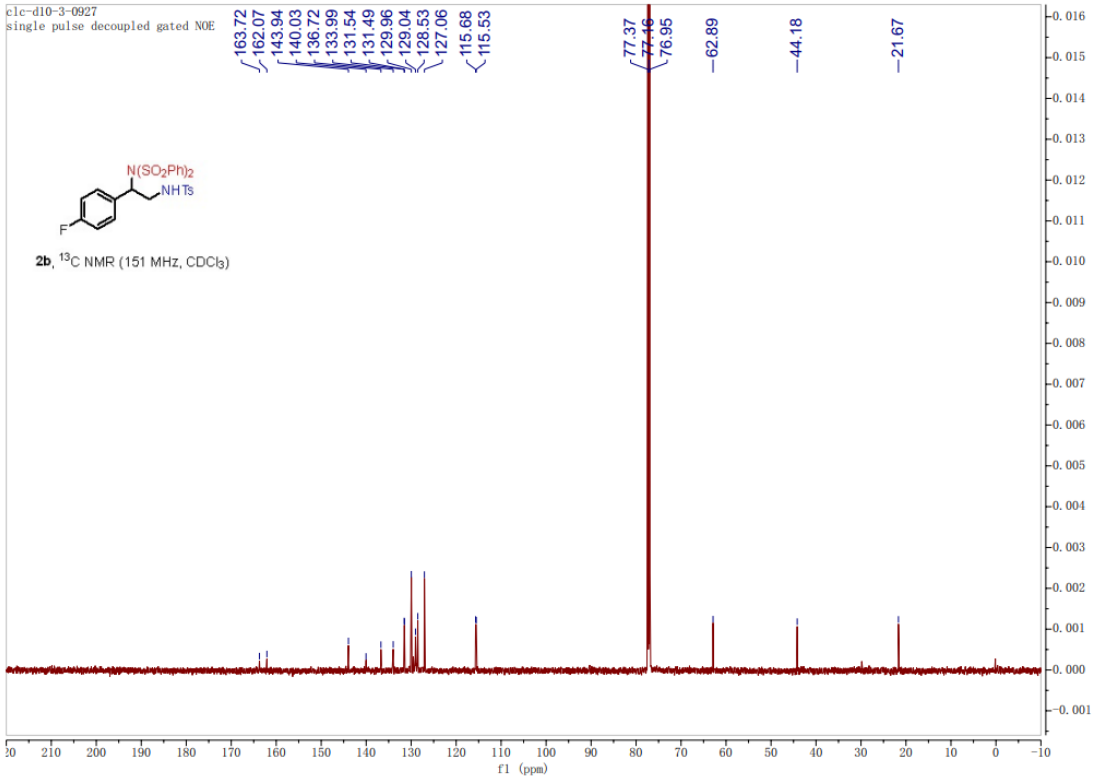
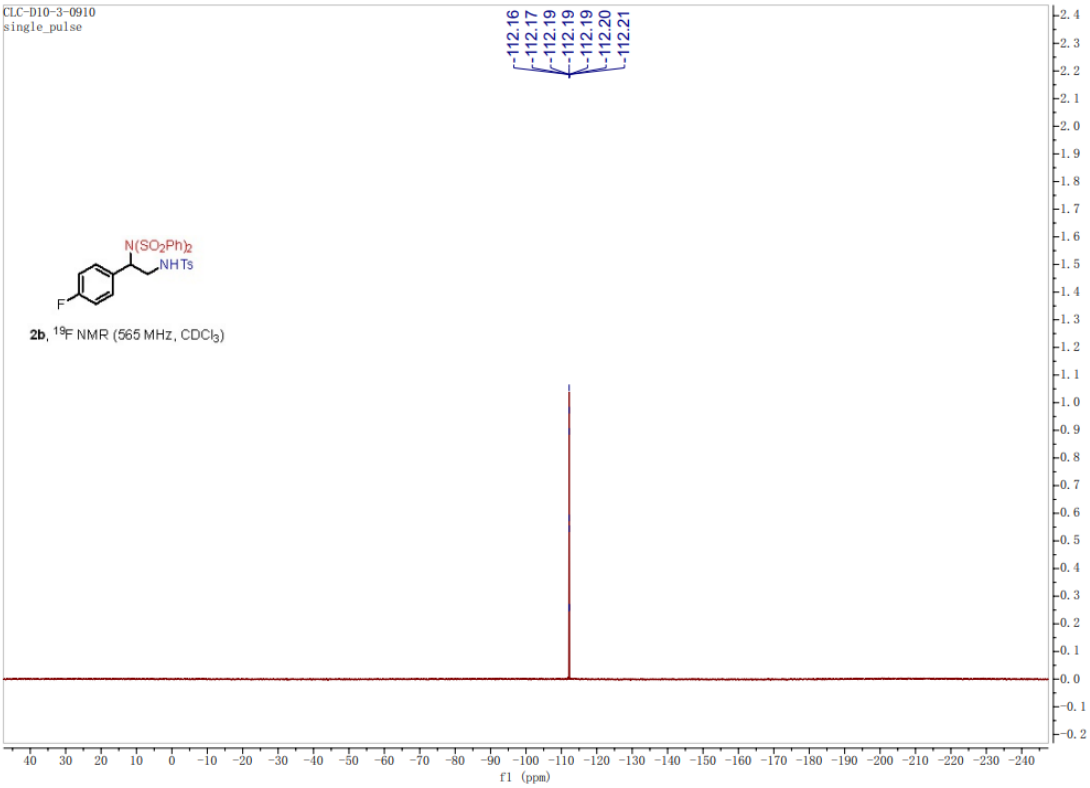
N(SO2Ph)2
NHTs
F
2b, 1H NMR (600 MHz, CDCl3)
EtOAc
CH2CH3
EtOAc
CH3CO
H2O
EtOAc
CH2CH3
f1 (ppm)


clc-d10-3-0927
single pulse decoupled gated NOE
N(SO2Ph)2
NHTs
F
2b, 13C NMR (151 MHz, CDCl3)
f1 (ppm)


CLC-D10-3-0910
single_pulse
-112.16
-112.17
-112.19
-112.19
-112.19
-112.20
-112.21
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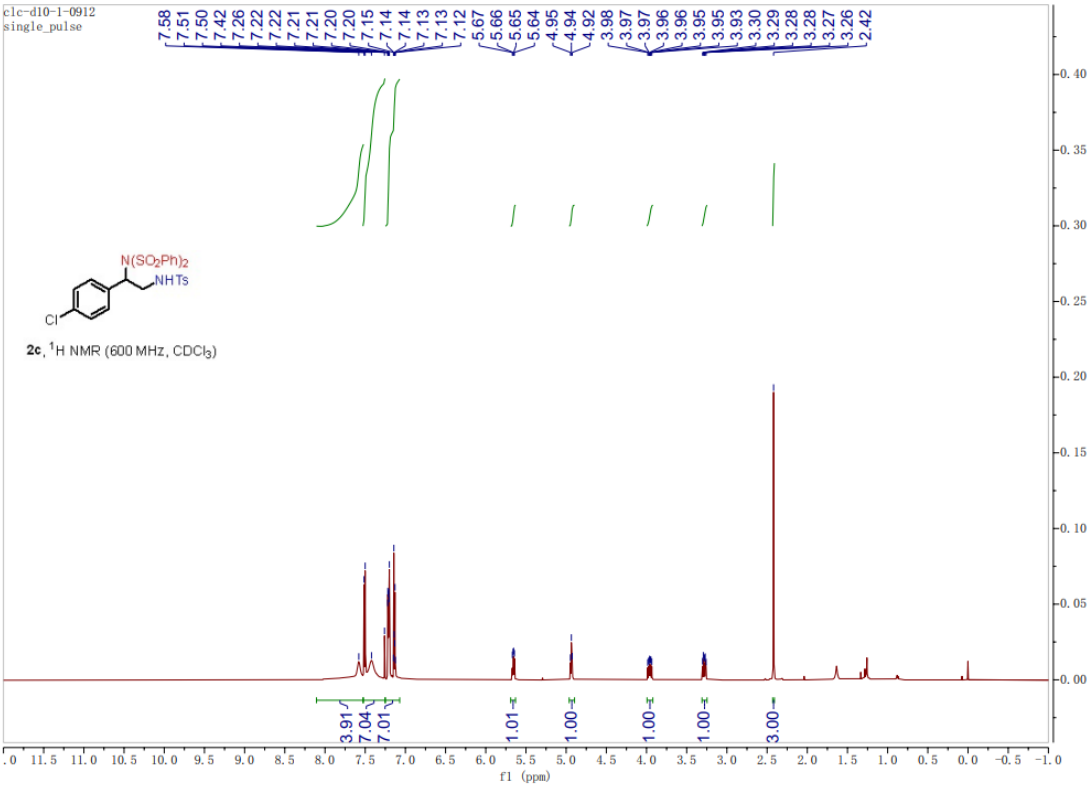
NHTs
F
2b, 19F NMR (565 MHz, CDCl3)
f1 (ppm)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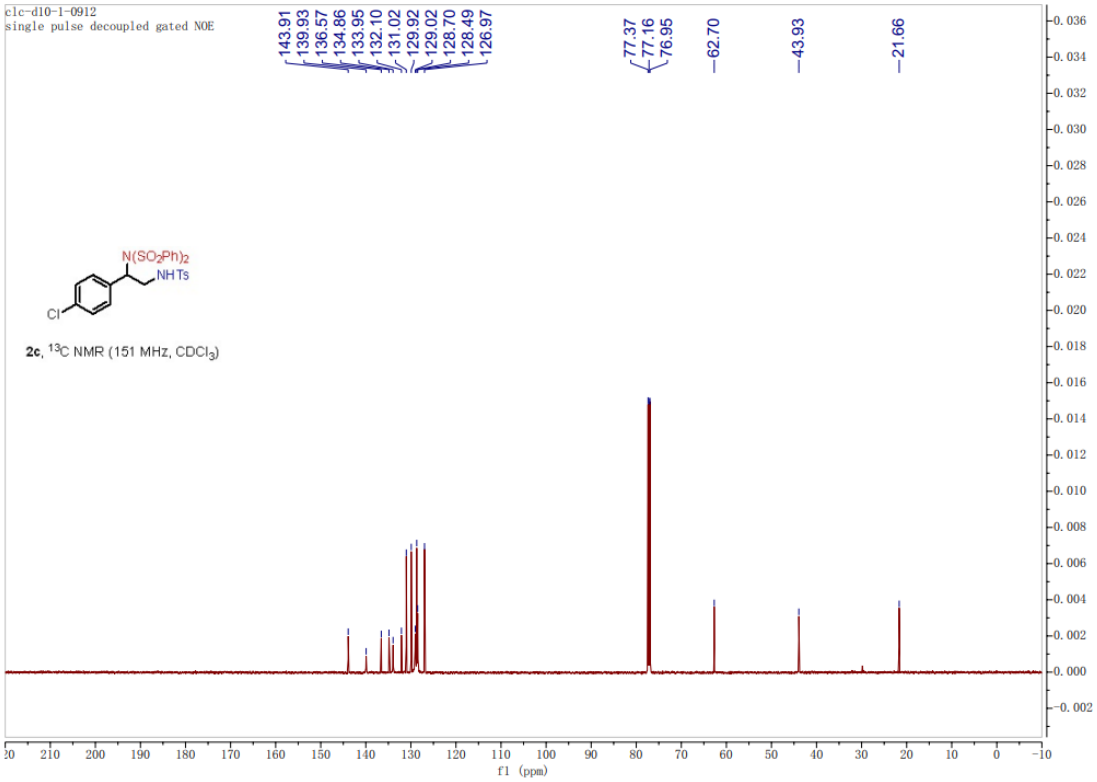
7.58
7.51
7.50
7.42
7.26
7.22
7.22
7.21
7.21
7.20
7.20
7.15
7.14
7.14
7.13
7.13
7.12
5.67
5.66
5.65
5.64
4.95
4.94
4.92
3.98
3.97
3.97
3.96
3.96
3.95
3.95
3.93
3.30
3.29
3.28
3.28
3.27
3.26
2.42
N(SO2Ph)2
NHTs
Cl
2c, 1H NMR (600 MHz, CDCl3)
3.91
7.04
7.01
1.01
1.00
1.00
1.00
3.00
f1 (ppm)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single pulse decoupled gated NOE
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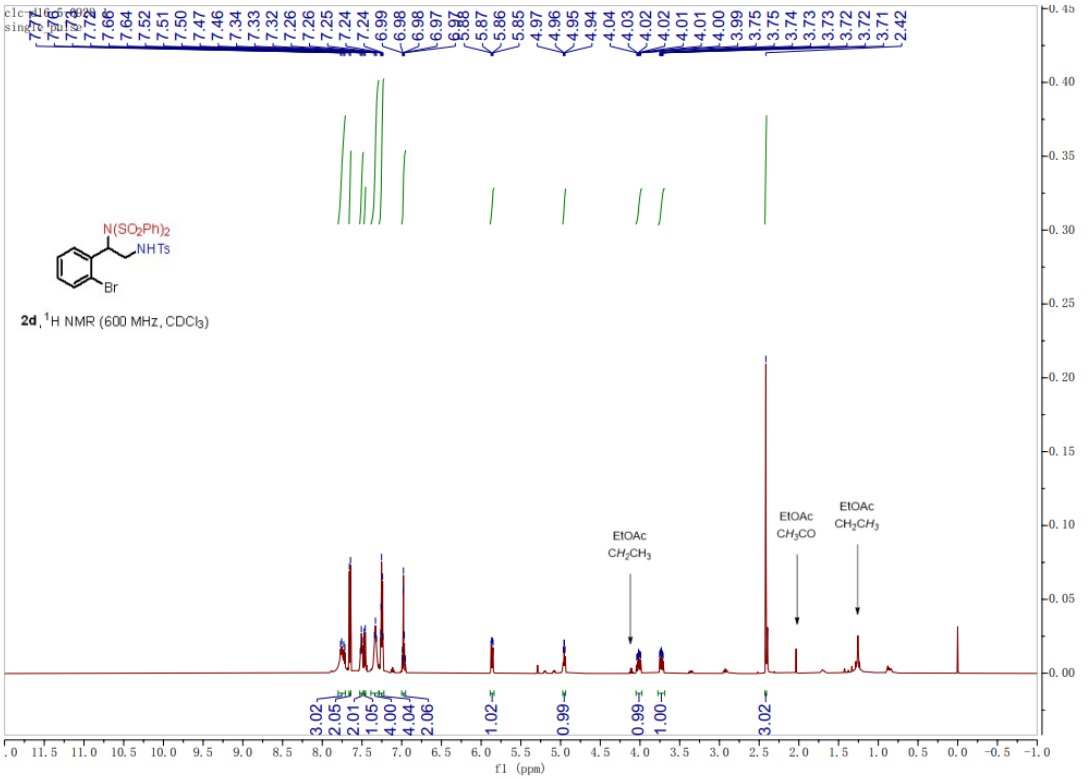
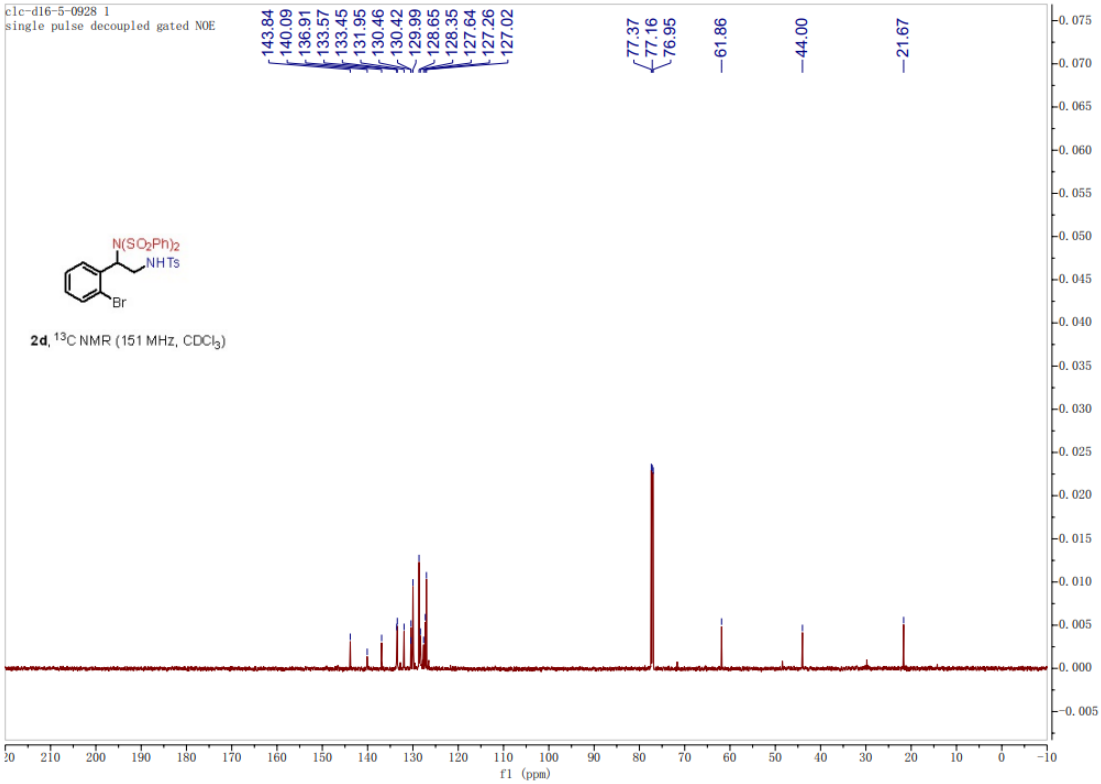
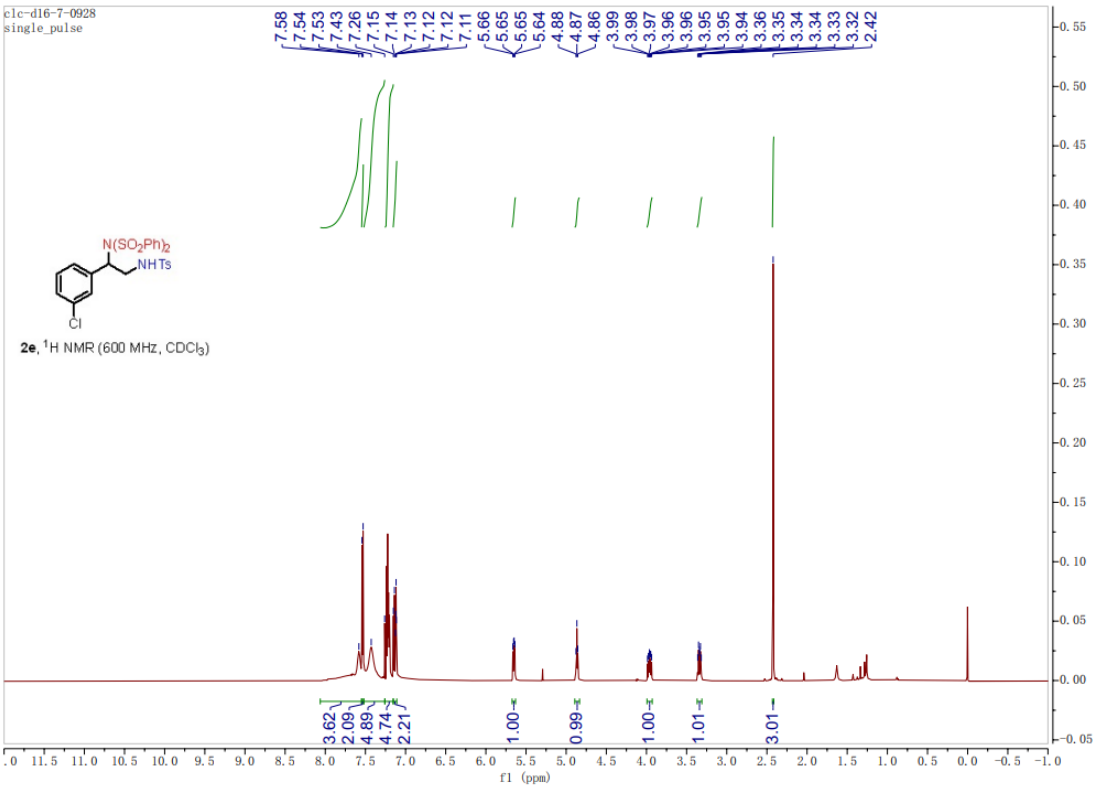
139.93
136.57
134.86
133.95
132.10
131.02
129.92
129.02
128.70
128.49
126.97
77.37
77.16
76.95
62.70
43.93
21.66
N(SO2Ph)2
NHTs
Cl
2c, 13C NMR (151 MHz, CDCl3)
f1 (ppm)


N(SO2Ph)2
NHTs
Br
2d, 1H NMR (600 MHz, CDCl3)
EtOAc
CH2CH3
EtOAc
CH3CO
EtOAc
CH2CH3
3.02
2.05
2.01
1.05
4.00
4.04
2.06
1.02
0.99
0.99
1.00
3.02
f1 (ppm)


clc-d16-5-0928 1
single pulse decoupled gated NOE
143.84
140.09
136.91
133.57
133.45
131.95
130.46
130.42
129.99
128.65
128.35
127.64
127.26
127.02
77.37
77.16
76.95
61.86
44.00
21.67
N(SO2Ph)2
NHTs
Br
2d, 13C NMR (151 MHz, CDCl3)
f1 (ppm)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single_pulse
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7.54
7.53
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7.26
7.15
7.14
7.13
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7.12
7.11
5.66
5.65
5.65
5.64
4.88
4.87
4.86
3.99
3.98
3.97
3.96
3.96
3.95
3.95
3.94
3.36
3.35
3.34
3.34
3.33
3.32
2.42
N(SO2Ph)2
NHTs
Cl
2e, 1H NMR (600 MHz, CDCl3)
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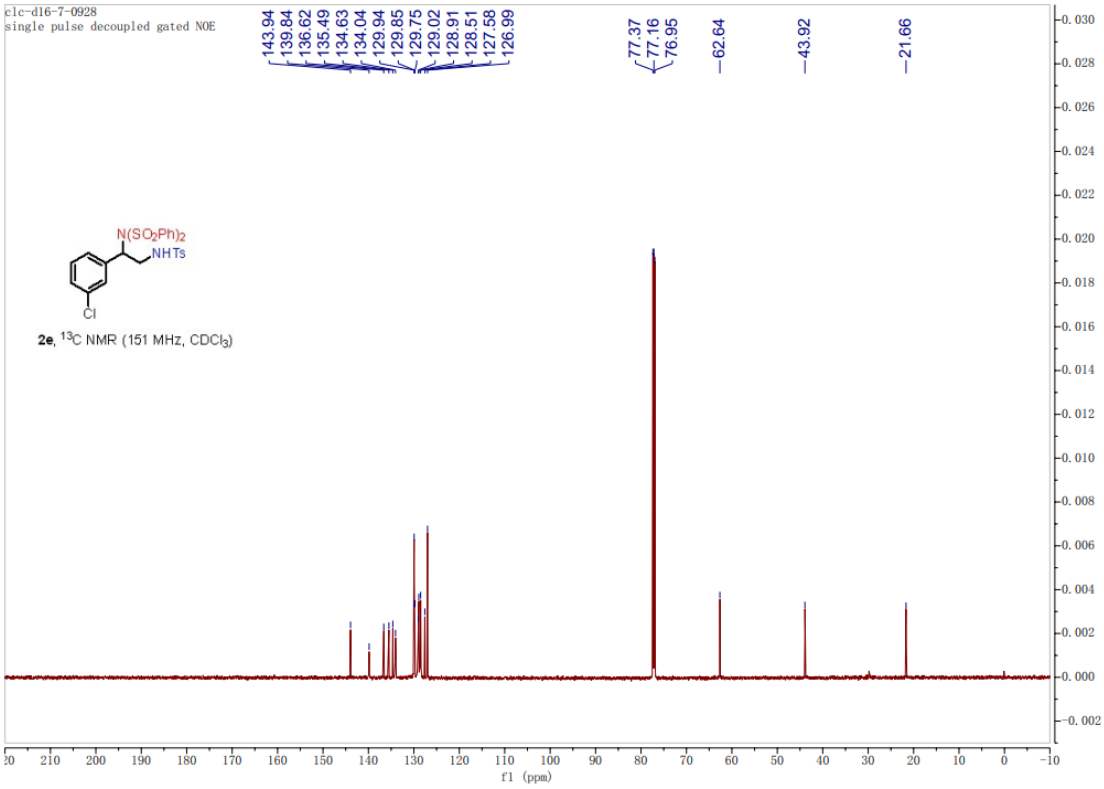
2.09
4.89
4.74
2.21
1.00
0.99
1.00
1.01
3.01
f1 (ppm)


clc-d16-7-0928
single pulse decoupled gated NOE
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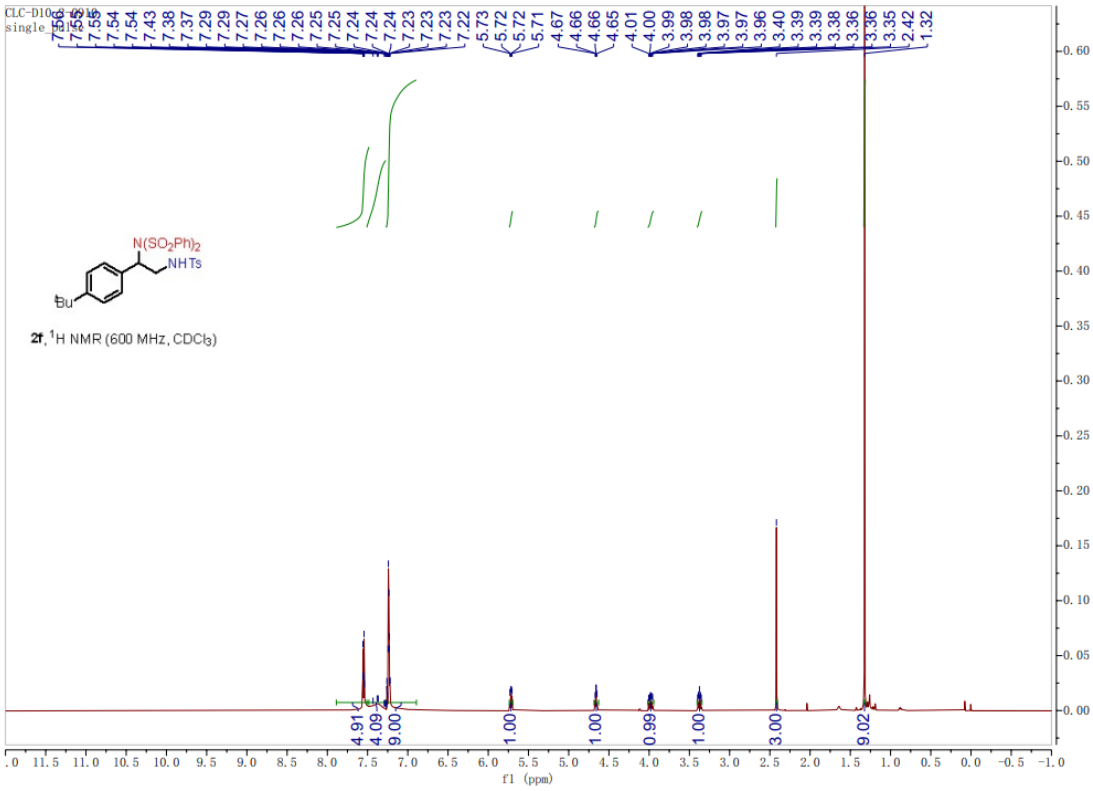
139.84
136.62
135.49
134.63
134.04
129.94
129.85
129.75
129.02
128.91
128.51
127.58
126.99
77.37
77.16
76.95
62.64
43.92
21.66
N(SO2Ph)2
NHTs
Cl
2e, 13C NMR (151 MHz, CDCl3)
f1 (ppm)


CLC-D10
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7.55
7.54
7.54
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7.38
7.37
7.29
7.29
7.27
7.26
7.26
7.26
7.25
7.25
7.24
7.24
7.24
7.23
7.23
7.23
7.22
5.73
5.72
5.72
5.71
4.67
4.66
4.66
4.65
4.01
4.00
3.99
3.98
3.98
3.97
3.97
3.96
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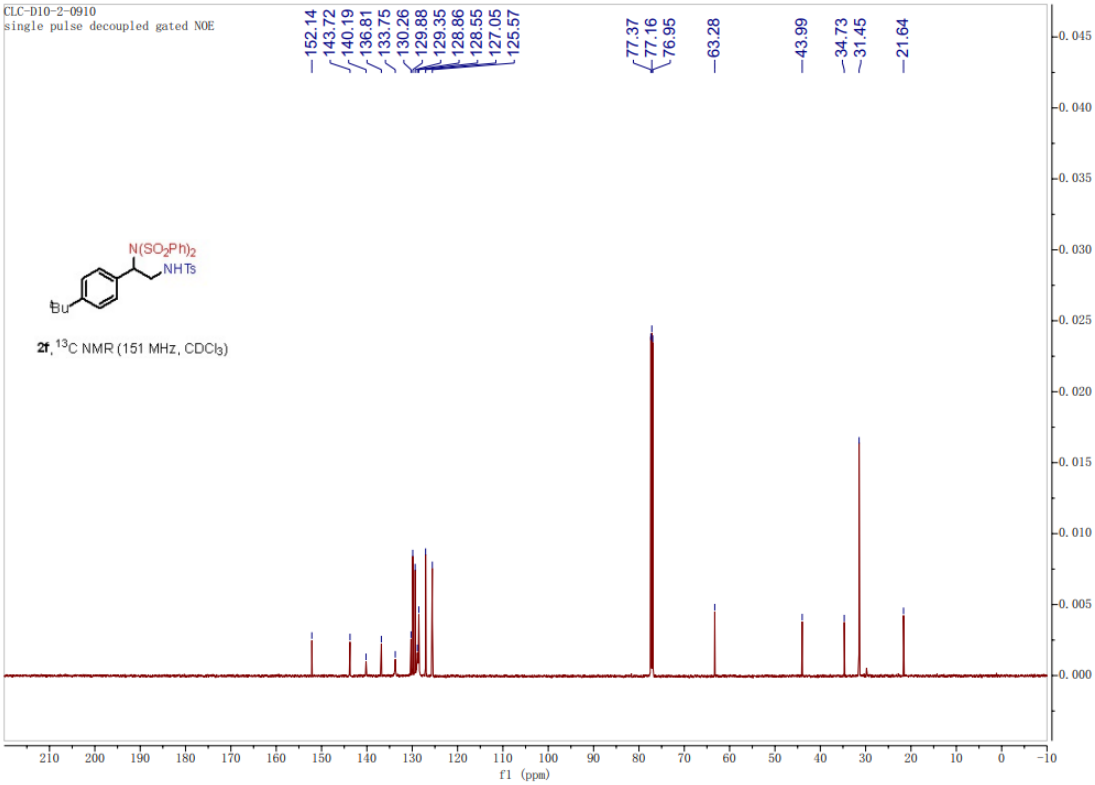
3.39
3.39
3.38
3.36
3.36
3.35
2.42
1.32
4.91
4.09
9.00
1.00
1.00
0.99
1.00
3.00
9.02
N(SO2Ph)2
NHTs
tBu
2f, 1H NMR (600 MHz, CDCl3)
f1 (ppm)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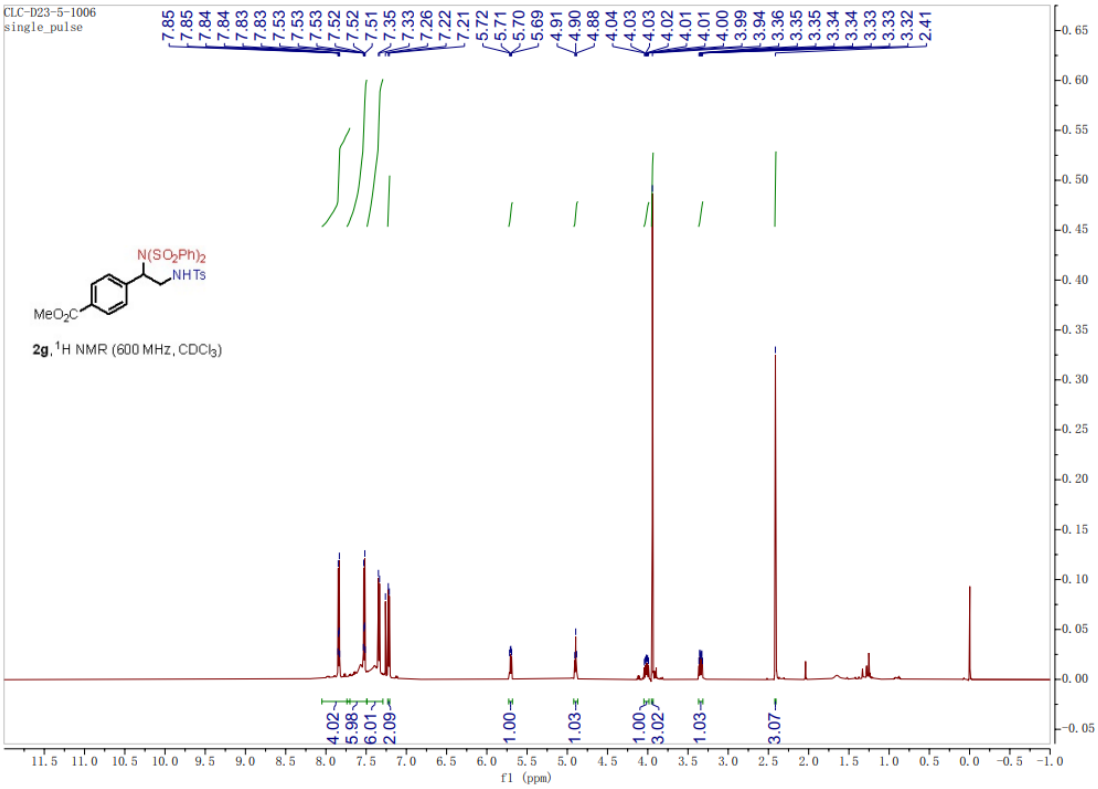
129.35
128.86
128.55
127.05
125.57
77.37
77.16
76.95
63.28
43.99
34.73
31.45
21.64
N(SO2Ph)2
NHTs
tBu
2f, 13C NMR (151 MHz, CDCl3)
f1 (ppm)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7.85
7.84
7.84
7.83
7.83
7.53
7.53
7.52
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7.35
7.33
7.26
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7.21
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5.69
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3.94
3.36
3.35
3.35
3.34
3.34
3.33
3.33
3.32
2.41
N(SO2Ph)2
NHTs
MeO2C
2g, 1H NMR (600 MHz, CDCl3)
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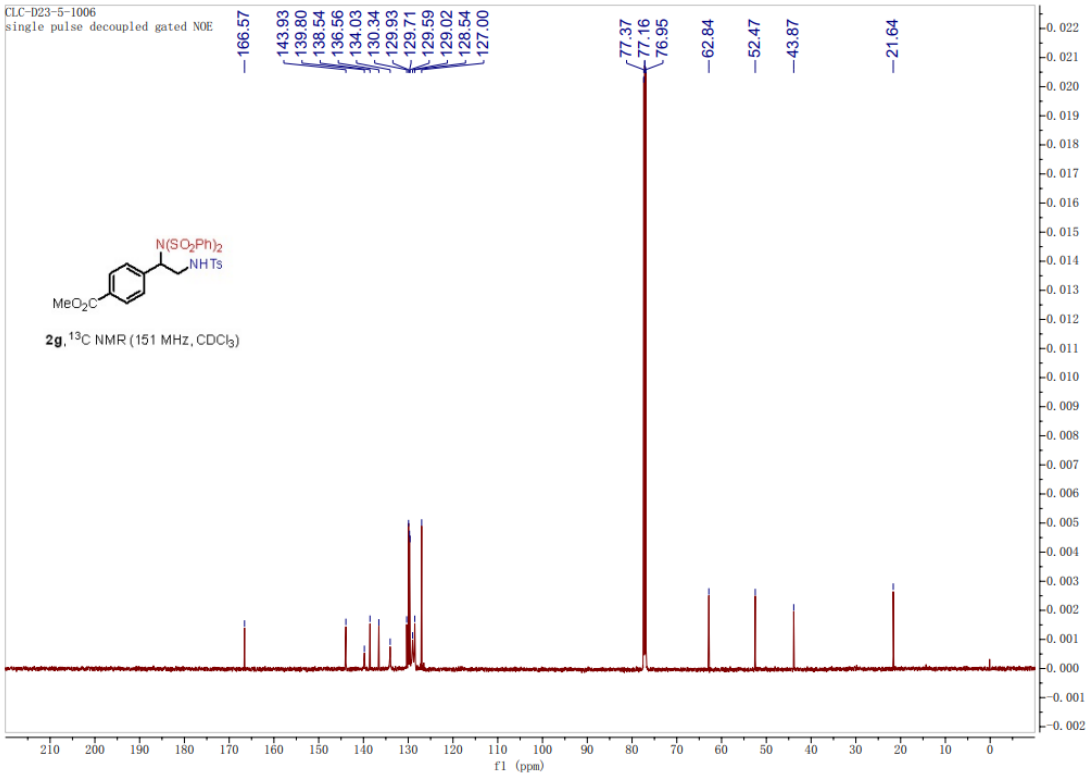
6.01
2.09
1.00
1.03
1.00
3.02
1.03
3.07
f1 (ppm)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136.56
134.03
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129.71
129.59
129.02
128.54
127.00
77.37
77.16
76.95
62.84
52.47
43.87
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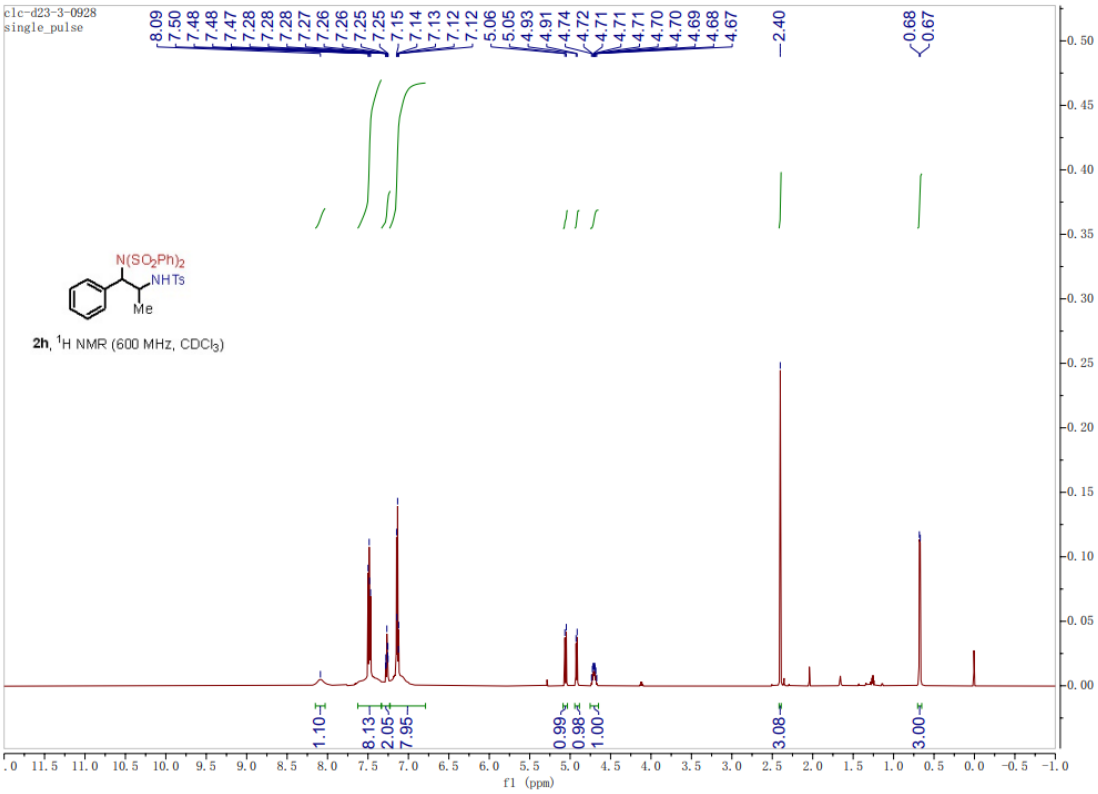
N(SO2Ph)2
NHTs
MeO2C
2g, 13C NMR (151 MHz, CDCl3)
f1 (ppm)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7.47
7.28
7.28
7.28
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7.26
7.25
7.25
7.15
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7.12
7.12
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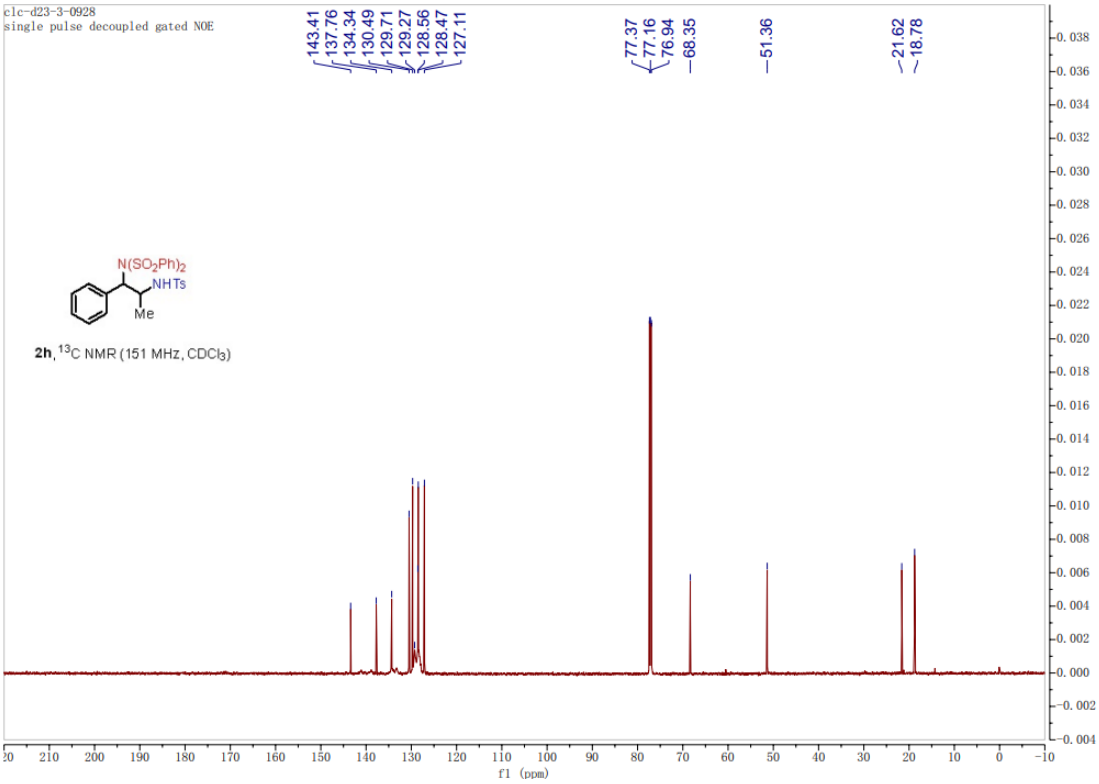
5.05
4.93
4.91
4.74
4.72
4.71
4.71
4.71
4.70
4.70
4.69
4.68
4.67
2.40
0.68
0.67
N(SO2Ph)2
NHTs
Me
2h, 1H NMR (600 MHz, CDCl3)
1.10
8.13
2.05
7.95
0.99
0.98
1.00
3.08
3.00
f1 (ppm)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single pulse decoupled gated NOE
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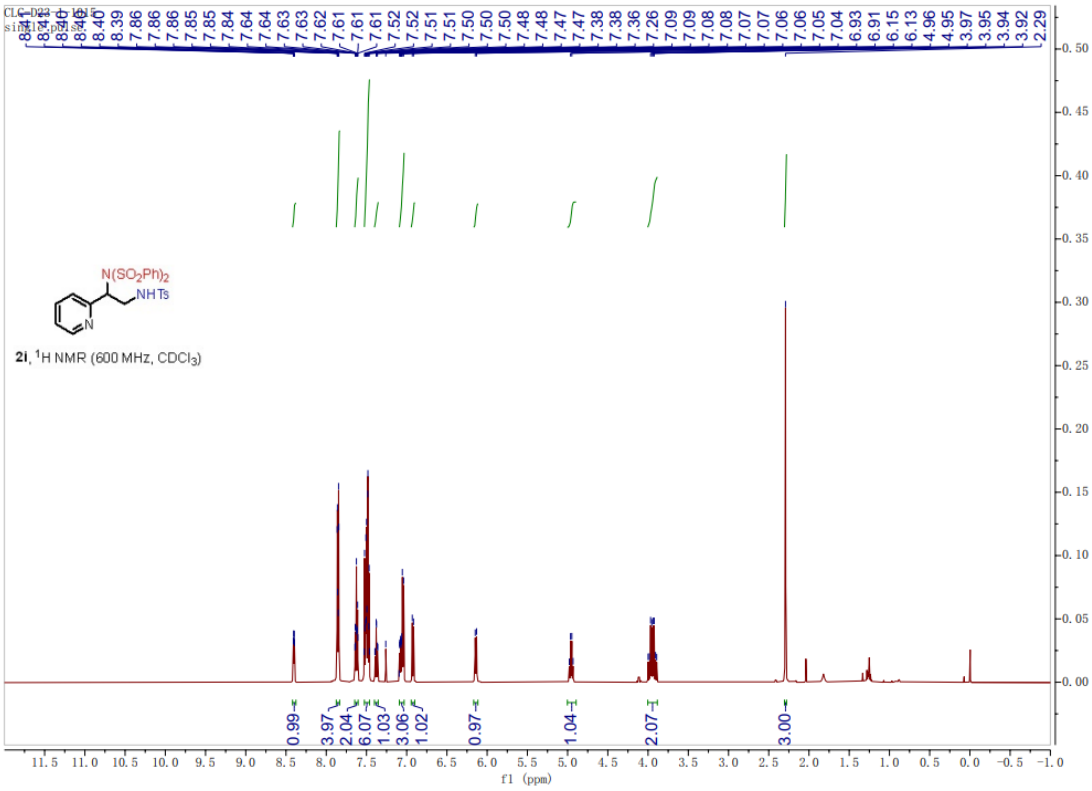
134.34
130.49
129.71
129.27
128.56
128.47
127.11
77.37
77.16
76.94
68.35
51.36
21.62
18.78
N(SO2Ph)2
NHTs
Me
2h, 13C NMR (151 MHz, CDCl3)
f1 (ppm)


N(SO2Ph)2
NHTs
N
2i, 1H NMR (600 MHz, CDCl3)
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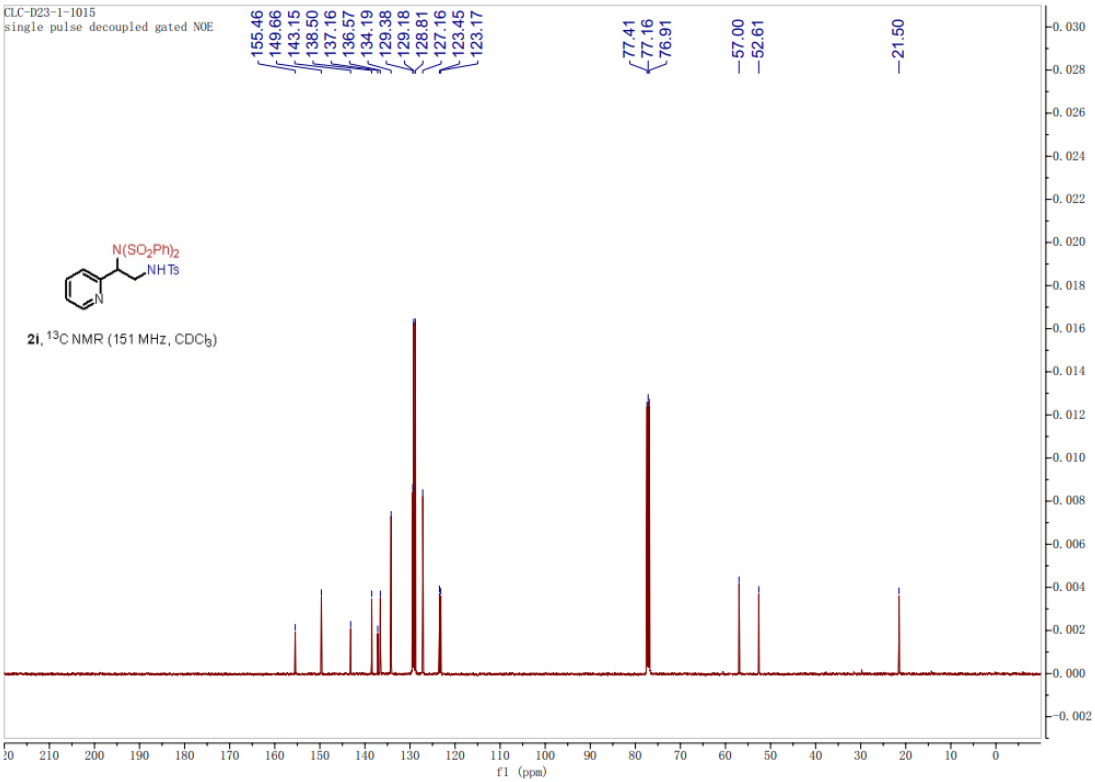
3.97
2.04
6.07
1.03
3.06
1.02
0.97
1.04
2.07
3.00
f1 (ppm)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134.19
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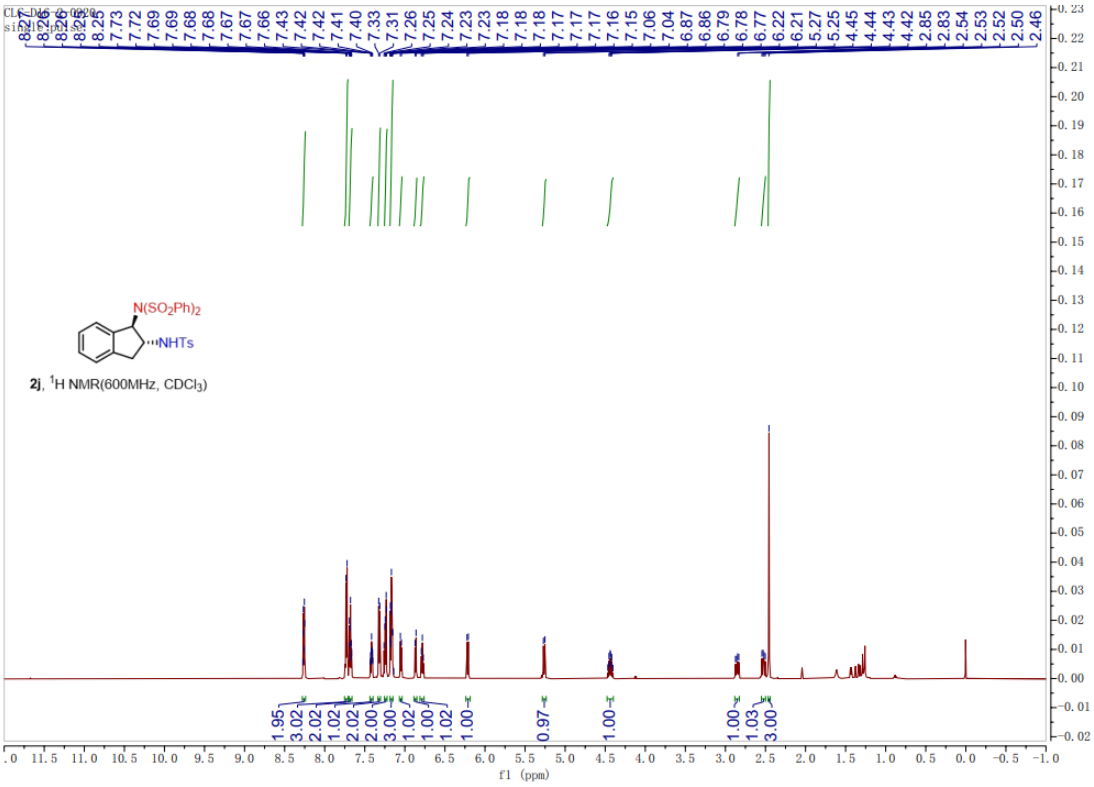
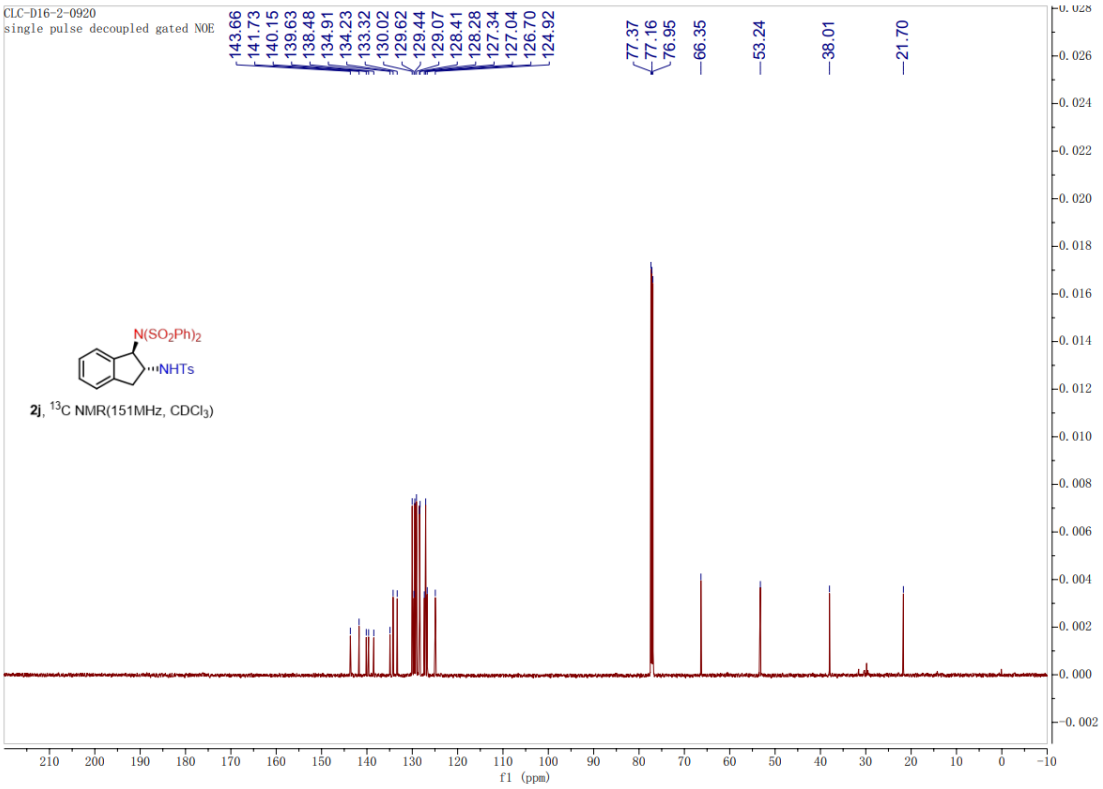
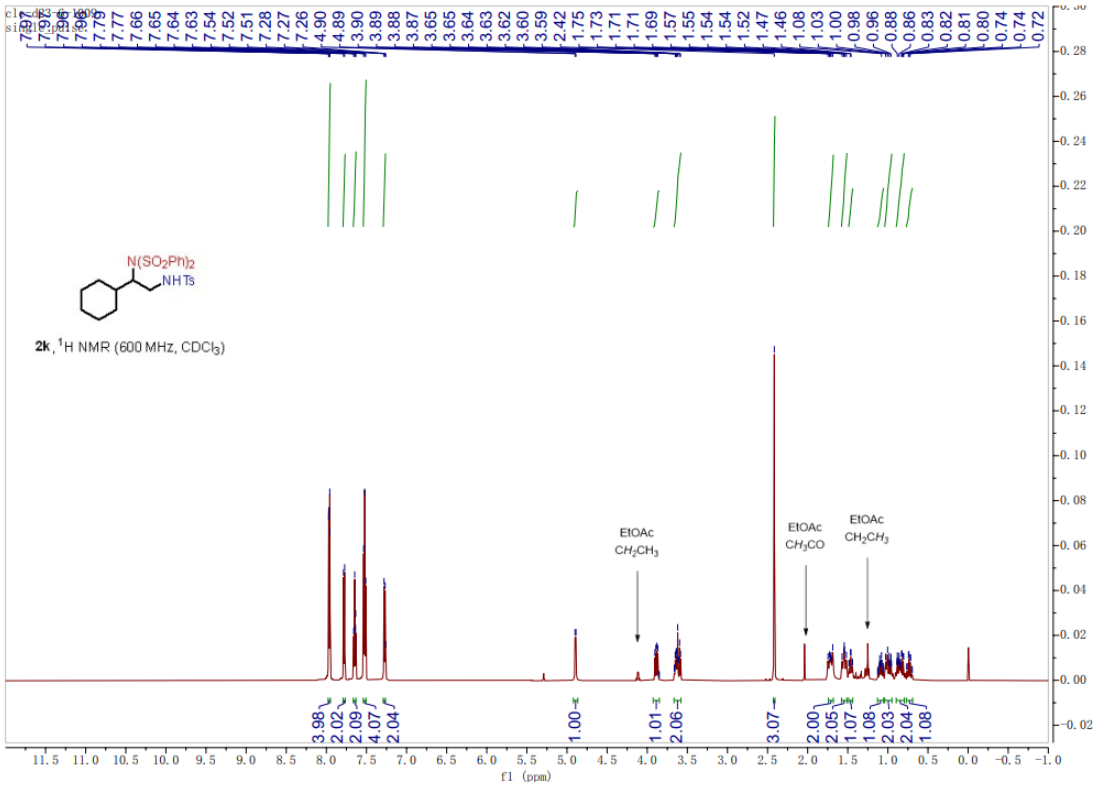
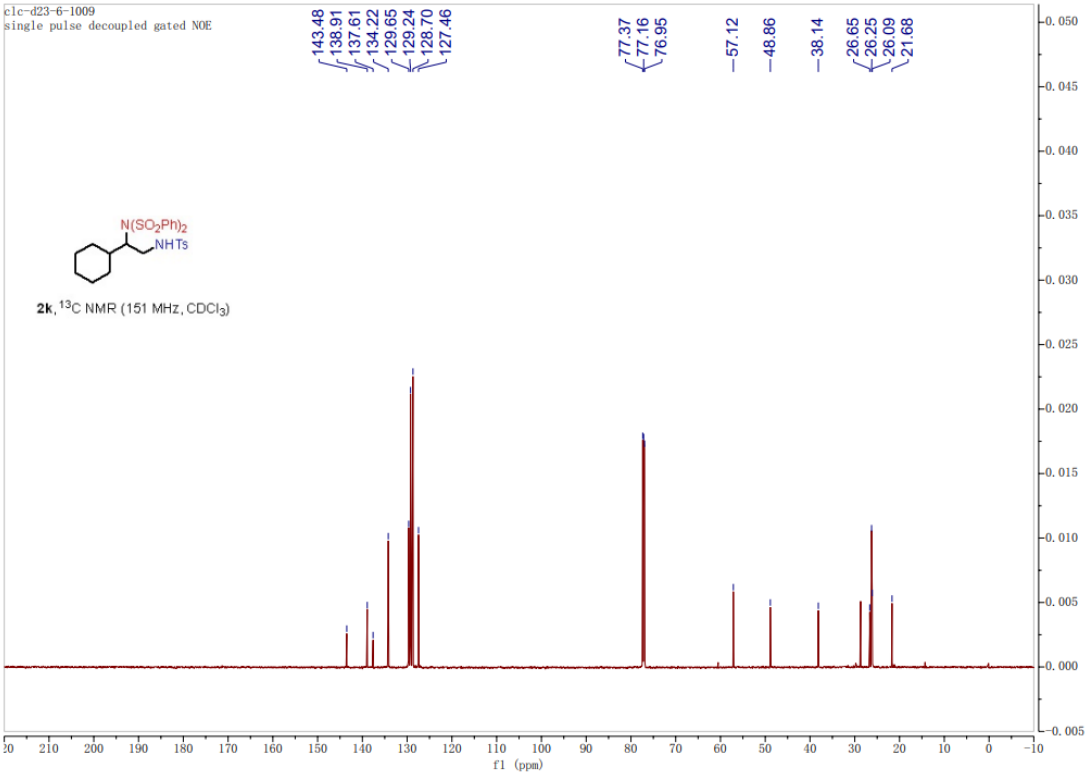
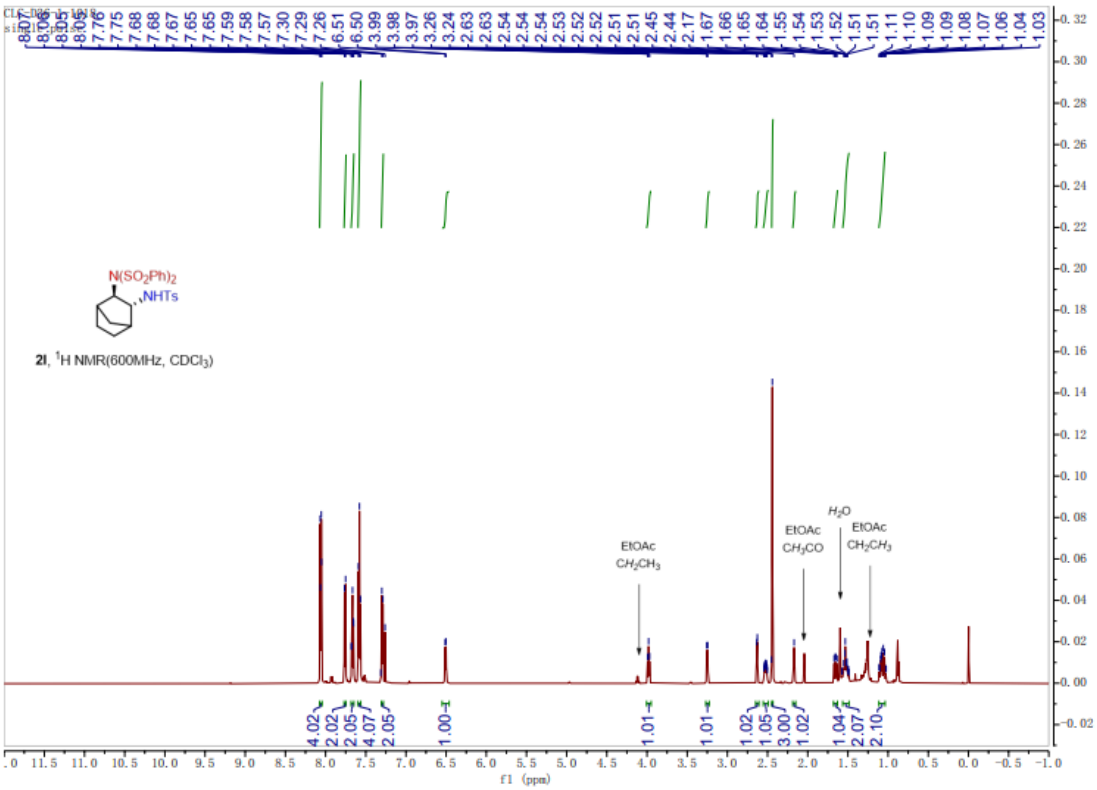
129.18
128.81
127.16
123.45
123.17
77.41
77.16
76.91
57.00
52.61
21.50
N(SO2Ph)2
NHTs
2i, 13C NMR (151 MHz, CDCl3)
f1 (ppm)

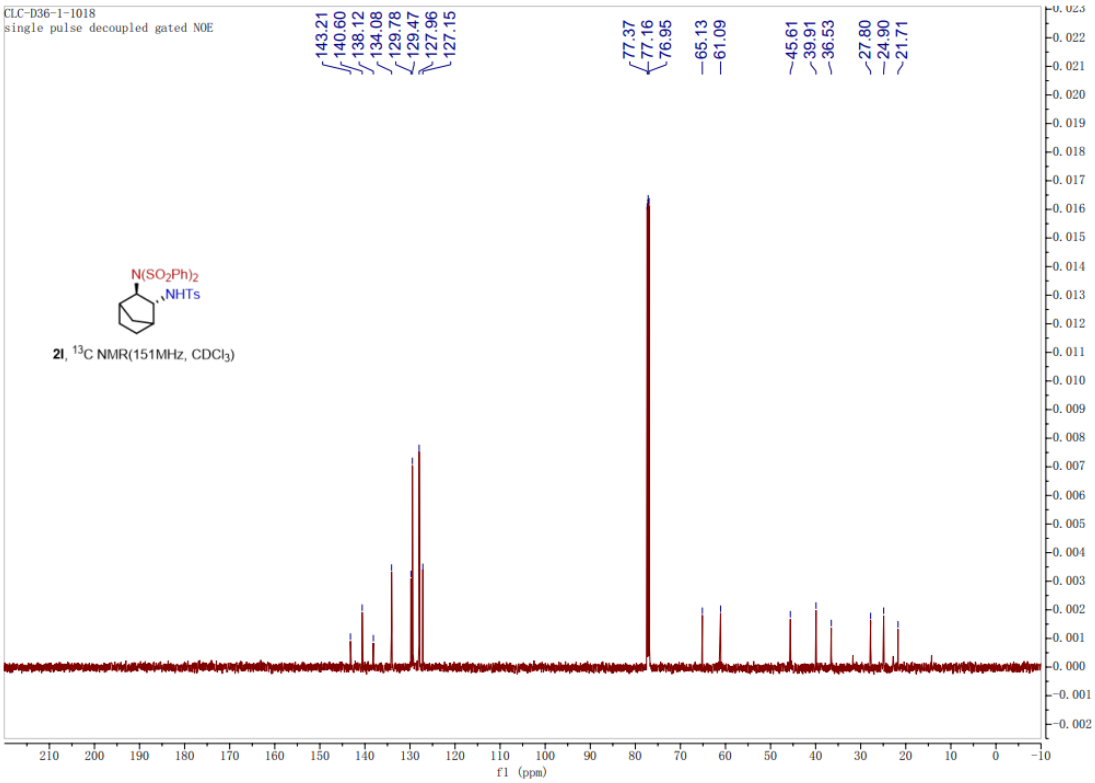

N(SO2Ph)2
NHTs
2j, 1H NMR(600MHz, CDCl3)
1.95
3.02
2.02
1.02
2.02
2.00
3.00
1.02
1.00
1.02
1.00
0.97
1.00
1.00
1.03
3.00
f1 (ppm)

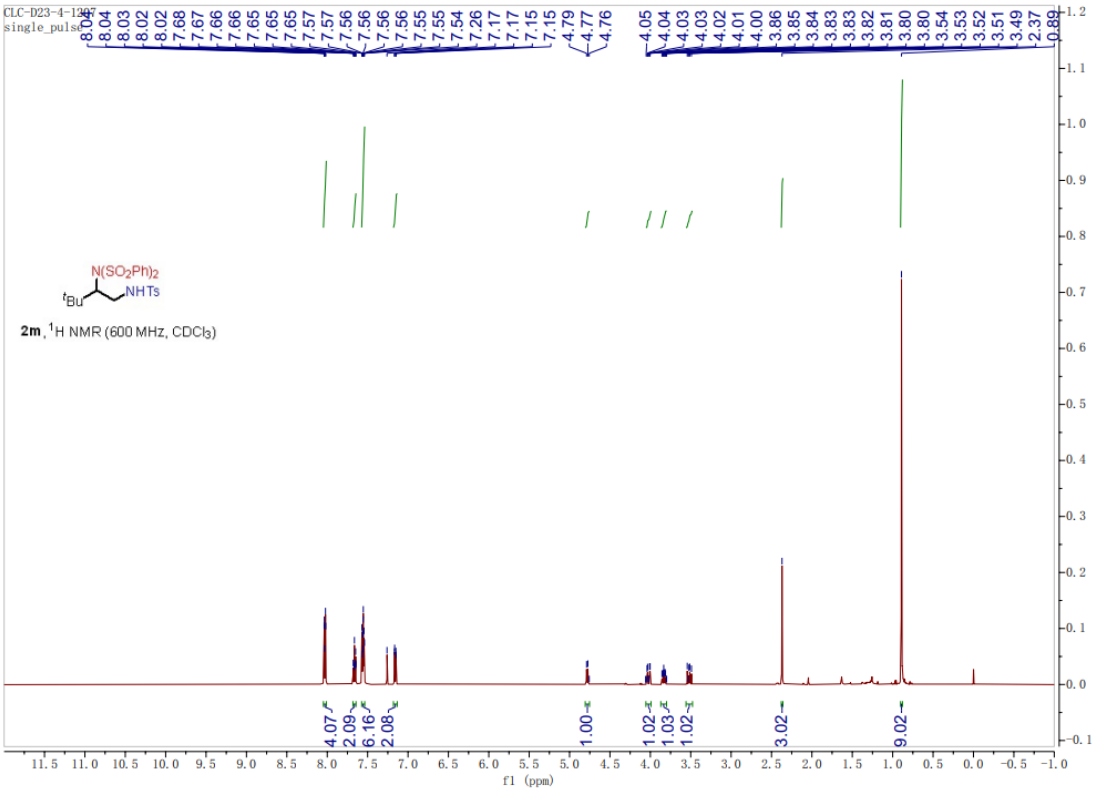

CLC-D16-2-0920
single pulse decoupled gated NOE
143.66
141.73
140.15
139.63
138.48
134.91
134.23
133.32
130.02
129.62
129.44
129.07
128.41
128.28
127.34
127.04
126.70
124.92
77.37
77.16
76.95
66.35
53.24
38.01
21.70
N(SO2Ph)2
NHTs
2j, 13C NMR(151MHz, CDCl3)
f1 (ppm)

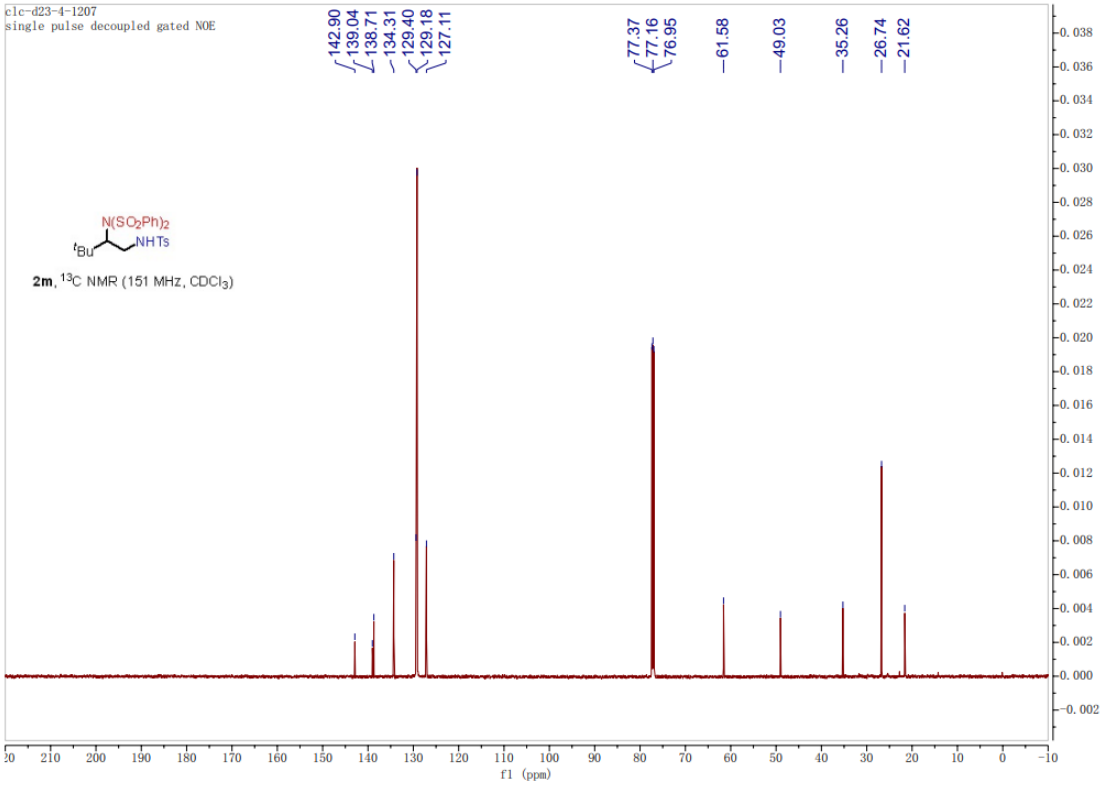

N(SO2Ph)2
NHTs
2k, 1H NMR (600 MHz, CDCl3)
EtOAc
CH2CH3
EtOAc
CH3CO
EtOAc
CH2CH3
3.98
2.02
2.09
4.07
2.04
1.00
1.01
2.06
3.07
2.00
2.05
1.07
1.08
2.03
2.04
1.08
f1 (ppm)

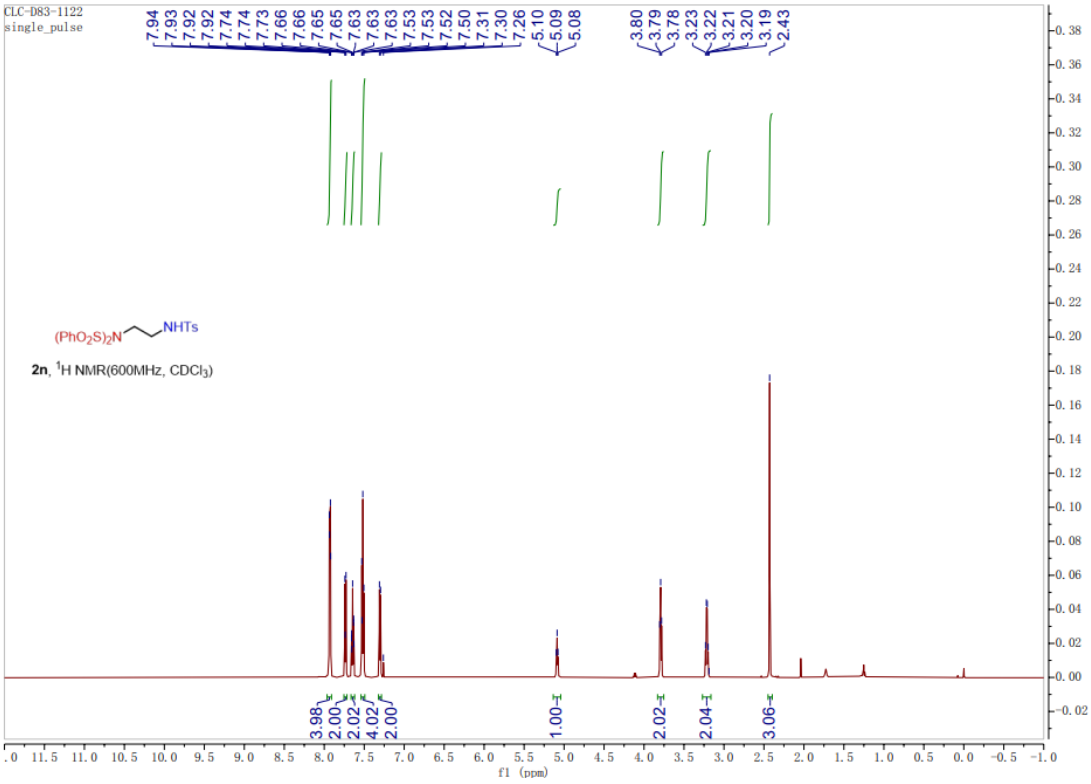

clc-d23-6-1009
single pulse decoupled gated NOE
143.48
138.91
137.61
134.22
129.65
129.24
128.70
127.46
77.37
77.16
76.95
57.12
48.86
38.14
26.65
26.25
26.09
21.68
N(SO2Ph)2
NHTs
2k, 13C NMR (151 MHz, CDCl3)
f1 (ppm)

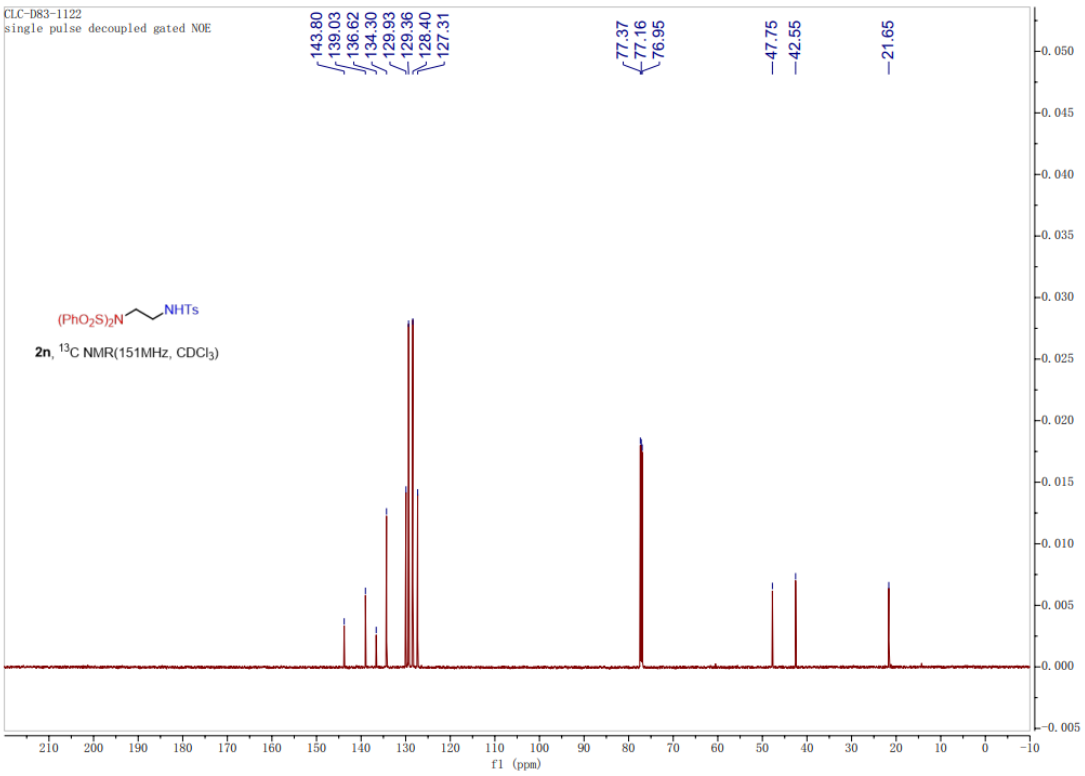

N(SO2Ph)2
NHTs
2l, 1H NMR(600MHz, CDCl3)
EtOAc
CH2CH3
EtOAc
CH3CO
H2O
EtOAc
CH2CH3
4.02
2.02
2.05
4.07
2.05
1.00
1.01
1.01
1.02
1.05
3.00
1.02
1.04
2.07
2.10
f1 (ppm)

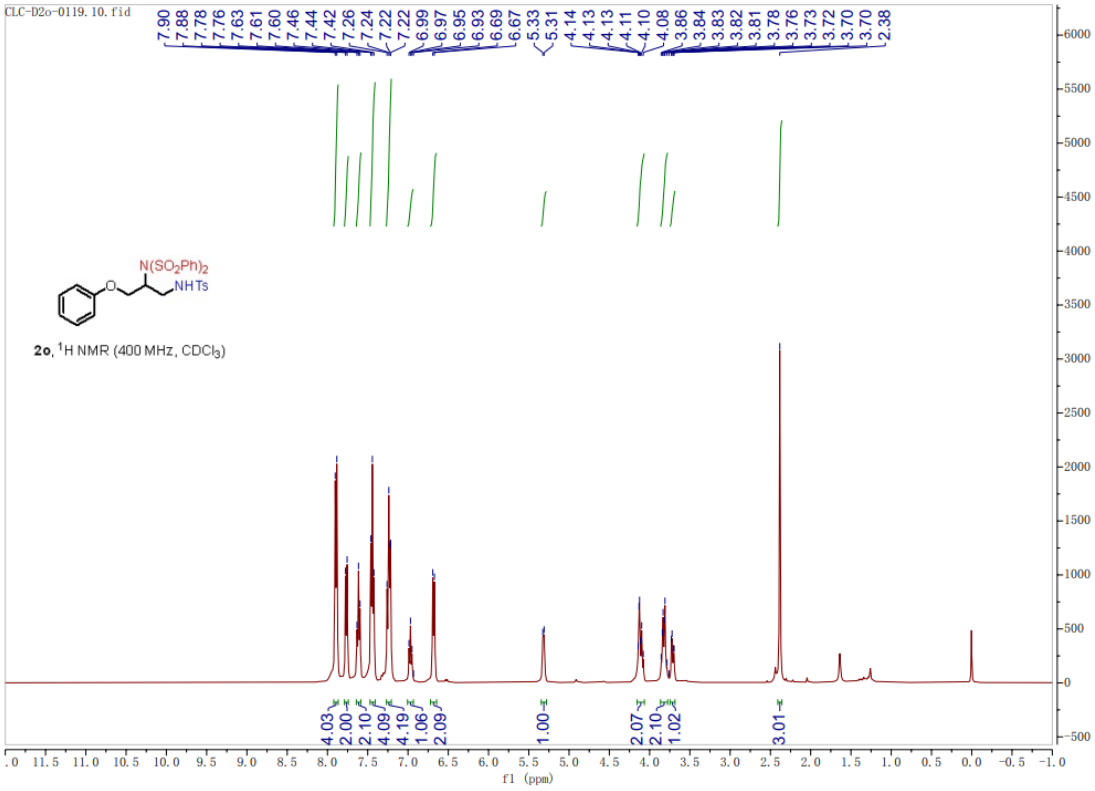

CLC-D36-1-1018
single pulse decoupled gated NOE
143.21
140.60
138.12
134.08
129.78
129.47
127.96
127.15
77.37
77.16
76.95
65.13
61.09
45.61
39.91
36.53
27.80
24.90
21.71
N(SO2Ph)2
NHTs
2l, 13C NMR(151MHz, CDCl3)
f1 (ppm)

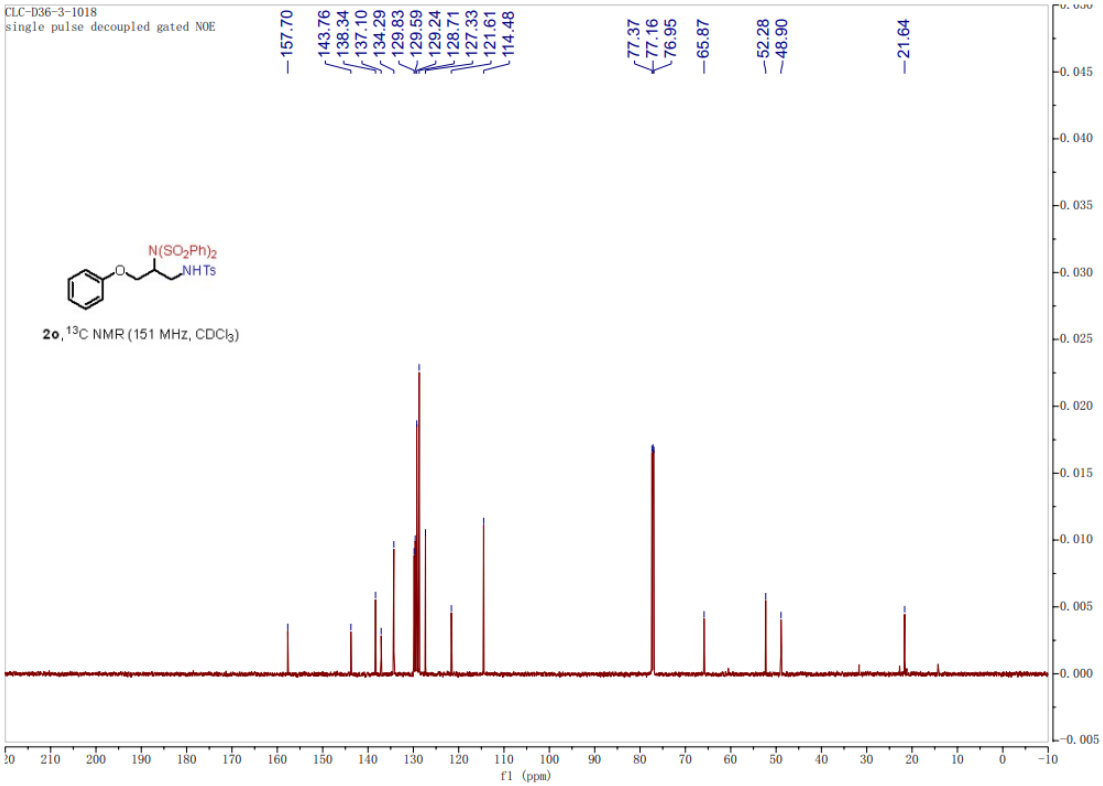

CLC-D23-4-1207
single_pulse
8.04
8.03
8.02
7.68
7.67
7.66
7.65
7.57
7.56
7.55
7.54
7.26
7.17
7.15
4.79
4.77
4.76
4.05
4.04
4.03
4.02
4.01
4.00
3.86
3.85
3.84
3.83
3.82
3.81
3.80
3.54
3.53
3.52
3.51
3.49
2.37
0.89
N(SO2Ph)2
tBu
NHTs
2m, 1H NMR (600 MHz, CDCl3)
4.07
2.09
6.16
2.08
1.00
1.02
1.03
1.02
3.02
9.02
f1 (ppm)

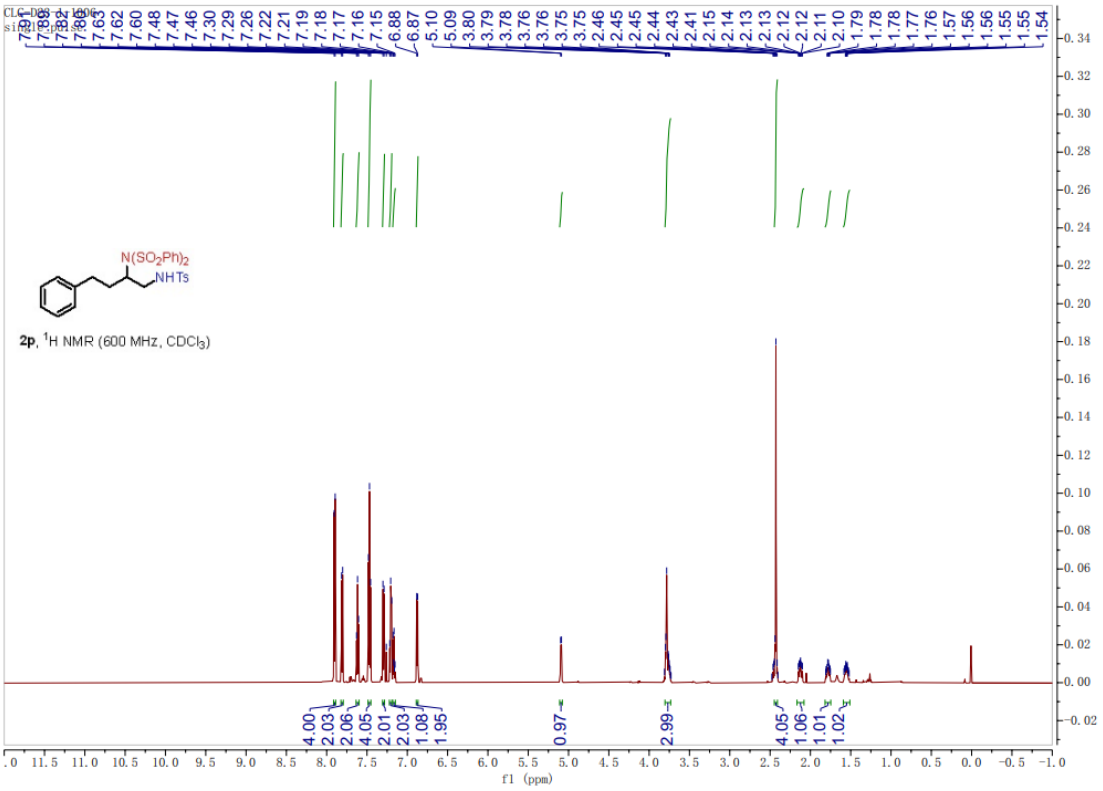

clc-d23-4-1207
single pulse decoupled gated NOE
142.90
139.04
138.71
134.31
129.40
129.18
127.11
77.37
77.16
76.95
61.58
49.03
35.26
26.74
21.62
N(SO2Ph)2
tBu
NHTs
2m, 13C NMR (151 MHz, CDCl3)
f1 (ppm)

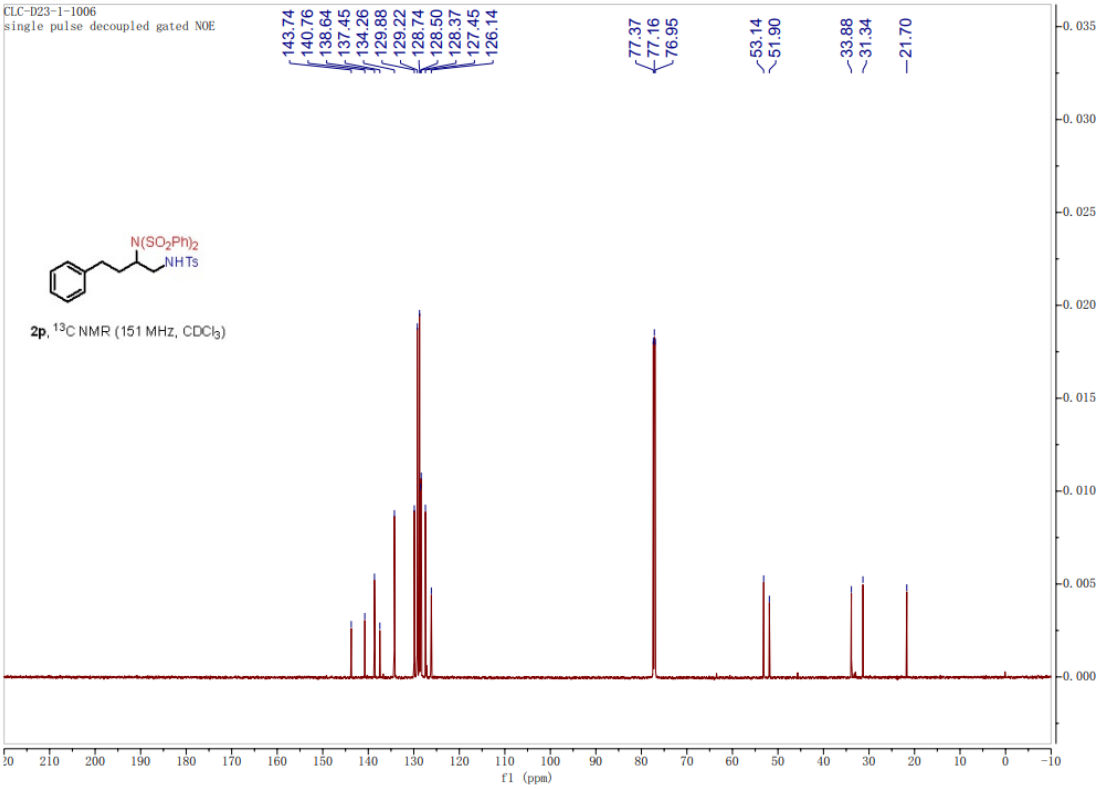

CLC-D83-1122
single_pulse
7.94
7.93
7.92
7.92
7.74
7.74
7.73
7.66
7.66
7.65
7.65
7.63
7.63
7.63
7.53
7.53
7.52
7.50
7.31
7.30
7.26
5.10
5.09
5.08
3.80
3.79
3.78
3.23
3.22
3.21
3.20
3.19
2.43
(PhO2S)2N
NHTs
2n, 1H NMR(600MHz, CDCl3)
3.98
2.00
2.02
4.02
2.00
1.00
2.02
2.04
3.06
f1 (ppm)

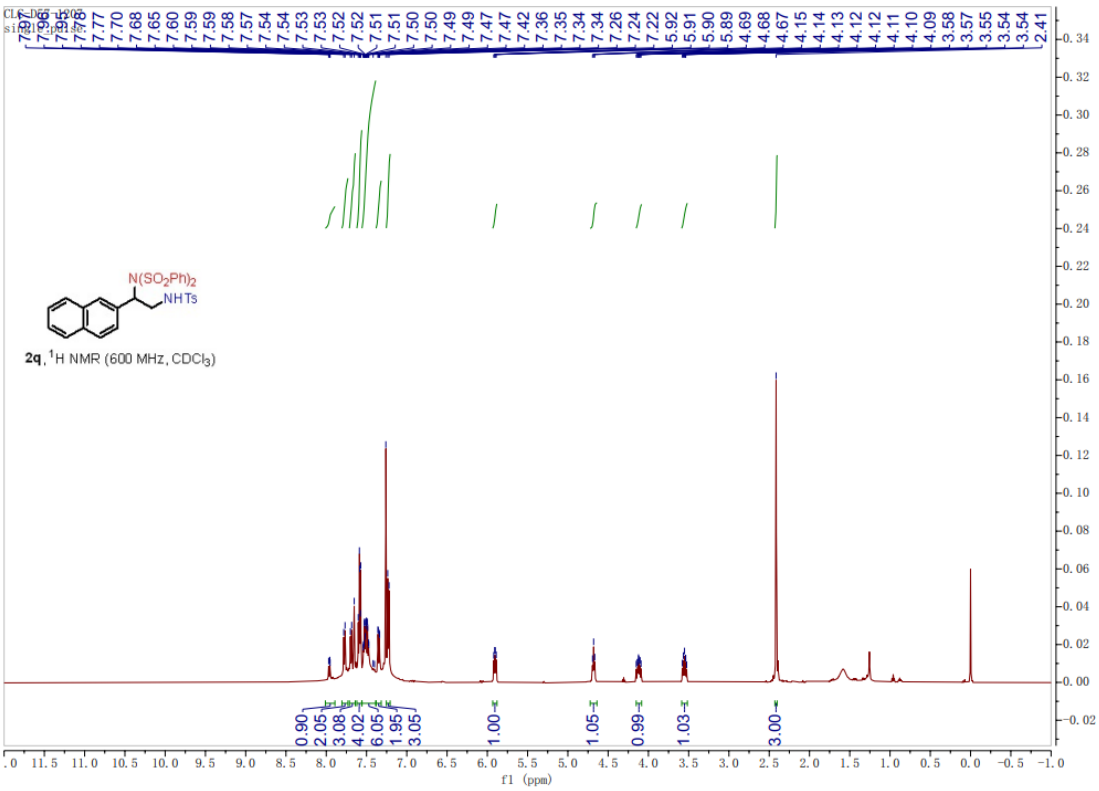

CLC-D83-1122
single pulse decoupled gated NOE
143.80
139.03
136.62
134.30
129.93
129.36
128.40
127.31
77.37
77.16
76.95
47.75
42.55
21.65
(PhO2S)2N
NHTs
2n, 13C NMR(151MHz, CDCl3)
f1 (ppm)

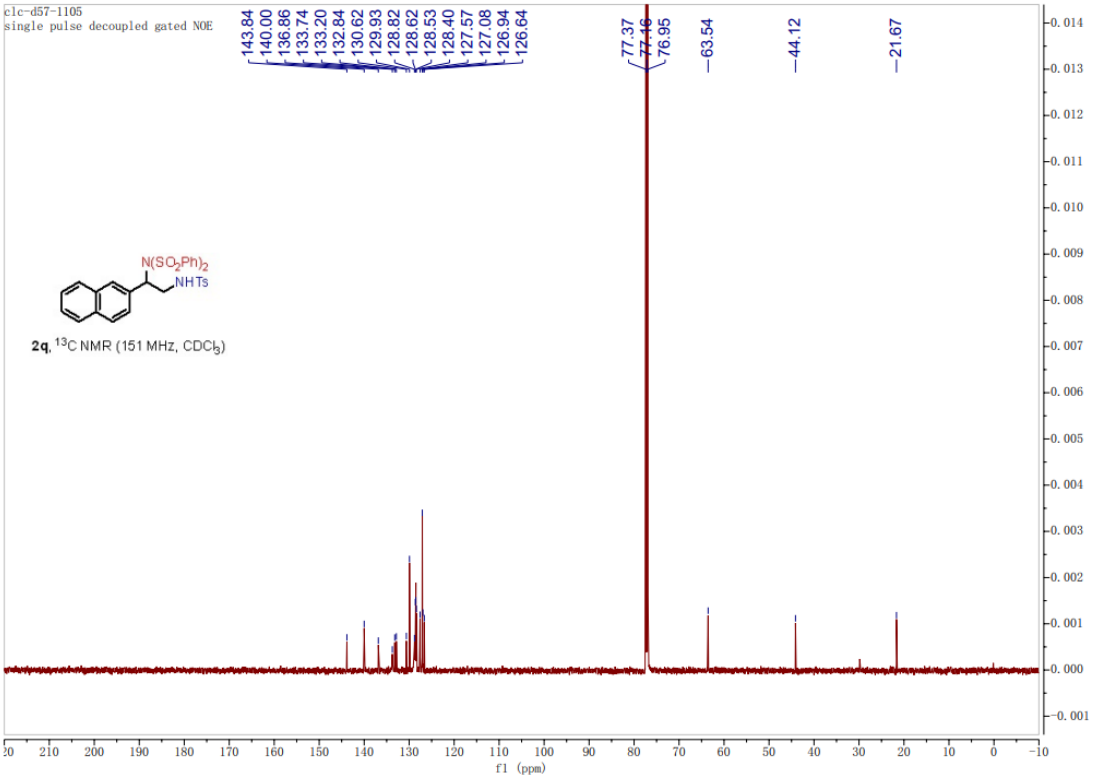

CLC-D2o-0119.10.fid
7.90
7.88
7.78
7.76
7.63
7.61
7.60
7.46
7.44
7.42
7.26
7.24
7.22
7.22
6.99
6.97
6.95
6.93
6.69
6.67
5.33
5.31
4.14
4.13
4.13
4.11
4.10
4.08
3.86
3.84
3.83
3.82
3.81
3.78
3.76
3.73
3.72
3.70
3.70
2.38
N(SO2Ph)2
NHTs
2o, 1H NMR (400 MHz, CDCl3)
4.03
2.00
2.10
4.09
4.19
1.06
2.09
1.00
2.07
2.10
1.02
3.01
f1 (ppm)

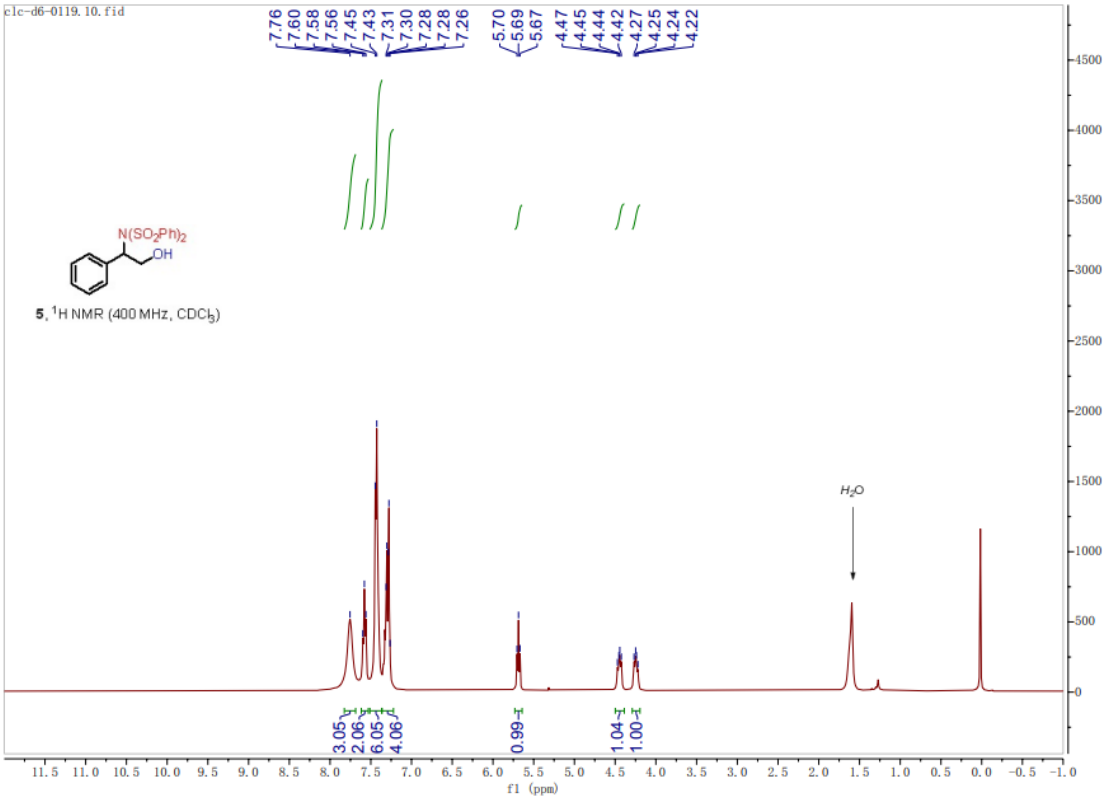

CLC-D36-3-1018
single pulse decoupled gated NOE
157.70
143.76
138.34
137.10
134.29
129.83
129.59
129.24
128.71
127.33
121.61
114.48
77.37
77.16
76.95
65.87
52.28
48.90
21.64
N(SO2Ph)2
NHTs
2o, 13C NMR (151 MHz, CDCl3)
f1 (ppm)

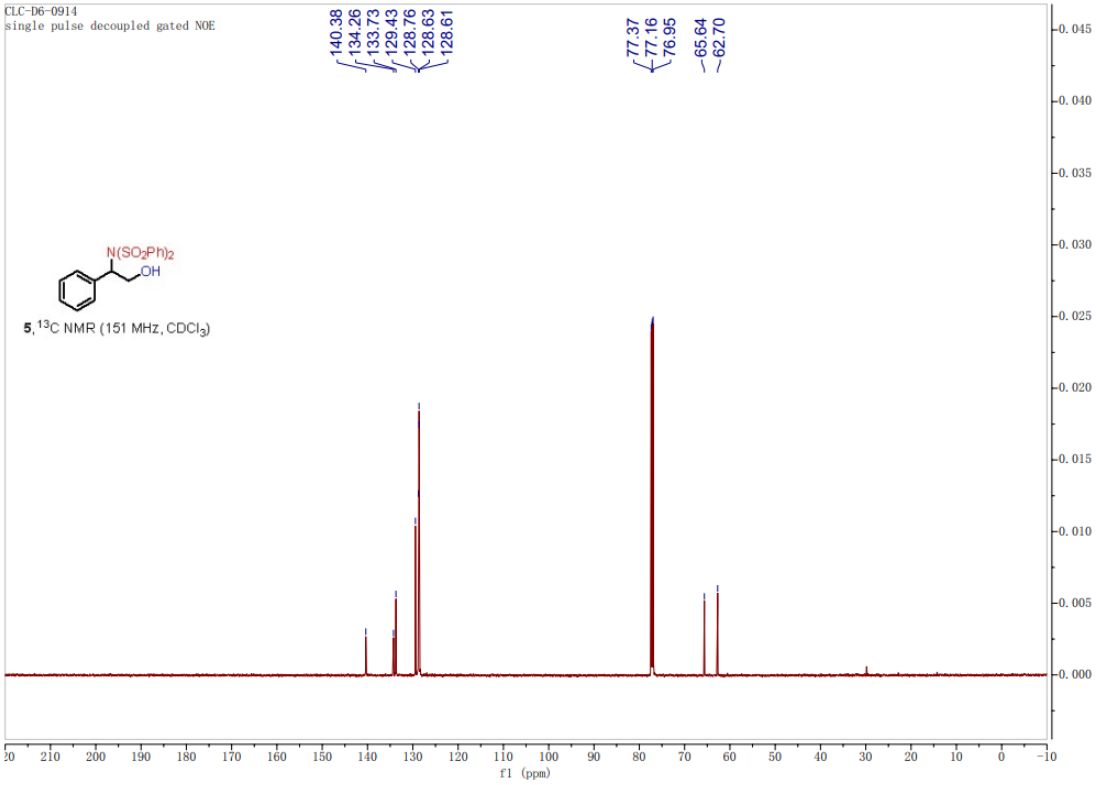

N(SO2Ph)2
NHTs
2p, 1H NMR (600 MHz, CDCl3)
4.00
2.03
2.06
4.05
2.01
2.03
1.08
1.95
0.97
2.99
4.05
1.06
1.01
1.02
f1 (ppm)

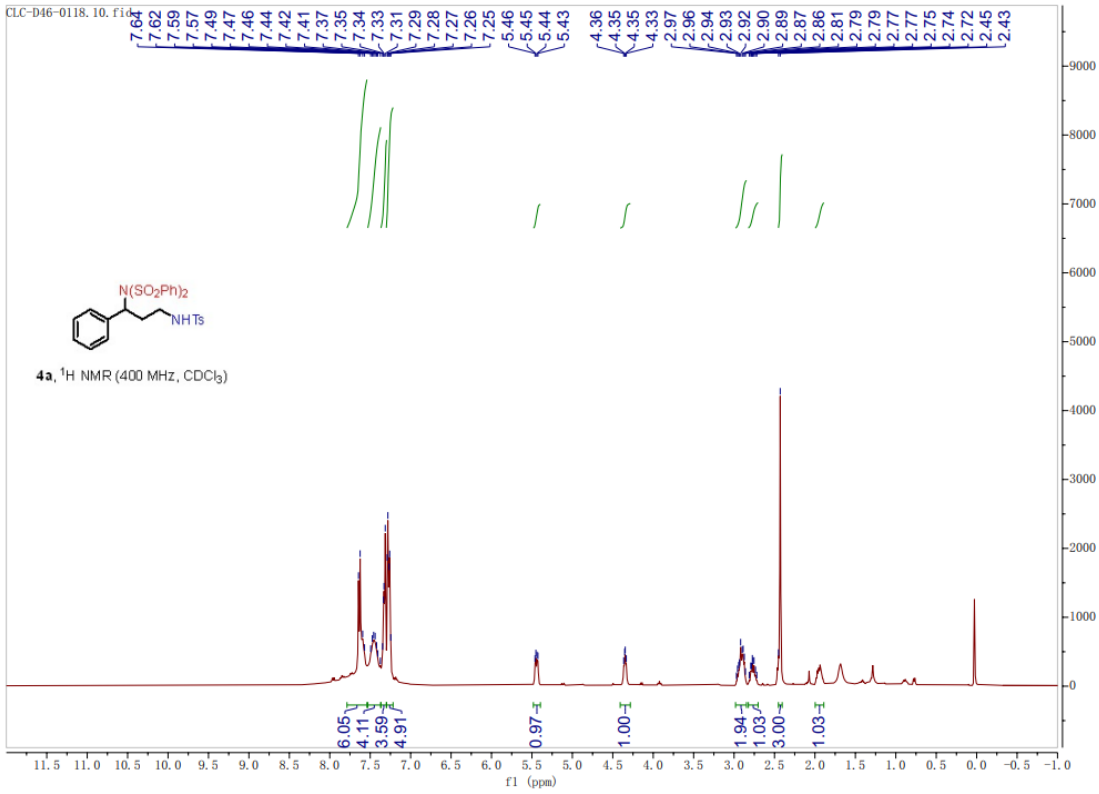

CLC-D23-1-1006
single pulse decoupled gated NOE
143.74
140.76
138.64
137.45
134.26
129.88
129.22
128.74
128.50
128.37
127.45
126.14
77.37
77.16
76.95
53.14
51.90
33.88
31.34
21.70
N(SO2Ph)2
NHTs
2p, 13C NMR (151 MHz, CDCl3)
f1 (ppm)

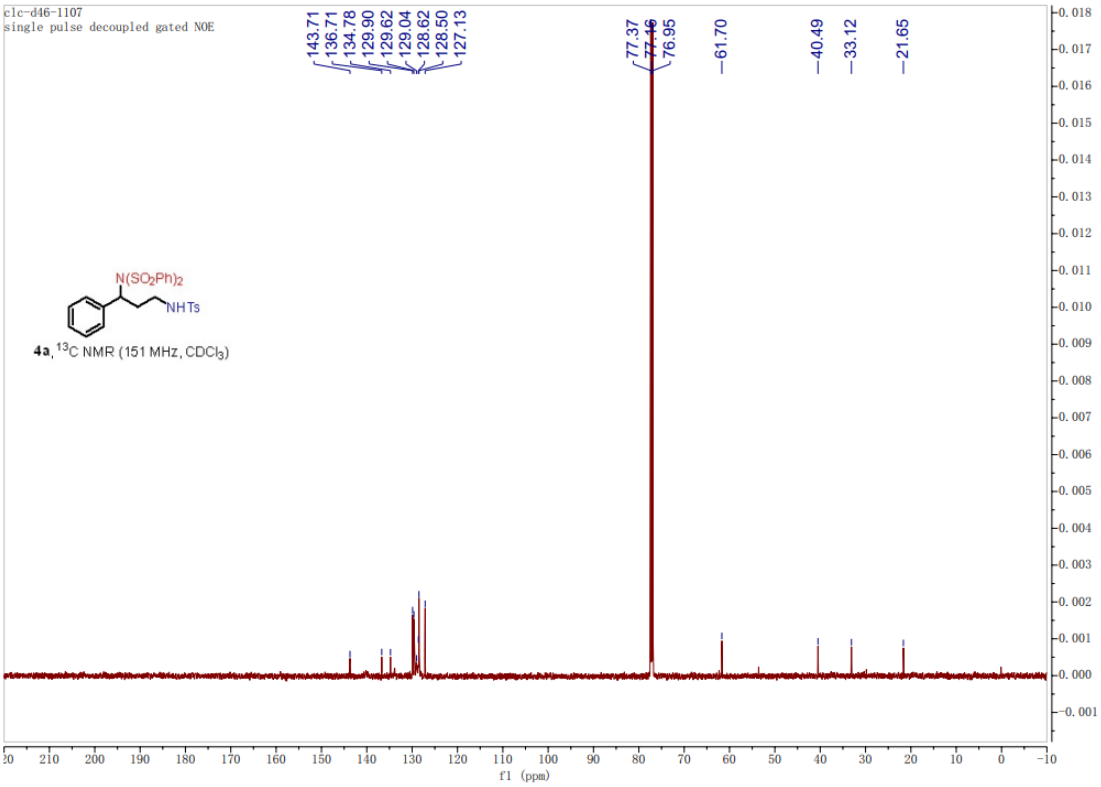

N(SO2Ph)2
NHTs
2q, 1H NMR (600 MHz, CDCl3)
0.90
2.05
3.08
4.02
6.05
1.95
3.05
1.00
1.05
0.99
1.03
3.00
f1 (ppm)

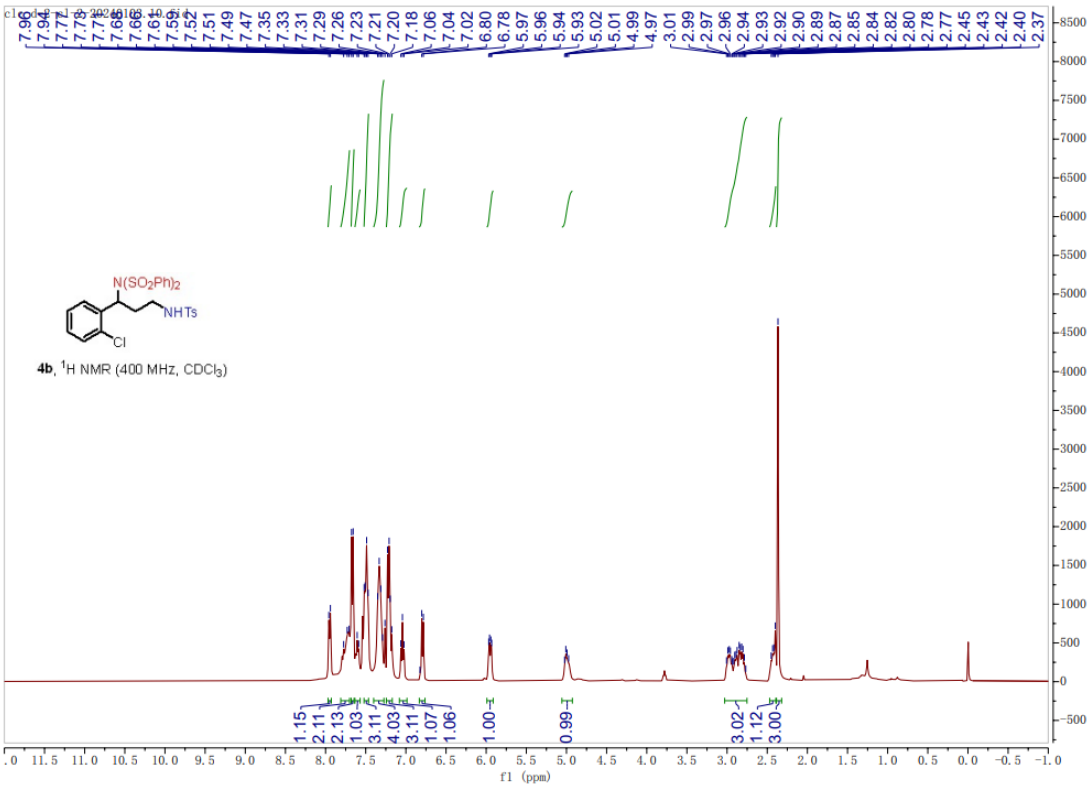

clc-d57-1105
single pulse decoupled gated NOE
143.84
140.00
136.86
133.74
133.20
132.84
130.62
129.93
128.82
128.62
128.53
128.40
127.57
127.08
126.94
126.64
77.37
77.16
76.95
63.54
44.12
21.67
N(SO2Ph)2
NHTs
2q, 13C NMR (151 MHz, CDCl3)
f1 (ppm)

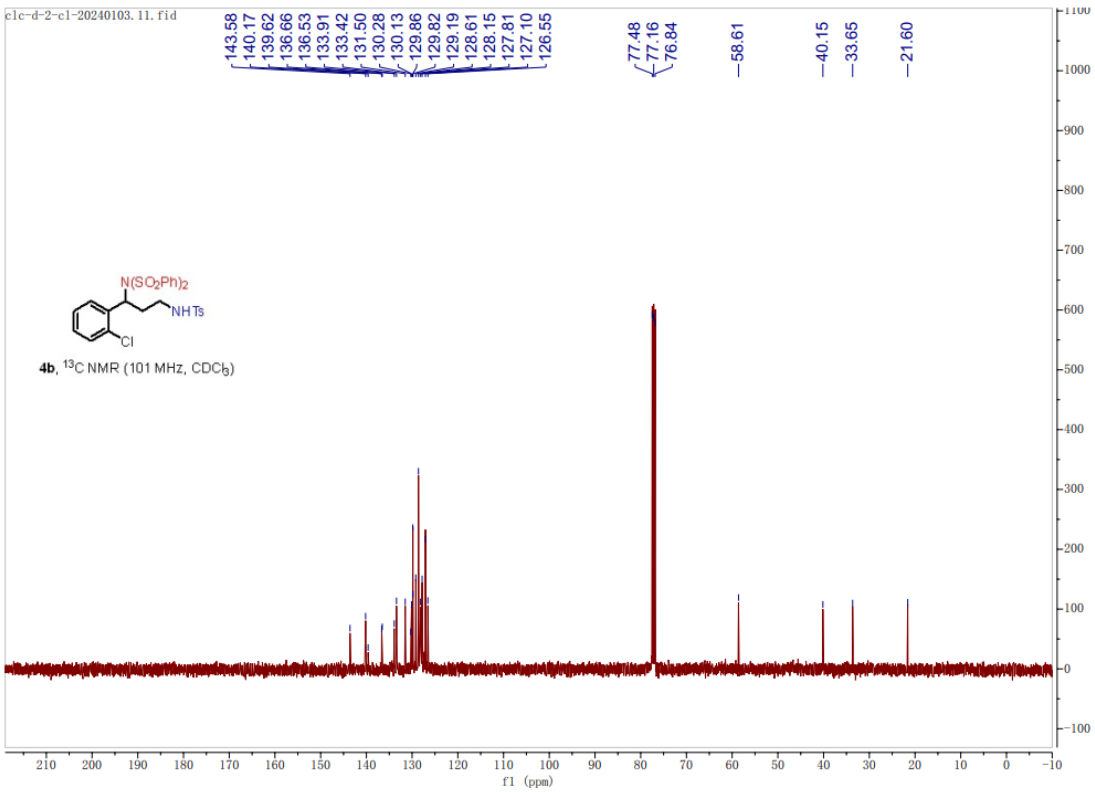

clc-d6-0119.10.fid
7.76
7.60
7.58
7.56
7.45
7.43
7.31
7.30
7.28
7.28
7.26
5.70
5.69
5.67
4.47
4.45
4.44
4.42
4.27
4.25
4.24
4.22
N(SO2Ph)2
OH
5, 1H NMR (400 MHz, CDCl3)
H2O
3.05
2.06
6.05
4.06
0.99
1.04
1.00
f1 (ppm)

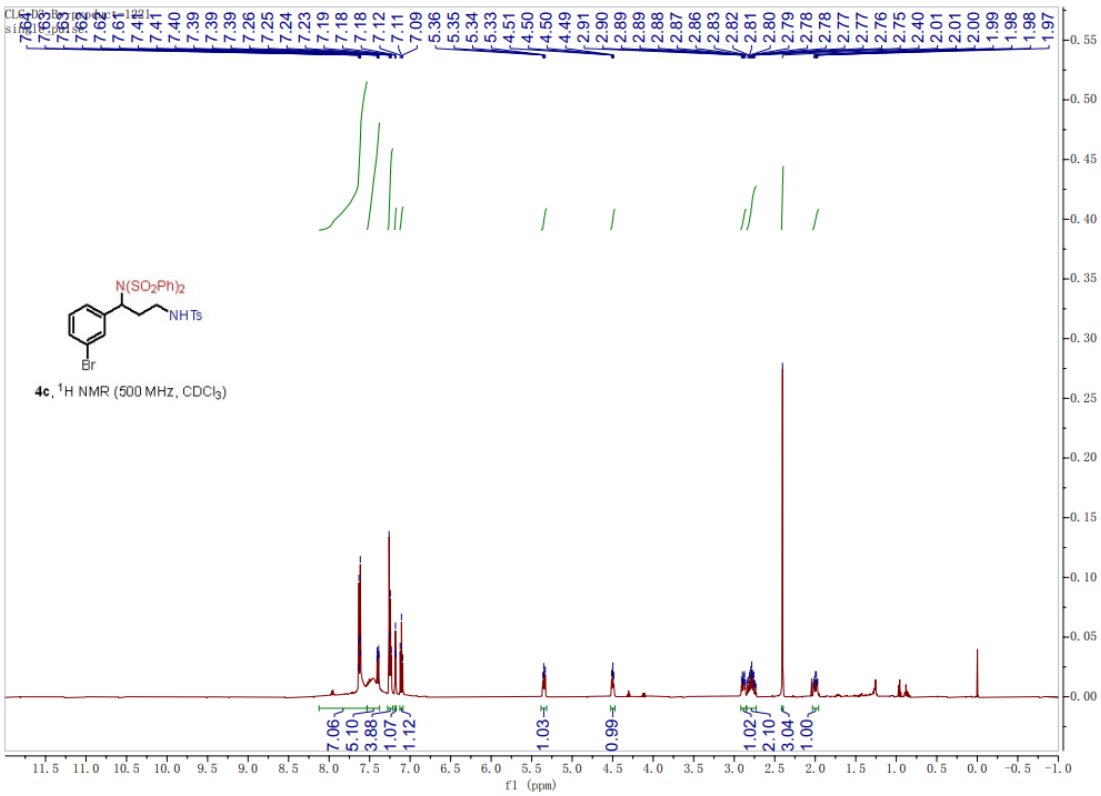

CLC-D6-0914
single pulse decoupled gated NOE
140.38
134.26
133.73
129.43
128.76
128.63
128.61
77.37
77.16
76.95
65.64
62.70
N(SO2Ph)2
OH
5, 13C NMR (151 MHz, CDCl3)
f1 (ppm)

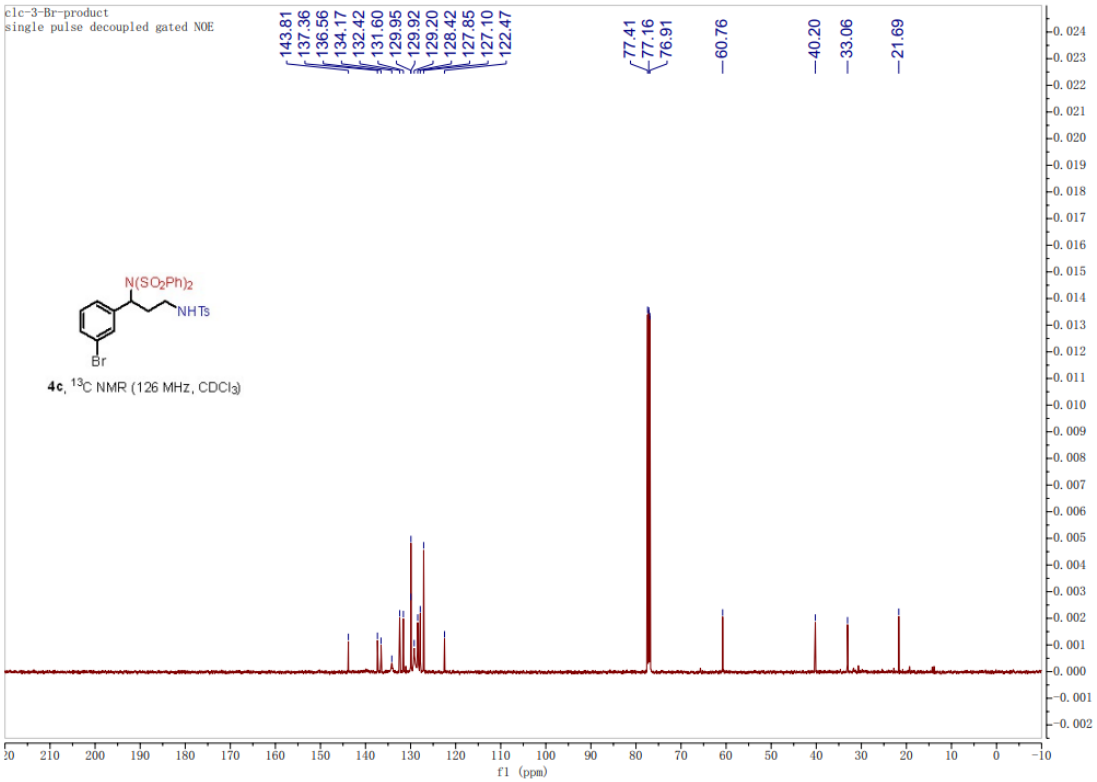

CLC-D46-0118.10.fid
7.64
7.62
7.59
7.57
7.49
7.47
7.46
7.44
7.42
7.41
7.37
7.35
7.34
7.33
7.31
7.29
7.28
7.27
7.26
7.25
5.46
5.45
5.44
5.43
4.36
4.35
4.35
4.33
2.97
2.96
2.94
2.93
2.92
2.90
2.89
2.87
2.86
2.81
2.79
2.79
2.77
2.77
2.75
2.74
2.72
2.45
2.43
N(SO2Ph)2
NHTs
4a, 1H NMR (400 MHz, CDCl3)
6.05
4.11
3.59
4.91
0.97
1.00
1.94
1.03
3.00
1.03
f1 (ppm)


clc-d46-1107
single pulse decoupled gated NOE
143.71
136.71
134.78
129.90
129.62
129.04
128.62
128.50
127.13
77.37
77.16
76.95
61.70
40.49
33.12
21.65
N(SO2Ph)2
NHTs
4a, 13C NMR (151 MHz, CDCl3)
f1 (ppm)

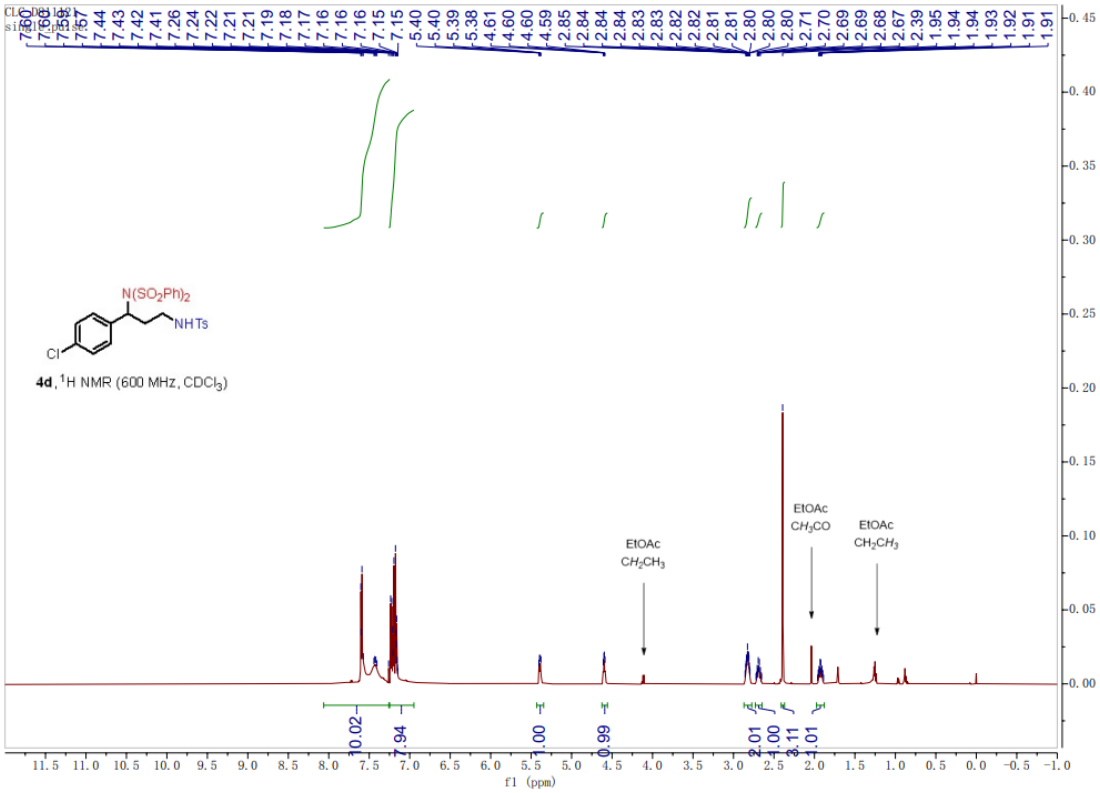

N(SO2Ph)2
NHTs
Cl
4b, 1H NMR (400 MHz, CDCl3)
1.15
2.11
2.13
1.03
3.11
4.03
3.11
1.07
1.06
1.00
0.99
3.02
1.12
3.00
f1 (ppm)


clc-d-2-cl-20240103.11.fid
143.58
140.17
139.62
136.66
136.53
133.91
133.42
131.50
130.28
130.13
129.86
129.82
129.19
128.61
128.15
127.81
127.10
126.55
77.48
77.16
76.84
58.61
40.15
33.65
21.60
N(SO2Ph)2
NHTs
Cl
4b, 13C NMR (101 MHz, CDCl3)
f1 (ppm)

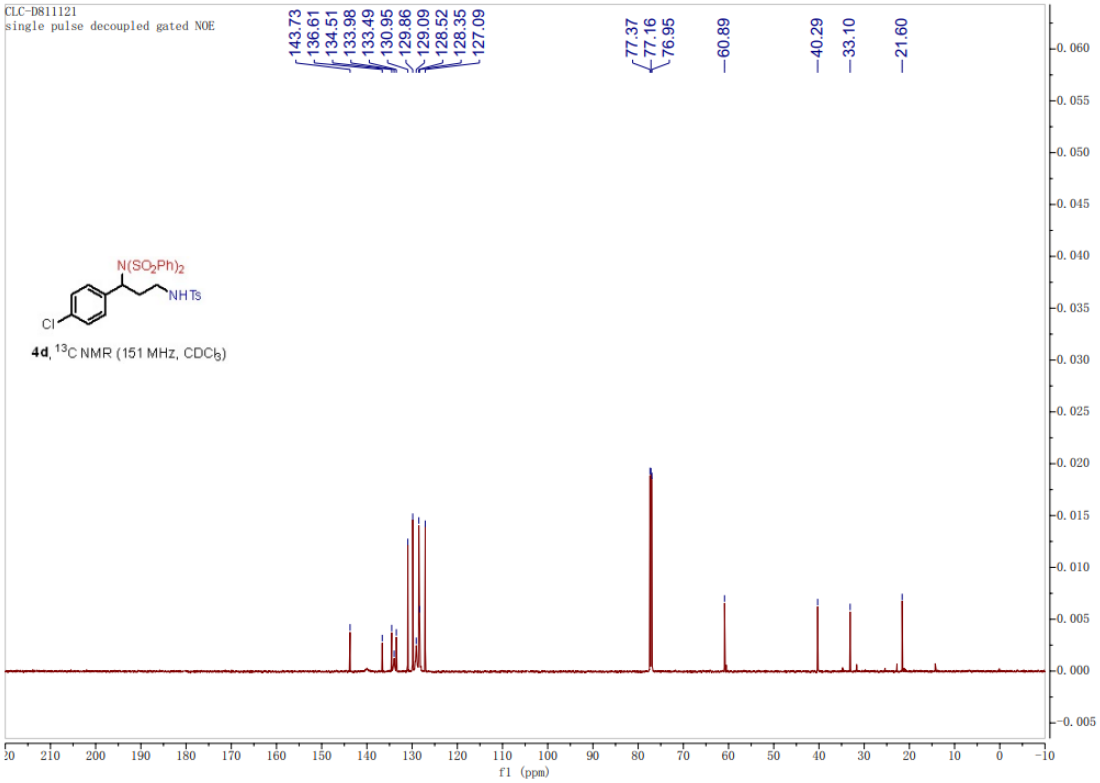

N(SO2Ph)2
NHTs
Br
4c, 1H NMR (500 MHz, CDCl3)
7.06
5.10
3.88
1.07
1.12
1.03
0.99
1.02
2.10
3.04
1.00
f1 (ppm)

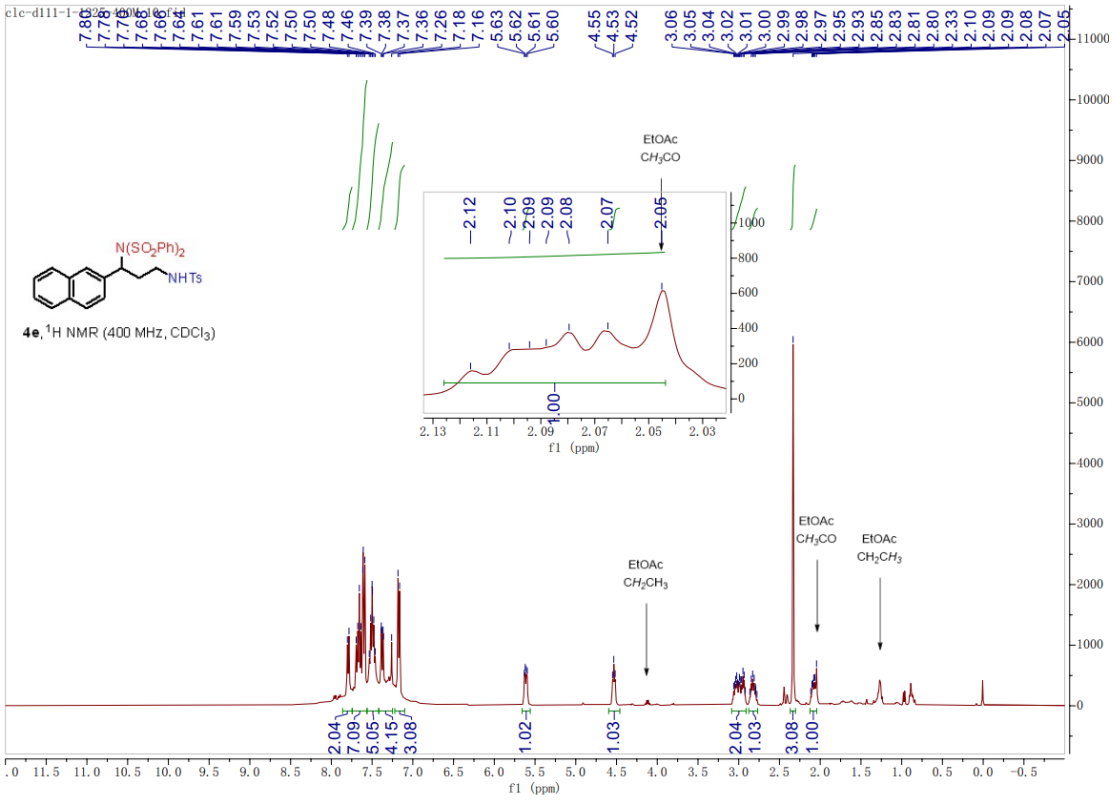


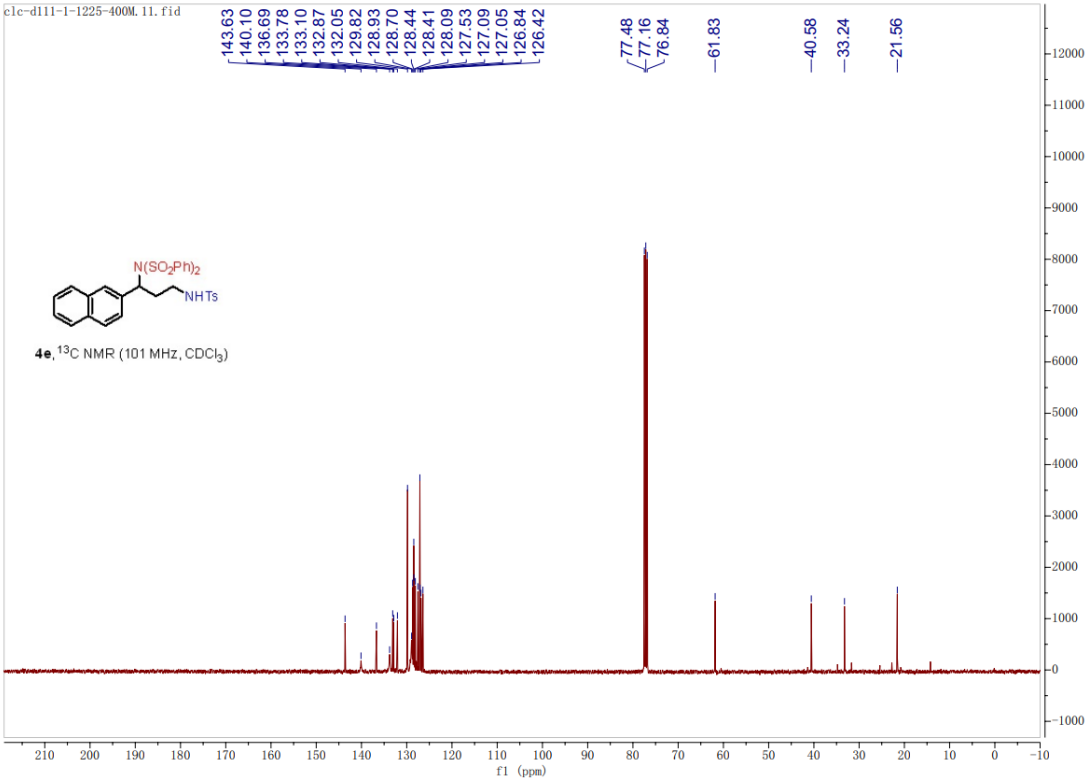
4c, ^{13}C NMR (126 MHz, $CDCl_3$)



4d, ^{1}H NMR (600 MHz, $CDCl_3$)

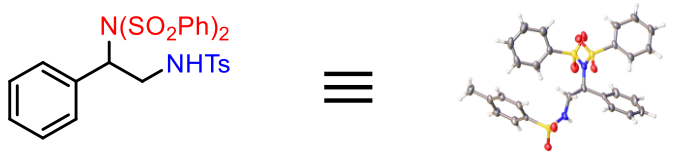

CLC-D811121
single pulse decoupled gated NOE
143.73
136.61
134.51
133.98
133.49
130.95
129.86
129.09
128.52
128.35
127.09
77.37
77.16
76.95
60.89
40.29
33.10
21.60
N(SO2Ph)2
NHTs
Cl
4d, 13C NMR (151 MHz, CDCl3)
f1 (ppm)


N(SO2Ph)2
NHTs
4e, 1H NMR (400 MHz, CDCl3)
EtOAc
CH3CO
EtOAc
CH3CH3
EtOAc
CH2CH3
2.12
2.10
2.09
2.09
2.08
2.07
2.05
1.00
2.04
7.09
5.05
4.15
3.08
1.02
1.03
2.04
1.03
3.08
1.00
f1 (ppm)


clc-d111-1-1225-400M.11.fid
143.63
140.10
136.69
133.78
133.10
132.87
132.05
129.82
128.93
128.70
128.44
128.41
128.09
127.53
127.09
127.05
126.84
126.42
77.48
77.16
76.84
61.83
40.58
33.24
21.56
N(SO2Ph)2
NHTs
4e, 13C NMR (101 MHz, CDCl3)
f1 (ppm)

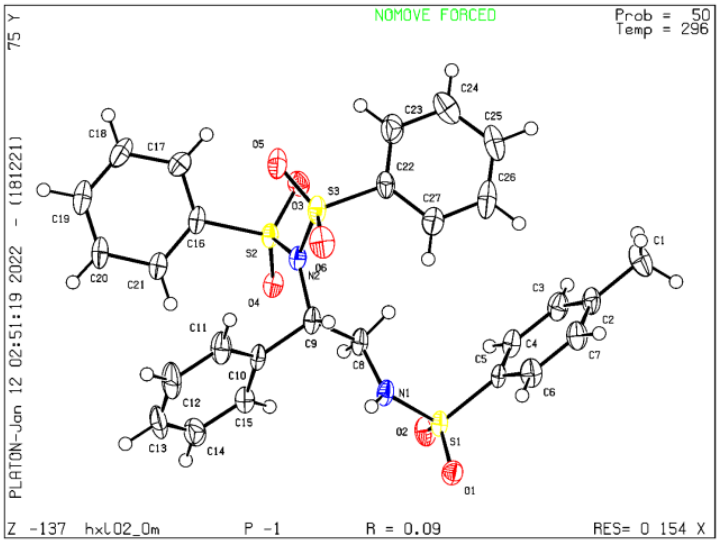
10.X-ray Crystallographic Information

Crystal data and structure refinement for 2a



2a ≡ **CDCC 2141473**

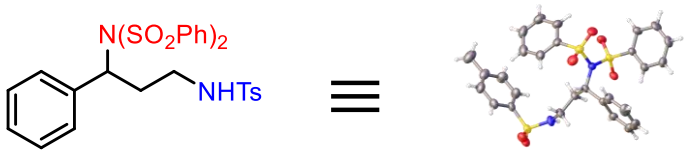
Datablock hxl02_0m - ellipsoid plot



Datablock: hxl02_0m

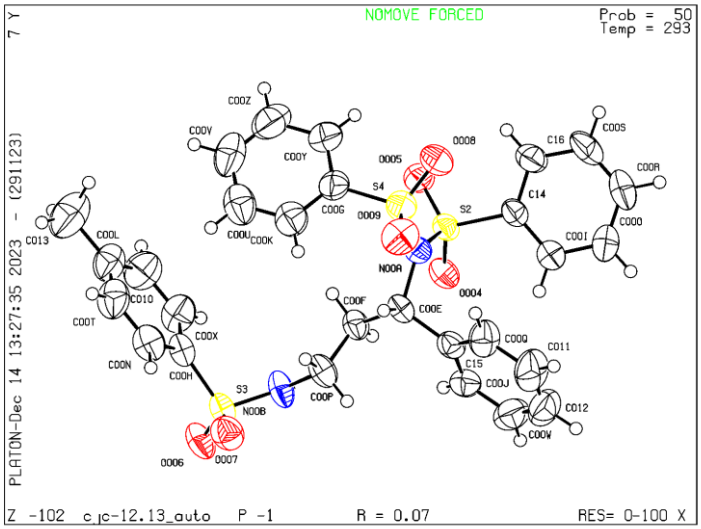
```
Bond precision:   C-C = 0.0064 A          Wavelength=0.71073

Cell:           a=10.094(4)       b=10.648(6)       c=13.883(9)
                alpha=73.30(3)    beta=70.165(18)   gamma=72.632(17)
Temperature:    296 K

                 Calculated                  Reported
Volume           1310.6(13)                  1310.5(13)
Space group      P -1                        P -1
Hall group       -P 1                        -P 1
Moiety formula   C27 H26 N2 O6 S3            C27 H26 N2 O6 S3
Sum formula      C27 H26 N2 O6 S3            C27 H26 N2 O6 S3
Mr               570.68                      570.68
Dx,g cm-3        1.446                       1.446
Z                2                           2
Mu (mm-1)        0.329                       0.329
F000             596.0                       596.0
F000'            597.00
h,k,lmax         12,12,16                    12,12,16
Nref             4729                        4557
Tmin,Tmax        0.961,0.968
Tmin'            0.961

Correction method= Not given

Data completeness= 0.964          Theta(max)= 25.223

R(reflections)= 0.0936( 3951)                wR2(reflections)=
                                             0.3043( 4557)
S = 1.415                 Npar= 344
```

Crystal data and structure refinement for 4a



4a **CDCC 2322479**

Datablock cjc-12.13_auto - ellipsoid plot



Datablock: cjc-12.13_auto

```
Bond precision:   C-C = 0.0086 A          Wavelength=1.54184

Cell:           a=9.9841(2)        b=9.9889(2)       c=15.0529(5)
                alpha=76.184(3)    beta=78.526(2)    gamma=74.084(2)
Temperature:    293 K

                Calculated                Reported
Volume          1387.52(6)                1387.52(7)
Space group     P -1                      P -1
Hall group      -P 1                      -P 1
Moiety formula  C28 H28 N2 O6 S3          C28 H28 N2 O6 S3
Sum formula     C28 H28 N2 O6 S3          C28 H28 N2 O6 S3
Mr              584.70                    584.70
Dx,g cm-3       1.400                     1.400
Z               2                         2
Mu (mm-1)       2.827                     2.827
F000            612.0                     612.0
F000'           615.66
h,k,lmax        12,12,18                  12,12,18
Nref            5803                      5497
Tmin,Tmax       0.791,0.868               0.888,1.000
Tmin'           0.718

Correction method= # Reported T Limits: Tmin=0.888 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.947          Theta(max)= 76.237

R(reflections)= 0.0685( 4746)                    wR2(reflections)=
                                                 0.2129( 5497)
S = 1.088                Npar= 353
```