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Aza-Morita–Baylis–Hillman Reactions Catalyzed by a Cyclopropenylidene

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General and Additional Information

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1 General Experimental

Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker AVA 400, Bruker AVA 500, Bruker PRO 500, and Bruker AVA 600 spectrometers, respectively. These spectrometers operate at the following frequencies: 400 MHz, 500 MHz, or 600 MHz for ^{1}H NMR; 100 MHz, 125 MHz, or 150 MHz for ^{13}C NMR; 128 MHz or 160 MHz for ^{11}B NMR; 128 MHz for ^{19}F NMR. Chemical shifts (δ) were quoted in parts per million (ppm) down-field to tetramethylsilane (TMS; δ = 0 ppm), or in the scale relative to the corresponding NMR solvent used as an internal reference. Coupling constants (*J*) are quoted to the nearest 0.1 Hz. Abbreviations used in the description of resonances are: s (singlet), d (doublet), t (triplet), q (quartet), sept (septet), m (multiplet), and br (broad). Infrared (IR) spectra were recorded on a Shimadzu IR Affinity–1 instrument using the corresponding isolated NMR sample in $CDCl_3$ (attenuated total reflectance sampling technique). High-resolution mass spectra (HRMS) were recorded on a Finnigan MAT 900 XLT spectrometer [electrospray ionization (ESI) technique]. Chiral HPLC analyses were performed on a Shimadzu LC–20AT apparatus with an SPD–20A detector using 4.6 x 250 mm columns from DAICEL CHIRALPAK. Thin-layer chromatography (TLC) was carried out on pre-coated silica gel plates from Merck (DF Alufolien 60F_{254}; 0.2 mm). Preparative thin-layer Chromatography (PTLC) was carried out on self-prepared plates using silica gel from Wakogel (B–5F; particle size: 45 μm). Flash column chromatography was carried out using silica gel from Fisher Scientific (60 Å; particle size: 40–63 μm). Product spots were visualized by UV light at 254 nm, or with an appropriate stain solution. Melting points were recorded on a Gallenkamp melting point apparatus (uncorrected).

All bases were purchased with the highest available purity: LiHMDS (97%, Aldrich), NaHMDS (99%, Aldrich), KHMDS (0.5 M in toluene, Aldrich), LDA (97%, Aldrich), LTMP (97%, Aldrich), NaO*t*Bu (99.9%, Aldrich), KO*t*Bu (99.99%, Aldrich), Li_2CO_3 (≥99.0%, Aldrich), Na_2CO_3 (≥99.0%, Aldrich), K_2CO_3 (99.9995%, Aldrich), Cs_2CO_3 (99.9995%, Aldrich), 1,8-diazabicyclo[5.4.0]undec-7-ene (≥99.0%, Aldrich), *N*,*N*,*N*,*N*-tetramethyl-guanidine (TMG, ≥99.0%, Aldrich), proton sponge (≥99.0%, Aldrich), 1,4-diazabi-cyclo[2.2.2]octane (DABCO; 99%, Aldrich), 4-dimethylaminopyridine (DMAP; >99%, Aldrich), triphenylphosphine (99%, Aldrich), tributylphosphine (99%, Aldrich), tricyclohexyl-phosphine (1 M in toluene, Aldrich). All NHC precursors for control experiments were purchased with the highest available purity: **1a**•HCl (95%, Aldrich), **1b**•HBF_4 (96%, Aldrich), **1c**•HBF_4 (97%, Aldrich), **1d**•HBF_4 (97%, Aldrich), **1e**•HCl (97%, Aldrich), **1f**•HBF_4 (95%, Aldrich), **1g**•HI (98%, Aldrich), **1h**•HBr (≥98%, Aldrich) and **1i**•HBr (98%, Aldrich). CAAC precursor **2**•$(HCl)_2$ was donated from Rhodia (Marseille, France).

Bis(dialkylamino)cyclo-propenylidene precursors **3a**•HBF_4,[1] **3b**•$HBPh_4$,[2] **3c**•$HBPh_4$,[2] and **3d**•$HBPh_4$[2] were prepared according to slightly modified literature methods. Imines **4a,j,l,s–u**,[3] **4b**,[4] **4c–e,h,k,z**,[5] **4f,p**,[6] **4g**,[7] **4m,q**,[8] **4n–o**,[9] **4r**,[10] **4v**,[11] **4w**,[12] **4x–y**,[13] are literature-known and were prepared accordingly. Imine **4h** was unknown and prepared according to a literature method.[3] Michael acceptors **5a** (98%, Aldrich), **5c** (98%, Aldrich), **5d** (99%, Aldrich), **5f** (99%, Aldrich), **5g** (90%, Aldrich), **5h** (98%, Aldrich), **5i** (97%, Aldrich), and **5j** (99%, Aldrich) were purchased, distilled before use, and stored over activated molecular sieves (4 Å) in a nitrogen glove box. Michael acceptors **5b**[14] and **5e**[15] were prepared according to literature methods, respectively. The obtained analytical data were in full agreement with the reported data. Unless otherwise stated, all reagents purchased from commercial suppliers were used directly without further purification. THF, toluene, and diethyl ether were distilled over sodium–benzophenone, and stored over activated molecular sieves (4 Å) in a nitrogen glove box. All other solvents –including dioxane, DME, DCM, DCE, and MeCN– were used non-distilled, but stored over activated molecular sieves (4 Å) in a nitrogen glove box. Solvent dryness was confirmed using a Karl–Fischer apparatus.

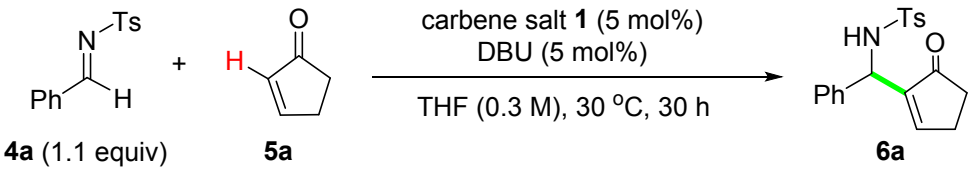
All catalytic reactions were carried out in oven-dried glassware (sealed screw-capped test tubes) under an inert atmosphere. Conventional stirring and heating was carried out using a magnetic stirring bar and a hot plate magnetic stirrer (sand bath).

2 Additional Experiments

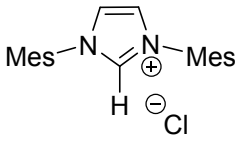
2.1 Control Experiments with *N*-Heterocyclic Carbenes (NHCs; Table S–1)

Results for the control experiments with NHCs –under optimized conditions– are summarized in Table S–1.

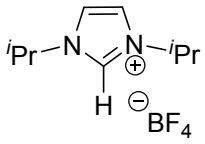
Table S–1: Control experiments with NHCs.[a]



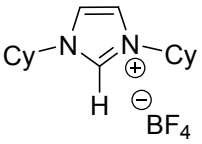
4a (1.1 equiv) **5a** **6a**



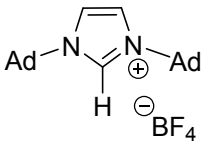
1a•HCl
68%



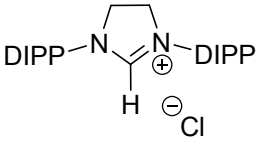
1b•HBF_4
54%



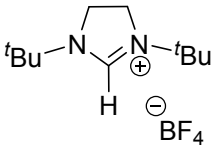
1c•HBF_4
NR



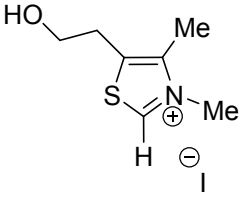
1d•HBF_4
NR



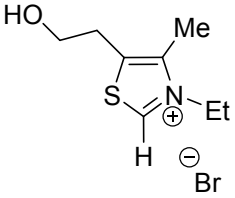
1e•HCl
68%



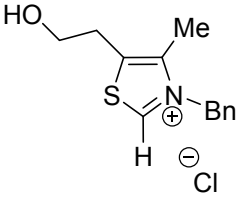
1f•HBF_4
NR



1g•HI
51%



1h•HBr
63%



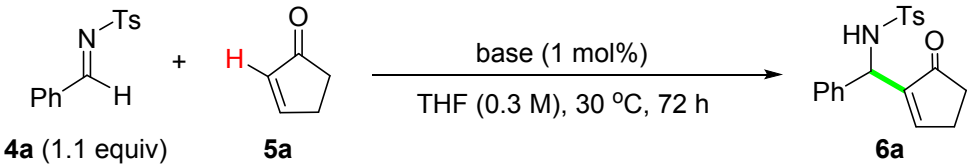
1i•HCl
53%

[a] The yield was determined by ^{1}H NMR spectroscopic analysis of an aliquot of the reaction mixture; internal standard: dibenzyl ether (25 mol% in mesitylene). [b] NR = no reaction; product **6a** was not detected – only starting materials were recovered (^{1}H NMR spectroscopic analysis of an aliquot of the reaction mixture).

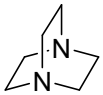
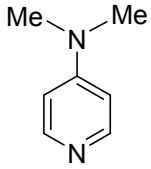
2.2 Control Experiments with *N*- and *P*-Centered Lewis Bases (Table S–2)

Results for the control experiments with *N*- and *P*-centered Lewis bases –at 1 mol% catalyst loading– are summarized in Table S–2.

Table S–2: Control experiments with *N*- and *P*-centered Lewis bases.[a]



4a (1.1 equiv) **5a** **6a**

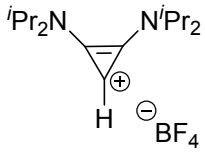
		PPh_3	PBu_3	PCy_3
68%	60%	49%	54%	41%

[a] The yield was determined by ^1H NMR spectroscopic analysis of an aliquot of the reaction mixture; internal standard: dibenzyl ether (25 mol% in mesitylene).

3 General Procedures

3.1 Preparation of Bis(dialkylamino)cyclopropenylidene Salts 3a–d•HX

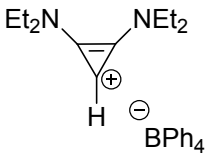
*Bis(diisopropylamino)cyclopropenium tetrafluoroborate (**3a**•HBF_4)*



3a•HBF_4

The compound was prepared according to Bertrand's reported literature procedure.[1] Diisopropylamine (11.1 g, 110 mmol, 5.00 equiv) was added drop-wise to a stirred solution of tetrachlorocyclopropene (3.87 g, 22.0 mmol, 1.00 equiv) in CH_2Cl_2 (150 mL) at 0 °C under a nitrogen atmosphere. After 6 h at 0 °C, the solution was warmed to room temperature and sodium tetrafluoroborate (7.50 g, 22.0 mmol, 1.00 equiv) was added. The suspension was stirred overnight and refluxed for 4 h. After cooling to room temperature were added successively triphenylphosphine (5.71 g, 22.0 mmol, 1.00 equiv) and water (100 mL), and the mixture was stirred overnight (open air). The organic layer was washed with water (3 x 250 mL), dried ($MgSO_4$), and concentrated *in vacuo*. After washing with pentane (100 mL) and drying *in vacuo*, the solid obtained was recrystallized from CH_2Cl_2/Et_2O at –20 °C to give **3a**•HBF_4 as a yellow solid.

*Bis(diethylamino)cyclopropenium tetraphenylborate (**3b**•$HBPh_4$)*

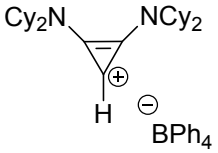


3b•$HBPh_4$

The compound was prepared according to a reported literature procedure.[2] Diethylamine (4.70 mL, 45.0 mmol, 4.50 equiv) was added drop-wise to a stirred solution of tetrachlorocyclopropene (1.38 mL, 12.0 mmol, 1.00 equiv) in CH_2Cl_2 (200 mL) at –78 °C under a nitrogen atmosphere. The reaction mixture was warmed to room temperature over 3 h and cooled to –78 °C. Triphenylphosphine (2.96 g, 12.0 mmol, 1.00 equiv) was added quickly, and the mixture was warmed to room temperature. At that stage, distilled water (40 mL) was added, and the two-phase mixture was stirred vigorously for 16 h before adding sodium tetraphenylborate (3.86 g, 12.0 mmol, 1.00 equiv). The organic layer was successively washed with aqueous HCl (0.5 M; 15 mL), aqueous $NaHCO_3$ (saturated; 15

mL), and water (10 mL), dried (Na_2SO_4), and concentrated *in vacuo*. Recrystallization from hot MeOH gave **3b**•$HBPh_4$ as a colorless solid (4.30 g, 92% yield).

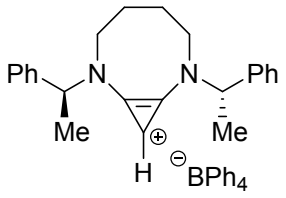
Bis(dicyclohexylamino)cyclopropenium tetraphenylborate (***3c***•*$HBPh_4$*)



3c•$HBPh_4$

The compound was prepared according to a modified literature procedure.[2] Dicyclohexylamine (5.14 mL, 45.0 mmol, 4.50 equiv) was added drop-wise to a stirred solution of tetrachlorocyclopropene (1.38 mL, 12.0 mmol, 1.00 equiv) in CH_2Cl_2 (200 mL) at –78 °C under a nitrogen atmosphere. The reaction mixture was warmed to room temperature over 3 h, distilled water (40 mL) was added, and the two-phase mixture was stirred vigorously for 16 h before adding sodium tetraphenylborate (3.86 g, 12.0 mmol, 1.00 equiv). The organic layer was successively washed with aqueous HCl (0.5 M; 15 mL), aqueous $NaHCO_3$ (saturated; 15 mL), and water (10 mL), dried (Na_2SO_4), and concentrated *in vacuo*. Recrystallization from hot MeOH gave the chlorocyclopropenium salt as a colorless solid (mp 132–133 °C). The chlorocyclopropenium salt (1.00 g, 1.30 mmol, 1.00 equiv) was dissolved in DCM (50 mL) and cooled to –78 °C. Triphenylphosphine (0.35 g, 1.30 mmol, 1.00 equiv) was added quickly, and the mixture was warmed to room temperature. At that stage, distilled water (10 mL) was added, and the two-phase mixture was stirred vigorously for 16 h. The organic layer was successively washed with aqueous HCl (0.5 M; 20 mL), aqueous $NaHCO_3$ (saturated; 20 mL), and water (15 mL), dried (Na_2SO_4), and concentrated *in vacuo*. Recrystallization from DCM/Et_2O gave **3c**•$HBPh_4$ as a light-yellow solid.

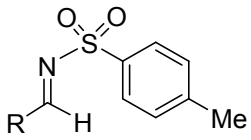
*2-(S)-1-Phenylethyl-7-[(S)-1-phenylethyl]-2,7-diazabicyclo[6.1.0]non-1(8)-en-9-ylium tetraphenylborate (**3d**•$HBPh_4$)*



3d•BPh_4

The compound was prepared according to a reported literature procedure.[2] Under a nitrogen atmosphere, a pre-cooled solution of *N,N'*-bis[(*S*)-phenylethyl]butane-1,4-diamine[23] (83.0 mg, 0.28 mmol, 1.00 equiv) in CH_2Cl_2 (0.6 mL) at –78 °C was slowly added to a solution of tetrachlorocyclopropene (34.0 µL, 0.28 mmol, 1.00 equiv) in CH_2Cl_2 (5.0 mL) at –78 °C. After addition of diisopropylethylamine (98.0 µL, 0.56 mmol, 2.00 equiv), the reaction mixture was warmed to room temperature and stirred at room temperature for 3 h. The flask was cooled to –78 °C, at which stage polystyrene-bound triphenylphosphine (3.0 mmol/g; 100 mg, 0.56 mmol, 2.00 equiv) was added in one portion. The reaction mixture was warmed to room temperature over 2 h before successive addition of distilled water (5 mL) and sodium tetraphenylborate (98.0 mg, 0.28 mmol, 1.00 equiv). The reaction mixture was stirred vigorously for 48 h before filtration and transfer of the filtrate to a separating funnel containing CH_2Cl_2. After phase separation, the organic layer was washed successively with aqueous HCl (0.5 M), aqueous $NaHCO_3$ (saturated), and water. The organic phase was dried (Na_2SO_4), filtered, and concentrated *in vacuo.* The crude product was purified by flash column chromatography on silica gel (eluent: acetone/DCM = 1:100) to obtain the pure product as a colorless solid (150 mg, 83% yield).

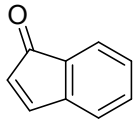
3.2 General Procedure for the Synthesis of Imines 4a–z



To an oven-dried 50 mL round-bottom flask with a magnetic stirring bar under an argon atmosphere were added *p*-toluenesulfonamide (1.00 equiv), tetraethyl orthosilicate (1.10 equiv), and the respective aldehyde (1.00 equiv). The flask was connected to a short distillation head (approximately 3–4 cm long) and a receptor flask. The reaction mixture was heated at 140–160 °C for 8–16 h; the by-product, ethanol, was collected in the receptor flask. After confirming the end-point of the reaction by ^{1}H NMR spectroscopic analysis, the reaction mixture was cooled to room temperature and washed with hexane (10 mL). The mixture was filtered, and volatiles were removed from the filtrate *in vacuo* to give a solid, which was recrystallized from ethyl acetate to yield the corresponding pure imine, which was powdered and dried over molecular sieves (4Å) in DCM prior to use in catalysis.

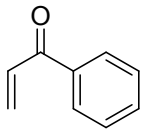
3.3 Procedures for the Synthesis of Michael Acceptors 5b and 5e

Procedure for the Synthesis of 5b[14]



NBS (1.95 g, 11.0 mmol, 1.10 equiv) and AIBN (20.0 mg, 0.11 mmol, 0.01 equiv) were added to a solution of 1-indanone (1.32 g, 10.0 mmol, 1.00 equiv) in CCl_4 (4 mL). The resulting mixture was stirred at 100 °C for 2.5 h, cooled to room temperature, filtered through celite, and washed with CCl_4. The filtrate was cooled to 0 °C, treated with triethylamine (2.80 mL, 20.0 mmol, 2.00 equiv) overnight, and concentrated *in vacuo*. Flash column chromatography on silica gel (eluent: EtOAc/PE = 1:5) gave product **5b** as a yellow liquid (10.7 g, 90% yield).

Procedure for the Synthesis of 5e[15]

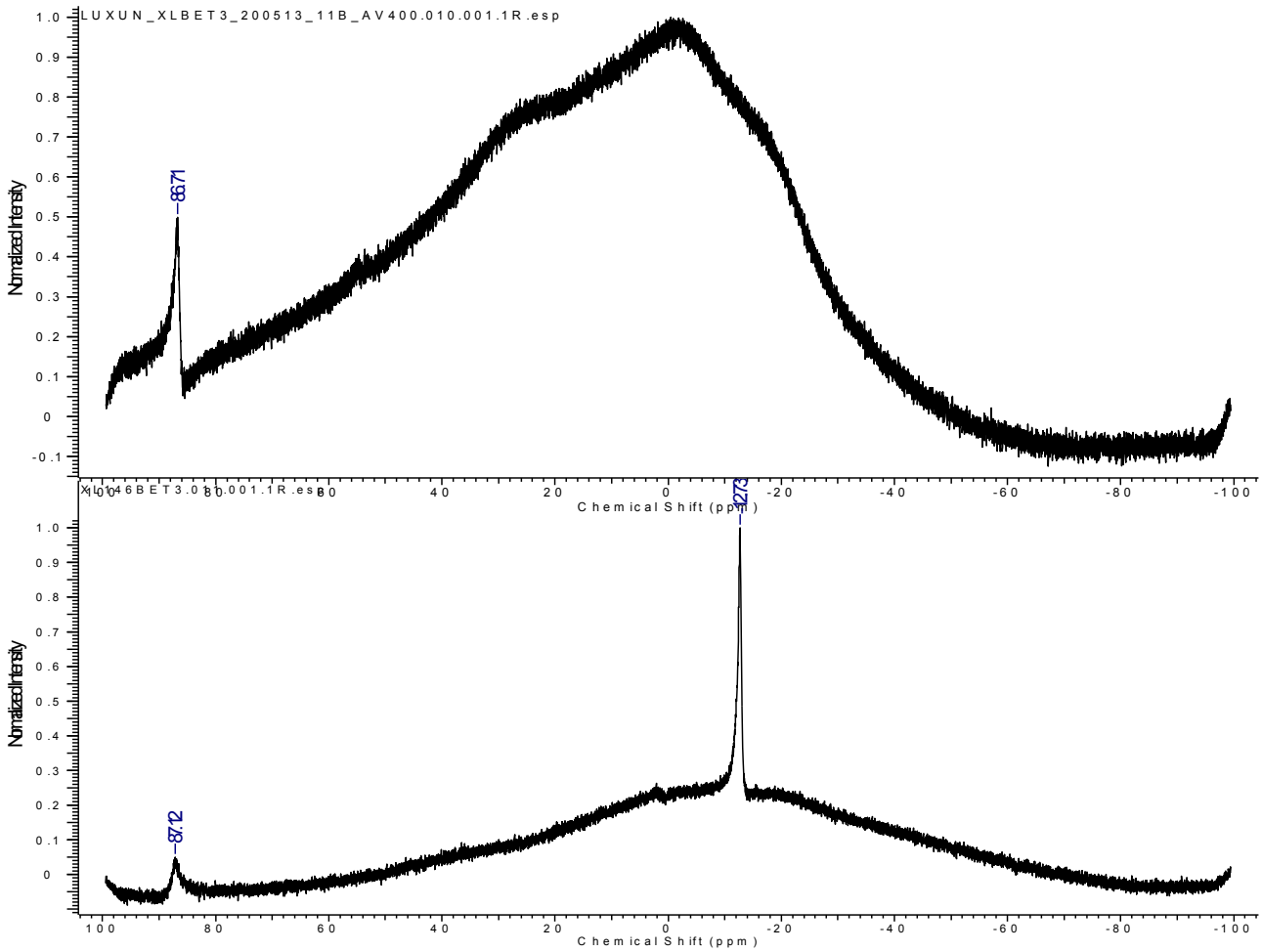


Triethylamine (2.47 g, 24.0 mmol, 2.40 equiv) was added drop-wise over 1 h to a stirred solution of 3-chloropropiophenone (1.68 g, 10.0 mmol, 1.00 equiv) in chloroform (20 mL) under a nitrogen atmosphere. The reaction mixture was stirred overnight at room temperature, followed by washing with aqueous HCl (1 M; 2 x 20 mL), distilled water (2 x 20 mL), aqueous $NaHCO_3$ (saturated; 2 x 20 mL), and brine (1 x 20 mL). The organic layer was dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (eluent: EtOAc/PE = 1:6) to give product **5e** as a colorless liquid (1.20 g, 90% yield).

3.4 General Procedures for BAC Catalysis

Deprotonation of 3a•HBF$_4$ and Formation of 3a•BEt$_3$

To an oven-dried test tube with a magnetic stirring bar in a nitrogen glovebox were added **3a**•HBF_4 (16.0 mg, 50 μmol, 1.00 equiv) and THF (400 μL). The reaction mixture was cooled to –78 °C and stirred for 15 min. KHMDS (0.5 M in toluene; 100 μL, 50 μmol, 1.00 equiv) was added drop-wise to the mixture, which was stirred at –78 °C for 15 min. The reaction mixture was warmed to room temperature and stirred for 30 min. Volatiles were removed *in vacuo*, and C_6D_6 (400 μL) was added to the test tube. The supernatant of the suspension was added to triethyl borane (1.0 M in hexane; 60.0 μL, 60 μmol, 1.20 equiv). The solution was then transferred to an NMR tube for ^{11}B NMR spectroscopic analysis; the upper chart corresponds to triethyl borane (BEt_3); the bottom chart corresponds to the formation of **3a**•BEt_3.



Procedure for Initial C–C Bond Formation

To an oven-dried test tube with a magnetic stirring bar in a nitrogen glovebox were added **3a**•HBF_4 (3.2 mg, 10 μmol, 1.00 equiv) and THF (80 μL). The reaction mixture was cooled to –78 °C and stirred for 15 min. KHMDS (20 μL, 10 μmol, 0.5 M in toluene, 1.00 equiv) was added dropwise to the mixture, and stirred at –78 °C for 15 min. The reaction mixture was warmed to room temperature and stirred for 30 min. Volatiles were removed *in vacuo*, and THF (100 μL) was added to the test tube to prepare a catalyst solution. To another oven-dried test tube with a magnetic stirring bar in a nitrogen glovebox were added imine **4a** (28.5 mg, 0.11 mmol, 1.10 equiv), Michael acceptor **5a** (8.2 mg, 0.10 mmol, 1.00 equiv), and THF (400 μL, 0.2 M in total). The reaction mixture was stirred at 30 °C for 24 h. ^{1}H NMR spectroscopic analysis was carried to detect the NMR yield of product **6a**.

General Procedure A **[imine scope]**

To an oven-dried test tube with a magnetic stirring bar in a nitrogen glovebox were added **3a**•HBF_4 (3.2 mg, 10 μmol, 5 mol%), the corresponding imine (0.22 mmol, 1.10 equiv), Michael acceptor **5a** (16.4 mg, 0.20 mmol, 1.00 equiv), THF (0.66 mL), and DBU (1.5 mg, 10 μmol, 5 mol%). The reaction mixture was stirred at 30 °C for 24–48 h, at which point TLC and/or ^{1}H NMR spectroscopic analysis indicated complete consumption of **5a**. Volatiles were removed *in vacuo*, and the residue was purified by PTLC or flash column chromatography on silica gel (eluent: EtOAc/PE = 1:2, or DCM/acetone = 100:1) to give the corresponding products.

General Procedure B **[Michael acceptor scope]**

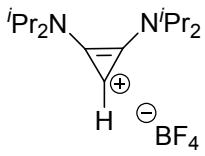
To an oven-dried test tube with a magnetic stirring bar in a nitrogen glovebox were added **3b**•$HBPh_4$ (5.0 mg, 10 μmol, 10 mol%), imine **4a** (28.5 mg, 0.11 mmol, 1.10 equiv), the corresponding Michael acceptor (0.10 mmol, 1.00 equiv), THF (0.33 mL), and DBU (1.5 mg, 10 μmol, 10 mol%). The reaction mixture was stirred at 40 °C for 24–72 h, at which point TLC and/or ^{1}H NMR analysis indicated complete consumption of the corresponding Michael acceptor. The volatiles were removed *in vacuo*, and the residue was purified by PTLC or flash column chromatography on silica gel (eluent: EtOAc/PE = 1:5) to give the corresponding products.

4 Analytical Data for Unknown Compounds

4.1 Analytical Data for Bis(dialkylamino)cyclopropenylidene Salts 3a–d•HX

The synthesized BAC precursor **3b**•$HBPh_4$ and **3d**•$HBPh_4$ are literature-known,[2] and the obtained analytical data are in full agreement with the reported data. The obtained analytical data for the novel BAC precursors **3a**•HBF_4 and **3c**•$HBPh_4$ are listed below.

Bis(diisopropylamino)cyclopropenium tetrafluoroborate (3a•HBF_4)



3a•HBF_4

Yellow solid (mp 132–134 °C).

Yield: 10.6 g (90%).

^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.46 (s, 1H), 4.05 (sept, *J* = 11.3 Hz, 2H), 3.86 (sept, *J* = 11.3 Hz, 2H), 1.41 (d, *J* = 11.3 Hz, 12H), 1.38 (d, *J* = 11.3 Hz, 12H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 133.8 (2C), 99.3, 56.9 (2C), 49.2 (2C), 20.8 (4C), 20.7 (4C) ppm.

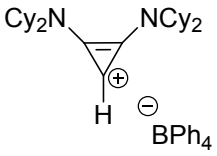
^{11}B NMR ($CDCl_3$, 128 MHz): δ = –1.70 ppm.

^{19}F NMR ($CDCl_3$, 128 MHz): δ = –152.2 ~ –152.3 (m) ppm.

IR (neat): ν = 3122, 2983, 2268, 1880, 1566, 1055, 1033, 912, 727 cm^{-1}.

HRMS (ESI+): calculated for $C_{15}H_{29}N_2^+$ = $[M]^+$: m/z = 237.2319, found: m/z = 237.2325.

Bis(dicyclohexylamino)cyclopropenium tetraphenylborate (3c•$HBPh_4$)



3c•$HBPh_4$

Light-yellow solid (mp 152–153 °C).

Yield: 0.81 g (85%).

^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.57 (br s, 8H), 7.09 (t, *J* = 8.5 Hz, 8H), 6.63 (t, *J* = 8.5 Hz, 4H), 4.61 (br s, 1H), 3.39 (q, *J* = 7.5 Hz, 2H), 3.36 (q, *J* = 7.5 Hz, 2H), 1.92–1.89 (m, 15H), 1.77–1.75 (m, 2H), 1.53–1.52 (m, 15H), 1.38–1.35 (m, 8H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 167.5 (q, *J* = 44.3 Hz, 4C), 138.9 (4C), 138.1 (2C), 127.5 (8C), 122.5 (8C), 99.2, 57.3 (4C), 31.2 (4C), 25.9 (8C), 25.4 (8C) ppm.

^{11}B NMR ($CDCl_3$, 160 MHz): δ = –6.14 ppm.

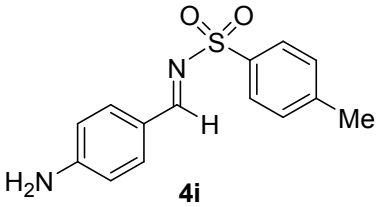
IR (neat): ν = 3110, 3045, 2984, 1620, 1593, 1567 cm^{-1}.

HRMS (ESI+): calculated for $C_{27}H_{45}N_2^+$ = $[M]^+$: m/z = 397.6578, found: m/z = 397.6581.

4.2 Analytical Data for Imines 4a–z

The synthesized imines **4a,j,l,s–u**,[3] **4b**,[4] **4c–e,h,k,z**,[5] **4f,p**,[6] **4g**,[7] **4m,q**,[8] **4n–o**,[9] **4r**,[10] **4v**,[11] **4w**,[12] **4x–y**,[13] are literature-known, and the obtained analytical data are in full agreement with the reported data. The obtained analytical data for the novel imine **4i** are listed below.

4-Methyl-*N*-[(4-amino)benzylidene]benzenesulfonamide (4i)



4i

Colorless liquid.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 9.72 (s, 1H), 7.73 (d, *J* = 7.0 Hz, 2H), 7.49 (d, *J* = 7.6 Hz, 2H), 7.33 (d, *J* = 7.0 Hz, 2H), 7.19 (d, *J* = 7.6 Hz, 2H), 6.39 (br s, NH_2, 2H), 2.32 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 150 MHz): δ = 168.1, 149.1, 144.3, 138.2, 132.7, 130.1 (2C), 129.7 (2C), 127.2 (2C), 114.3 (2C), 21.6 ppm.

IR (neat): ν = 3408, 2978, 2882, 1618, 1460, 1376, 1325, 1148, 856 cm^{-1}.

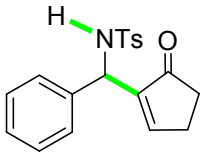
HRMS (ESI+): calculated for $C_{14}H_{14}NaN_2O_2S$ = $[M+Na]^+$: m/z = 297.0801, found: m/z = 297.0810.

4.3 Analytical Data for Michael Acceptors 5b and 5e

The synthesized Michael acceptors **5b**[14] and **5e**[15] are literature-known, and the obtained analytical data are in full agreement with the reported data.

4.4 Analytical Data for Products 6a–z and (*R*)-6a

4-Methyl-*N*-[(5-oxocyclopent-1-enyl)(phenyl)methyl]benzenesulfonamide (6a)[16]



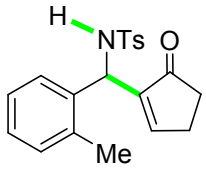
6a

Prepared from imine **4a** (57.0 mg, 0.22 mmol, 1.10 equiv) and Michael acceptor **5a** (16.4 mg, 0.20 mmol, 1.00 equiv) according to the *general procedure A* using **3a**•HBF_4 (3.20 mg, 10 µmol, 5 mol%) and DBU (1.5 mg, 10 µmol, 5 mol%) in THF (0.66 mL, 0.3 M) at 30 °C for 30 h. **6a** was purified by PTLC on silica gel (eluent: EtOAc/PE = 1:2). *The obtained analytical data were in full agreement with the reported data.*[16]

Colorless solid.

Yield: 64.2 mg (93%).

4-Methyl-*N*-[(5-oxocyclopent-1-enyl)(2-toluyl)methyl]benzenesulfonamide (6b)



6b

Prepared from imine **4b** (60.4 mg, 0.22 mmol, 1.10 equiv) and Michael acceptor **5a** (16.4 mg, 0.20 mmol, 1.00 equiv) according to the *general procedure A* using **3a**•HBF_4 (3.2 mg, 10 µmol, 5 mol%) and DBU (1.5 mg, 10 µmol, 5 mol%) in THF (0.66 mL, 0.3 M) at 30 °C for 24 h. **6b** was purified by PTLC on silica gel (eluent: EtOAc/PE = 1:2).

Colorless solid (mp 163–165 °C).

Yield: 64.7 mg (91%).

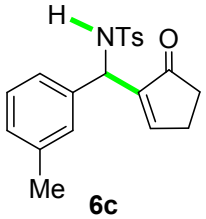
^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.60 (d, *J* = 8.4 Hz, 2H), 7.35 (t, *J* = 6.3 Hz, 1H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.12–7.03 (m, 4H), 5.82 (d, *J* = 7.6 Hz, 1H), 5.49 (d, *J* = 7.6 Hz, 1H), 2.49–2.13 (m, 4H), 2.38 (s, 3H), 2.28 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 150 MHz): δ = 208.3, 160.2, 143.9, 143.2, 137.3, 136.7, 135.7, 130.7, 129.3 (2C), 127.9, 127.4 (2C), 126.9, 126.3, 51.8, 34.9, 26.7, 21.5, 19.4 ppm.

IR (neat): ν = 3302, 2958, 1697, 1441, 1339, 1161, 904, 864, 741, 650 cm^{-1}.

HRMS (ESI+): calculated for $C_{20}H_{21}NaNO_3S$ = $[M+Na]^+$: m/z = 378.1134, found: m/z = 378.1120.

4-Methyl-*N*-[(5-oxocyclopent-1-enyl)(3-toluyl)methyl]benzenesulfonamide (6c)



6c

Prepared from imine **4c** (60.4 mg, 0.22 mmol, 1.10 equiv) and Michael acceptor **5a** (16.4 mg, 0.20 mmol, 1.00 equiv) according to the *general procedure A* using **3a**•HBF_4 (3.2 mg, 10 µmol, 5 mol%) and DBU (1.5 mg, 10 µmol, 5 mol%) in THF (0.66 mL, 0.3 M) at 30 °C for 24 h. **6c** was purified by PTLC on silica gel (eluent: EtOAc/PE = 1:2).

Colorless solid (mp 164–165 °C).

Yield: 63.1 mg (87%).

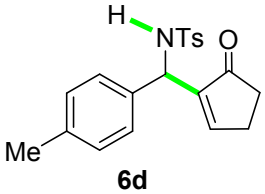
^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.61 (d, *J* = 8.2 Hz, 2H), 7.35 (t, *J* = 6.1 Hz, 1H), 7.19 (d, *J* = 8.2 Hz, 2H), 7.12–7.10 (m, 1H), 7.02 (d, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 7.6 Hz, 2H), 6.02 (d, *J* = 8.4 Hz, 1H), 5.25 (d, *J* = 8.4 Hz, 1H), 2.50–2.15 (m, 4H), 2.39 (s, 3H), 2.23 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 150 MHz): δ = 208.3, 160.4, 143.6, 143.1, 138.5, 138.3, 137.5, 129.3 (2C), 128.6, 128.5, 127.5, 127.4 (2C), 123.7, 55.4, 34.9, 26.7, 21.4, 21.3 ppm.

IR (neat): ν = 3275, 2920, 2849, 1695, 1437, 1330, 1159, 1091, 904, 815, 742, 665 cm^{-1}.

HRMS (ESI+): calculated for $C_{20}H_{21}NaNO_3S$ = $[M+Na]^+$: m/z = 378.1134, found: m/z = 378.1115.

4-Methyl-*N*-[(5-oxocyclopent-1-enyl)(4-toluyl)methyl]benzenesulfonamide (6d)[16]



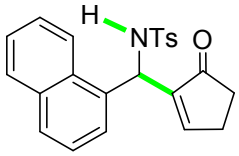
6d

Prepared from imine **4d** (60.4 mg, 0.22 mmol, 1.10 equiv) and Michael acceptor **5a** (16.4 mg, 0.20 mmol, 1.00 equiv) according to the *general procedure A* using **3a**•HBF_4 (3.2 mg, 10 µmol, 5 mol%) and DBU (1.50 mg, 10 µmol, 5 mol%) in THF (0.66 mL, 0.3 M) at 30 °C for 24 h. **6d** was purified by PTLC on silica gel (eluent: EtOAc/PE = 1:2). *The obtained analytical data were in full agreement with the reported data.*[16]

Colorless solid.

Yield: 57.9 mg (84%).

4-Methyl-*N*-[(5-oxocyclopent-1-enyl)(2-naphthalenyl)methyl]benzenesulfonamide (6e)



6e

Prepared from imine **4e** (68.2 mg, 0.22 mmol, 1.10 equiv) and Michael acceptor **5a** (16.4 mg, 0.20 mmol, 1.00 equiv) according to the *general procedure A* using **3a**•HBF_4 (3.2 mg, 10 μmol, 5 mol%) and DBU (1.5 mg, 10 μmol, 5 mol%) in THF (0.66 mL, 0.3 M) at 30 °C for 48 h. **6e** was purified by PTLC on silica gel (eluent: EtOAc/PE = 1:1).

Colorless solid (mp 176–178 °C).

Yield: 77.2 mg (93%).

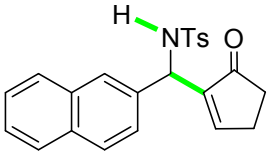
^{1}H NMR ($CDCl_3$, 600 MHz): δ = 8.07–8.06 (m, 1H), 7.84–7.82 (m, 1H), 7.76–7.74 (m, 1H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.49–7.47 (m, 2H), 7.42–7.41 (t, *J* = 6.3 Hz, 1H), 7.33–7.30 (m, 2H), 7.14 (d, *J* = 8.2 Hz, 2H), 6.10 (d, *J* = 7.8 Hz, 1H), 6.04 (d, *J* = 7.8 Hz, 1H), 2.46–2.19 (m, 4H), 2.39 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 150 MHz): δ = 208.4, 161.3, 143.4, 143.2, 137.0, 133.9, 130.3, 129.2 (2C), 128.9, 128.8, 127.5 (2C), 126.6, 126.2, 125.8, 125.3, 125.0, 123.1, 51.7, 34.9, 26.7, 21.4 ppm.

IR (neat): ν = 3163, 3005, 2943, 1440, 1375, 1037, 918, 748 cm^{-1}.

HRMS (ESI+): calculated for $C_{23}H_{21}NaNO_3S$ = $[M+Na]^+$: m/z = 414.1134, found: m/z = 414.1111.

4-Methyl-*N*-[(5-oxocyclopent-1-enyl)(2-naphthalenyl)methyl]benzenesulfonamide (6f)



6f

Prepared from imine **4f** (68.2 mg, 0.22 mmol, 1.10 equiv) and Michael acceptor **5a** (16.4 mg, 0.20 mmol, 1.00 equiv) according to the *general procedure A* using **3a**•HBF_4 (3.2 mg, 10 μmol, 5 mol%) and DBU (1.5 mg, 10 μmol, 5 mol%) in THF (0.66 mL, 0.3 M) at 30 °C for 30 h. **6f** was purified by PTLC on silica gel (eluent: EtOAc/PE = 1:1).

Colorless solid (mp 175–179 °C).

Yield: 76.2 mg (92%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.76–7.75 (m, 1H), 7.70 (d, *J* = 8.6 Hz, 2H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.59 (s, 1H), 7.45–7.44 (m, 2H), 7.42 (t, *J* = 5.4 Hz, 1H), 7.31–7.30 (m, 1H),

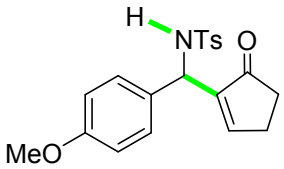
7.10 (d, *J* = 8.2 Hz, 2H), 6.18 (d, *J* = 8.4 Hz, 1H), 5.45 (d, *J* = 8.4 Hz, 1H), 2.54–2.20 (m, 4H), 2.30 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 150 MHz): δ = 208.5, 160.8, 139.5, 137.9, 133.7, 133.0, 132.8, 129.7, 129.3 (2C), 128.6, 127.9, 127.5, 127.4 (2C), 126.4, 126.3, 125.7, 125.4, 58.1, 32.5, 26.2, 21.3 ppm.

IR (neat): ν = 3165, 3003, 2943, 1701, 1436, 1375, 1161, 1039, 918, 736, 669 cm^{-1}.

HRMS (ESI+): calculated for $C_{23}H_{21}NaNO_3S$ = $[M+Na]^+$: m/z = 414.1134, found: m/z = 414.1093.

4-Methyl-*N*-[(5-oxocyclopent-1-enyl)(4-methoxylphenyl)methyl]benzenesulfonamide (6g)[16]



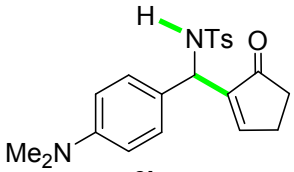
6g

Prepared from imine **4g** (63.8 mg, 0.22 mmol, 1.10 equiv) and Michael acceptor **5a** (16.4 mg, 0.20 mmol, 1.00 equiv) according to the *general procedure A* using **3a**•HBF_4 (3.2 mg, 10 μmol, 5 mol%) and DBU (1.5 mg, 10 μmol, 5 mol%) in THF (0.66 mL, 0.3 M) at 30 °C for 30 h. **6g** was purified by PTLC on silica gel (eluent: EtOAc/PE = 1:2). *The obtained analytical data were in full agreement with the reported data.*[16]

Colorless solid.

Yield: 70.2 mg (92%).

4-Methyl-*N*-[(5-oxocyclopent-1-enyl)(4-dimethylaminophenyl)methyl]benzenesulfonamide (6h)[17]



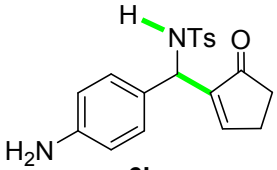
6h

Prepared from imine **4h** (67.1 mg, 0.22 mmol, 1.10 equiv) and Michael acceptor **5a** (16.4 mg, 0.20 mmol, 1.00 equiv) according to the *general procedure A* using **3a**•HBF_4 (3.2 mg, 10 μmol, 5 mol%) and DBU (1.5 mg, 10 μmol, 5 mol%) in THF (0.66 mL, 0.3 M) at 30 °C for 48 h. **6h** was purified by PTLC on silica gel (eluent: EtOAc/PE = 1:2). *The obtained analytical data were in full agreement with the reported data.*[17]

Pale-yellow solid.

Yield: 72.3 mg (92%).

4-Methyl-*N*-[(5-oxocyclopent-1-enyl)(4-aminophenyl)methyl]benzenesulfonamide (6i)



6i

Prepared from imine **4i** (60.2 mg, 0.22 mmol, 1.10 equiv) and Michael acceptor **5a** (16.4 mg, 0.20 mmol, 1.00 equiv) according to the *general procedure A* using **3a**•HBF_4 (3.2 mg, 10 µmol, 5 mol%) and DBU (1.5 mg, 10 µmol, 5 mol%) in THF (0.66 mL, 0.3 M) at 30 °C for 24 h. **6i** was purified by PTLC on silica gel (eluent: EtOAc/PE = 1:2).

Colorless solid (mp 157–159 °C).

Yield: 59.2 mg (83%).

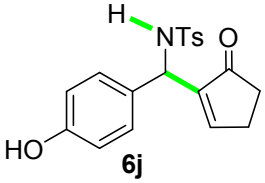
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.65 (br s, 2H), 7.66 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.26 (t, *J* = 5.4 Hz, 1H), 7.05 (d, *J* = 8.2 Hz, 2H), 6.62–6.59 (m, 2H), 5.85 (d, *J* = 8.2 Hz, 1H), 5.21 (d, *J* = 8.2 Hz, 1H), 2.52–2.17 (m, 4H), 2.41 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 208.3, 151.1, 146.3, 141.5, 139.9, 132.7, 131.7 (2C), 131.2, 129.5 (2C), 129.1 (2C), 116.1 (2C), 60.7, 35.1, 28.8, 23.9 ppm.

IR (neat): ν = 3028, 2924, 2835, 2291, 2250, 1705, 1587, 1494, 1346, 1180, 914, 825, 750, 700, 663, 623 cm^{-1}.

HRMS (ESI+): calculated for $C_{19}H_{20}NaN_2O_3S$ = $[M+Na]^+$: m/z = 356.4432, found: m/z = 356.4433.

4-Methyl-*N*-[(5-oxocyclopent-1-enyl)(4-hydroxyphenyl)methyl]benzenesulfonamide (6j)



6j

Prepared from imine **4j** (59.4 mg, 0.22 mmol, 1.10 equiv) and Michael acceptor **5a** (16.4 mg, 0.20 mmol, 1.00 equiv) according to the *general procedure A* using **3a**•HBF_4 (3.2 mg, 10 µmol, 5 mol%) and DBU (1.5 mg, 10 µmol, 5 mol%) in THF (0.66 mL, 0.3 M) at 30 °C for 24 h. **6j** was purified by PTLC on silica gel (eluent: EtOAc/PE = 1:2).

Colorless solid (mp 169–170 °C).

Yield: 50.0 mg (70%).

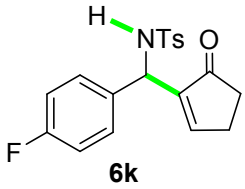
^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.80 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.45 (t, *J* = 5.3 Hz, 1H), 7.26 (d, *J* = 8.3 Hz, 2H), 6.93–6.91 (m, 2H), 6.10 (d, *J* = 8.4 Hz, 1H), 5.83 (br s, 1H), 5.25 (d, *J* = 8.4 Hz, 1H), 2.55–2.19 (m, 4H), 2.43 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 206.3, 157.8, 144.3, 139.5, 137.7, 130.7, 129.8 (2C), 129.5 (2C), 127.6, 125.1 (2C), 115.1 (2C), 58.1, 32.5, 26.2, 21.3 ppm.

IR (neat): ν = 3062, 2922, 2835, 2250, 1705, 1647, 1587, 1435, 1346, 180, 750, 698, 611 cm^{-1}.

HRMS (ESI+): calculated for $C_{19}H_{19}NaNO_4S$ = $[M+Na]^+$: m/z = 380.5824, found: m/z = 380.5821.

4-Methyl-*N*-[(5-oxocyclopent-1-enyl)(4-fluorophenyl)methyl]benzenesulfonamide (6k)[16]



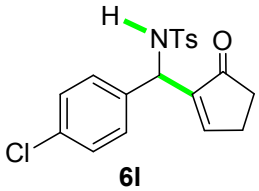
6k

Prepared from imine **4k** (71.0 mg, 0.22 mmol, 1.10 equiv) and Michael acceptor **5a** (16.4 mg, 0.20 mmol, 1.00 equiv) according to the *general procedure A* using **3a**•HBF_4 (3.2 mg, 10 μmol, 5 mol%) and DBU (1.5 mg, 10 μmol, 5 mol%) in THF (0.66 mL, 0.3 M) at 30 °C for 30 h. **6k** was purified by PTLC on silica gel (eluent: EtOAc/PE = 1:2). *The obtained analytical data were in full agreement with the reported data.*[16]

Colorless solid.

Yield: 66.3 mg (91%).

4-Methyl-*N*-[(5-oxocyclopent-1-enyl)(4-chlorophenyl)methyl]benzenesulfonamide (6l)[16]



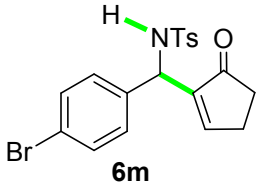
6l

Prepared from imine **4l** (64.6 mg, 0.22 mmol, 1.10 equiv) and Michael acceptor **5a** (16.4 mg, 0.20 mmol, 1.00 equiv) according to the *general procedure A* using **3a**•HBF_4 (3.2 mg, 10 μmol, 5 mol%) and DBU (1.5 mg, 10 μmol, 5 mol%) in THF (0.66 mL, 0.3 M) at 30 °C for 30 h. **6l** was purified by PTLC on silica gel (eluent: EtOAc/PE = 1:2). *The obtained analytical data were in full agreement with the reported data.*[16]

Colorless solid.

Yield: 72.3 mg (95%).

4-Methyl-*N*-[(5-oxocyclopent-1-enyl)(4-bromophenyl)methyl]benzenesulfonamide (6m)[17]



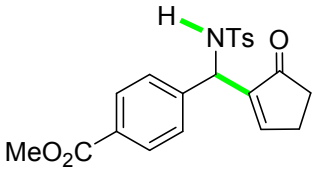
6m

Prepared from imine **4m** (67.4 mg, 0.22 mmol, 1.10 equiv) and Michael acceptor **5a** (16.4 mg, 0.20 mmol, 1.00 equiv) according to the *general procedure A* using **3a**•HBF_4 (3.2 mg, 10 µmol, 5 mol%) and DBU (1.5 mg, 10 µmol, 5 mol%) in THF (0.66 mL, 0.3 M) at 30 °C for 30 h. **6m** was purified by PTLC on silica gel (eluent: EtOAc/PE = 1:2). *The obtained analytical data were in full agreement with the reported data.*[17]

Colorless solid.

Yield: 80.2 mg (94%).

4-Methyl-*N*-[(5-oxocyclopent-1-enyl)(4-methoxycarbonylphenyl)methyl]benzene-sulfonamide (6n)



6n

Prepared from imine **4n** (69.8 mg, 0.22 mmol, 1.10 equiv) and Michael acceptor **5a** (16.4 mg, 0.20 mmol, 1.00 equiv) according to the *general procedure A* using **3a**•HBF_4 (3.2 mg, 10 µmol, 5 mol%) and DBU (1.5 mg, 10 µmol, 5 mol%) in THF (0.66 mL, 0.3 M) at 30 °C for 24 h. **6n** was purified by PTLC on silica gel (eluent: EtOAc/PE = 1:2).

Colorless solid (mp 181–183 °C).

Yield: 67.4 mg (94%).

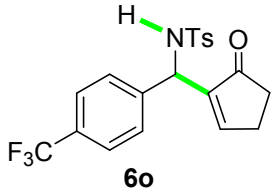
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.90 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.36 (t, *J* = 5.3 Hz, 1H), 7.26 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 6.12 (d, *J* = 8.7 Hz, 1H), 5.34 (d, *J* = 8.7 Hz, 1H), 3.90 (s, 3H), 2.56–2.14 (m, 4H), 2.40 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 207.3, 165.6, 160.0, 142.5, 142.4, 141.8, 136.3, 128.9 (2C), 128.6, 128.4 (2C), 126.3 (2C), 125.7 (2C), 54.2, 51.1, 33.9, 25.9, 20.5 ppm.

IR (neat): ν = 3258, 3032, 2917, 1743, 1613, 1431, 1256, 1121, 1099, 910, 812, 732, 654 cm^{-1}.

HRMS (ESI+): calculated for $C_{21}H_{21}NaNO_5S$ = $[M+Na]^+$: m/z = 422.5612, found: m/z = 466.5619.

4-Methyl-*N*-[(5-oxocyclopent-1-enyl)(4-trifluoromethyphenyl)methyl]benzenesulfonamide (6o)



6o

Prepared from imine **4o** (72.0 mg, 0.22 mmol, 1.10 equiv) and Michael acceptor **5a** (16.4 mg, 0.20 mmol, 1.00 equiv) according to the *general procedure A* using **3a**•HBF_4 (3.2 mg, 10 µmol, 5 mol%) and DBU (1.5 mg, 10 µmol, 5 mol%) in THF (0.66 mL, 0.3 M) at 30 °C for 24 h. **6o** was purified by PTLC on silica gel (eluent: EtOAc/PE = 1:2).

Colorless solid (mp 190–192 °C).

Yield: 76.4 mg (85%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.58 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.37 (t, *J* = 5.9 Hz, 1H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 6.19 (d, *J* = 8.6 Hz, 1H), 5.36 (d, *J* = 8.6 Hz, 1H), 2.56–2.18 (m, 4H), 2.39 (s, 3H) ppm.

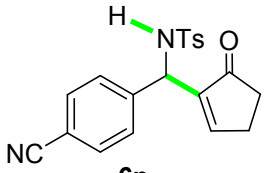
^{13}C NMR ($CDCl_3$, 150 MHz): δ = 208.4, 161.1, 144.3, 143.5, 142.7, 137.3, 132.0 (q, *J* = 1.3 Hz, 2C), 130.7 (q, *J* = 270.3 Hz), 129.4 (2C), 128.9 (q, *J* = 3.8 Hz, 2C), 127.2 (2C), 125.5 (q, *J* = 32.5 Hz), 55.2, 34.9, 26.9, 21.4 ppm.

^{19}F NMR ($CDCl_3$, 128 MHz): δ = – 62.7 (s, 3F) ppm.

IR (neat): ν = 3275, 2916, 2850, 1693, 1436, 1328, 1159, 906, 745, 665 cm^{-1}.

HRMS (ESI+): calculated for $C_{20}H_{18}F_3NaNO_3S$ = $[M+Na]^+$: m/z = 432.0852, found: m/z = 432.0857.

4-Methyl-*N*-[(5-oxocyclopent-1-enyl)(4-cyanophenyl)methyl]benzenesulfonamide (6p)



6p

Prepared from imine **4p** (62.6 mg, 0.22 mmol, 1.10 equiv) and Michael acceptor **5a** (16.4 mg, 0.20 mmol, 1.00 equiv) according to the *general procedure A* using **3a**•HBF_4 (3.2 mg, 10 µmol, 5 mol%) and DBU (1.5 mg, 10 µmol, 5 mol%) in THF (0.66 mL, 0.3 M) at 30 °C for 24 h. **6p** was purified by PTLC on silica gel (eluent: EtOAc/PE = 1:2).

Colorless solid (mp 170–172 °C).

Yield: 67.8 mg (91%).

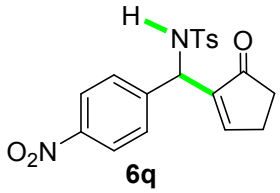
^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.60 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.34 (t, *J* = 4.8 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 6.19 (d, *J* = 8.8 Hz, 1H), 5.33 (d, *J* = 8.8 Hz, 1H), 2.56–2.20 (m, 4H), 2.41 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 150 MHz): δ = 208.3, 161.4, 143.8, 143.7, 142.3, 137.7, 132.4 (2C), 129.5 (2C), 127.5 (2C), 127.3 (2C), 118.4, 111.8, 55.0, 34.9, 26.9, 21.5 ppm.

IR (neat): ν = 3319, 2898, 2819, 2234, 1716, 1672, 1567, 1423, 1398, 1189, 934, 783, 643 cm^{-1}.

HRMS (ESI+): calculated for $C_{20}H_{18}NaN_2O_3S$ = $[M+Na]^+$: m/z = 389.5345, found: m/z = 389.5350.

4-Methyl-*N*-[(5-oxocyclopent-1-enyl)(4-nitrophenyl)methyl]benzenesulfonamide (6q)[16,17]



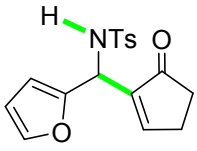
6q

Prepared from imine **4q** (67.1 mg, 0.22 mmol, 1.10 equiv) and Michael acceptor **5a** (16.4 mg, 0.20 mmol, 1.00 equiv) according to the *general procedure A* using **3a**•HBF_4 (3.2 mg, 10 µmol, 5 mol%) and DBU (1.5 mg, 10 µmol, 5 mol%) in THF (0.66 mL, 0.3 M) at 30 °C for 24 h. **6q** was purified by PTLC on silica gel (eluent: EtOAc/PE = 1:2). *The obtained analytical data were in full agreement with the reported data.*[16,17]

Pale-yellow solid.

Yield: 72.3 mg (93%).

4-Methyl-*N*-[(5-oxocyclopent-1-enyl)(2-furanyl)methyl]benzenesulfonamide (6r)[16]



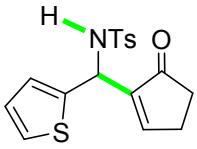
6r

Prepared from imine **4r** (54.8 mg, 0.22 mmol, 1.10 equiv) and Michael acceptor **5a** (16.4 mg, 0.20 mmol, 1.00 equiv) according to the *general procedure A* using **3a**•HBF_4 (3.2 mg, 10 µmol, 5 mol%) and DBU (1.5 mg, 10 µmol, 5 mol%) in THF (0.66 mL, 0.3 M) at 30 °C for 24 h. **6r** was purified by PTLC on silica gel (eluent: EtOAc/PE = 1:2). *The obtained analytical data were in full agreement with the reported data.*[16]

Yellow solid.

Yield: 55.9 mg (83%).

4-Methyl-*N*-[(5-oxocyclopent-1-enyl)(2-thienyl)methyl]benzenesulfonamide (6s)



6s

Prepared from imine **4s** (58.4 mg, 0.22 mmol, 1.10 equiv) and Michael acceptor **5a** (16.4 mg, 0.20 mmol, 1.00 equiv) according to the *general procedure A* using **3a**•HBF_4 (3.2 mg, 10 µmol, 5 mol%) and DBU (1.5 mg, 10 µmol, 5 mol%) in THF (0.66 mL, 0.3 M) at 30 °C for 24 h. **6s** was purified by PTLC on silica gel (eluent: EtOAc/PE = 1:2).

Pale-yellow solid (mp 160–164 °C).

Yield: 70.4 mg (92%).

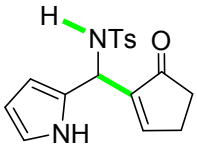
^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.66 (d, *J* = 8.1 Hz, 2H), 7.41 (t, *J* = 5.2 Hz, 1H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.16–7.15 (m, 1H), 6.86–6.84 (m, 1H), 6.78–6.77 (m, 1H), 6.03 (d, *J* = 9.0 Hz, 1H), 5.54 (d, *J* = 9.0 Hz, 1H), 2.56–2.17 (m, 4H), 2.41 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 150 MHz): δ = 208.1, 160.4, 143.4, 143.0, 142.3, 141.9, 137.4, 129.4 (2C), 127.4 (2C), 126.9, 125.4, 51.3, 34.9, 26.3, 21.5 ppm.

IR (neat): ν = 3163, 3001, 2943, 1735, 1442, 1375, 1246, 1039, 918, 748 cm^{-1}.

HRMS (ESI+): calculated for $C_{17}H_{17}NaNO_3S_2$ = $[M+Na]^+$: m/z = 370.0542, found: m/z = 370.0540.

4-Methyl-N-[(5-oxocyclopent-1-enyl)(2-pyrrolyl)methyl]benzenesulfonamide (6t)



6t

Prepared from imine **4t** (54.6 mg, 0.22 mmol, 1.10 equiv) and Michael acceptor **5a** (16.4 mg, 0.20 mmol, 1.00 equiv) according to the *general procedure A* using **3a**•HBF_4 (3.2 mg, 10 µmol, 5 mol%) and DBU (1.5 mg, 10 µmol, 5 mol%) in THF (0.66 mL, 0.3 M) at 30 °C for 48 h. **6t** was purified by PTLC on silica gel (eluent: EtOAc/PE = 1:2).

Brown solid (mp 145–147 °C).

Yield: 64.8 mg (88%).

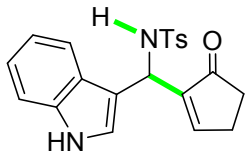
^{1}H NMR ($CDCl_3$, 600 MHz): δ = 8.61 (br s, NH, 1H), 7.67 (d, *J* = 8.1 Hz, 2H), 7.46 (t, *J* = 5.6 Hz, 1H), 7.26 (d, *J* = 8.1 Hz, 2H), 7.25–7.23 (m, 1H), 6.15–6.13 (m, 1H), 6.02–6.01 (m, 1H), 5.86 (d, *J* = 9.0 Hz, 1H), 5.29 (d, *J* = 9.0 Hz, 1H), 2.55–2.29 (m, 4H), 2.42 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 206.8, 144.3, 137.9, 137.5, 130.9, 129.7 (2C), 128.6, 127.5 (2C), 123.5, 111.9, 110.3, 58.3, 32.9, 26.3, 20.9 ppm.

IR (neat): ν = 3001, 2941, 2252, 1707, 1440, 1375, 1346, 1182, 916, 754, 702 cm^{-1}.

HRMS (ESI+): calculated for $C_{17}H_{18}NaN_2O_3S$ = $[M+Na]^+$: m/z = 353.5632, found: m/z = 353.5634.

4-Methyl-*N*-[(5-oxocyclopent-1-enyl)(1*H*-indol-3-yl)methyl]benzenesulfonamide (6u)



6u

Prepared from imine **4u** (65.6 mg, 0.22 mmol, 1.10 equiv) and Michael acceptor **5a** (16.4 mg, 0.20 mmol, 1.00 equiv) according to the *general procedure A* using **3a**•HBF_4 (3.2 mg, 10 µmol, 5 mol%) and DBU (1.5 mg, 10 µmol, 5 mol%) in THF (0.66 mL, 0.3 M) at 30 °C for 48 h. **6u** was purified by PTLC on silica gel (eluent: EtOAc/PE = 1:2).

Colorless solid (mp 175–179 °C).

Yield: 63.2 mg (83%).

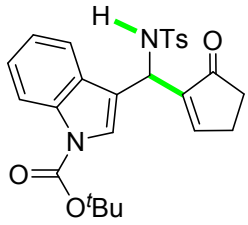
^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.68–7.65 (m, 2H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.34 (t, *J* = 5.0 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.12–7.08 (m, 1H), 7.00–6.97 (m, 1H), 6.73–6.72 (m, 1H), 6.02 (d, *J* = 8.4 Hz, 1H), 5.17 (br s, NH, 1H), 4.20 (d, *J* = 8.4 Hz, 1H), 2.53–2.16 (m, 4H), 2.38 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 208.3, 146.3, 139.9, 139.0, 132.7, 131.7 (2C), 130.9, 129.8, 129.5 (2C), 127.7, 124.2, 124.1, 122.2, 121.3, 113.6, 60.1, 34.9, 28.6, 23.7 ppm.

IR (neat): ν = 2924, 2251, 1703, 1662, 1587, 1346, 1180, 914, 752, 696 cm^{-1}.

HRMS (ESI+): calculated for $C_{21}H_{20}NaN_2O_3S$ = $[M+Na]^+$: m/z = 403.6171, found: m/z = 403.6174.

4-Methyl-*N*-[(5-oxocyclopent-1-enyl)(1*H*-indol-1-carboxlic acid-3-yl)methyl]benzenesulfonamide (6v)



6v

Prepared from imine **4v** (87.6 mg, 0.22 mmol, 1.10 equiv) and Michael acceptor **5a** (16.4 mg, 0.20 mmol, 1.00 equiv) according to the *general procedure A* using **3a**•HBF_4 (3.2 mg,

10 μmol, 5 mol%) and DBU (1.5 mg, 10 μmol, 5 mol%) in THF (0.66 mL, 0.3 M) at 30 °C for 30 h. **6v** was purified by PTLC on silica gel (eluent: EtOAc/PE = 1:2).

Colorless solid (mp 189–194 °C).

Yield: 95.4 mg (89%).

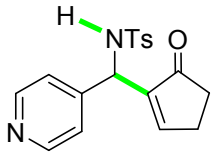
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.23 (d, *J* = 8.1 Hz, 1H), 8.02–8.00 (m, 1H), 7.78 (d, *J* = 8.1 Hz, 2H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.22–7.20 (m, 1H), 7.10–7.08 (m, 1H), 6.73 (t, *J* = 5.7 Hz, 1H), 6.08 (d, *J* = 8.4 Hz, 1H), 5.34 (d, *J* = 8.4 Hz, 1H), 2.54–2.18 (m, 4H), 2.39 (s, 3H), 1.44 (s, 9H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 206.3, 149.3, 144.3, 139.5, 135.4, 130.7, 129.7 (2C), 129.2, 128.5, 128.1, 127.6 (2C), 126.7, 122.9, 120.2, 119.2, 115.2, 81.4, 58.1, 32.5, 28.2, 26.2, 21.3 ppm.

IR (neat): ν = 3061, 3028, 2922, 2833, 2250, 1703, 1574, 1346, 1180, 914, 750, 698 cm^{-1}.

HRMS (ESI+): calculated for $C_{26}H_{28}NaN_2O_5S$ = $[M+Na]^+$: m/z = 503.7325, found: m/z = 503.7330.

4-Methyl-*N*-[(5-oxocyclopent-1-enyl)(4-pyridinyl)methyl]benzenesulfonamide (6w)



6w

Prepared from imine **4v** (87.6 mg, 0.22 mmol, 1.10 equiv) and Michael acceptor **5a** (16.4 mg, 0.20 mmol, 1.00 equiv) according to the *general procedure A* using **3a**•HBF_4 (3.2 mg, 10 μmol, 5 mol%) and DBU (1.5 mg, 10 μmol, 5 mol%) in THF (0.66 mL, 0.3 M) at 30 °C for 48 h. **6v** was purified by PTLC on silica gel (eluent: EtOAc/PE = 1:2).

Pale-yellow solid (mp 160–164 °C).

Yield: 95.4 mg (84%).

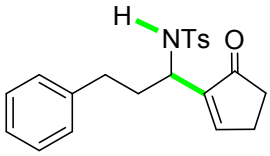
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.55–8.53 (m, 2H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.20–7.18 (m, 2H), 6.72 (t, *J* = 5.2 Hz, 1H), 6.02 (d, *J* = 8.4 Hz, 1H), 5.23 (d, *J* = 8.4 Hz, 1H), 2.58–2.22 (m, 4H), 2.40 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 206.3, 149.8, 144.3, 139.5, 137.9, 130.7, 130.0, 129.7 (2C), 129.4, 129.1, 127.6 (2C), 120.7, 57.9, 32.3, 25.9, 21.1 ppm.

IR (neat): ν = 3030, 2924, 2291, 2251, 1703, 1654, 1587, 1438, 1346, 1180, 1165, 914, 750 cm^{-1}.

HRMS (ESI+): calculated for $C_{18}H_{18}NaN_2O_3S$ = $[M+Na]^+$: m/z = 365.5734, found: m/z = 365.5743.

4-Methyl-*N*-[(5-oxocyclopent-1-enyl)(3-phenylpropyl)methyl]benzenesulfonamide (6x)



6x

Prepared from imine **4x** (63.2 mg, 0.22 mmol, 1.10 equiv) and Michael acceptor **5a** (16.4 mg, 0.20 mmol, 1.00 equiv) according to the *general procedure A* using **3a**•HBF_4 (3.2 mg, 10 µmol, 5 mol%) and DBU (1.5 mg, 10 µmol, 5 mol%) in THF (0.66 mL, 0.3 M) at 30 °C for 30 h. **6x** was purified by PTLC on silica gel (eluent: EtOAc/PE = 1:2).

Colorless solid (mp 178–182 °C).

Yield: 75.0 mg (92%).

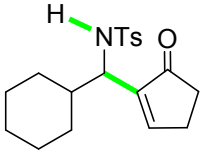
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.69 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.28–7.25 (m, 2H), 7.17–7.14 (m, 3H), 6.69 (d, *J* = 5.4 Hz, 1H), 6.12 (d, *J* = 8.4 Hz, 1H), 4.93 (t, *J* = 8.4 Hz, 1H), 2.55–2.50 (m, 2H), 2.42 (s, 3H), 2.38–2.30 (m, 4H), 2.21 (q, *J* = 7.4 Hz, 2H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 208.4, 164.3, 144.3, 140.8, 130.8, 129.7 (2C), 129.1, 128.7 (2C), 128.4 (2C), 127.9, 127.5 (2C), 58.1, 32.9, 32.5, 30.7, 26.2, 21.3 ppm.

IR (neat): ν = 3324, 2976, 2913, 2876, 2423, 2231, 1897, 1701, 1687, 1512, 1428, 1387, 1176, 1143, 921, 754 cm^{-1}.

HRMS (ESI+): calculated for $C_{21}H_{23}NaNO_3S$ = $[M+Na]^+$: m/z = 392.2453, found: m/z = 392.2459.

4-Methyl-*N*-[(5-oxocyclopent-1-enyl)(3-cyclohexyl)methyl]benzenesulfonamide (6y)



6y

Prepared from imine **4y** (58.4 mg, 0.22 mmol, 1.10 equiv) and Michael acceptor **5a** (16.4 mg, 0.20 mmol, 1.00 equiv) according to the *general procedure A* using **3a**•HBF_4 (3.2 mg, 10 µmol, 5 mol%) and DBU (1.5 mg, 10 µmol, 5 mol%) in THF (0.66 mL, 0.3 M) at 30 °C for 30 h. **6y** was purified by PTLC on silica gel (eluent: EtOAc/PE = 1:2).

Pale-yellow solid (mp 130–132 °C).

Yield: 70.4 mg (91%).

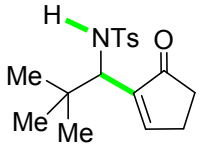
^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.62 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.00 (t, *J* = 5.4 Hz, 1H), 5.72 (d, *J* = 8.9 Hz, 1H), 3.81 (dd, *J* = 8.9, 9.3 Hz, 1H), 2.40 (s, 3H), 2.39–2.38 (m, 1H), 2.19–2.18 (m, 1H), 2.09–2.08 (m, 1H), 1.96–1.95 (m, 2H), 1.94–1.92 (m, 4H), 1.42–1.39 (m, 1H), 1.15–1.10 (m, 3H), 0.90–0.81 (m, 2H) ppm.

^{13}C NMR ($CDCl_3$, 150 MHz): δ = 209.1, 160.6, 142.9, 141.9, 137.9, 129.2 (2C), 127.4 (2C), 57.4, 40.8, 34.8, 29.9, 29.4 (2C), 26.6 (2C), 26.1, 21.4 ppm.

IR (neat): ν = 3396, 3176, 2997, 2941, 1597, 1575, 1411, 1375, 1037, 918, 688 cm^{-1}.

HRMS (ESI+): calculated for $C_{19}H_{25}NaNO_3S$ = $[M+Na]^+$: m/z = 370.1447, found: m/z = 370.1438.

4-Methyl-*N*-[(5-oxocyclopent-1-enyl)(2,2-dimethylpropyl)methyl]benzenesulfonamide (6z)



6z

Prepared from imine **4z** (52.6 mg, 0.22 mmol, 1.10 equiv) and Michael acceptor **5a** (16.4 mg, 0.20 mmol, 1.00 equiv) according to the *general procedure A* using **3a**•HBF_4 (3.2 mg, 10 μmol, 5 mol%) and DBU (1.5 mg, 10 μmol, 5 mol%) in THF (0.66 mL, 0.3 M) at 30 °C for 30 h. **6z** was purified by PTLC on silica gel (eluent: EtOAc/PE = 1:2).

Colorless solid (mp 106–110 °C).

Yield: 56.8 mg (78%).

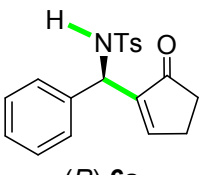
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.60 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 6.99 (t, *J* = 5.4 Hz, 1H), 5.70 (d, *J* = 8.1 Hz, 1H), 4.95 (d, *J* = 8.1 Hz, 1H), 2.50–2.14 (m, 4H), 2.32 (s, 3H), 0.82 (s, 9H) ppm.

^{13}C NMR ($CDCl_3$, 150 MHz): δ = 206.1, 144.3, 137.9, 130.7, 129.7 (2C), 129.4, 127.5 (2C), 57.8, 35.4, 32.2, 26.3 (3C), 26.2, 20.9 ppm.

IR (neat): ν = 3401, 3198, 2978, 2939, 2897, 1603, 1577, 1423, 1398, 1365, 1045, 923, 712, 685 cm^{-1}.

HRMS (ESI+): calculated for $C_{17}H_{23}NaNO_3S$ = $[M+Na]^+$: m/z = 344.5376, found: m/z = 344.5381.

(*R*)-4-Methyl-*N*-[(5-oxocyclopent-1-enyl)(phenyl)methyl]benzenesulfonamide[(*R*)-6a][24]



(*R*)-**6a**

Prepared from imine **4a** (57.0 mg, 0.22 mmol, 1.10 equiv) and Michael acceptor **5a** (16.4 mg, 0.20 mmol, 1.00 equiv) according to the *general procedure A* using **3d**•HBF_4 (6.50 mg, 10 μmol, 5 mol%) and DBU (1.5 mg, 10 μmol, 5 mol%) in THF (0.66 mL, 0.3 M) at 30 °C for 24 h. (*R*)-**6a** was purified by PTLC on silica gel (eluent: EtOAc/PE = 1:2). *The obtained analytical data was in full agreement with the reported data and the absolute configuration was assigned in analogy.*[24]

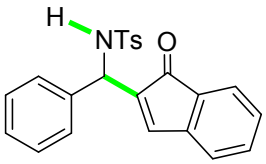
Colorless solid.

Yield: 53.8 mg (78%), 35% *ee*.

The enantiomeric excess was determined by chiral HPLC analysis using a DAICEL Chiracel IB column (eluent: hexane/^{i}PrOH = 80:20; flow rate: 0.8 mL/min; 220 nm, 25 ^{o}C): t_r (S) = 10.8 min, t_r (R) = 12.9 min.

4.5 Analytical Data for Products 6ab–aj

4-Methyl-*N*-[(inden-1-one)(phenyl)methyl]benzenesulfonamide (6ab)



6ab

Prepared from imine **4a** (28.5 mg, 0.11 mmol, 1.10 equiv) and Michael acceptor **5b** (12.5 mg, 0.10 mmol, 1.00 equiv) according to the *general procedure B* using **3b**•$HBPh_4$ (5.0 mg, 10 µmol, 10 mol%) and DBU (1.5 mg, 10 µmol, 10 mol%) in THF (0.33 mL, 0.3 M) at 40 °C for 24 h. **6ab** was purified by PTLC on silica gel (eluent: EtOAc/PE = 1:5).

Colorless solid (mp 172–177 °C).
Yield: 39.1 mg (90%).

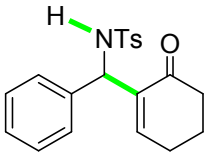
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.98 (t, *J* = 5.2 Hz, 1H), 7.77–7.70 (m, 3H), 7.61–7.59 (m, 2H), 7.57–7.54 (m, 1H), 7.32 (d, *J* = 8.3 Hz, 2H), 7.27–7.19 (m, 5H), 6.15 (d, *J* = 9.3 Hz, 1H), 5.09 (d, *J* = 9.3 Hz, 1H), 2.32 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 194.5, 144.3, 143.5, 139.5, 137.9, 133.7, 130.7, 129.7 (2C), 129.2 (2C), 128.9 (2C), 128.6, 128.4, 127.5 (2C), 127.0, 126.9, 126.1, 121.7, 58.1, 21.4 ppm.

IR (neat): ν = 3394, 3214, 2989, 2902, 2896, 1954, 1756, 1698, 1585, 1432, 1376, 1389, 1187, 916, 787, 698 cm^{-1}.

HRMS (ESI+): calculated for $C_{23}H_{19}NaNO_3S$ = $[M+Na]^+$: m/z = 412.2145, found: m/z = 412.2152.

4-Methyl-*N*-[(6-oxocyclohex-1-enyl)(phenyl)methyl]benzenesulfonamide (6ac)[16]



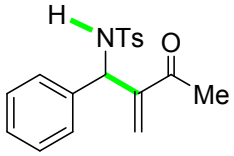
6ac

Prepared from imine **4a** (28.5 mg, 0.11 mmol, 1.10 equiv) and Michael acceptor **5c** (10.4 mg, 0.10 mmol, 1.00 equiv) according to the *general procedure B* using **3b**•$HBPh_4$ (5.0 mg, 10 µmol, 10 mol%) and DBU (1.5 mg, 10 µmol, 10 mol%) in THF (0.33 mL, 0.3 M) at 40 °C for 48 h. **6ac** was purified by PTLC on silica gel (eluent: EtOAc/PE = 1:5). *The obtained analytical data were in full agreement with the reported data.*[16]

Colorless solid.

Yield: 66.7 mg (92%).

4-Methyl-*N*-(2-methozoyl-1-benzylallyl)benzenesulfonamide (6ad)[18]

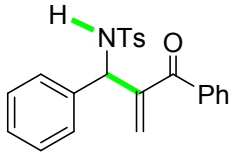


6ad

Prepared from imine **4a** (28.5 mg, 0.11 mmol, 1.10 equiv) and Michael acceptor **5d** (8.2 mg, 0.10 mmol, 1.00 equiv) according to the *general procedure B* using **3b**•$HBPh_4$ (5.0 mg, 10 μmol, 10 mol%) and DBU (1.5 mg, 10 μmol, 10 mol%) in THF (0.33 mL, 0.3 M) at 40 °C for 48 h. **6ad** was purified by PTLC on silica gel (eluent: EtOAc/PE = 1:5). *The obtained analytical data were in full agreement with the reported data.*[18]

Colorless solid.
Yield: 30.8 mg (95%).

4-Methyl-*N*-(2-benzoyl-1-benzylallyl)benzenesulfonamide (6ae)[19]

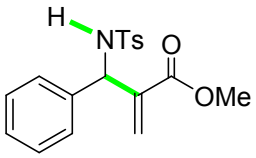


6ae

Prepared from imine **4a** (28.5 mg, 0.11 mmol, 1.10 equiv) and Michael acceptor **5e** (13.1 mg, 0.10 mmol, 1.00 equiv) according to the *general procedure B* using **3b**•$HBPh_4$ (5.0 mg, 10 μmol, 10 mol%) and DBU (1.5 mg, 10 μmol, 10 mol%) in THF (0.33 mL, 0.3 M) at 40 °C for 72 h. **6ae** was purified by PTLC on silica gel (eluent: EtOAc/PE = 1:5). *The obtained analytical data were in full agreement with the reported data.*[19]

Colorless solid.
Yield: 37.4 mg (94%).

Methyl-α–Methylene-β-[(*p*-toluenesulfonyl)-amino]-3-phenylpropionate (6af)[20,21]

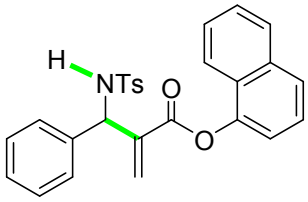


6af

Prepared from imine **4a** (28.5 mg, 0.11 mmol, 1.10 equiv) and Michael acceptor **5f** (9.3 mg, 0.10 mmol, 1.00 equiv) according to the *general procedure B* using **3b**•$HBPh_4$ (5.0 mg, 10 μmol, 10 mol%) and DBU (1.5 mg, 10 μmol, 10 mol%) in THF (0.33 mL, 0.3 M) at 40 °C for 72 h. **6af** was purified by PTLC on silica gel (eluent: EtOAc/PE = 1:5). *The obtained analytical data were in full agreement with the reported data.*[20,21]

Colorless solid.
Yield: 32.1 mg (93%).

1-Naphthyl-2-[phenyl-(toluene-4-sulfonylamino)methyl]acrylate (6ag)[20,21]

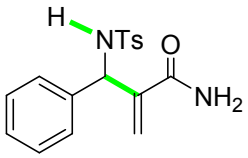


6ag

Prepared from imine **4a** (28.5 mg, 0.11 mmol, 1.10 equiv) and Michael acceptor **5g** (19.8 mg, 0.10 mmol, 1.00 equiv) according to the *general procedure B* using **3b**•$HBPh_4$ (5.0 mg, 10 μmol, 10 mol%) and DBU (1.5 mg, 10 μmol, 10 mol%) in THF (0.33 mL, 0.3 M) at 40 °C for 48 h. **6ag** was purified by PTLC on silica gel (eluent: EtOAc/PE = 1:3). *The obtained analytical data were in full agreement with the reported data.*[20,21]

Colorless solid.
Yield: 41.9 mg (96%).

2-[Phenyl-(toluene-4-sulfonylamino)methyl]-acrylamide (6ah)[22]

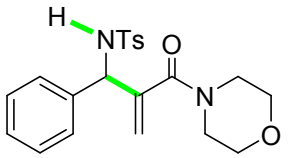


6ah

Prepared from imine **4a** (28.5 mg, 0.11 mmol, 1.10 equiv) and Michael acceptor **5h** (7.1 mg, 0.10 mmol, 1.00 equiv) according to the *general procedure B* using **3b**•$HBPh_4$ (5.0 mg, 10 μmol, 10 mol%) and DBU (1.5 mg, 10 μmol, 10 mol%) in THF (0.33 mL, 0.3 M) at 40 °C for 72 h. **6ah** was purified by PTLC on silica gel (eluent: EtOAc/PE = 1:5). *The obtained analytical data were in full agreement with the reported data.*[24]

Colorless solid.
Yield: 29.3 mg (88%)

2-[Phenyl-(toluene-4-sulfonylmorphlinyl)methyl]acrylamide (6ai)



6ai

Prepared from imine **4a** (28.5 mg, 0.11 mmol, 1.10 equiv) and Michael acceptor **5i** (14.1 mg, 0.10 mmol, 1.00 equiv) according to the *general procedure B* using **3b**•$HBPh_4$ (5.0 mg, 10 μmol, 10 mol%) and DBU (1.5 mg, 10 μmol, 10 mol%) in THF (0.33 mL, 0.3 M) at 40 °C for 72 h. **6ai** was purified by PTLC on silica gel (eluent: EtOAc/PE = 1:5).

Colorless solid (mp 156–159 °C).

Yield: 33.1 mg (74%).

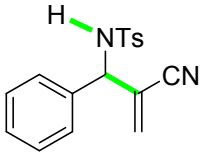
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.60 (d, *J* = 8.7 Hz, 2H), 7.32 (d, *J* = 8.7 Hz, 2H), 7.26–7.22 (m, 3H), 7.14–7.11 (m, 2H), 6.26 (d, *J* = 8.1 Hz, 1H), 6.19 (s, 1H), 5.94 (s, 1H), 5.70 (d, *J* = 8.1 Hz, 1H), 3.64–3.57 (m, 8H), 2.32 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 166.7, 144.3, 139.6, 137.6, 129.7, 129.2, 128.9 (2C), 128.6 (2C), 127.6 (2C), 126.9 (2C), 114.3, 66.4 (2C), 58.1, 44.1 (2C), 21.3 ppm.

IR (neat): ν = 3421, 3100, 3080, 2975, 2635, 1682, 1645, 1523, 1459, 1324, 1130, 990, 910, 720 cm^{-1}.

HRMS (ESI+): calculated for $C_{21}H_{24}N_2O_4NaS$ = $[M+Na]^+$: m/z = 400.4965, found: m/z = 400.4974.

4-methyl-*N*-(2-Cyano-1-phenylpropen-2-yl)benzenesulfonamide (6aj)[20]



6aj

Prepared from imine **4a** (28.5 mg, 0.11 mmol, 1.10 equiv) and Michael acceptor **5j** (5.3 mg, 0.10 mmol, 1.00 equiv) according to the *general procedure B* using **3b**•$HBPh_4$ (5.0 mg, 10 μmol, 10 mol%) and DBU (1.5 mg, 10 μmol, 10 mol%) in THF (0.33 mL, 0.3 M) at 40 °C for 48 h. **6aj** was purified by PTLC on silica gel (eluent: EtOAc/PE = 1:5). *The obtained analytical data were in full agreement with the reported data.*[20]

Colorless solid.

Yield: 30.1 mg (96%).

5 References

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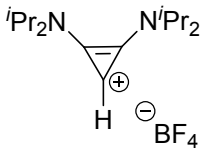
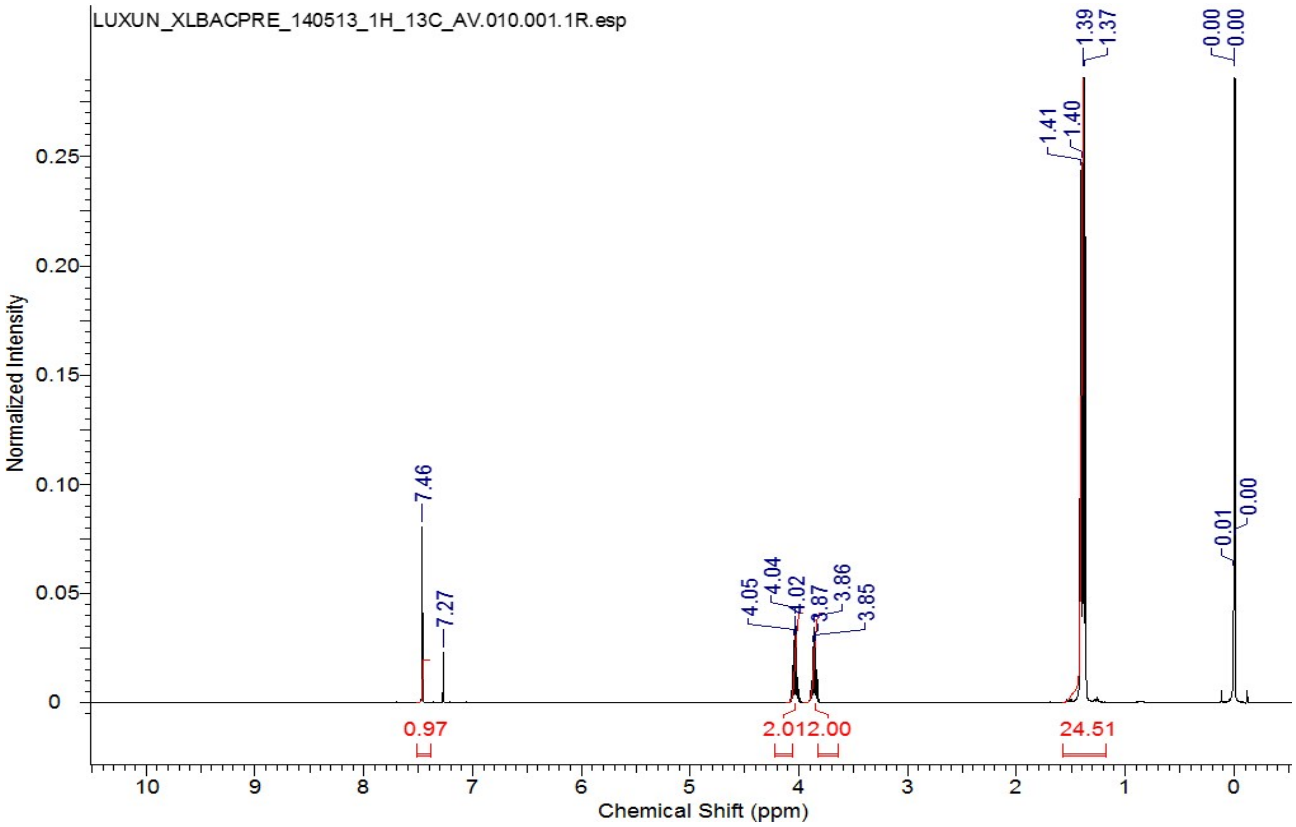
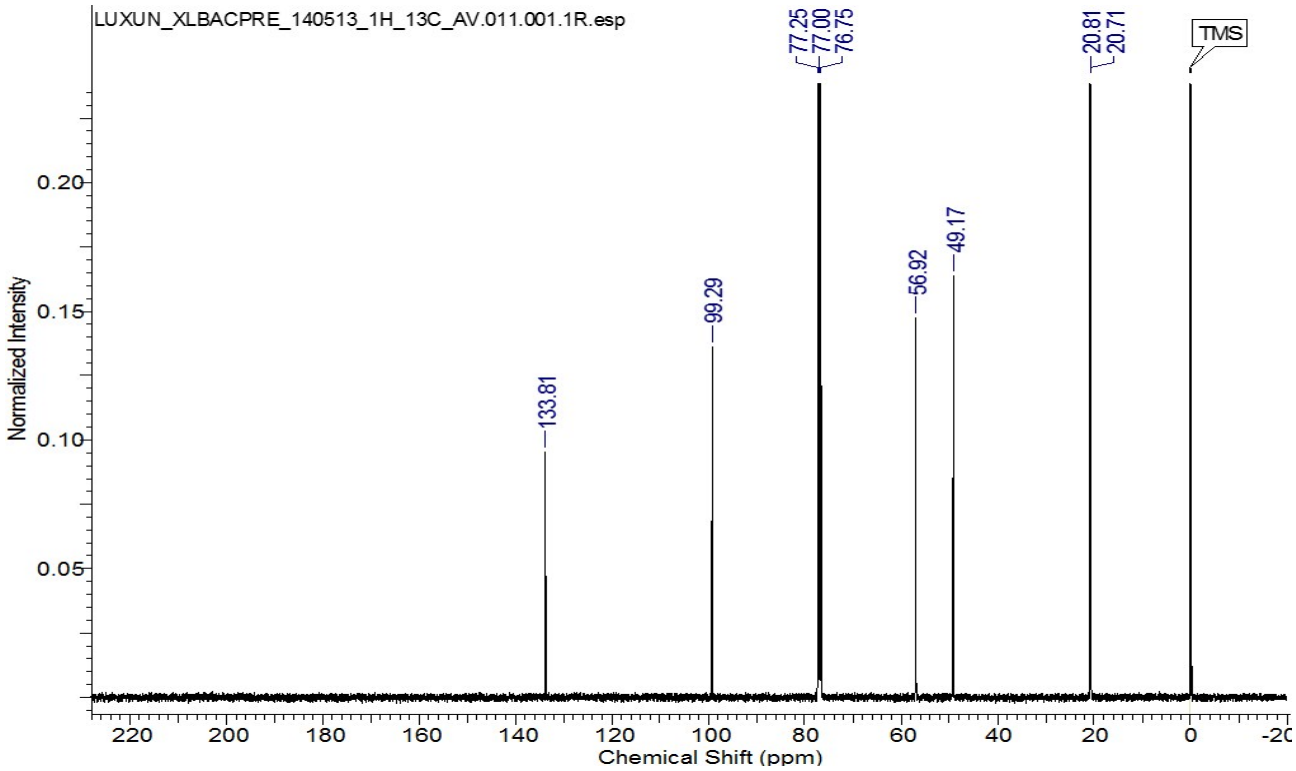
6 Copies of NMR Spectra of Substrates and Products



3a•HBF_4





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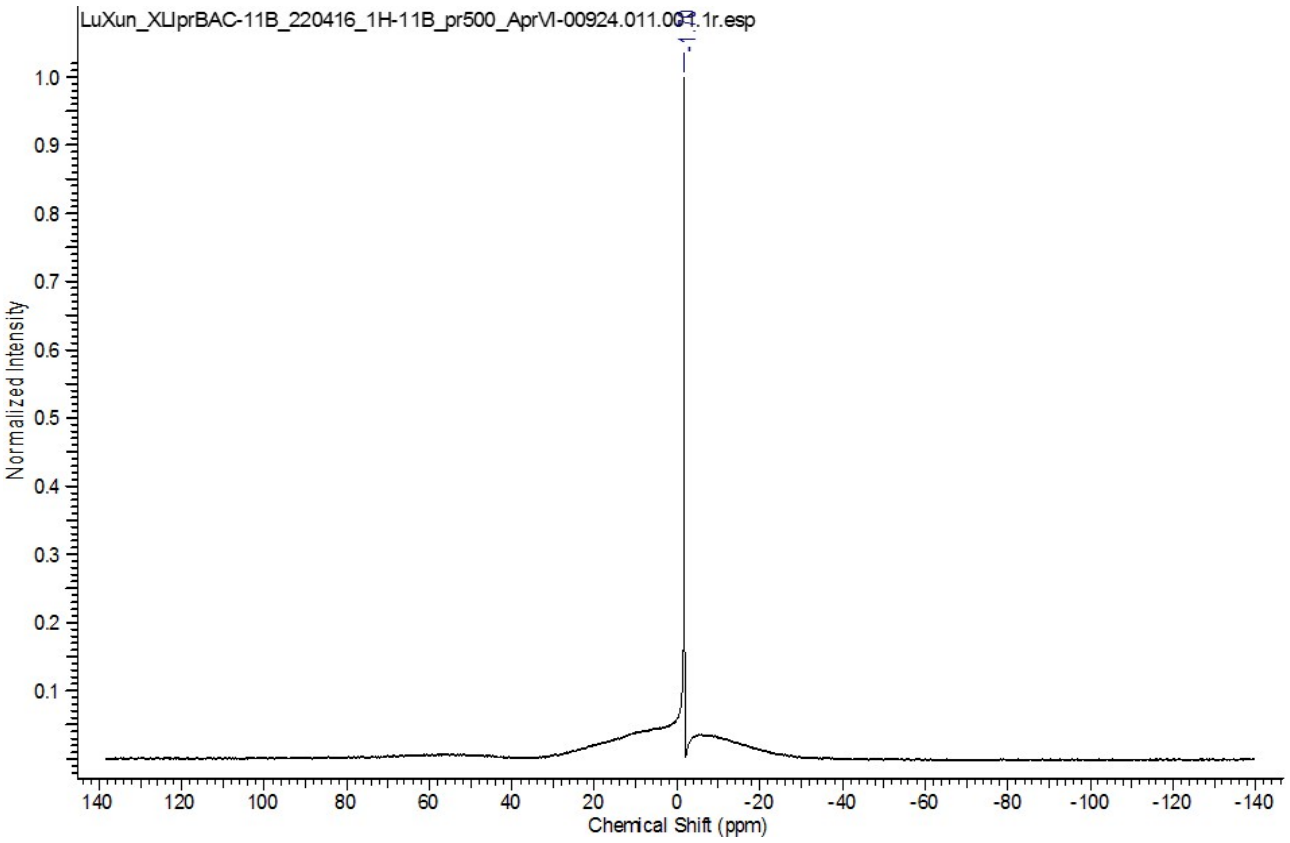
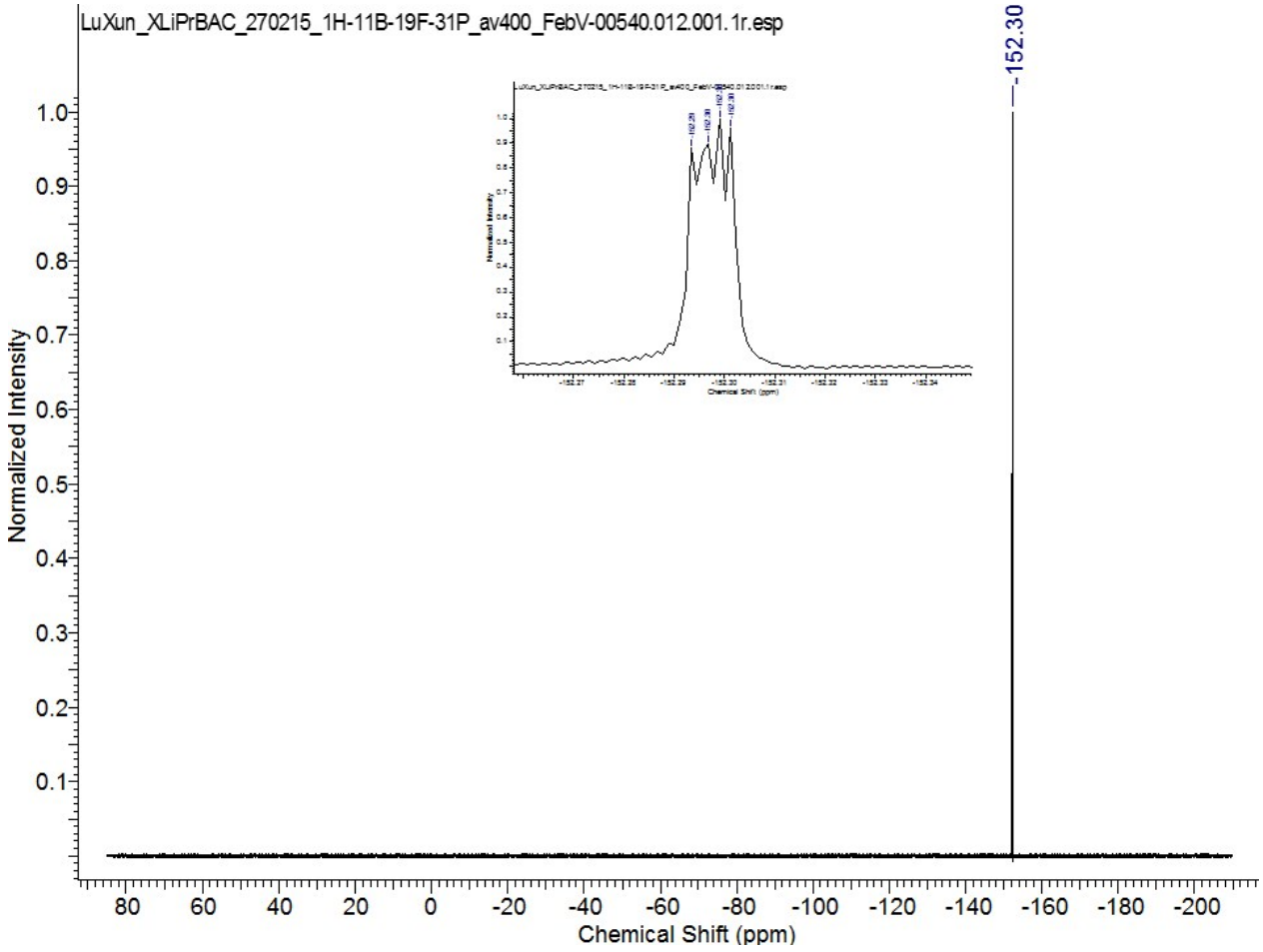
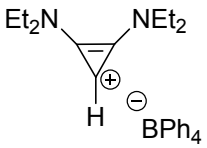


^{19}F NMR

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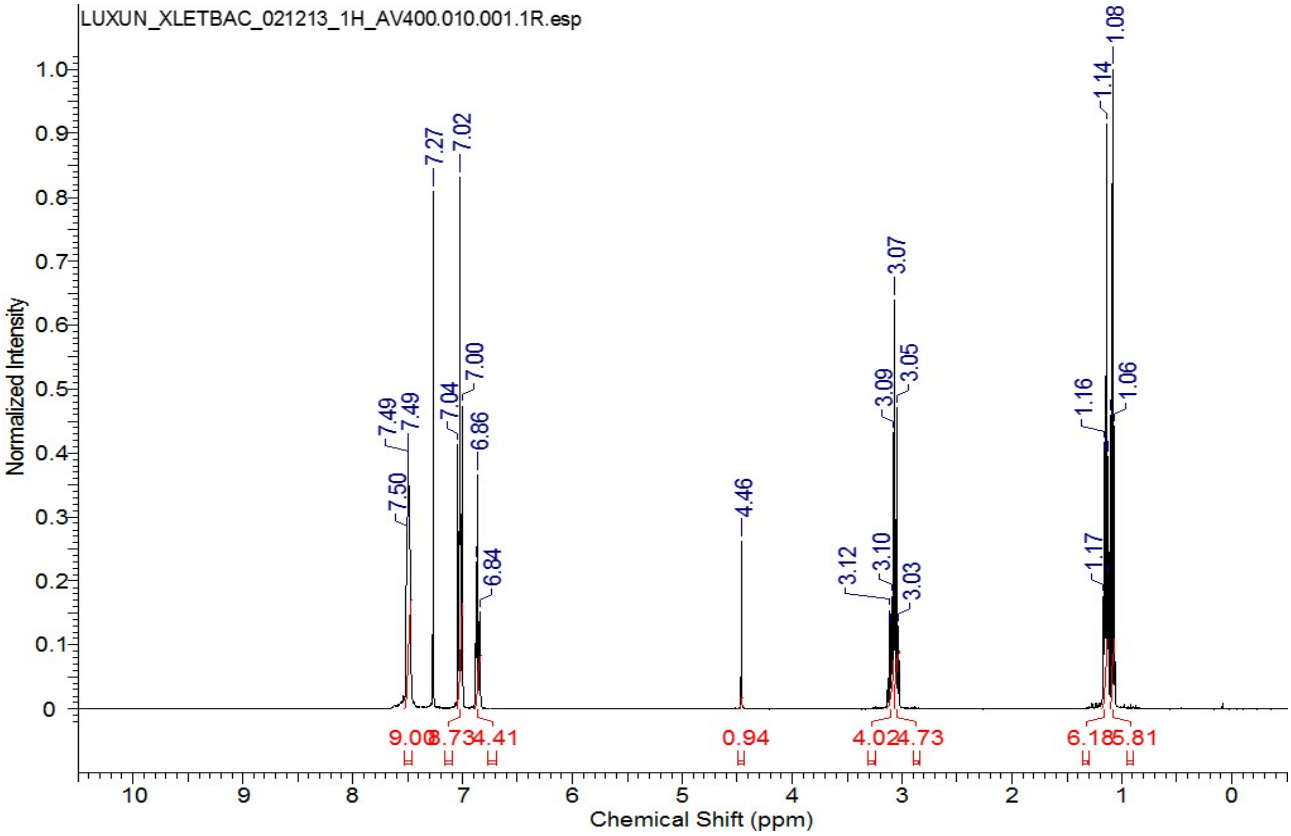
NEt2
H
BPh4

3b•$HBPh_4$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7.50
7.04
7.00
6.86
6.84
4.46
3.12
3.10
3.07
3.09
3.05
3.03
1.16
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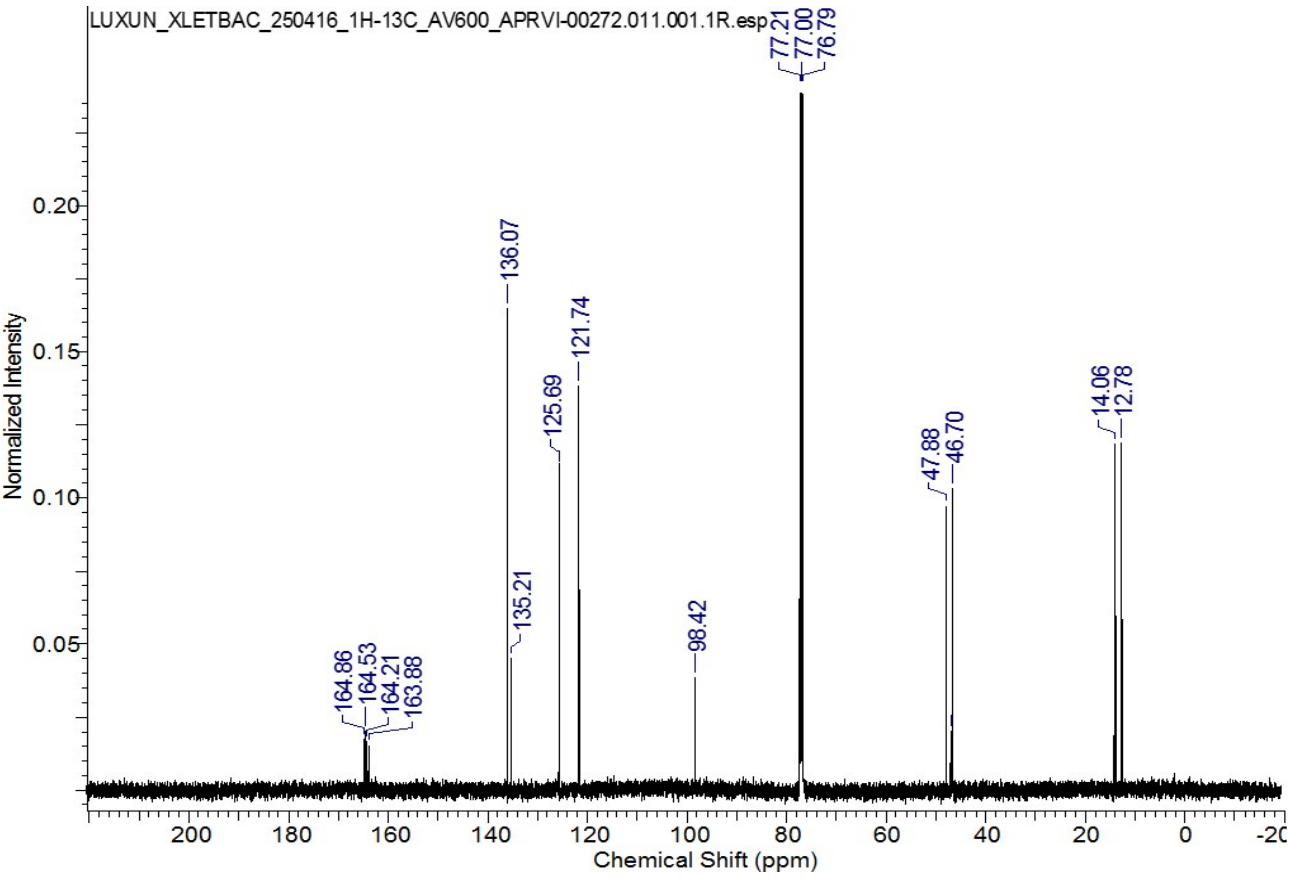
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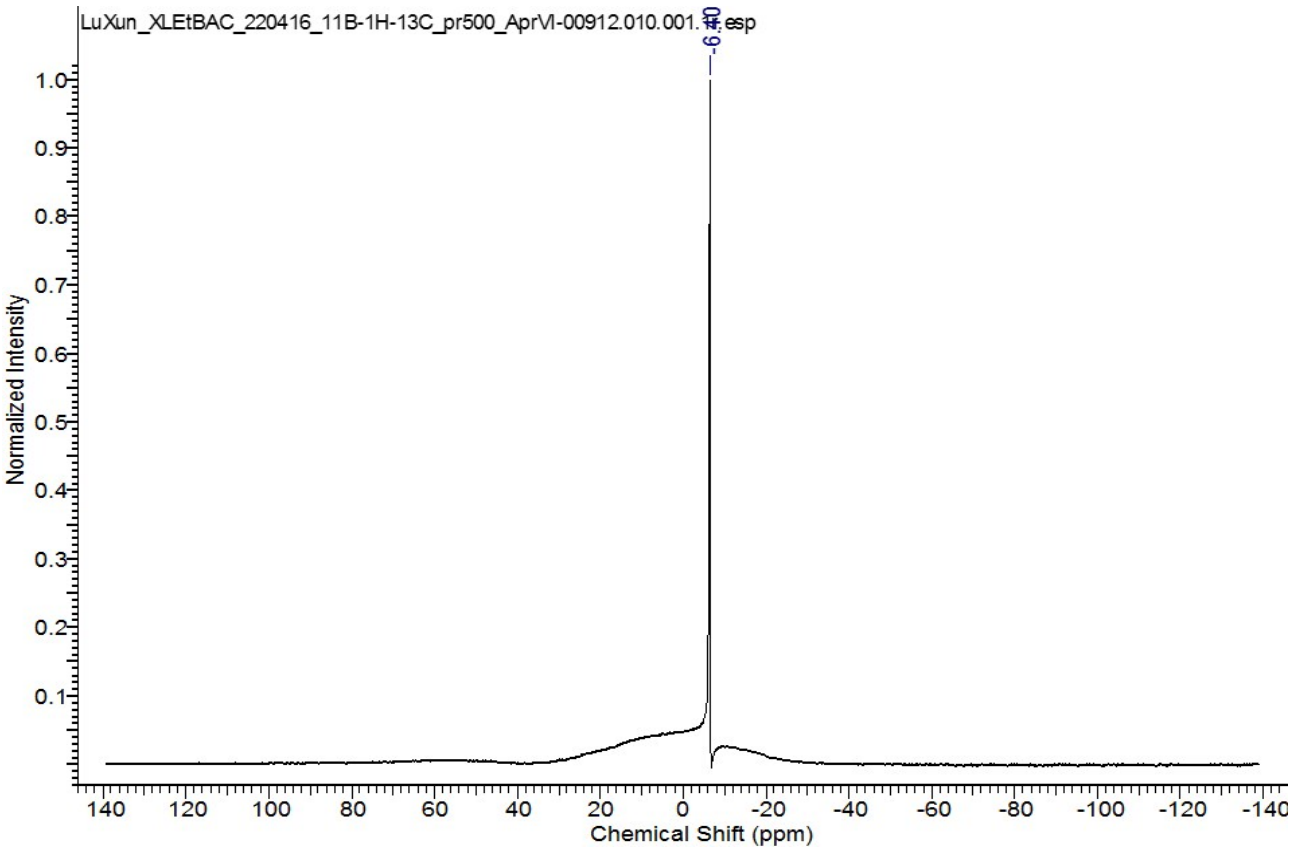
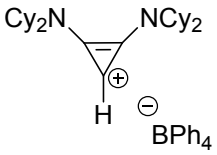
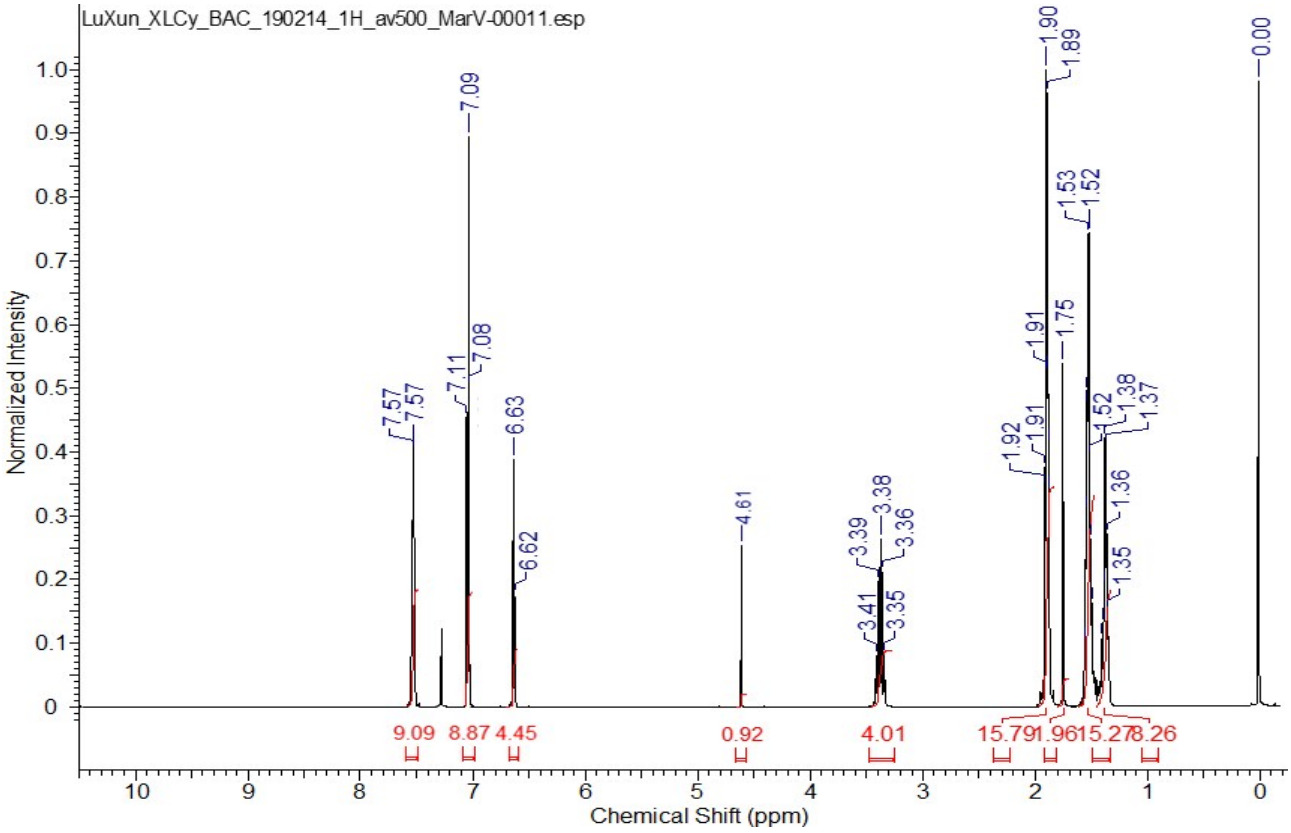
Chemical Shift (ppm)
77.21
77.00
76.79
136.07
121.74
125.69
135.21
98.42
47.88
46.70
14.06
12.78
164.86
164.53
164.21
163.88

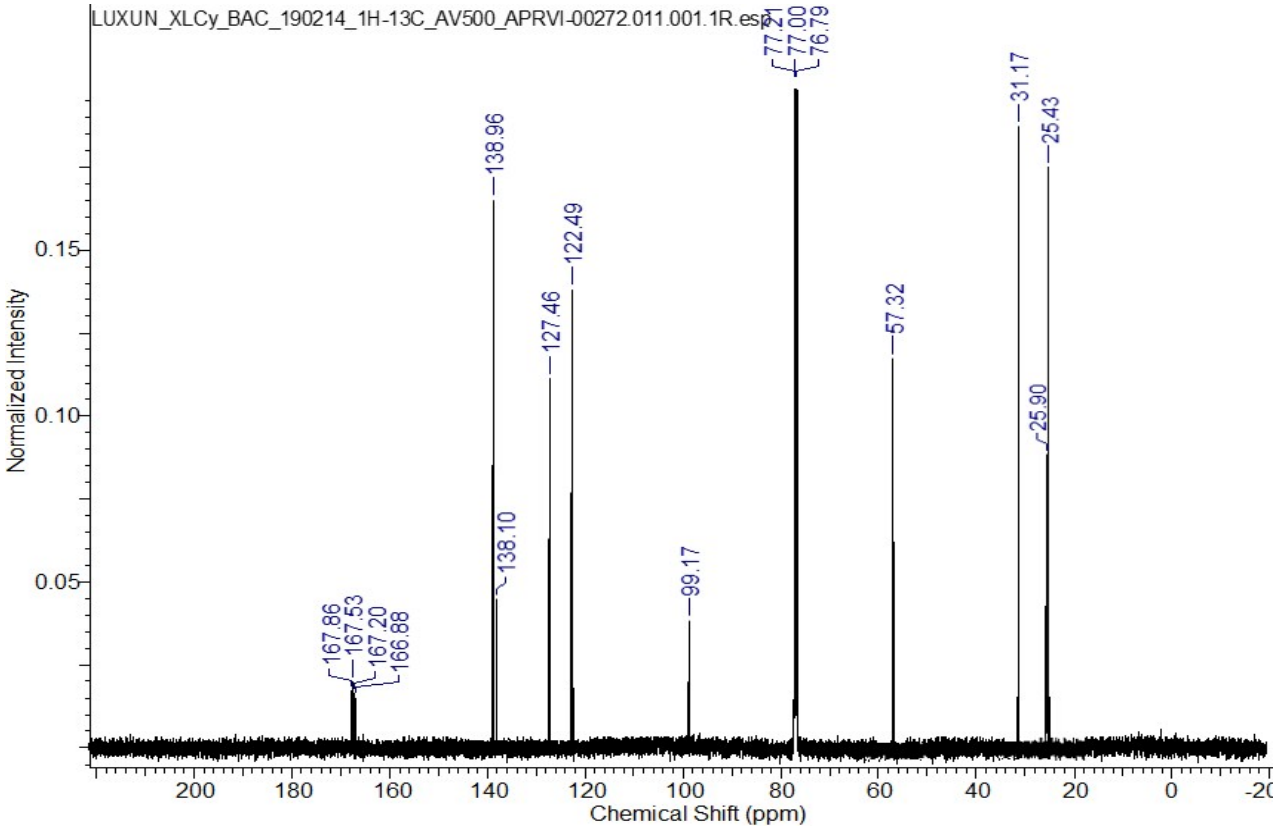
^{11}B NMR


LuXun_XLEtBAC_220416_11B-1H-13C_pr500_AprVI-00912.010.001.1r.esp
6.40
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
Chemical Shift (ppm)

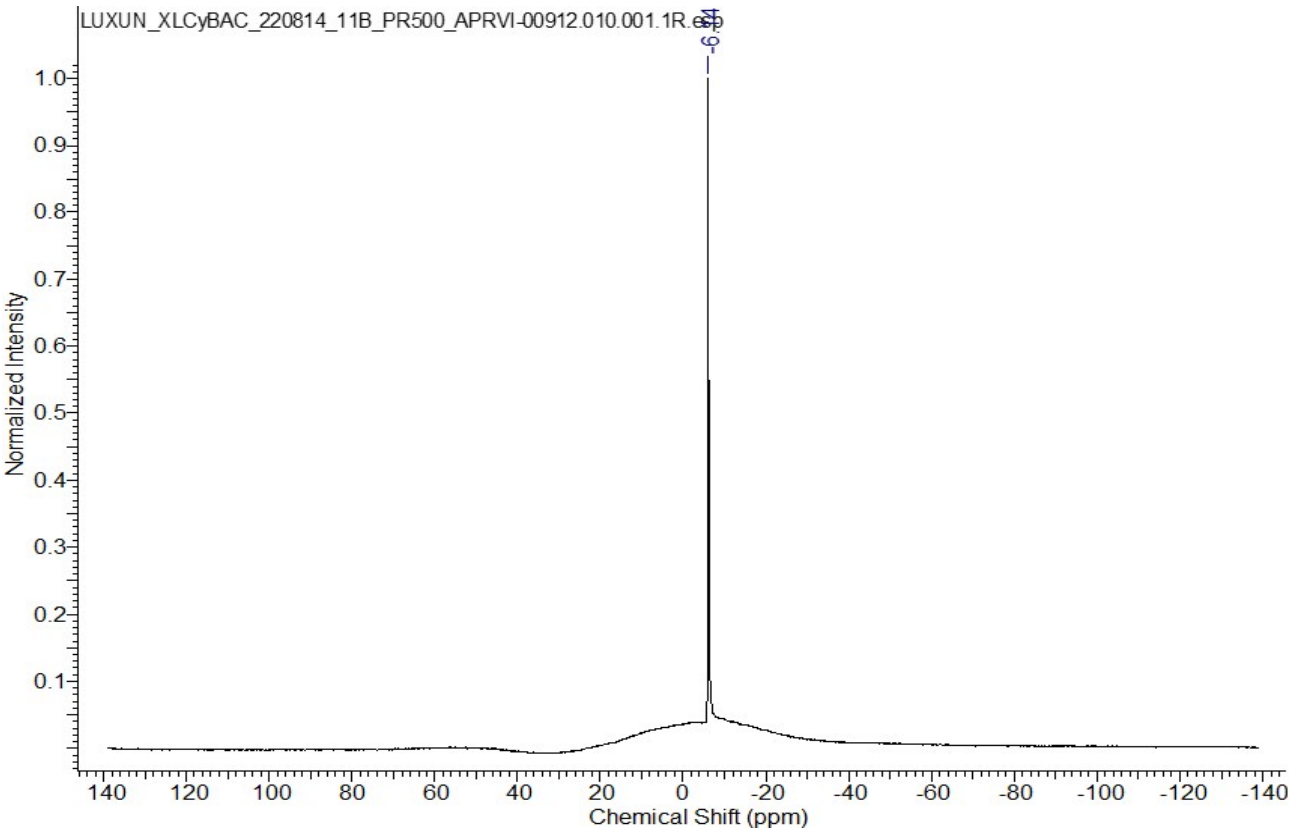

Cy2N
NCy2
H
BPh4

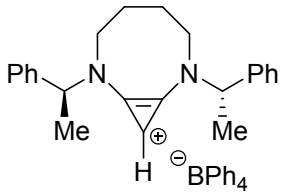
3c•$HBPh_4$


LuXun_XLCy_BAC_190214_1H_av500_MarV-00011.esp
Normalized Intensity
Chemical Shift (ppm)
9.09
8.87
4.45
0.92
4.01
15.79
1.96
15.27
8.26

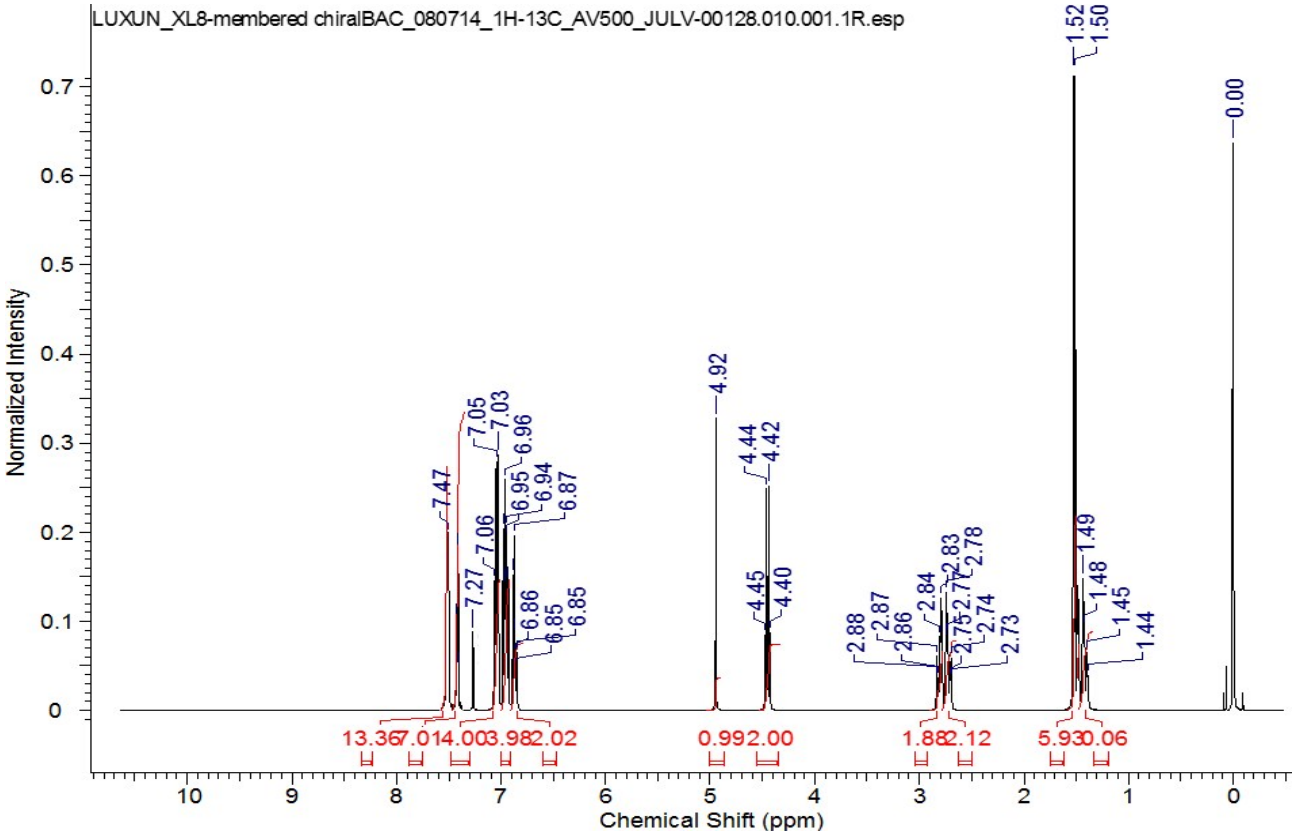

LUXUN_XLCy_BAC_190214_1H-13C_AV500_APRVI-00272.011.001.1R.esp
Normalized Intensity
Chemical Shift (ppm)

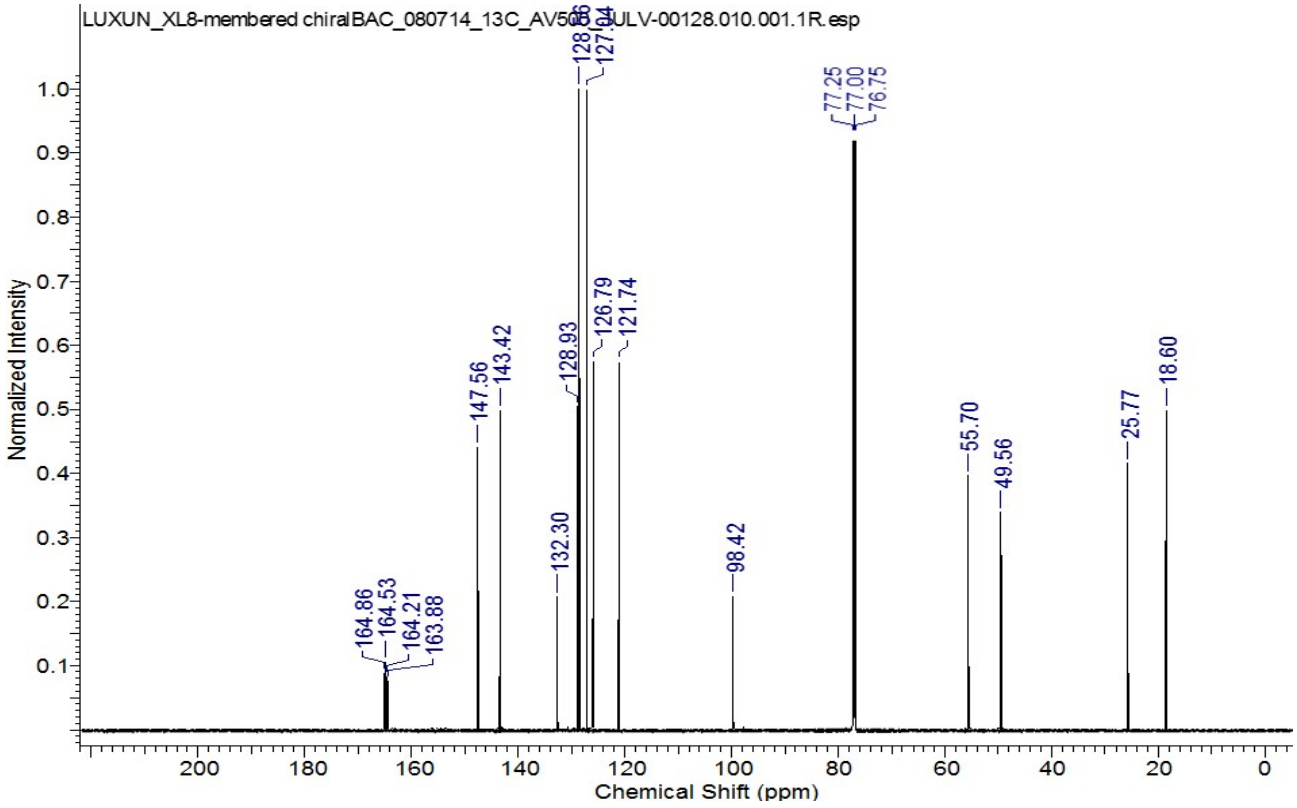
^{11}B NMR


LUXUN_XLCyBAC_220814_11B_PR500_APRVI-00912.010.001.1R.esp
6.44
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
Chemical Shift (ppm)

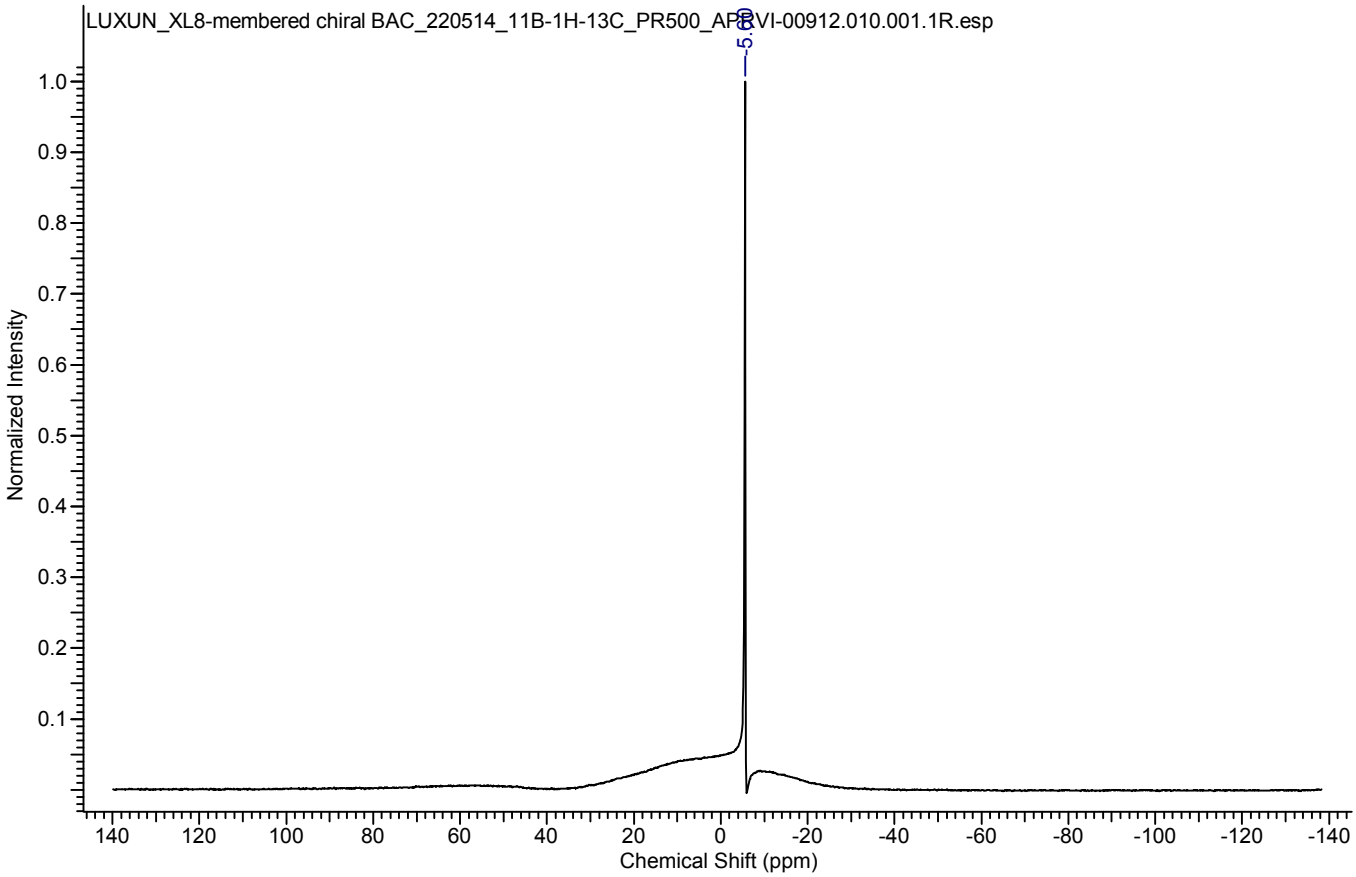

Ph
N
N
Ph
Me
Me
H
BPh4

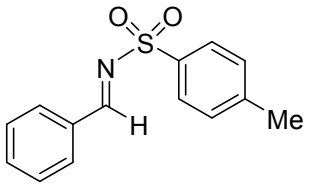
3d•BPh_4


LUXUN_XL8-membered chiralBAC_080714_1H-13C_AV500_JULV-00128.010.001.1R.esp
Normalized Intensity
Chemical Shift (ppm)
13.36
7.01
4.00
3.98
2.02
0.99
2.00
1.88
2.12
5.93
0.06

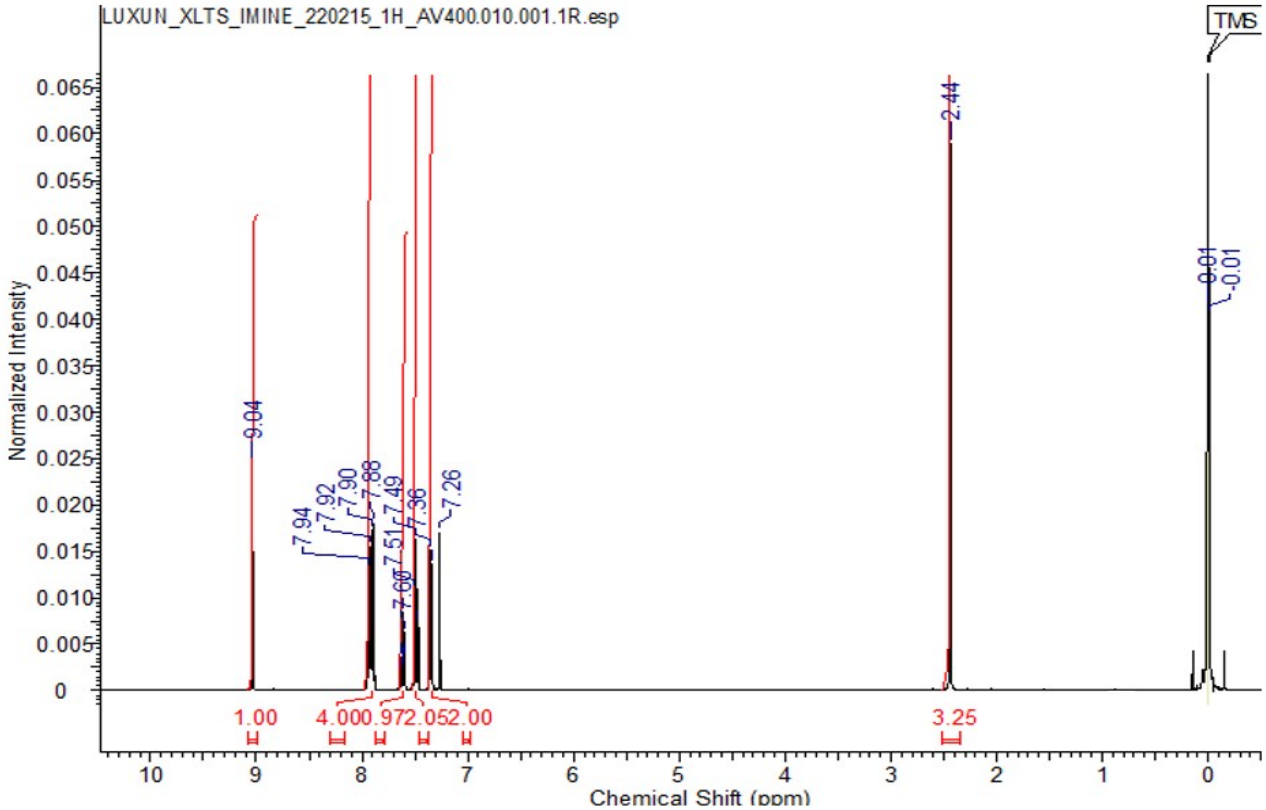

LUXUN_XL8-membered chiralBAC_080714_13C_AV500_JULV-00128.010.001.1R.esp
Normalized Intensity
Chemical Shift (ppm)

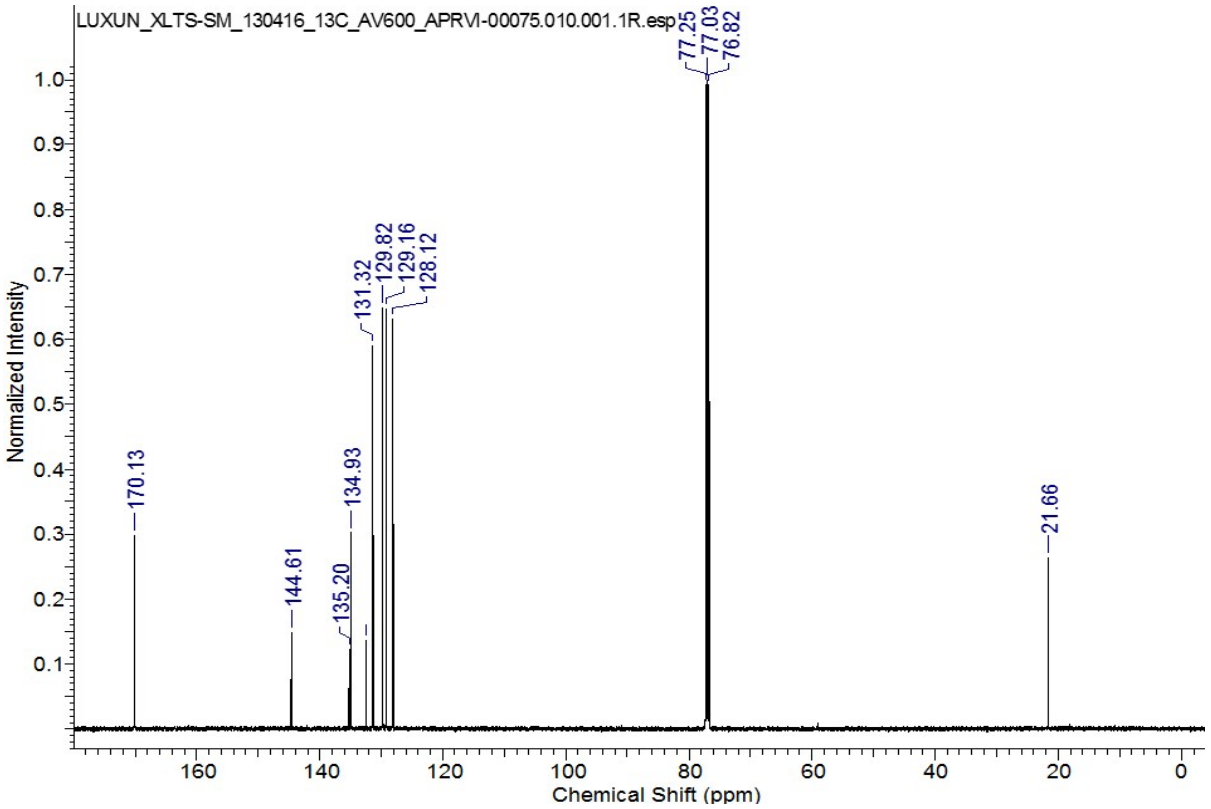
^{11}B NMR

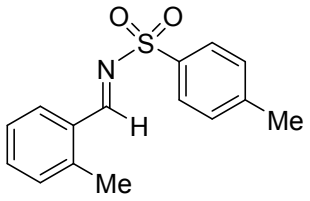

LUXUN_XL8-membered chiral BAC_220514_11B-1H-13C_PR500_APBVI-00912.010.001.1R.esp
5.69
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
Chemical Shift (ppm)


O
O
S
N
H
Me

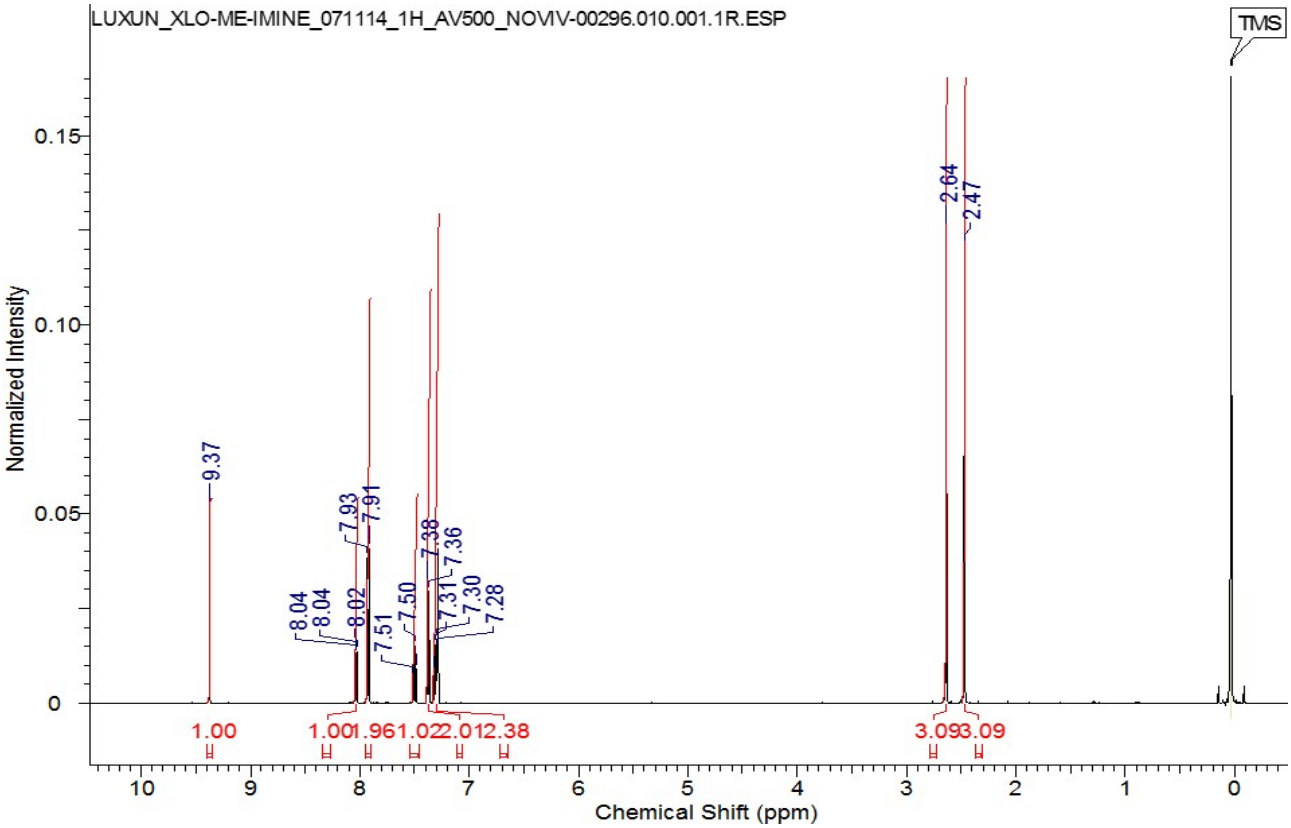
4a

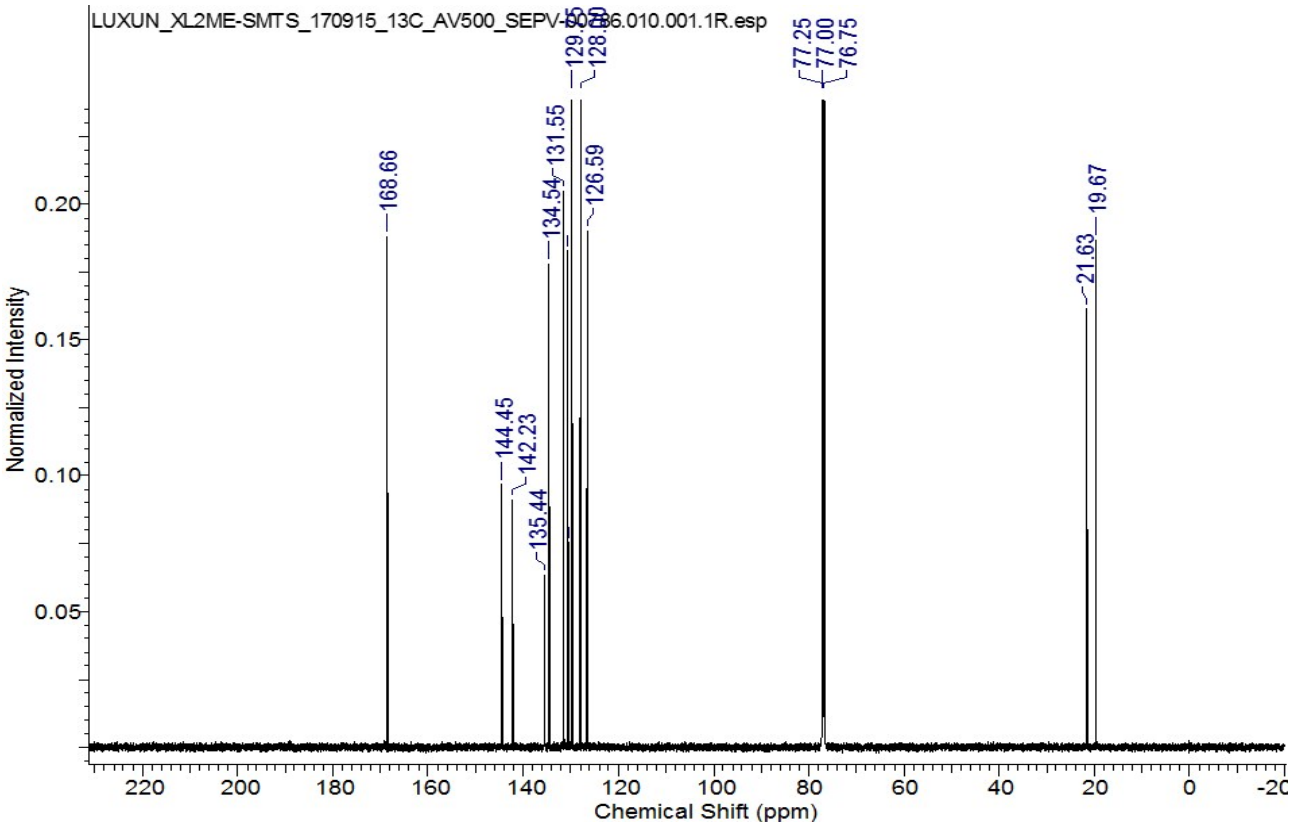

LUXUN_XLTS_IMINE_220215_1H_AV400.010.001.1R.esp
TMS
Normalized Intensity
Chemical Shift (ppm)
9.04
7.94
7.92
7.90
7.88
7.49
7.51
7.36
7.26
2.44
0.01
-0.01
1.00
4.00
0.97
2.05
2.00
3.25

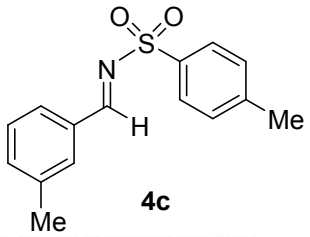

LUXUN_XLTS-SM_130416_13C_AV600_APRVI-00075.010.001.1R.esp
Normalized Intensity
Chemical Shift (ppm)
77.25
77.03
76.82
131.32
129.82
129.16
128.12
170.13
144.61
135.20
134.93
21.66


O
O
S
N
H
Me
Me

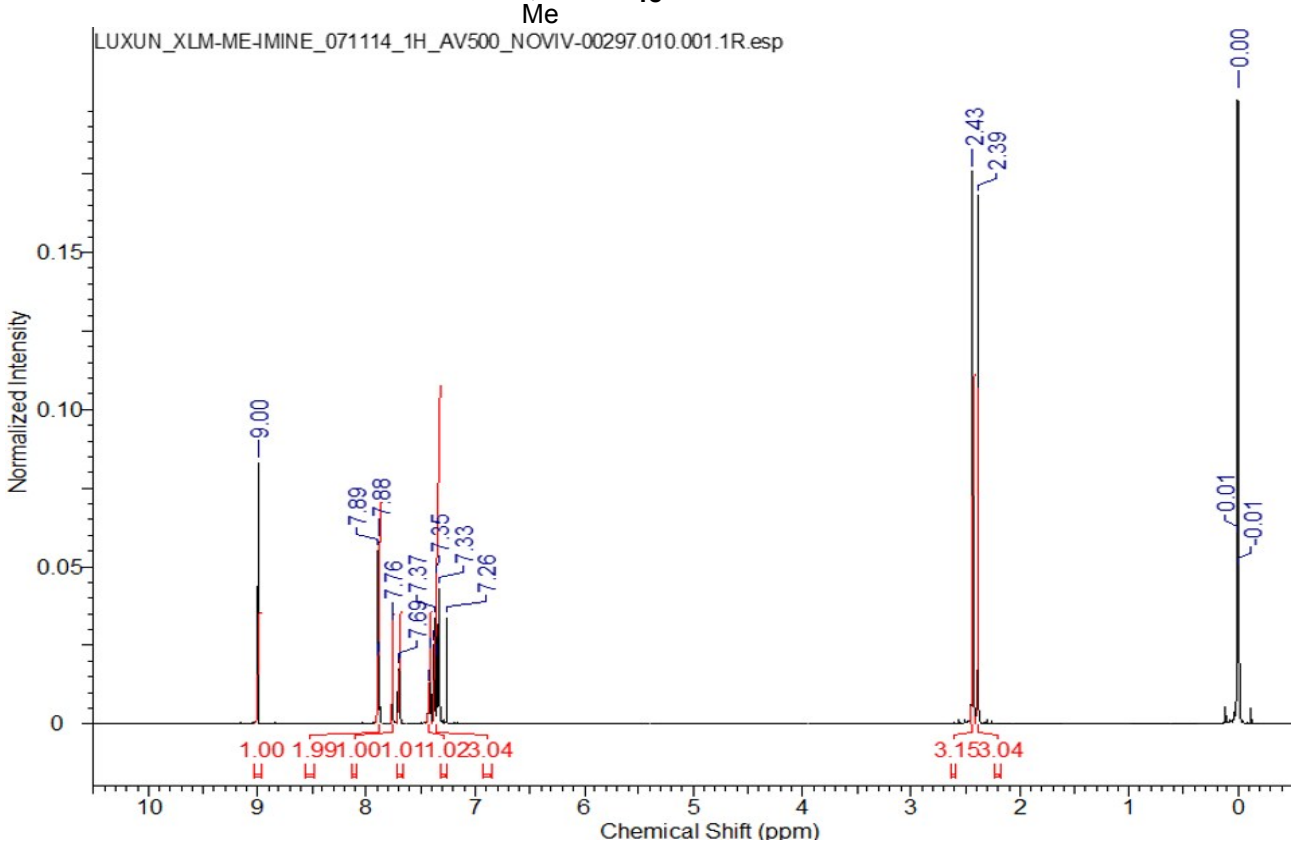
4b

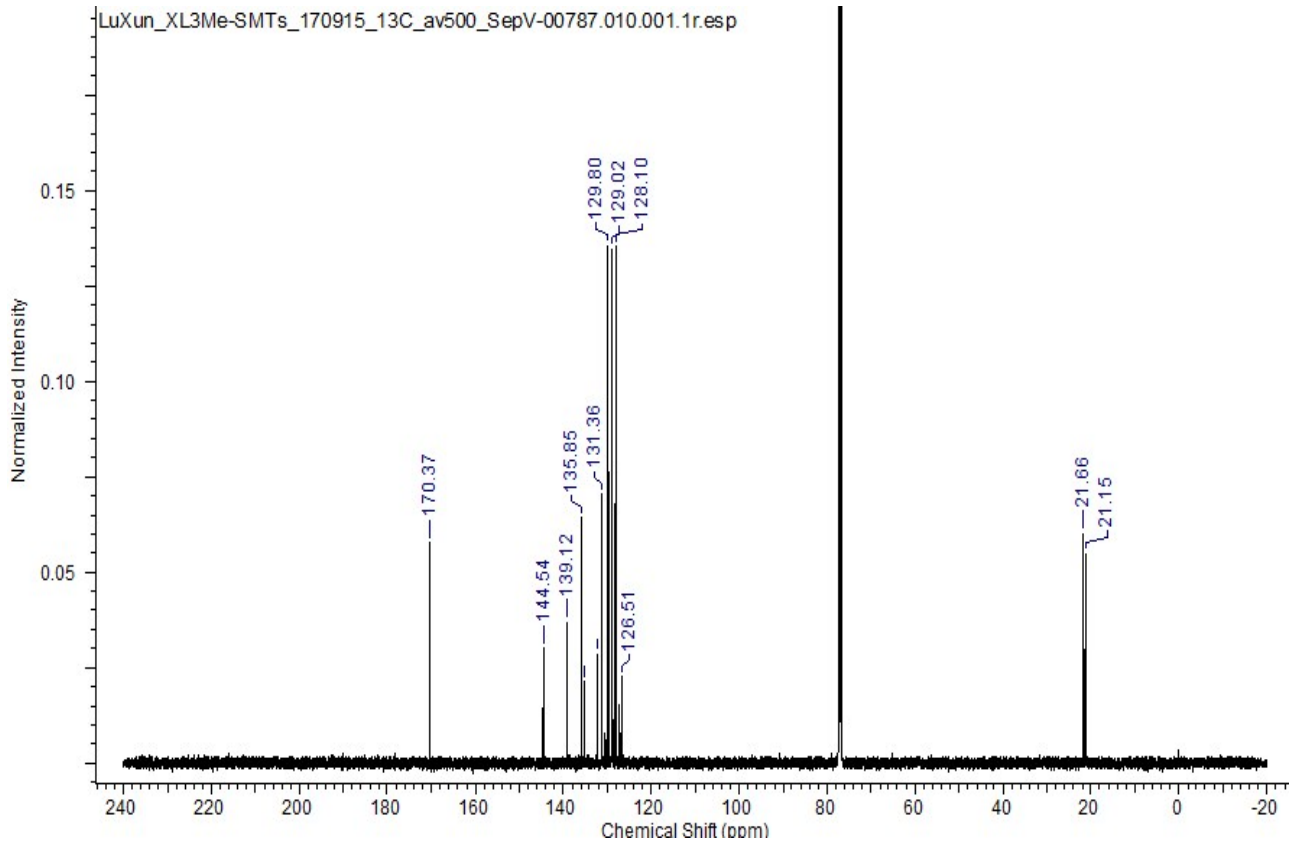

LUXUN_XLO-ME-IMINE_071114_1H_AV500_NOVIV-00296.010.001.1R.ESP
TMS
Normalized Intensity
Chemical Shift (ppm)
9.37
8.04
8.04
8.02
7.93
7.91
7.51
7.50
7.38
7.36
7.31
7.30
7.28
2.64
2.47
1.00
1.00
1.96
1.02
2.01
2.38
3.09
3.09

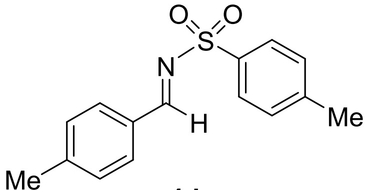

LUXUN_XL2ME-SMTS_170915_13C_AV500_SEPV-00296.010.001.1R.esp
Normalized Intensity
Chemical Shift (ppm)
168.66
144.45
142.23
135.44
134.54
131.55
129.50
128.80
126.59
77.25
77.00
76.75
21.63
19.67


O
O
S
N
H
Me
Me

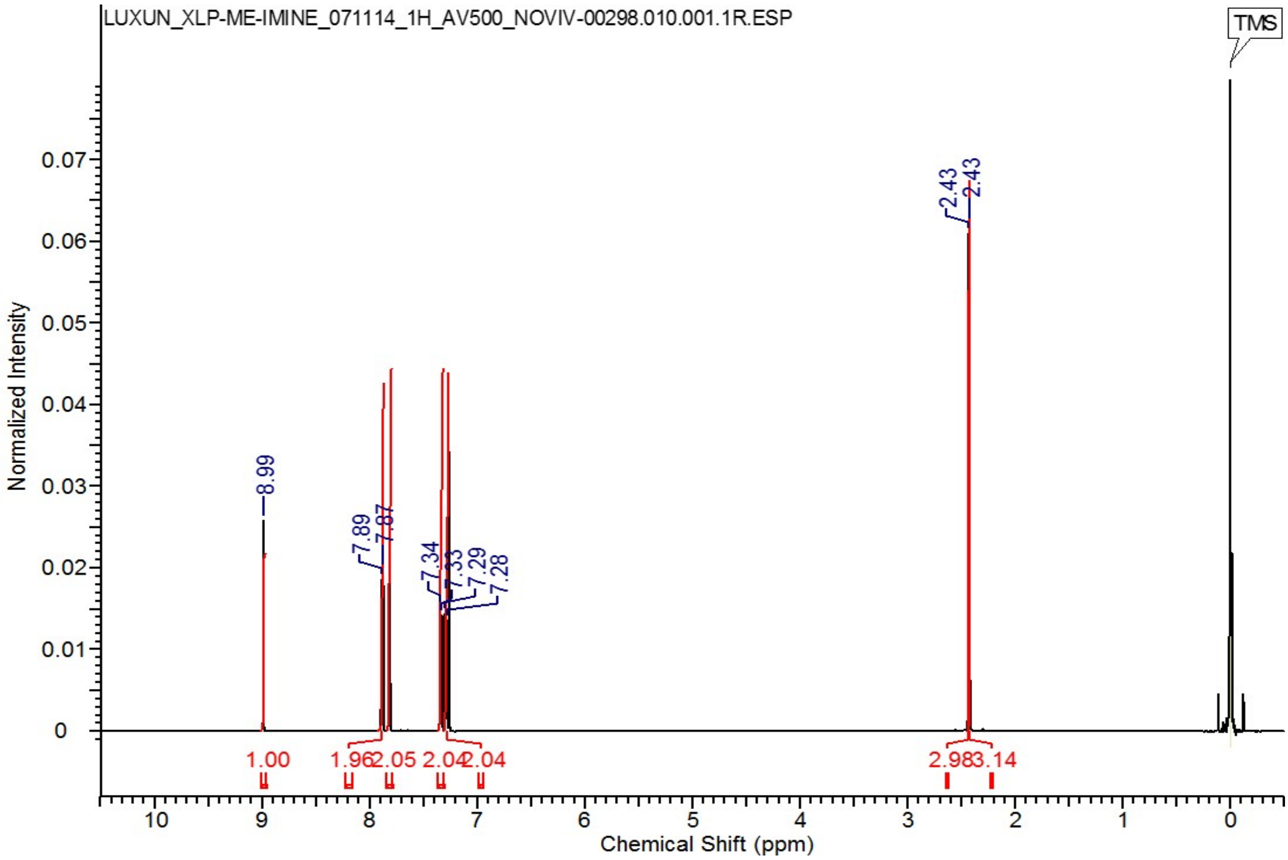
4c

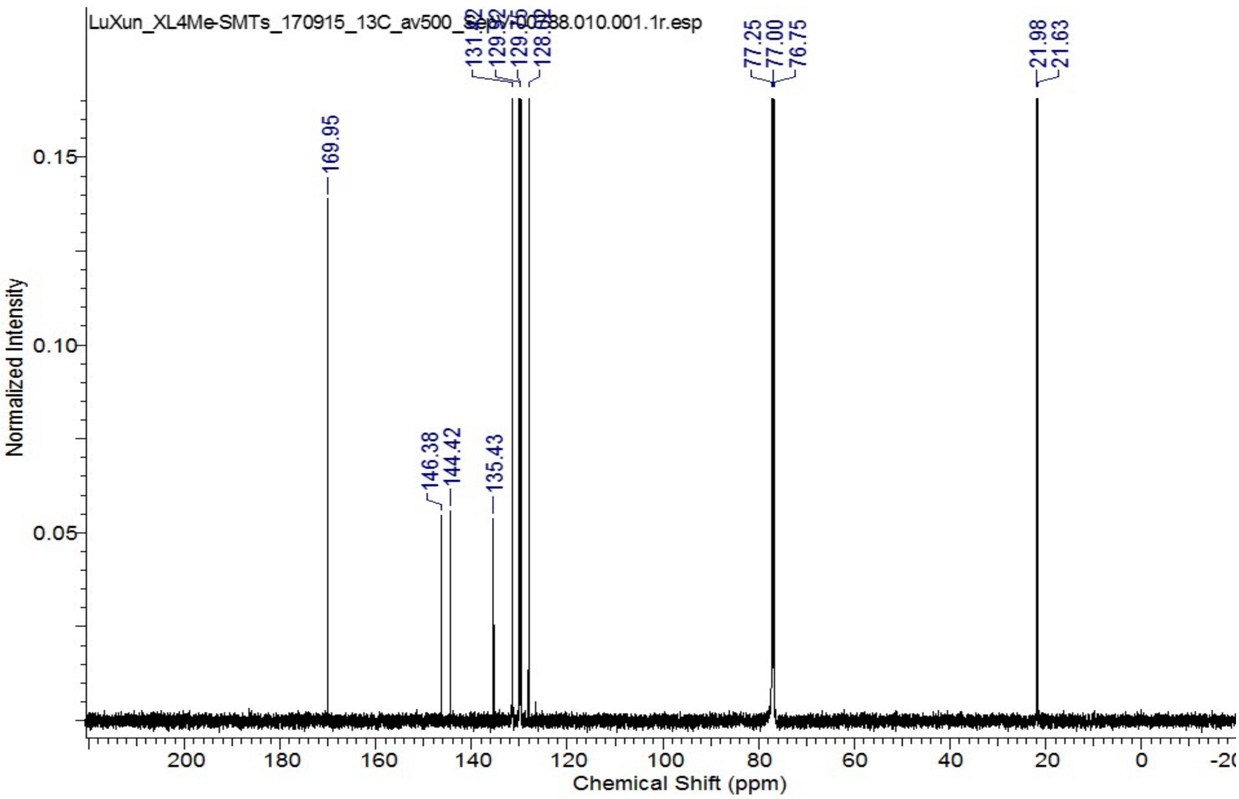

LUXUN_XLM-ME-IMINE_071114_1H_AV500_NOVIV-00297.010.001.1R.esp
Normalized Intensity
0.15
0.10
0.05
0
9.00
7.89
7.88
7.76
7.69
7.37
7.35
7.33
7.26
2.43
2.39
0.00
0.01
-0.01
1.00 1.99 1.00 1.01 1.02 3.04
3.15 3.04
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

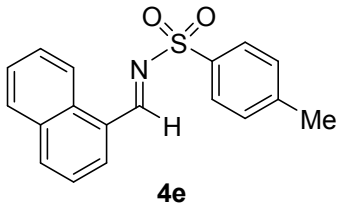

LuXun_XL3Me-SMTs_170915_13C_av500_SepV-00787.010.001.1r.esp
Normalized Intensity
0.15
0.10
0.05
170.37
144.54
139.12
135.85
131.36
129.80
129.02
128.10
126.51
21.66
21.15
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)


O
O
S
N
H
Me
Me

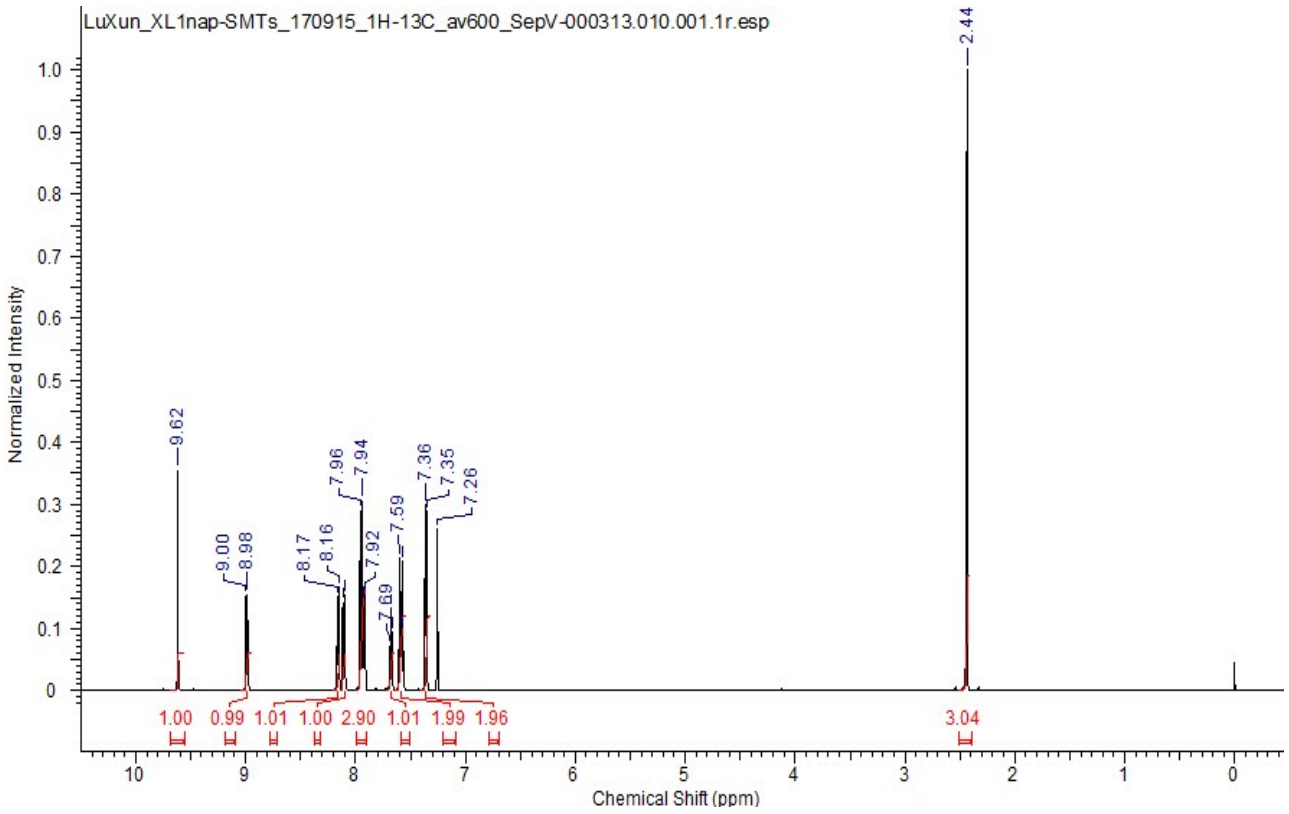
4d

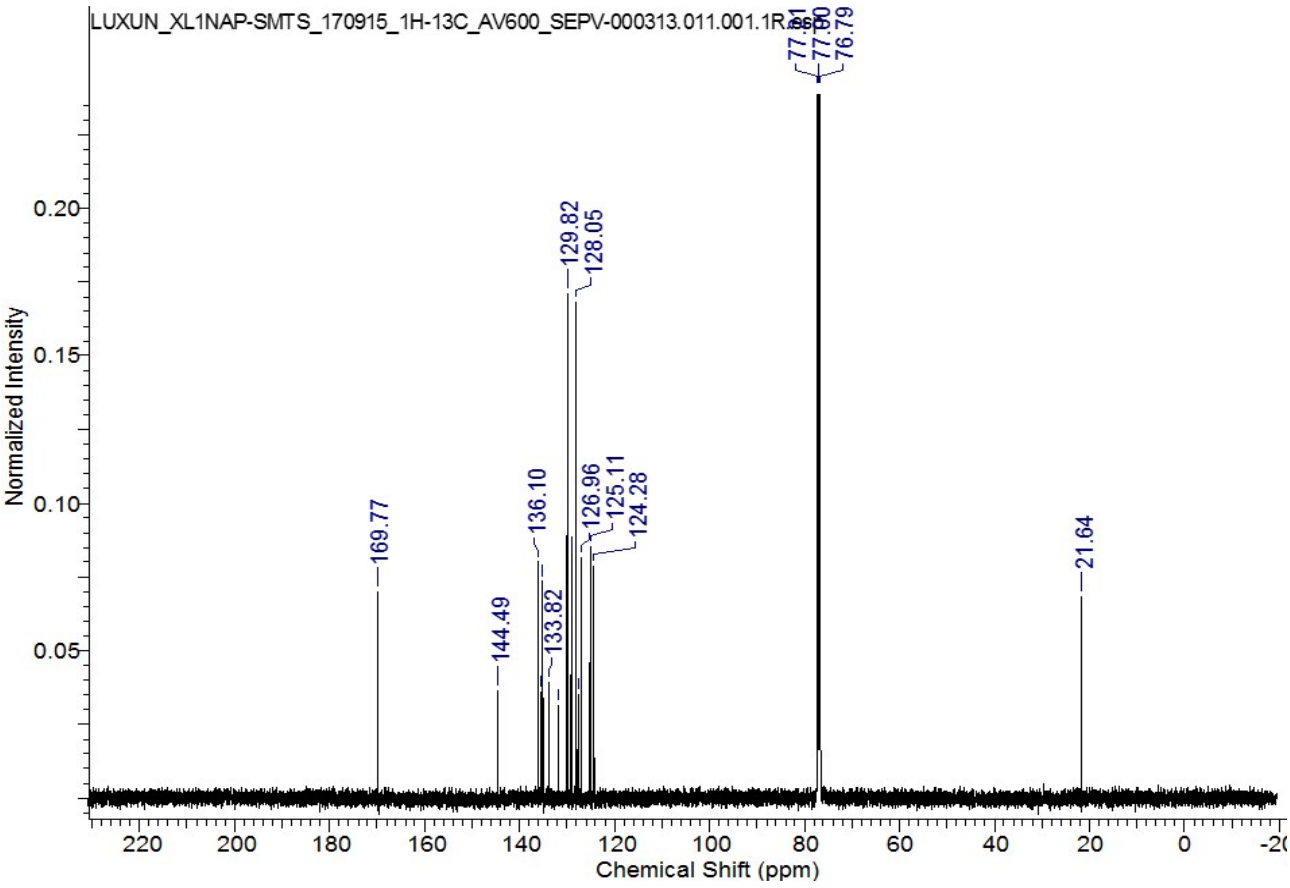

LUXUN_XLP-ME-IMINE_071114_1H_AV500_NOVIV-00298.010.001.1R.ESP
TMS
8.99
7.89
7.87
7.34
7.33
7.29
7.28
2.43
2.43
1.00
1.96
2.05
2.04
2.04
2.98
3.14
Normalized Intensity
Chemical Shift (ppm)

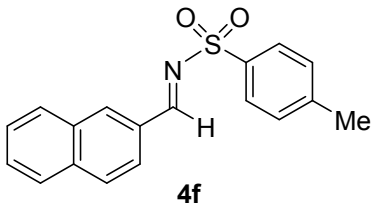

169.95
146.38
144.42
135.43
77.25
77.00
76.75
21.98
21.63
Normalized Intensity
Chemical Shift (ppm)


O
O
S
N
H
Me

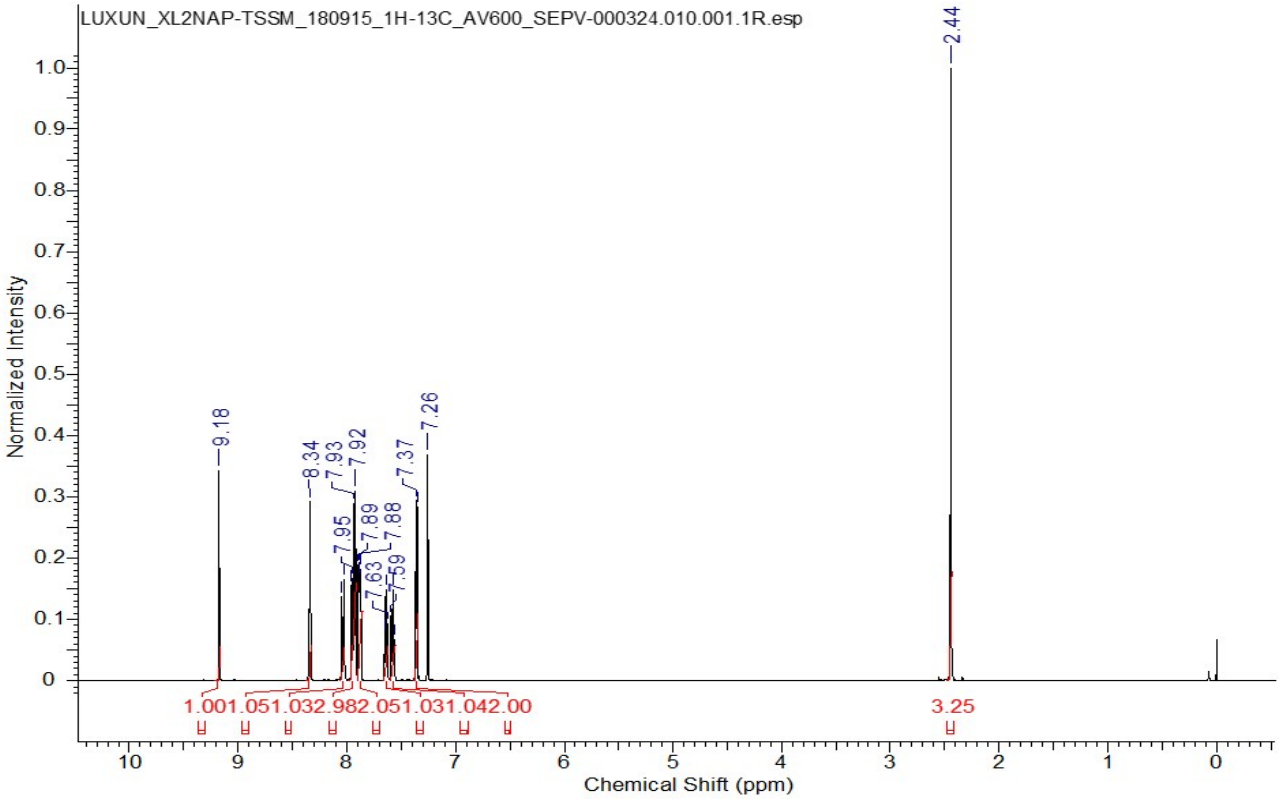
4e

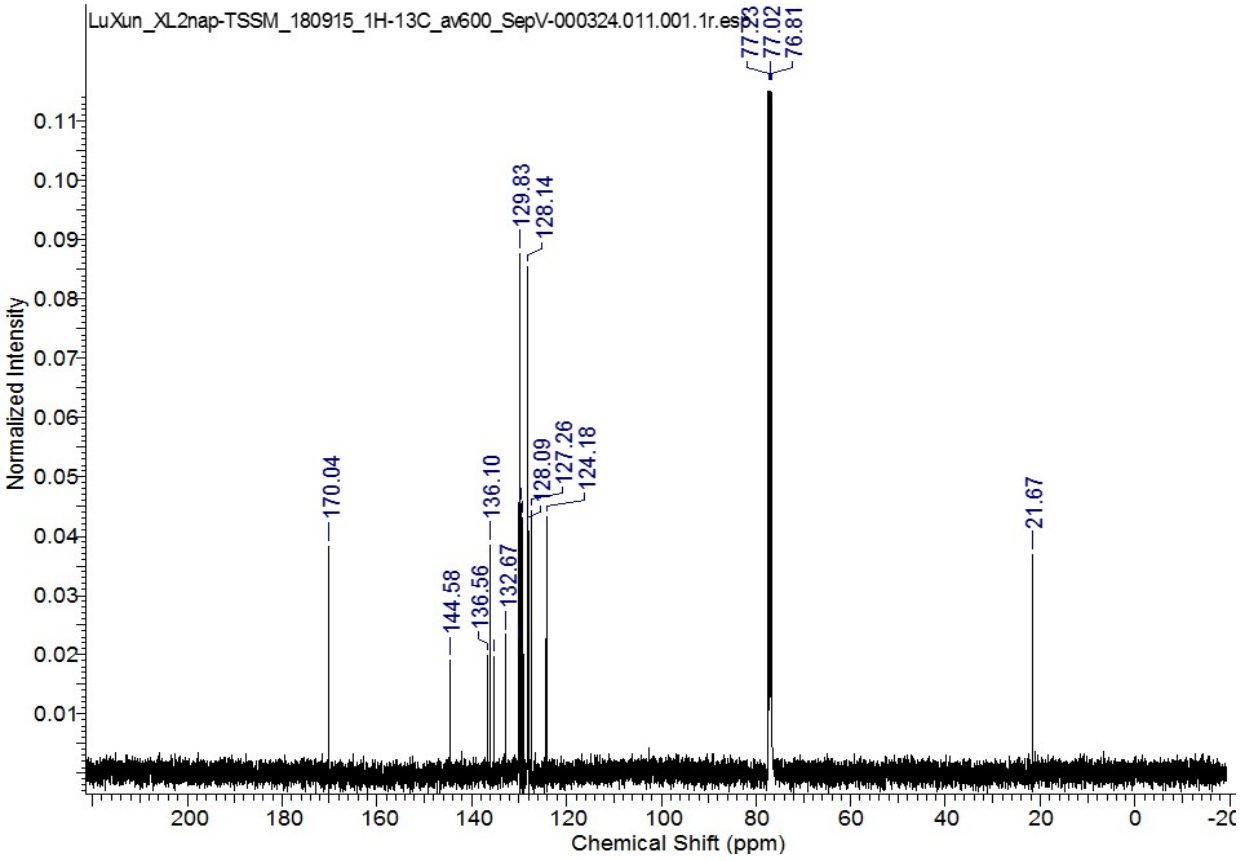

LuXun_XL1nap-SMTs_170915_1H-13C_av600_SepV-000313.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
9.62
9.00
8.98
8.17
8.16
7.96
7.94
7.92
7.69
7.59
7.36
7.35
7.26
2.44
1.00 0.99 1.01 1.00 2.90 1.01 1.99 1.96
3.04

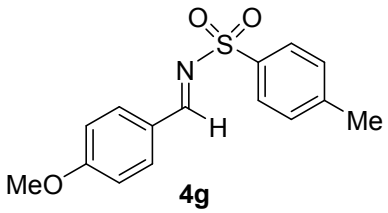

LUXUN_XL1NAP-SMTS_170915_1H-13C_AV600_SEPV-000313.011.001.1R.esp
Normalized Intensity
Chemical Shift (ppm)
77.41
77.00
76.79
129.82
128.05
169.77
144.49
136.10
133.82
126.96
125.11
124.28
21.64


O
O
S
N
H
Me

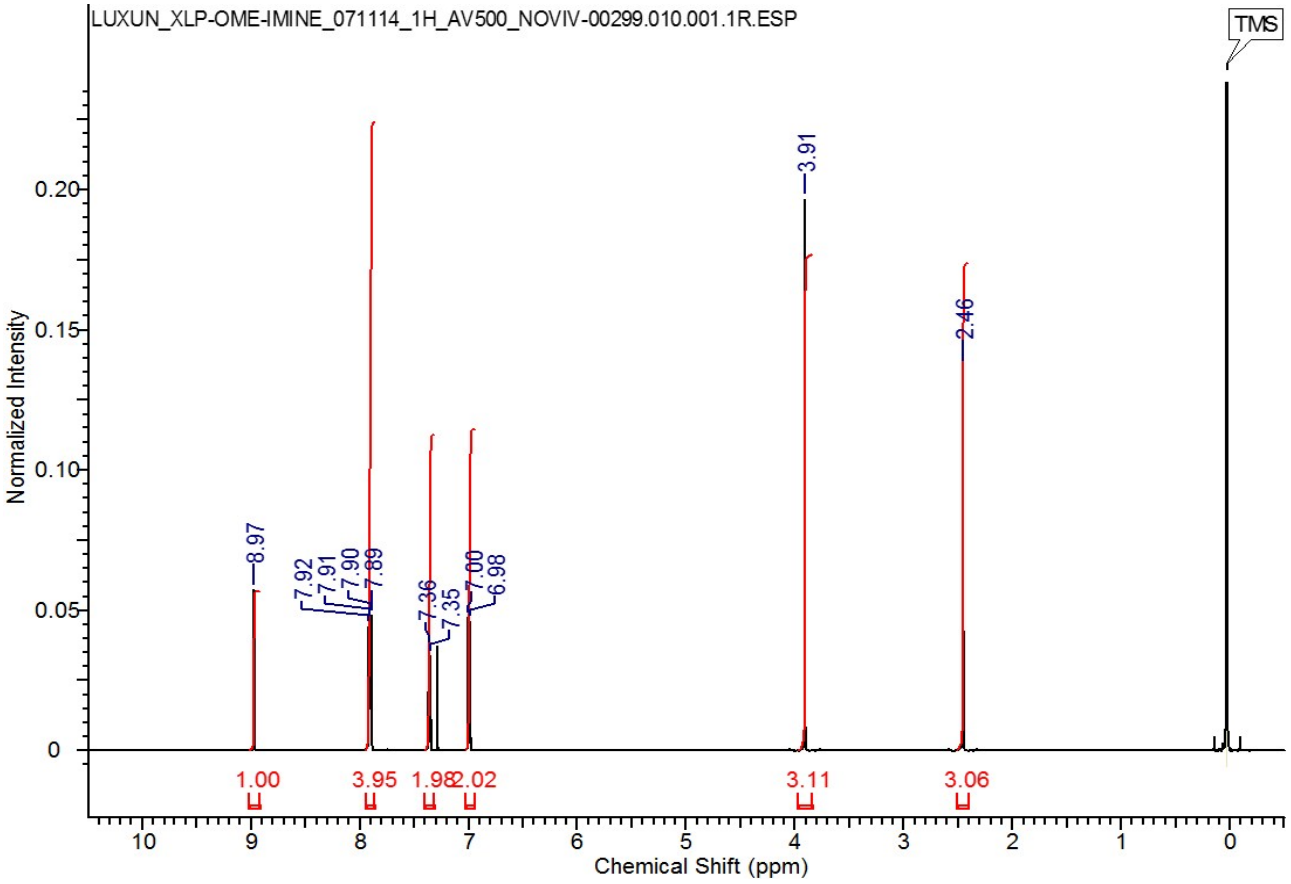
4f

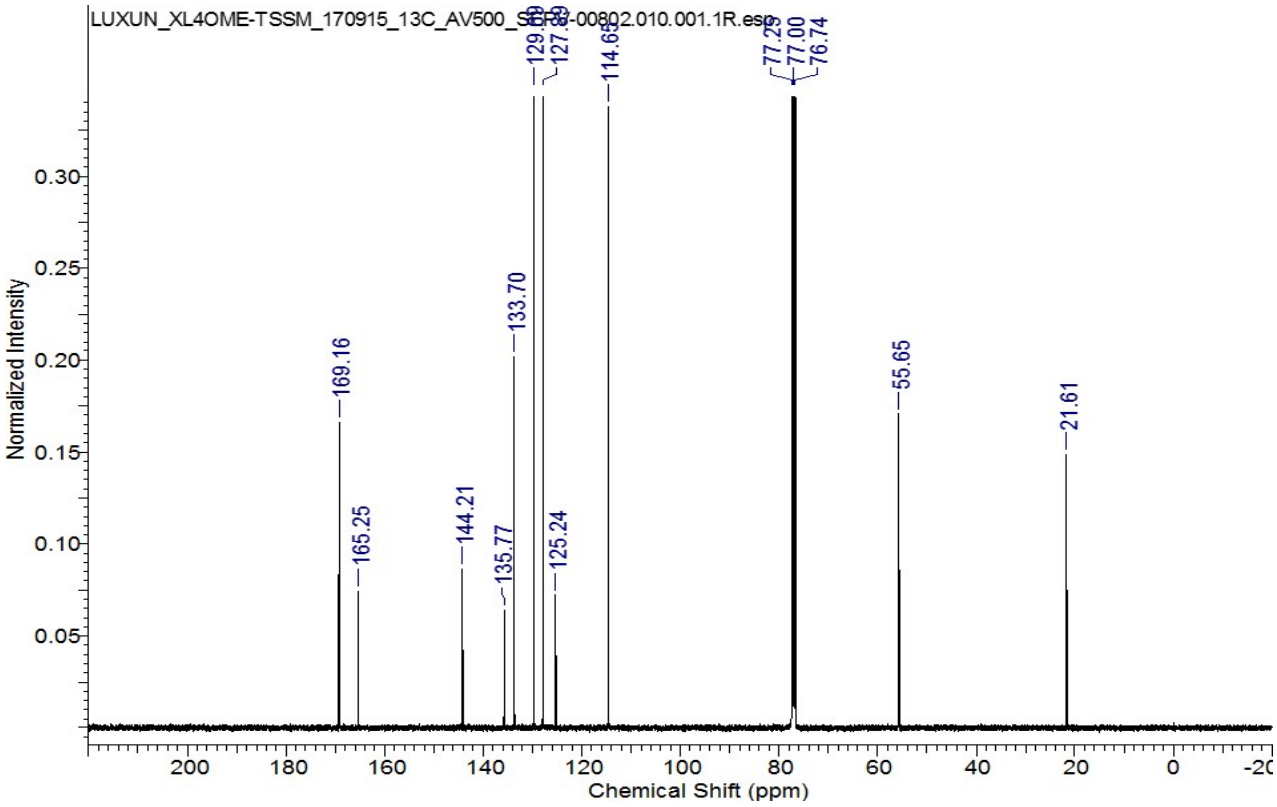

LUXUN_XL2NAP-TSSM_180915_1H-13C_AV600_SEPV-000324.010.001.1R.esp
Normalized Intensity
Chemical Shift (ppm)
9.18
8.34
7.93
7.92
7.95
7.89
7.88
7.63
7.59
7.37
7.26
2.44
1.00 1.05 1.03 2.98 2.05 1.03 1.04 2.00
3.25

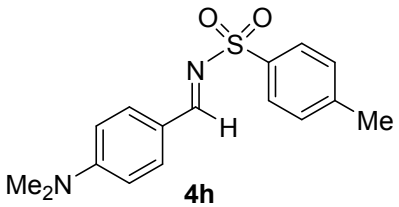

LuXun_XL2nap-TSSM_180915_1H-13C_av600_SepV-000324.011.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
77.23
77.02
76.81
129.83
128.14
128.09
127.26
124.18
170.04
144.58
136.56
136.10
132.67
21.67


O
O
S
N
H
Me
MeO

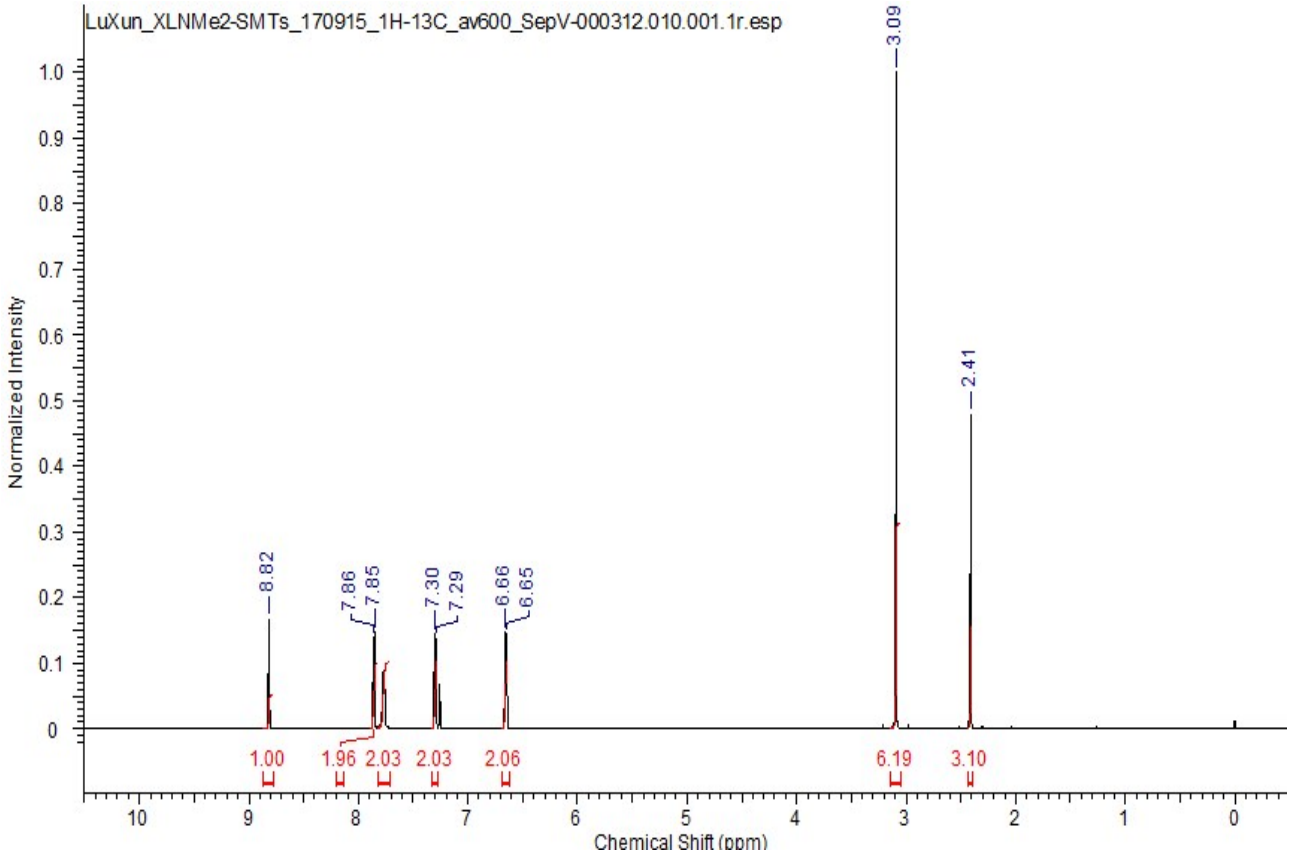
4g

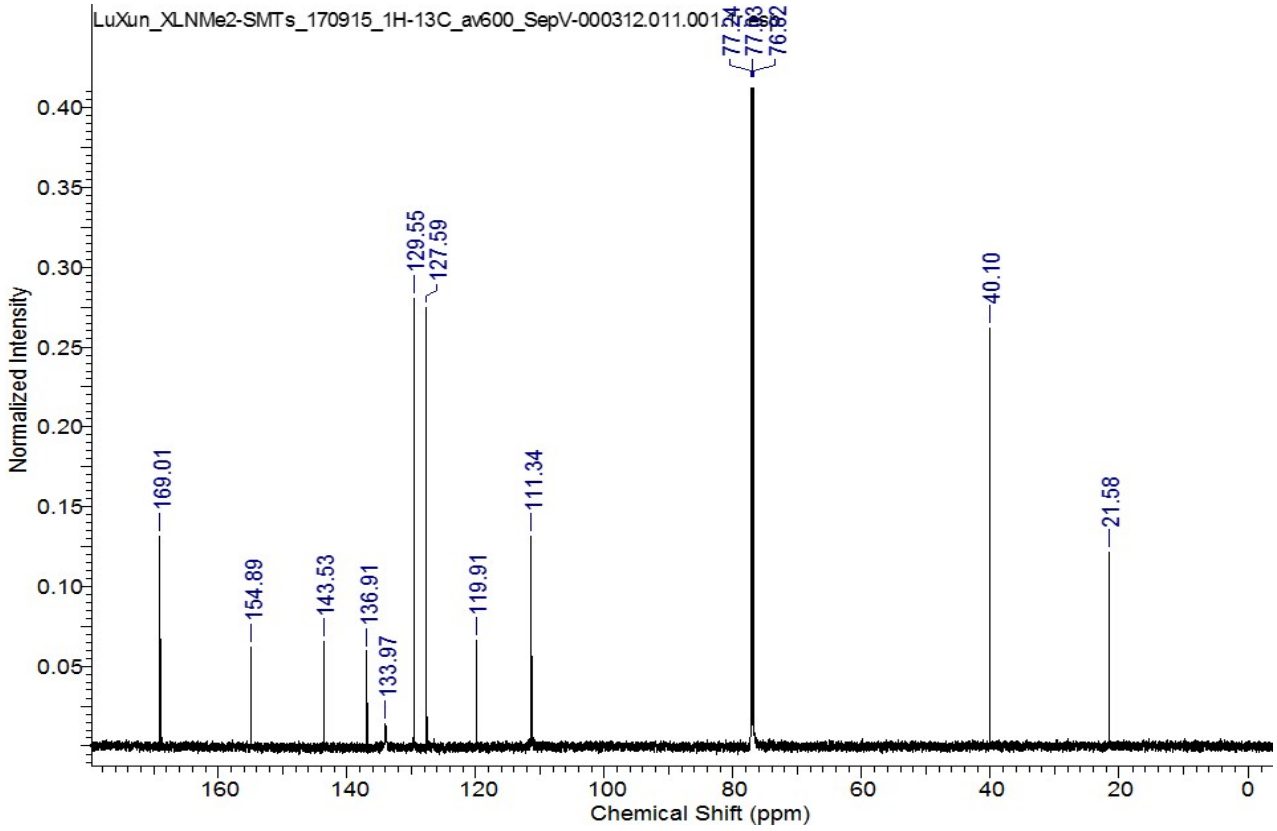

LUXUN_XLP-OME-IMINE_071114_1H_AV500_NOVIV-00299.010.001.1R.ESP
TMS
Normalized Intensity
Chemical Shift (ppm)
8.97
7.92
7.91
7.90
7.89
7.36
7.35
7.00
6.98
3.91
2.46
1.00
3.95
1.98
2.02
3.11
3.06

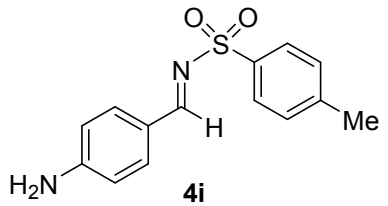

LUXUN_XL4OME-TSSM_170915_13C_AV500_S
Normalized Intensity
Chemical Shift (ppm)
169.16
165.25
144.21
135.77
133.70
129.60
127.39
125.24
114.65
77.29
77.00
76.74
55.65
21.61


O
O
S
N
H
Me
Me2N

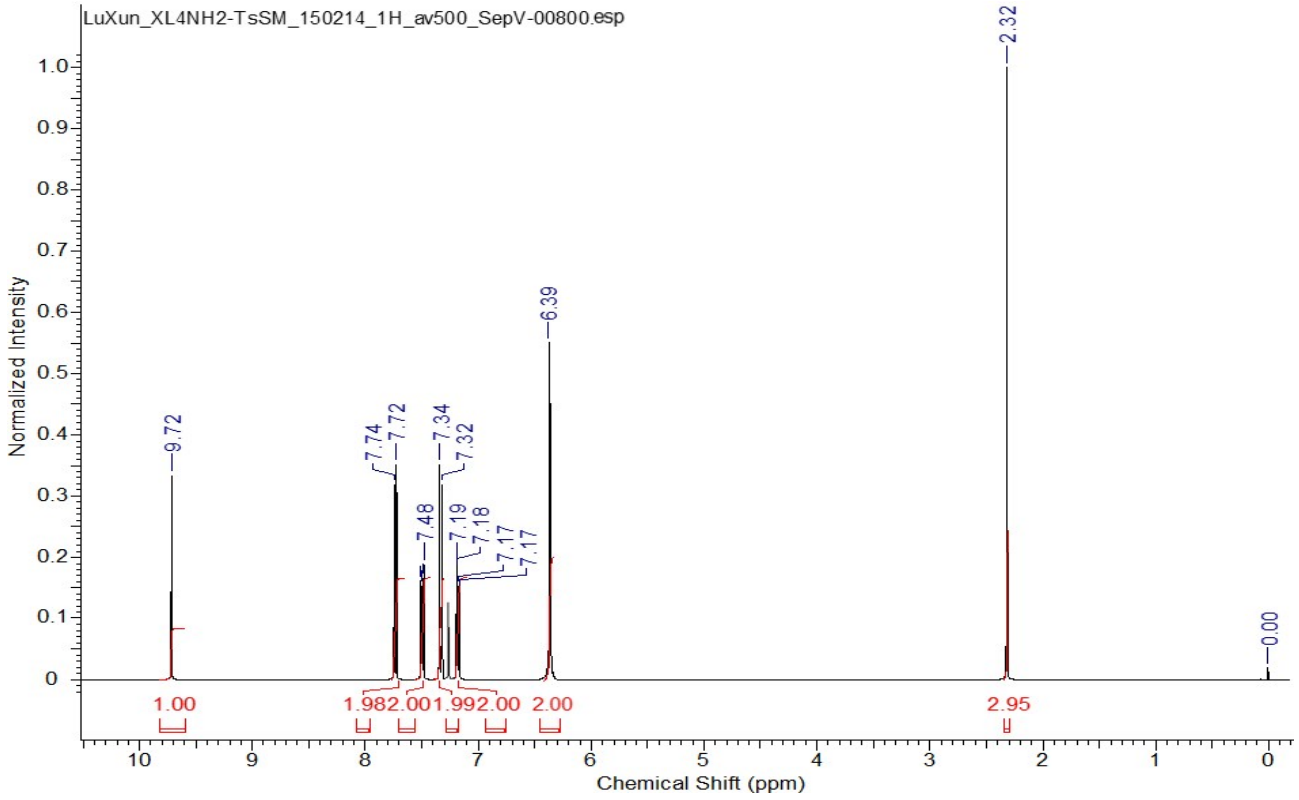
4h

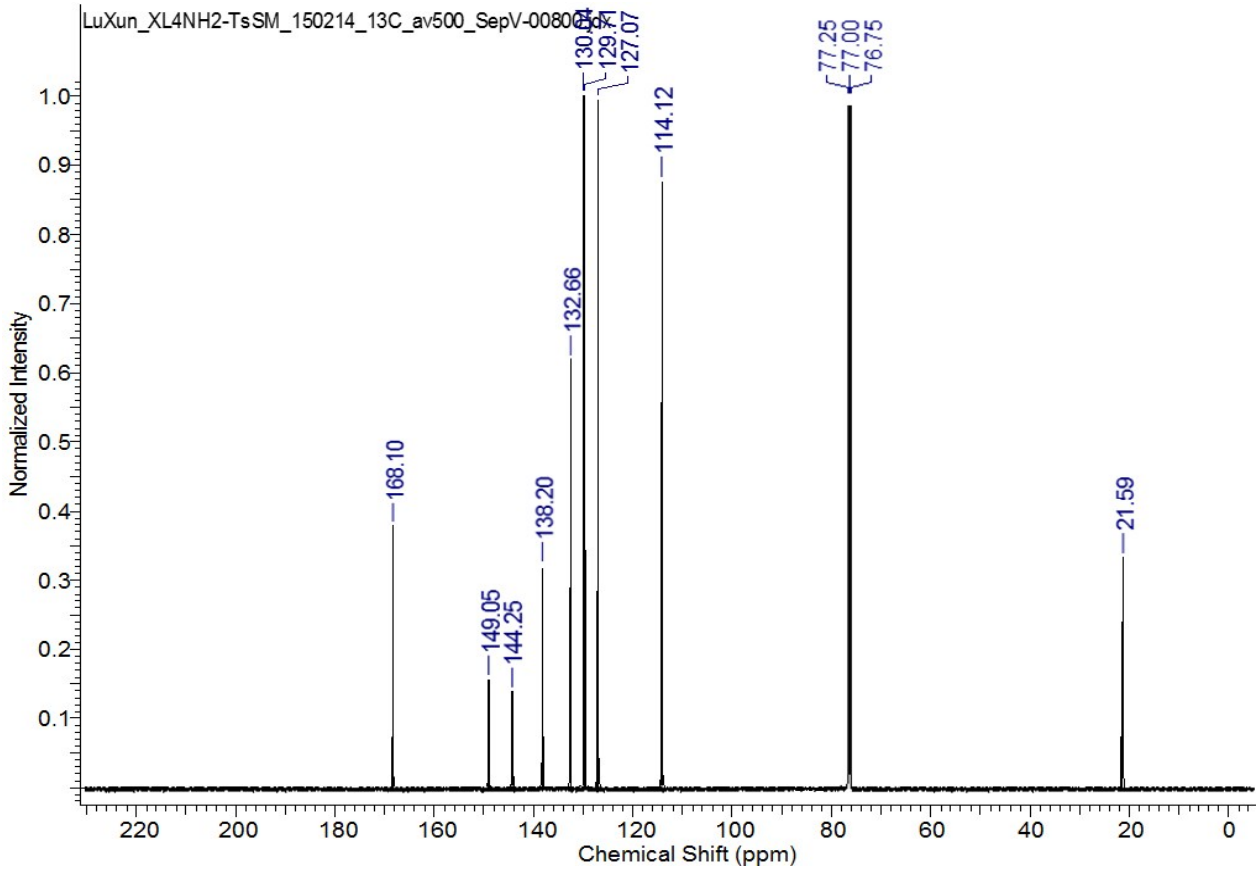

LuXun_XLNMe2-SMTs_170915_1H-13C_av600_SepV-000312.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
8.82
7.86
7.85
7.30
7.29
6.66
6.65
3.09
2.41
1.00
1.96
2.03
2.03
2.06
6.19
3.10

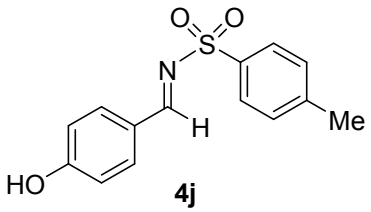

LuXun_XLNMe2-SMTs_170915_1H-13C_av600_SepV-000312.011.001.2r.esp
Normalized Intensity
Chemical Shift (ppm)
169.01
154.89
143.53
136.91
133.97
129.55
127.59
119.91
111.34
77.24
77.03
76.82
40.10
21.58


O
O
S
N
H
Me
H_2N

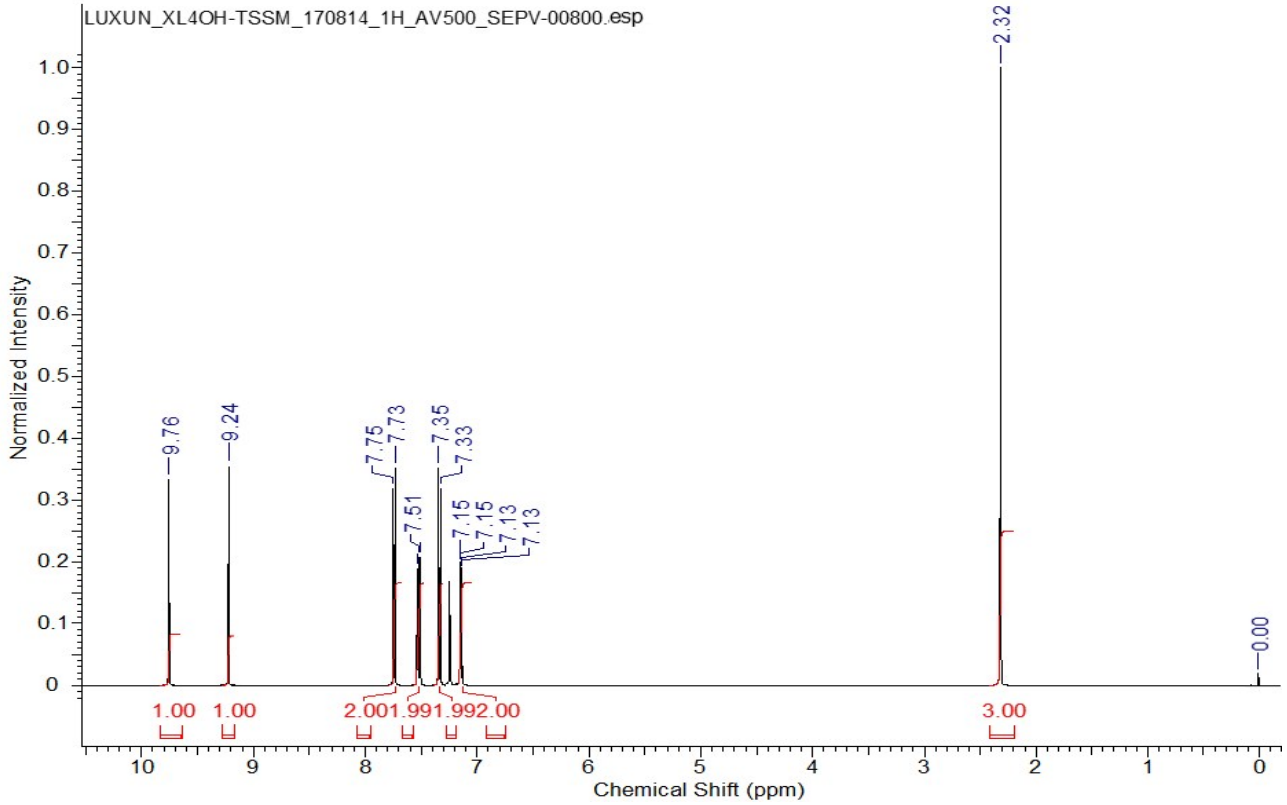
4i

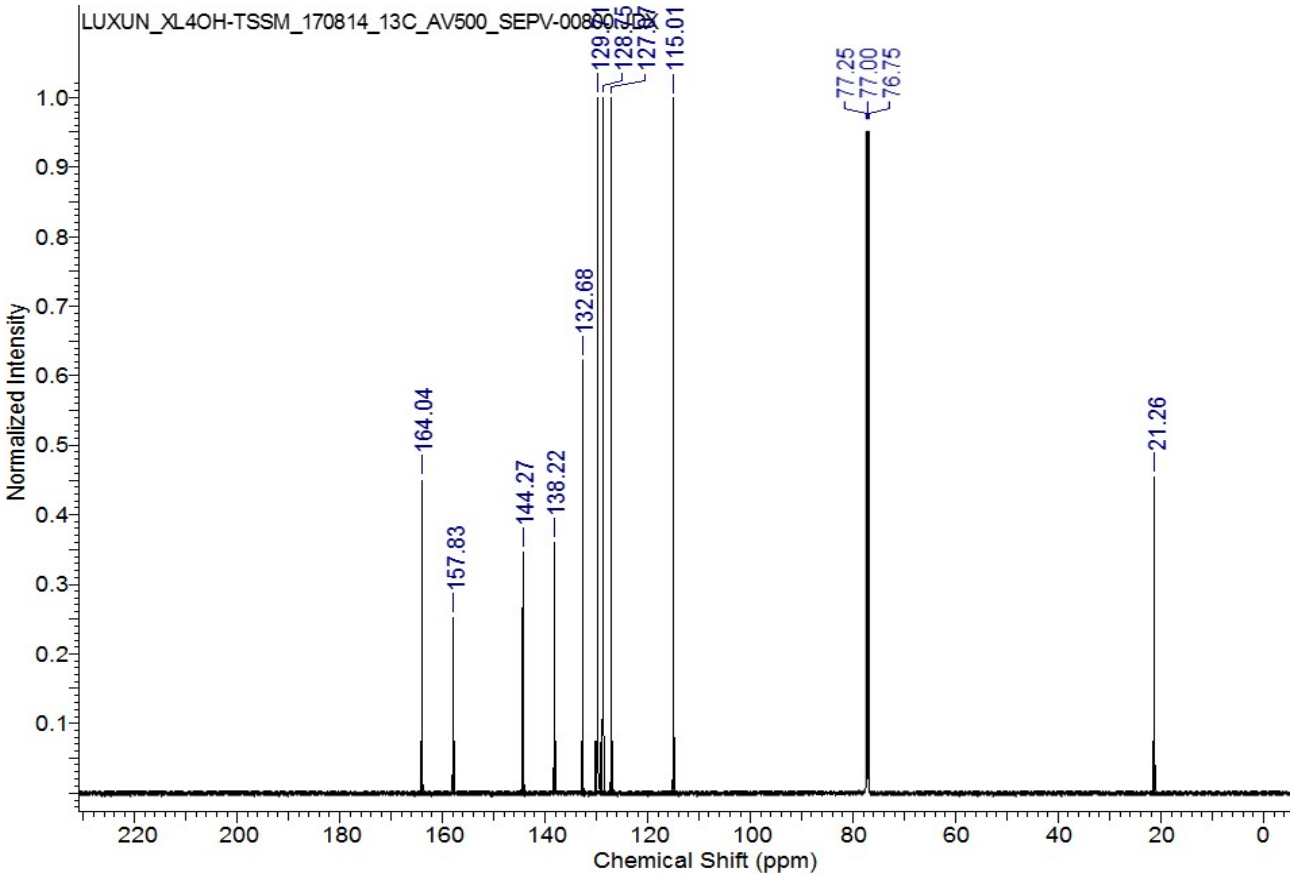

LuXun_XL4NH2-TsSM_150214_1H_av500_SepV-00800.esp
Normalized Intensity
Chemical Shift (ppm)
9.72
7.74
7.72
7.48
7.34
7.32
7.19
7.18
7.17
7.17
6.39
2.32
0.00
1.00
1.98
2.00
1.99
2.00
2.00
2.95

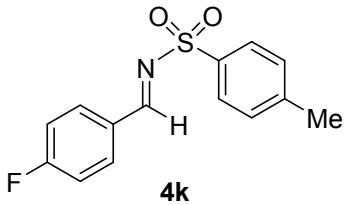

LuXun_XL4NH2-TsSM_150214_13C_av500_SepV-00800.esp
Normalized Intensity
Chemical Shift (ppm)
168.10
149.05
144.25
138.20
132.66
130.04
129.71
127.07
114.12
77.25
77.00
76.75
21.59


O
O
S
N
H
Me
HO

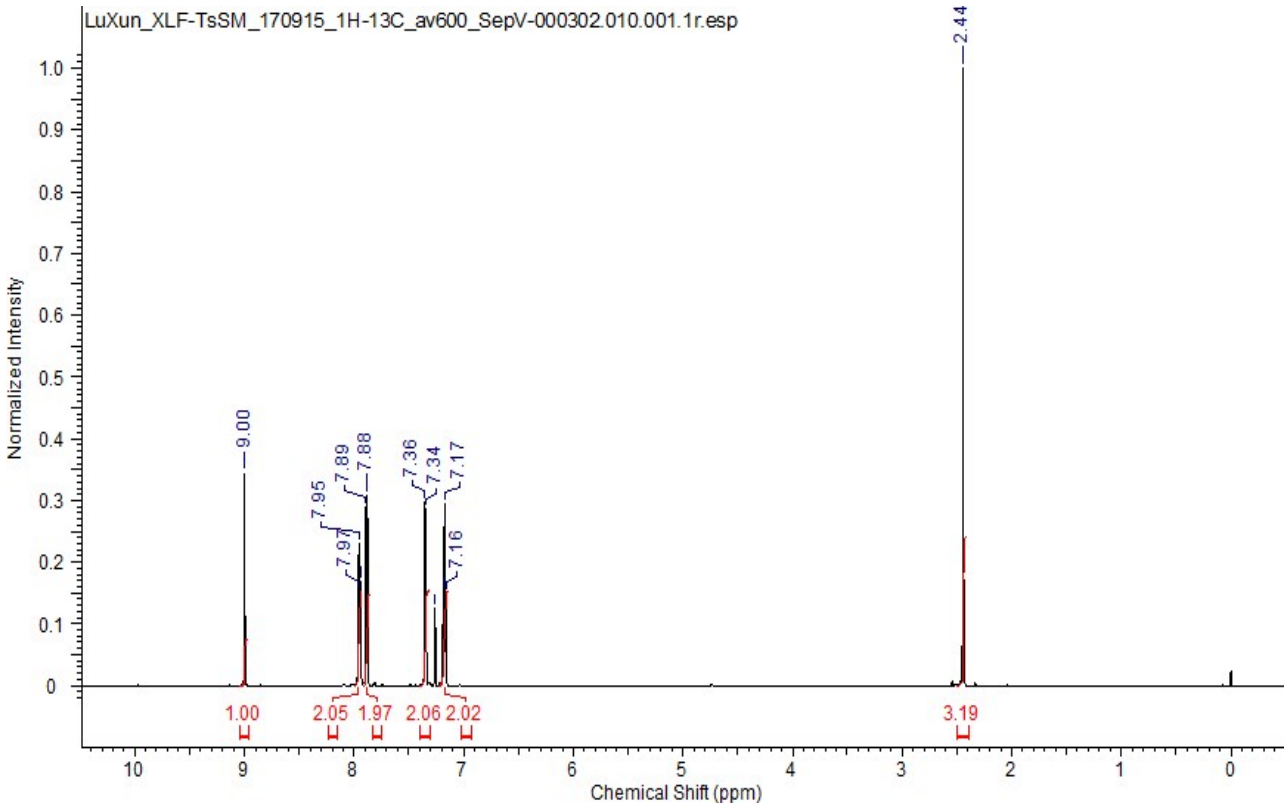
4j

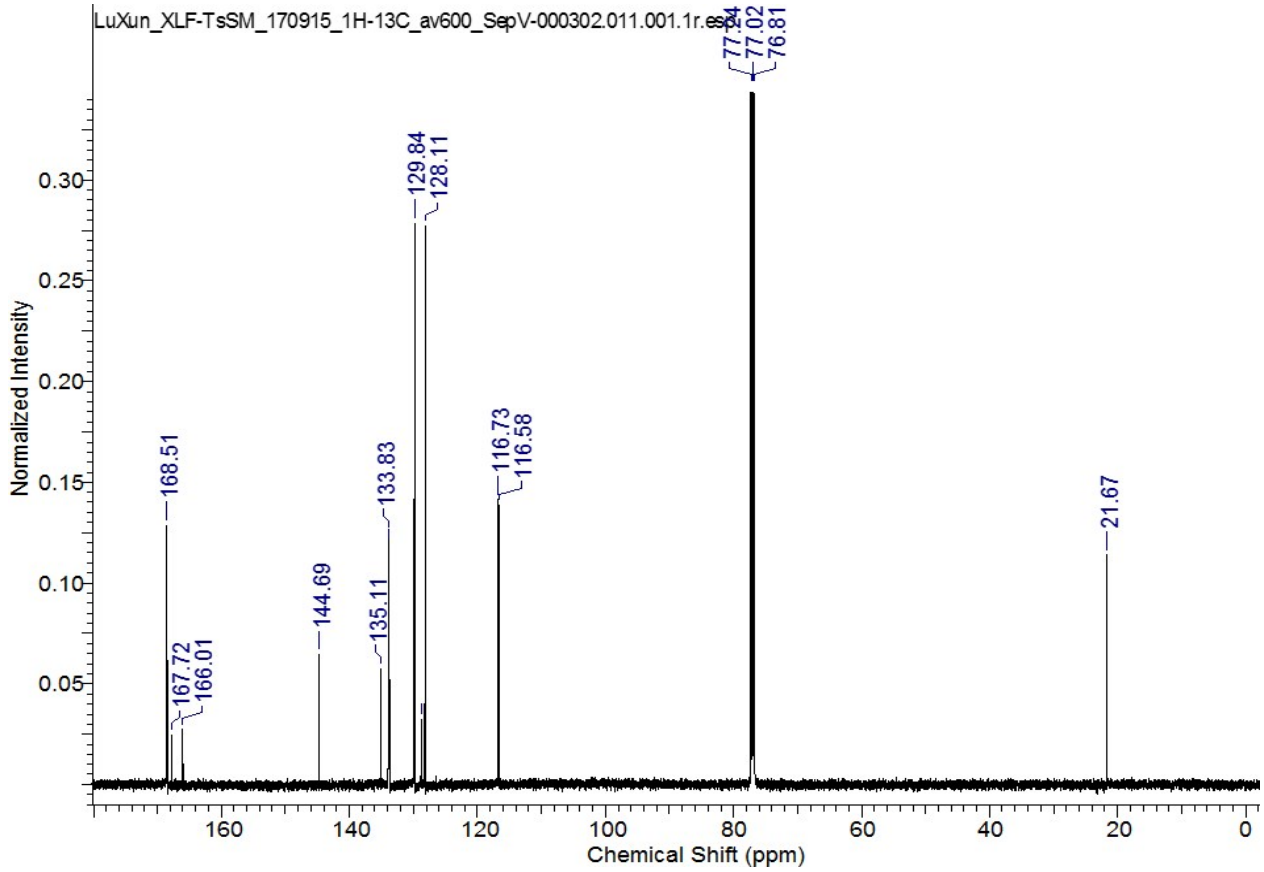

LUXUN_XL4OH-TSSM_170814_1H_AV500_SEPV-00800.esp
Normalized Intensity
Chemical Shift (ppm)
9.76
9.24
7.75
7.73
7.51
7.35
7.33
7.15
7.15
7.13
7.13
2.32
0.00
1.00
1.00
2.00
1.99
1.99
2.00
3.00

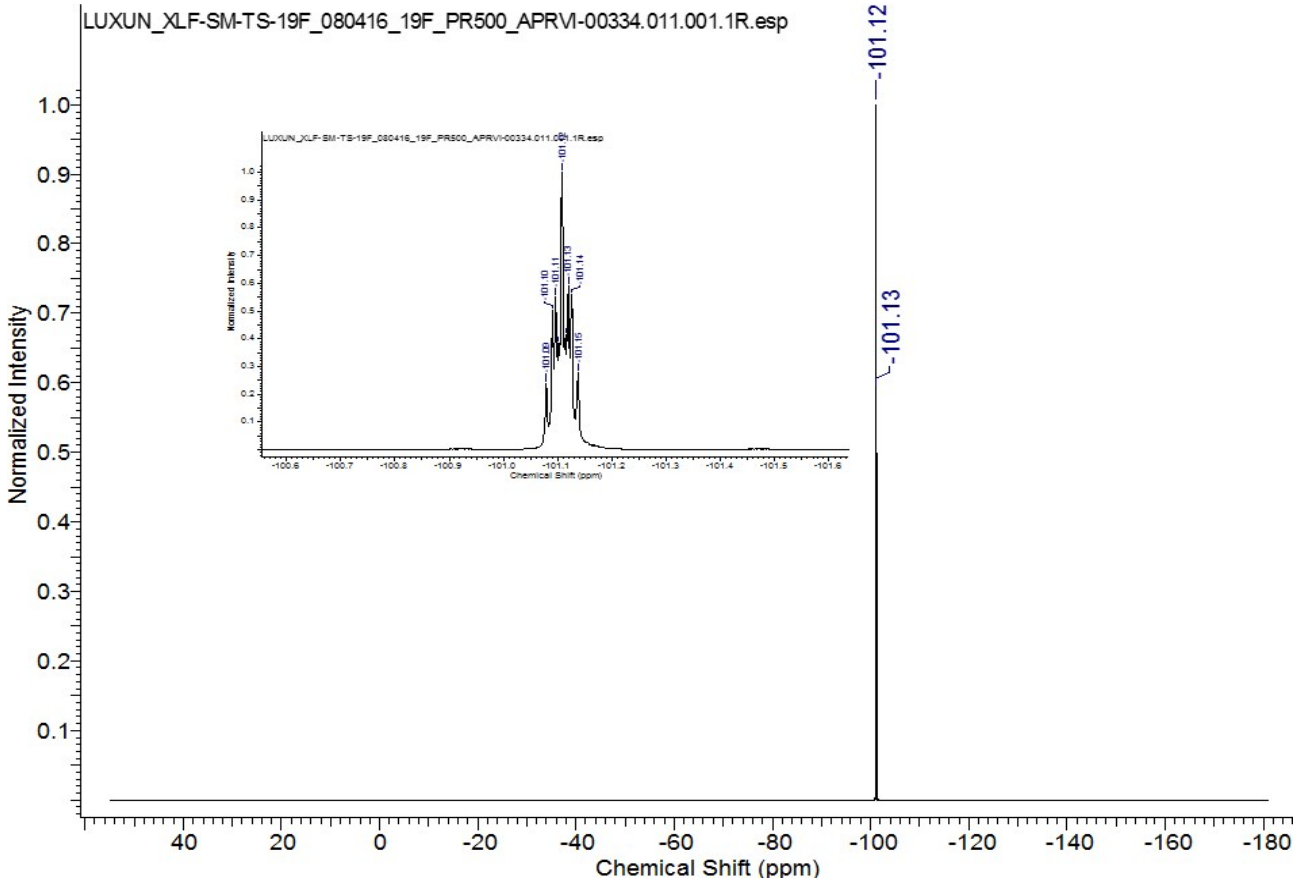

LUXUN_XL4OH-TSSM_170814_13C_AV500_SEPV-00800
Normalized Intensity
Chemical Shift (ppm)
164.04
157.83
144.27
138.22
132.68
129.21
128.75
127.87
115.01
77.25
77.00
76.75
21.26

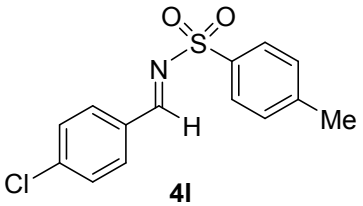

O
O
S
N
H
Me
F

4k

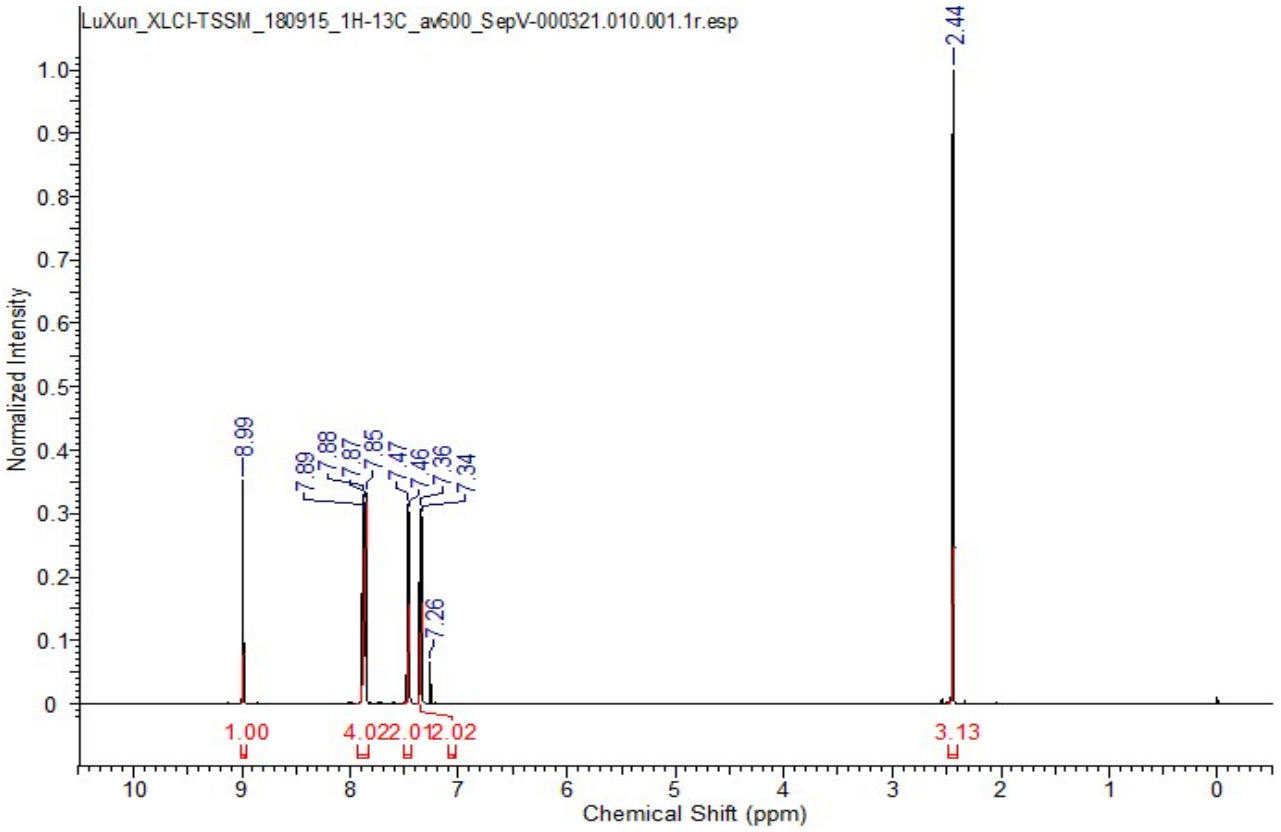

LuXun_XLF-TsSM_170915_1H-13C_av600_SepV-000302.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
9.00
7.95
7.89
7.88
7.97
7.36
7.34
7.17
7.16
2.44
1.00
2.05
1.97
2.06
2.02
3.19

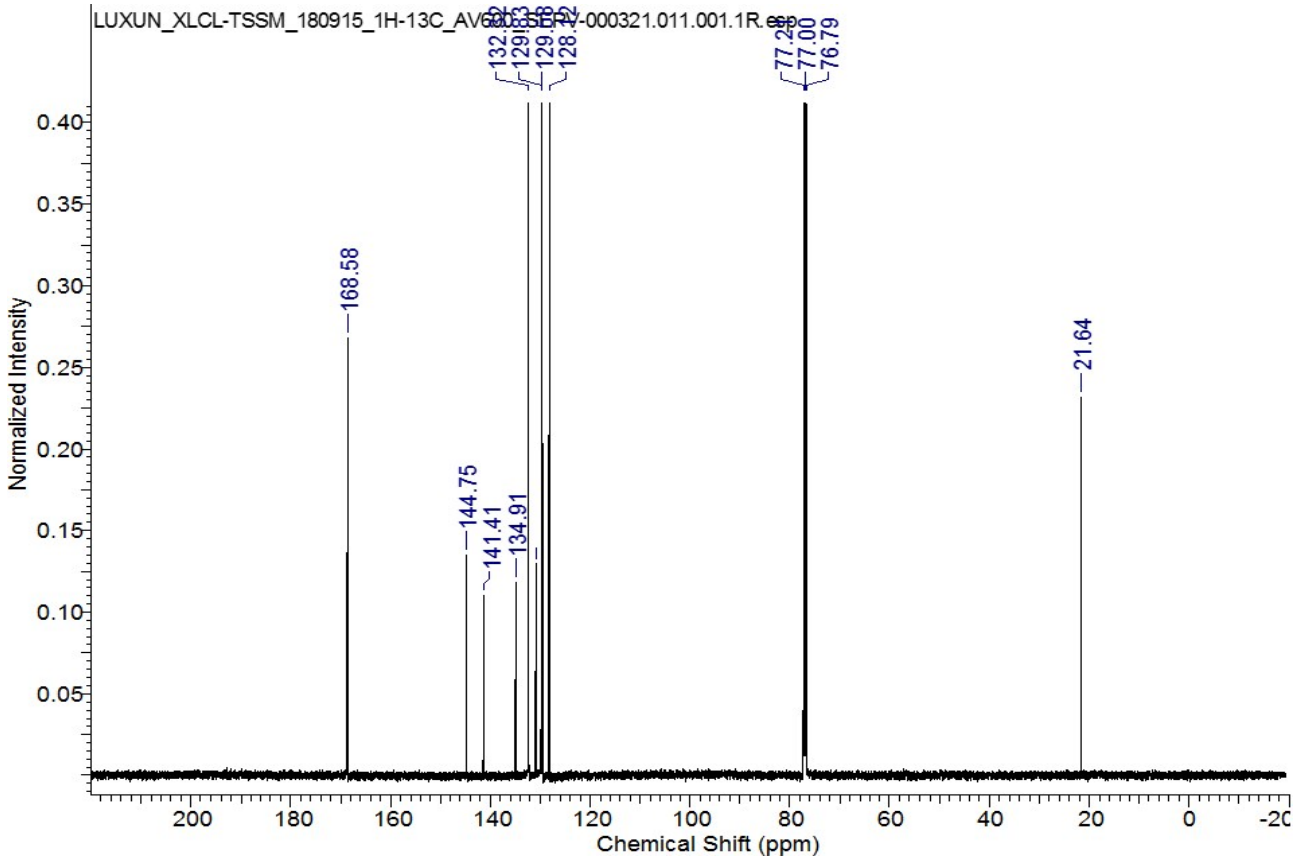

LuXun_XLF-TsSM_170915_1H-13C_av600_SepV-000302.011.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
77.24
77.02
76.81
129.84
128.11
168.51
133.83
116.73
116.58
144.69
135.11
167.72
166.01
21.67

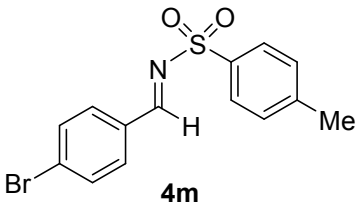

LUXUN_XLF-SM-TS-19F_080416_19F_PR500_APRVI-00334.011.001.1R.esp
-101.12
-101.13
Normalized Intensity
Chemical Shift (ppm)


O
O
S
N
H
Me
Cl

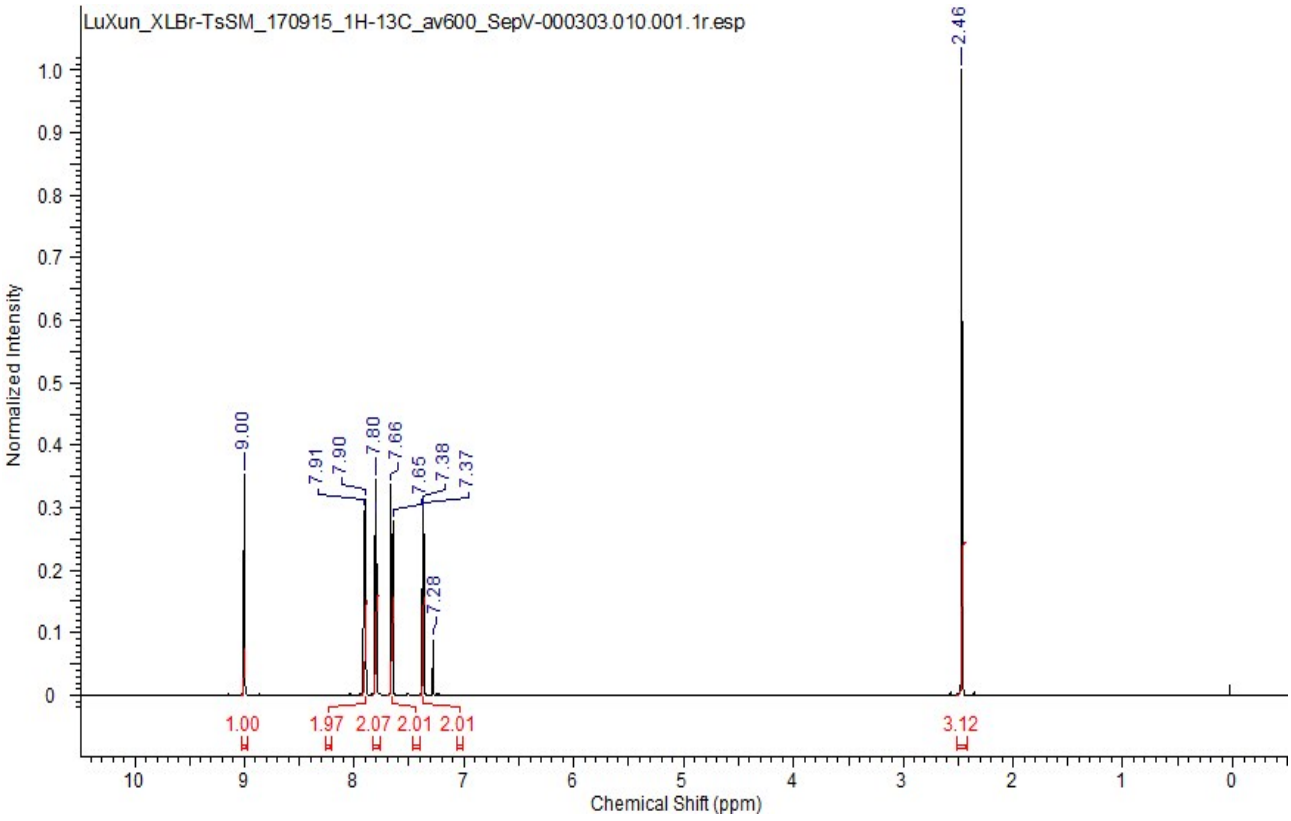
4l

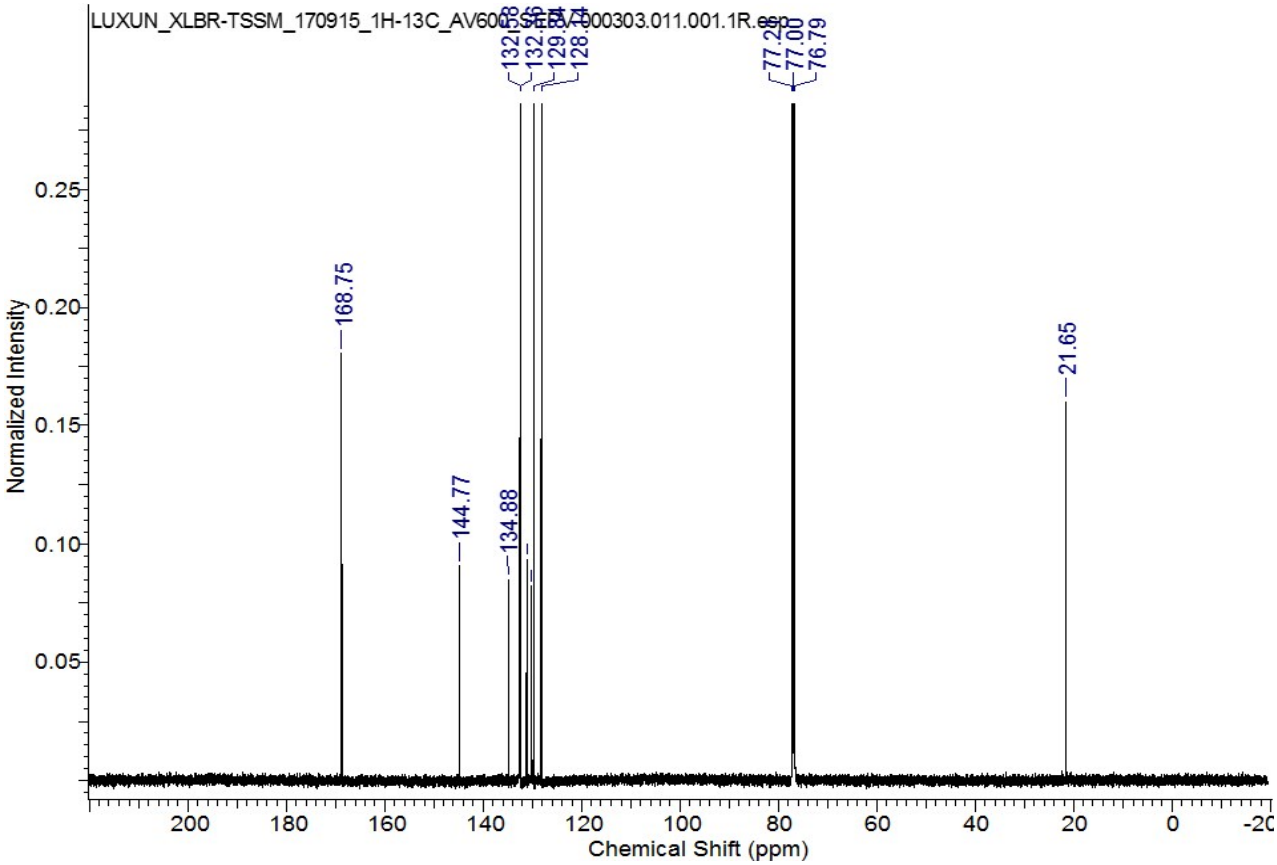

LuXun_XLCl-TSSM_180915_1H-13C_av600_SepV-000321.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
8.99
7.89
7.88
7.87
7.85
7.47
7.46
7.36
7.34
7.26
2.44
1.00
4.02
2.01
2.02
3.13

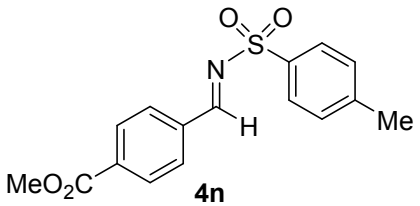

LUXUN_XLCL-TSSM_180915_1H-13C_AV600_SEPV-000321.011.001.1R.esp
Normalized Intensity
Chemical Shift (ppm)
168.58
144.75
141.41
134.91
77.25
77.00
76.79
21.64


O
O
S
N
H
Me
Br

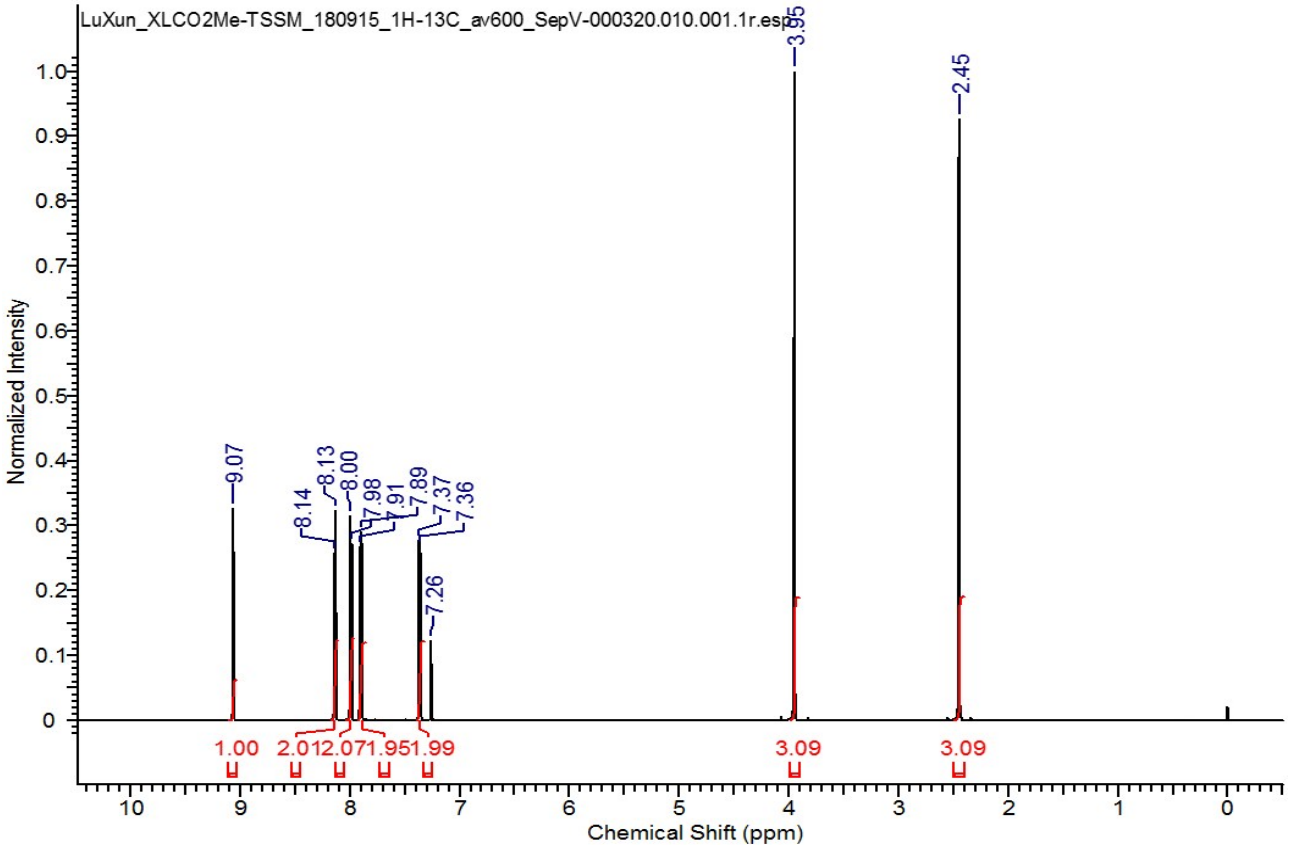
4m

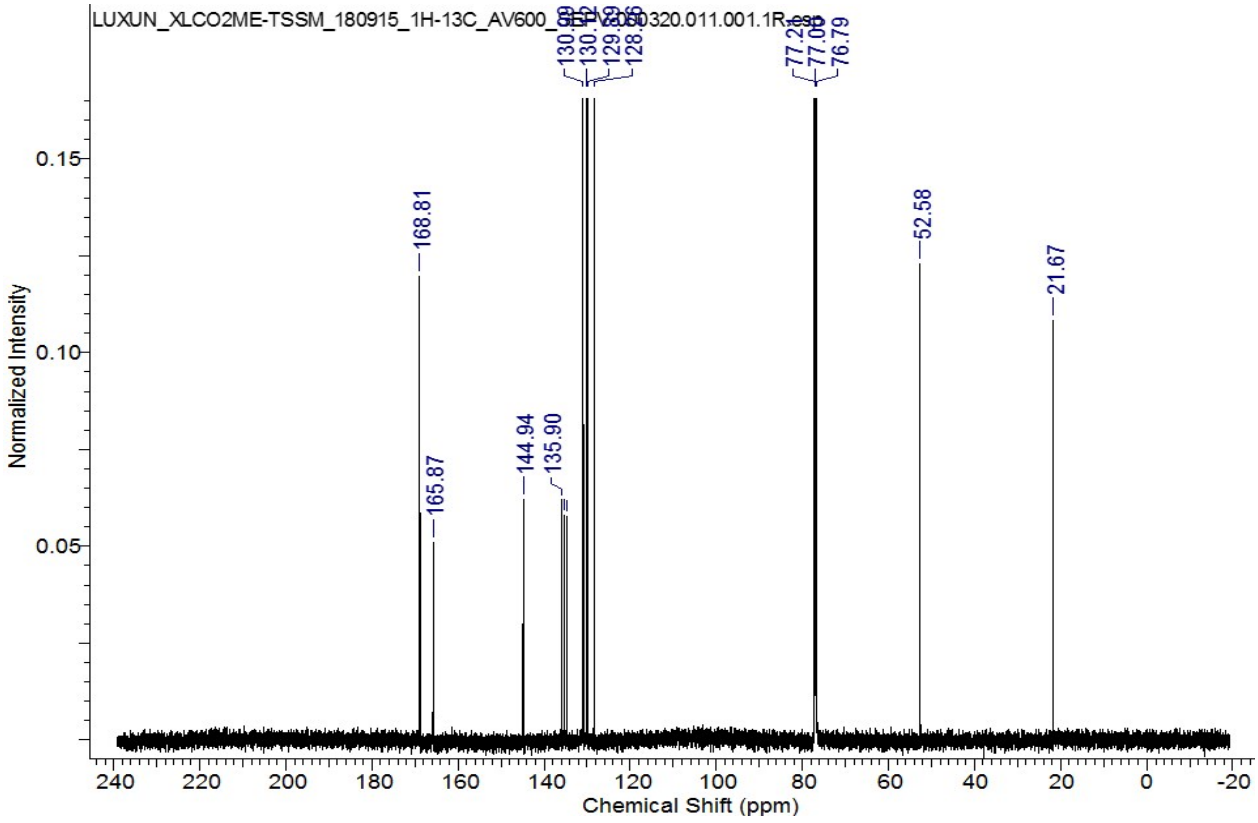

LuXun_XLBr-TsSM_170915_1H-13C_av600_SepV-000303.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
9.00
7.91
7.90
7.80
7.66
7.65
7.38
7.37
7.28
2.46
1.00
1.97
2.07
2.01
2.01
3.12

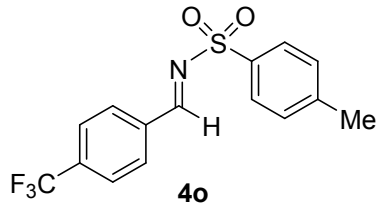

LUXUN_XLBR-TSSM_170915_1H-13C_AV600_SepV-000303.011.001.1R.esp
Normalized Intensity
Chemical Shift (ppm)
168.75
144.77
134.88
77.20
77.00
76.79
21.65


O
O
S
N
H
Me
MeO2C

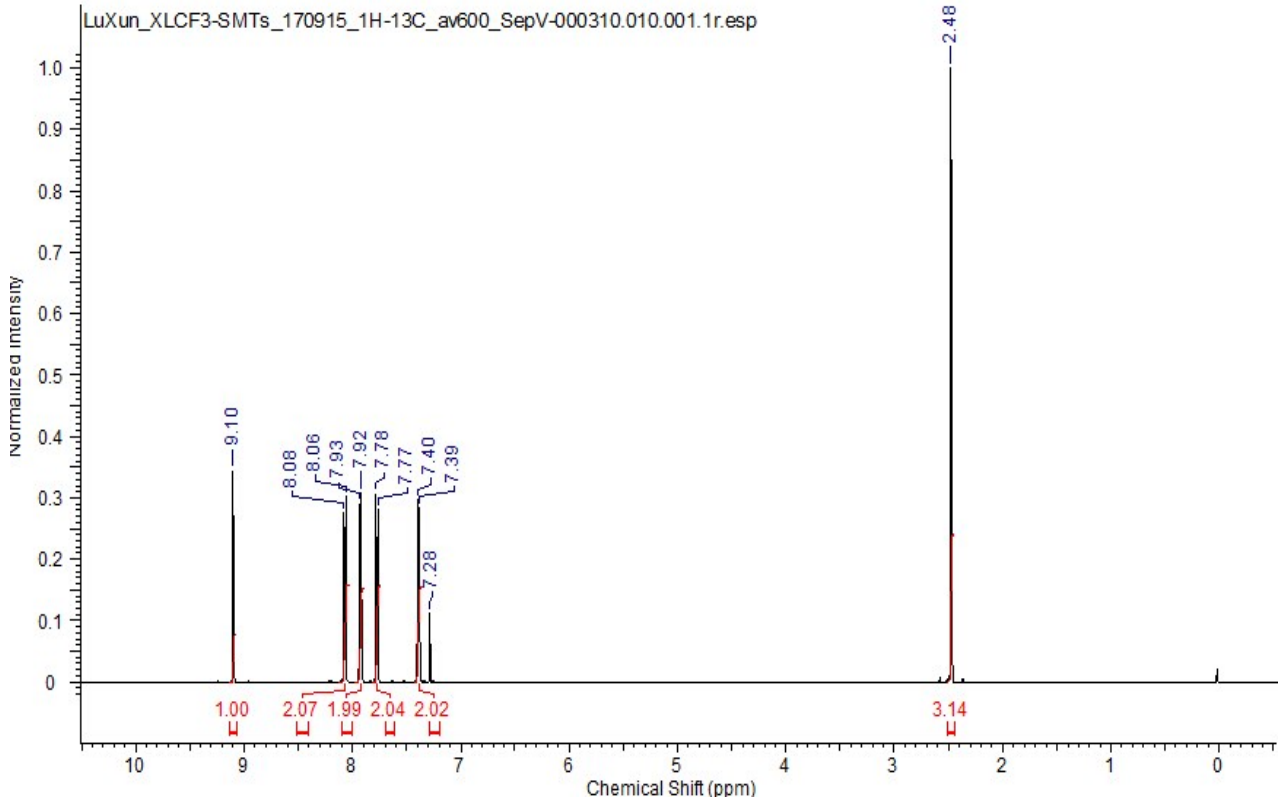
4n

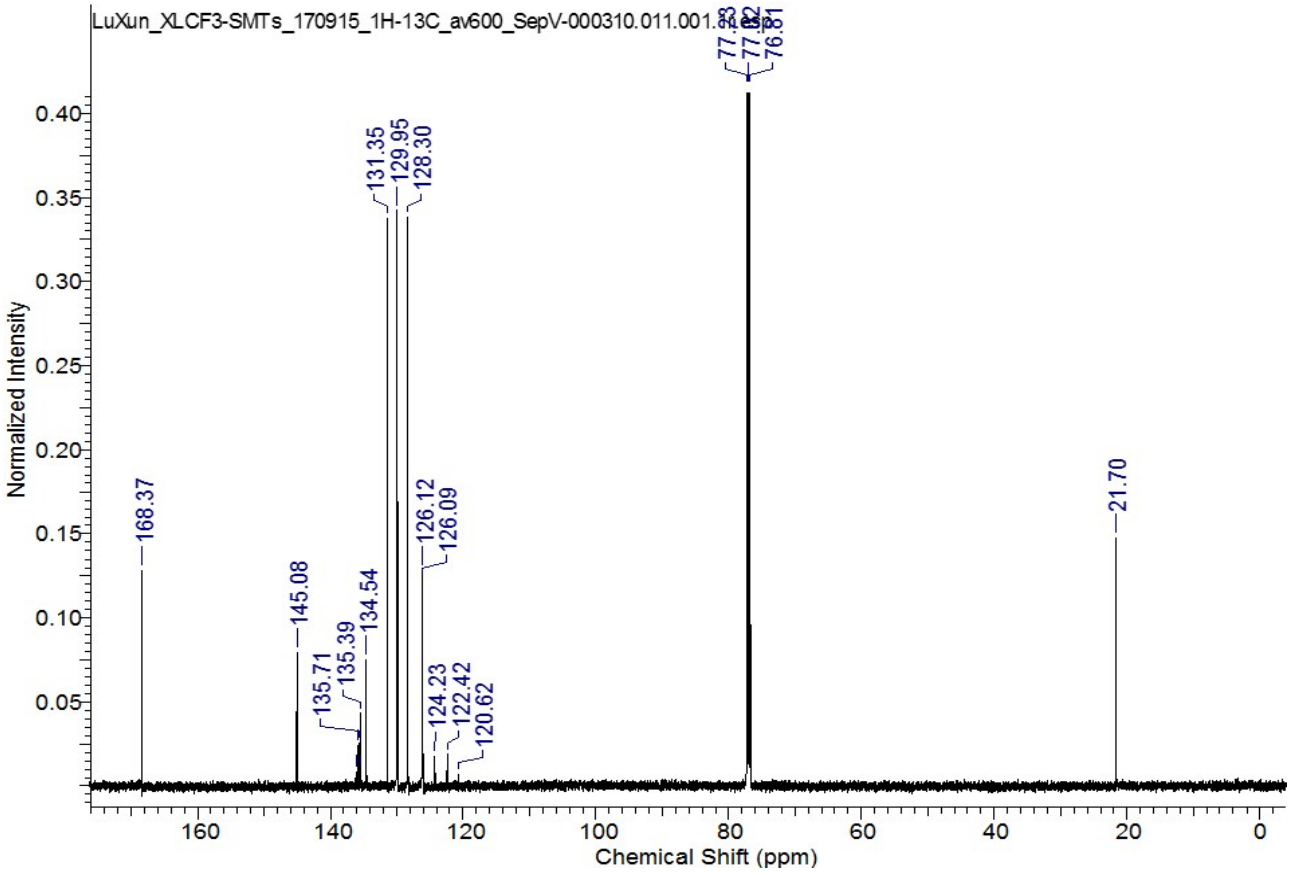

LuXun_XLCO2Me-TSSM_180915_1H-13C_av600_SepV-000320.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
9.07
8.14
8.13
8.00
7.98
7.91
7.89
7.37
7.36
7.26
3.95
2.45
1.00
2.01
2.07
1.95
1.99
3.09
3.09

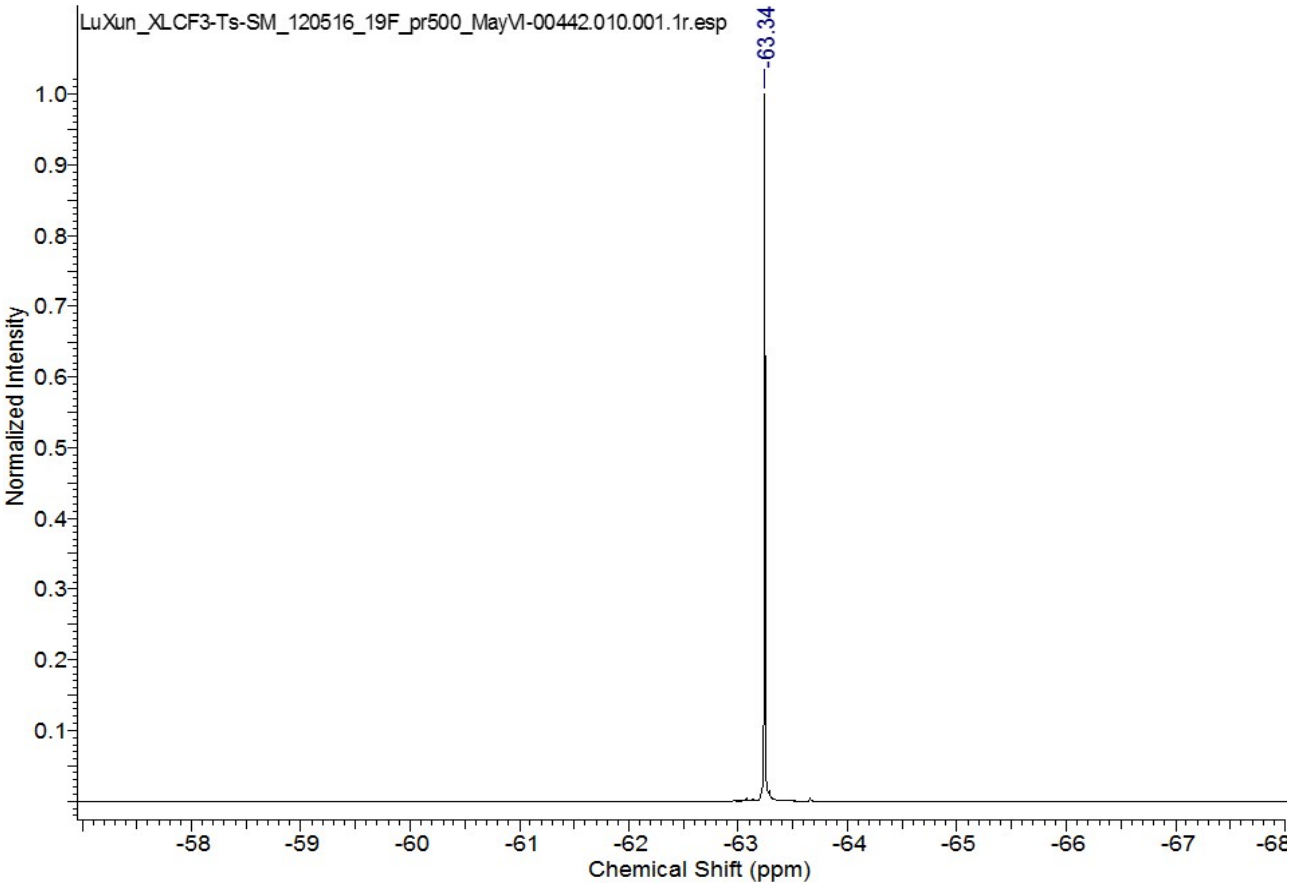

LUXUN_XLCO2ME-TSSM_180915_1H-13C_AV600_SEPV-000320.011.001.1R.esp
Normalized Intensity
Chemical Shift (ppm)
168.81
165.87
144.94
135.90
77.28
77.00
76.79
52.58
21.67

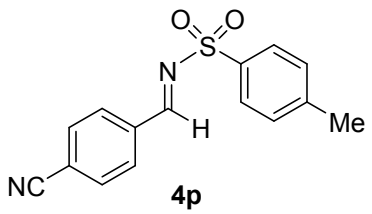

O
O
S
N
H
Me
F3C

4o

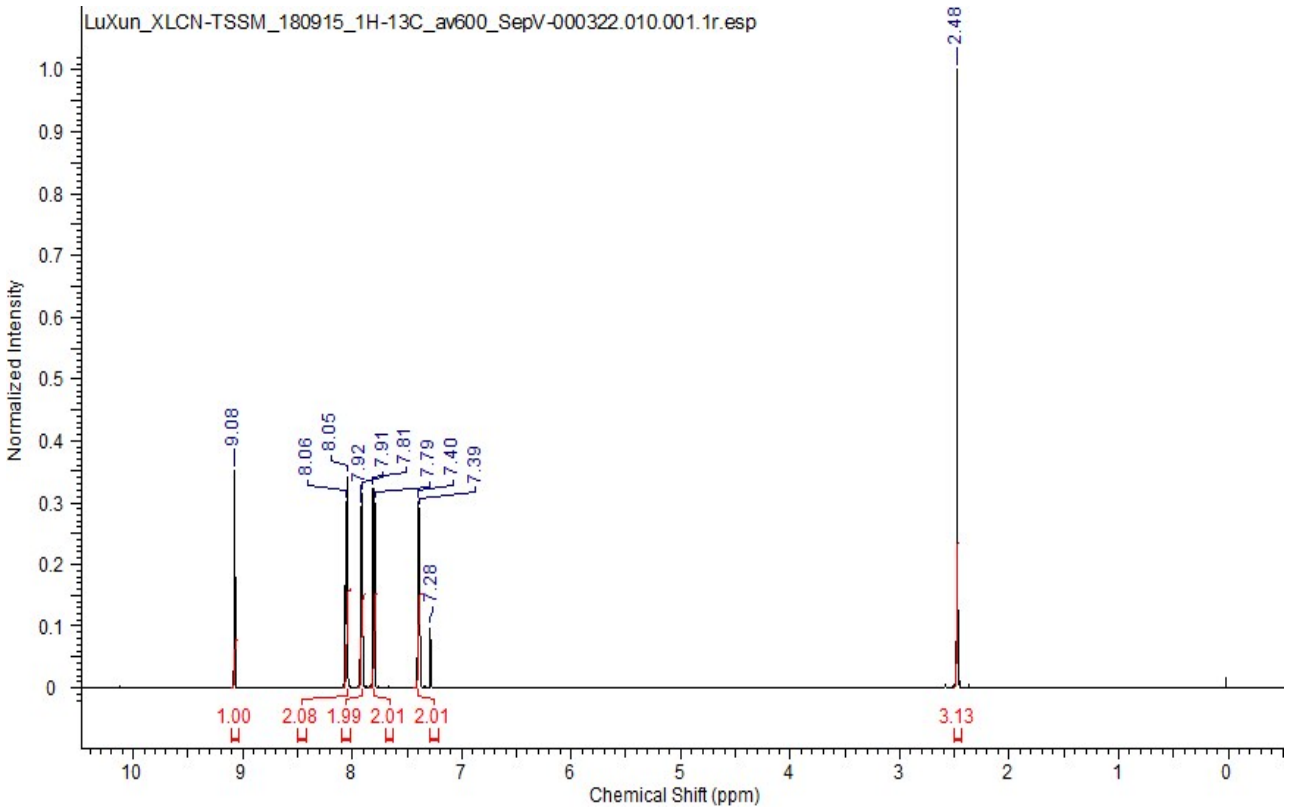

LuXun_XLCF3-SMTs_170915_1H-13C_av600_SepV-000310.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
9.10
8.08
8.06
7.93
7.92
7.78
7.77
7.40
7.39
7.28
2.48
1.00
2.07
1.99
2.04
2.02
3.14

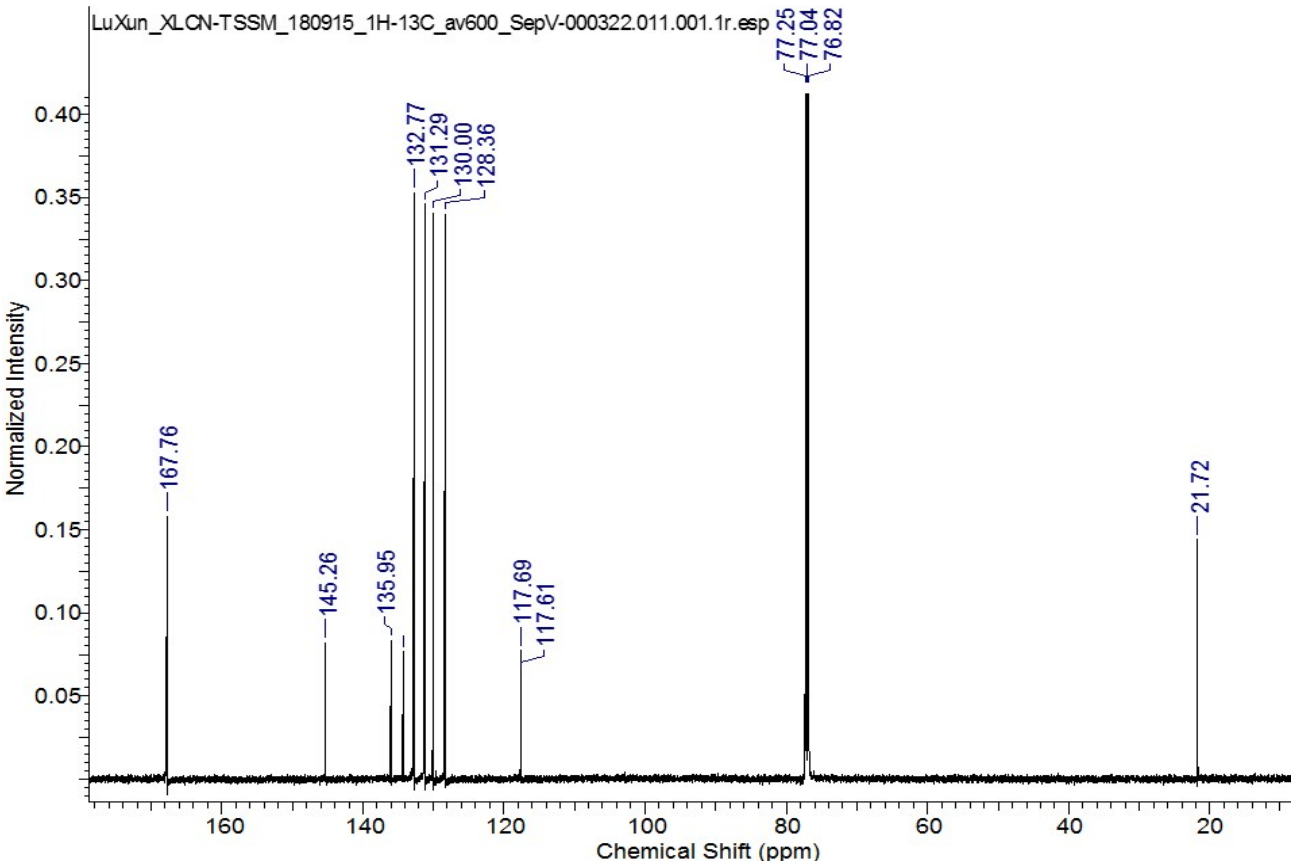

LuXun_XLCF3-SMTs_170915_1H-13C_av600_SepV-000310.011.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
168.37
145.08
135.71
135.39
134.54
131.35
129.95
128.30
126.12
126.09
124.23
122.42
120.62
77.33
77.02
76.81
21.70

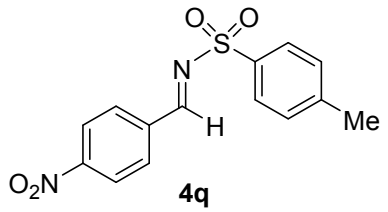

LuXun_XLCF3-Ts-SM_120516_19F_pr500_MayVI-00442.010.001.1r.esp
-63.34
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
-58
-59
-60
-61
-62
-63
-64
-65
-66
-67
Chemical Shift (ppm)


O
O
S
N
H
Me
NC

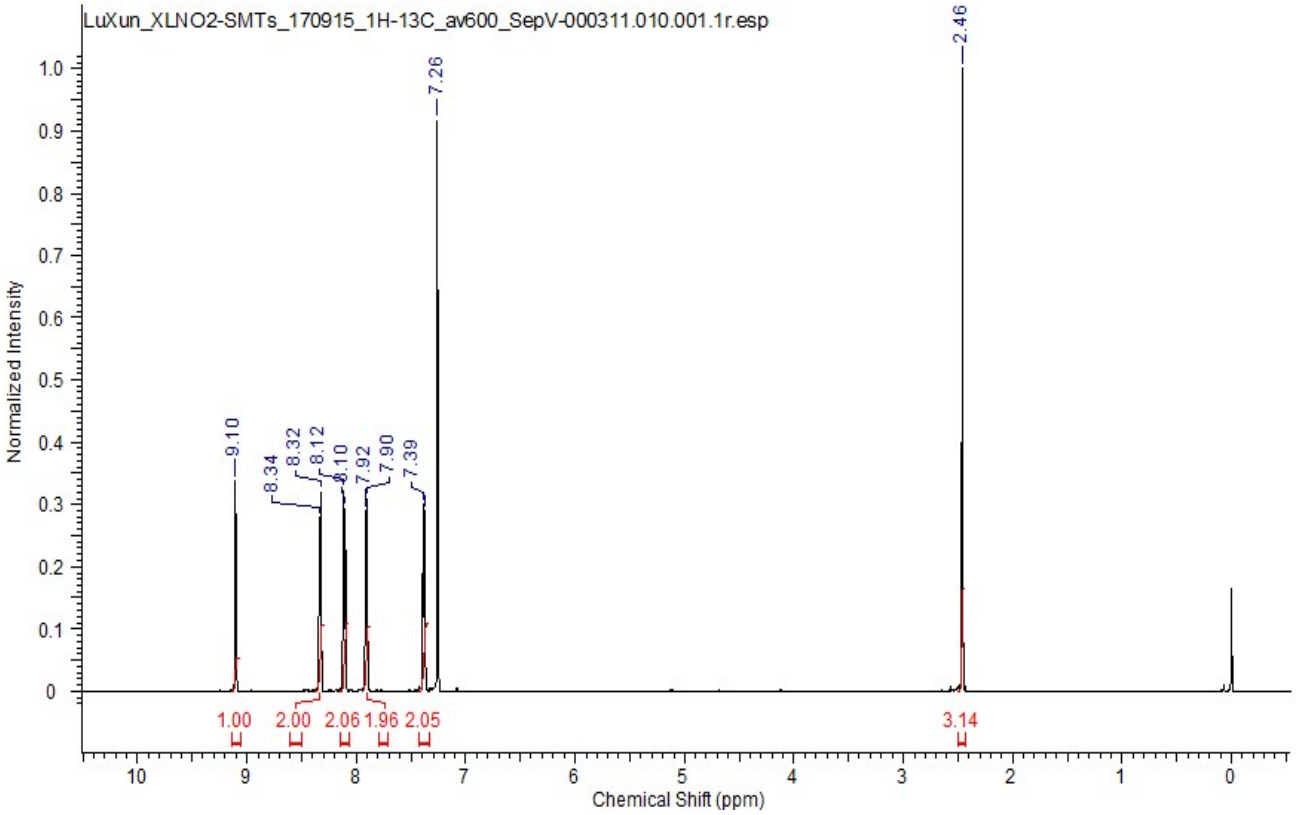
4p

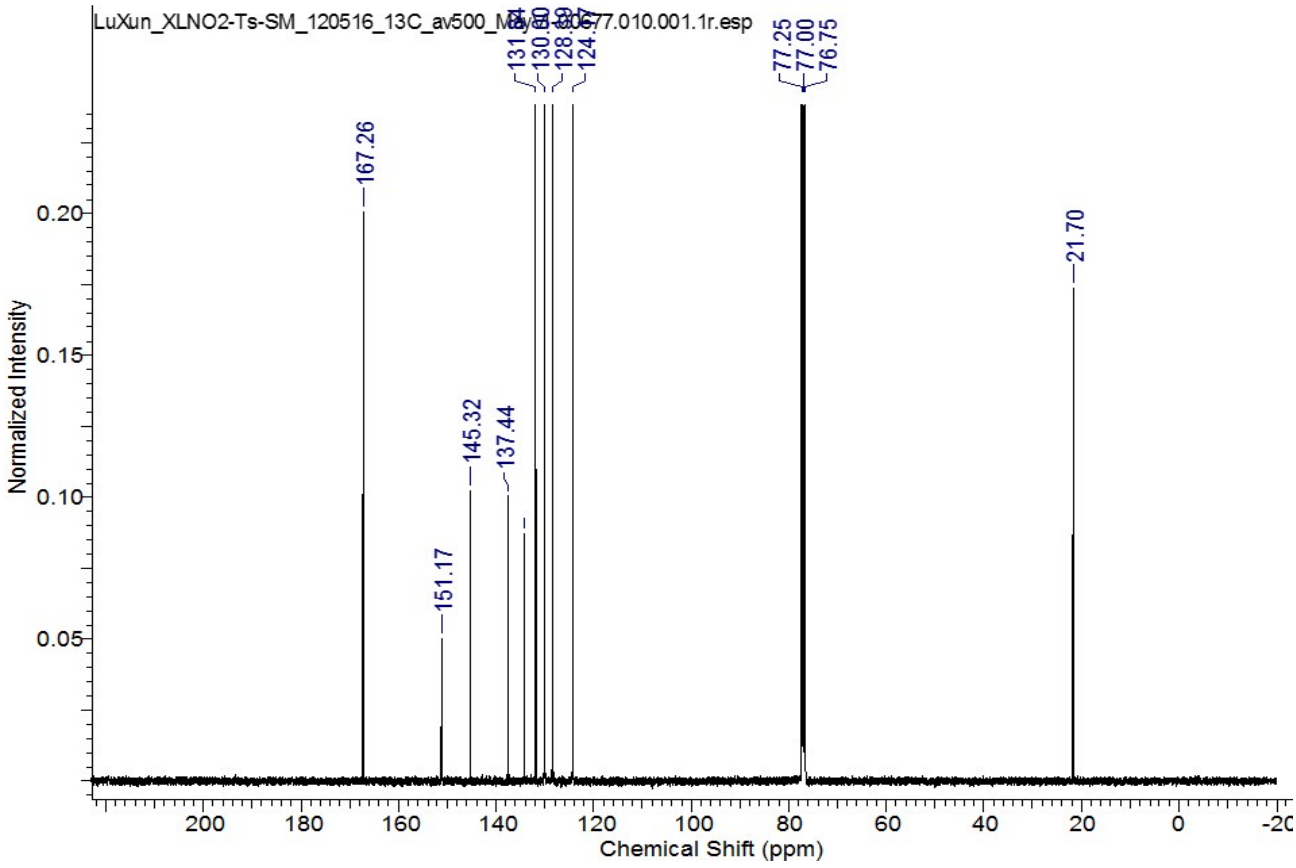

LuXun_XLCN-TSSM_180915_1H-13C_av600_SepV-000322.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
9.08
8.06
8.05
7.92
7.91
7.81
7.79
7.40
7.39
7.28
2.48
1.00
2.08
1.99
2.01
2.01
3.13

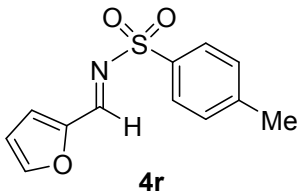

LuXun_XLCN-TSSM_180915_1H-13C_av600_SepV-000322.011.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
167.76
145.26
135.95
132.77
131.29
130.00
128.36
117.69
117.61
77.25
77.04
76.82
21.72


O
O
S
N
H
Me
O_2N

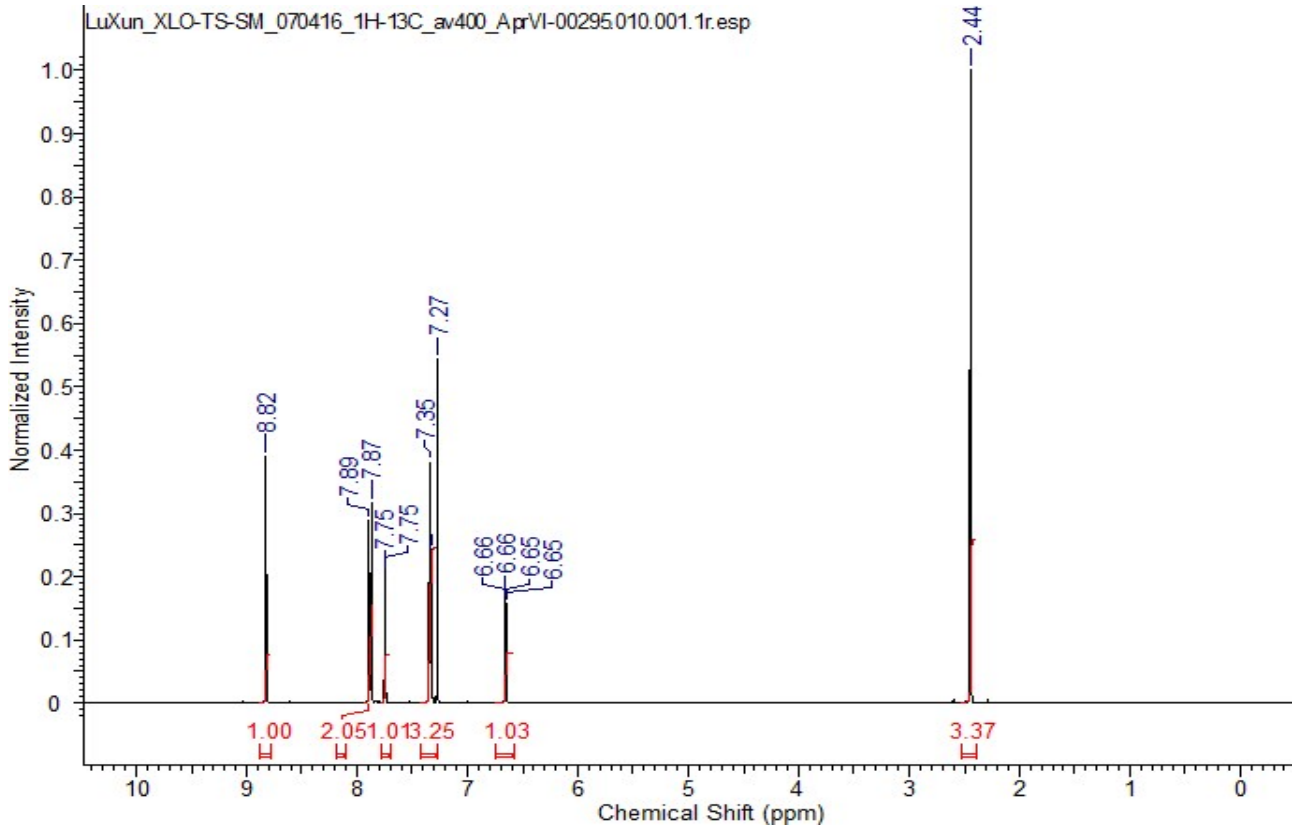
4q

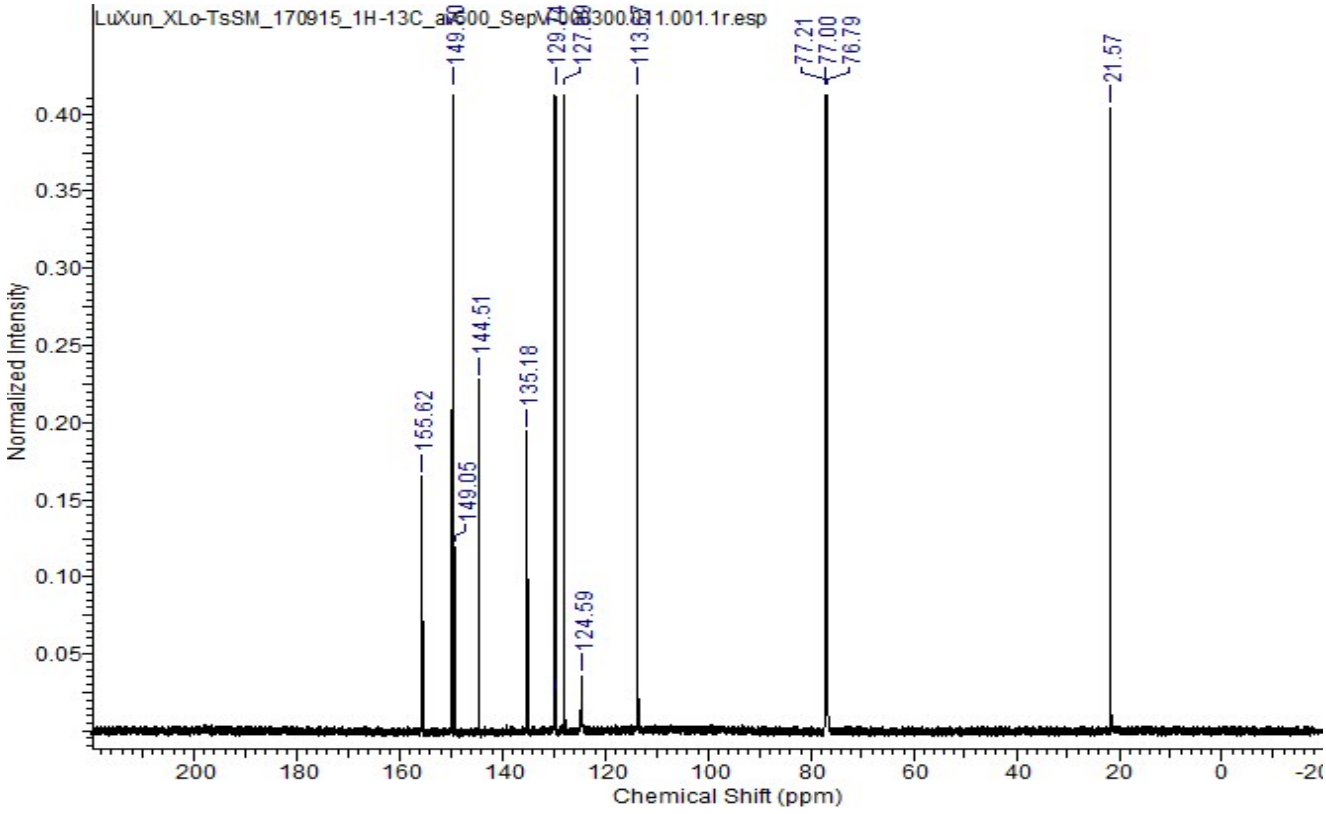

LuXun_XLNO2-SMTs_170915_1H-13C_av600_SepV-000311.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
9.10
8.34
8.32
8.12
8.10
7.92
7.90
7.39
7.26
2.46
1.00
2.00
2.06
1.96
2.05
3.14

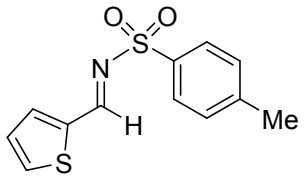

LuXun_XLNO2-Ts-SM_120516_13C_av500_MeOD-000677.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
167.26
151.17
145.32
137.44
77.25
77.00
76.75
21.70


O
O
S
N
H
O
Me

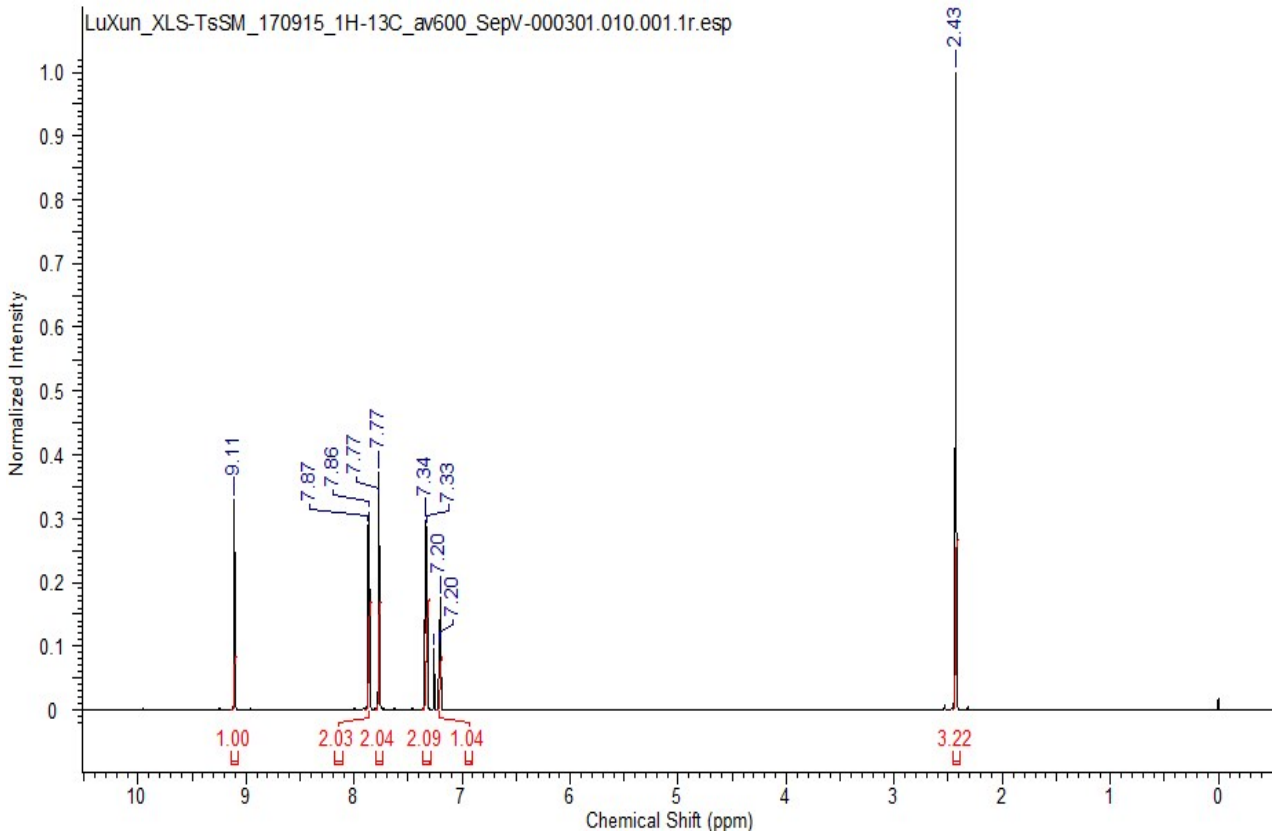
4r

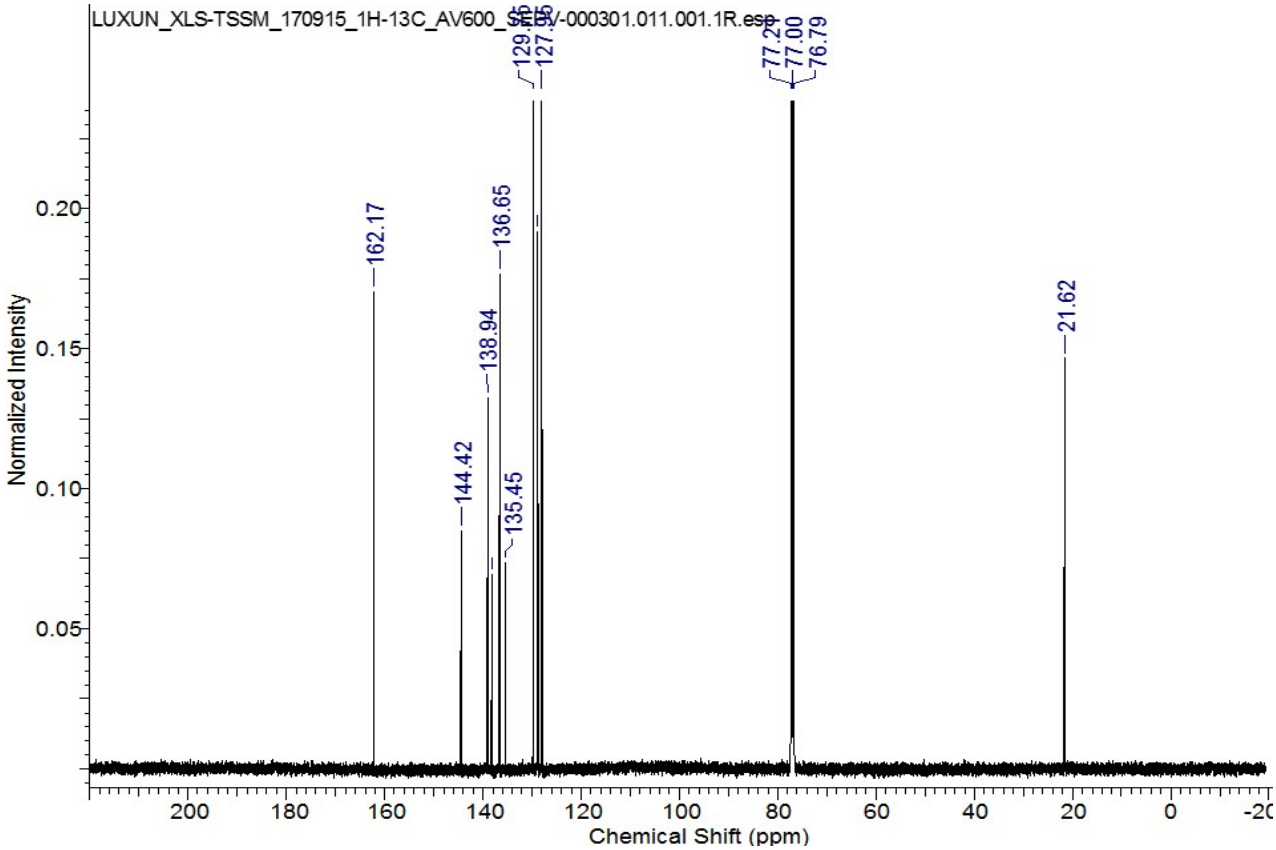

LuXun_XLO-TS-SM_070416_1H-13C_av400_AprVI-00295.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
8.82
7.89
7.87
7.75
7.75
7.35
7.27
6.66
6.66
6.65
6.65
2.44
1.00
2.05
1.01
3.25
1.03
3.37

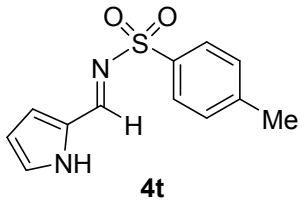

Normalized Intensity
Chemical Shift (ppm)
155.62
149.05
144.51
135.18
124.59
77.21
77.00
76.79
21.57


O
O
S
N
H
Me
S

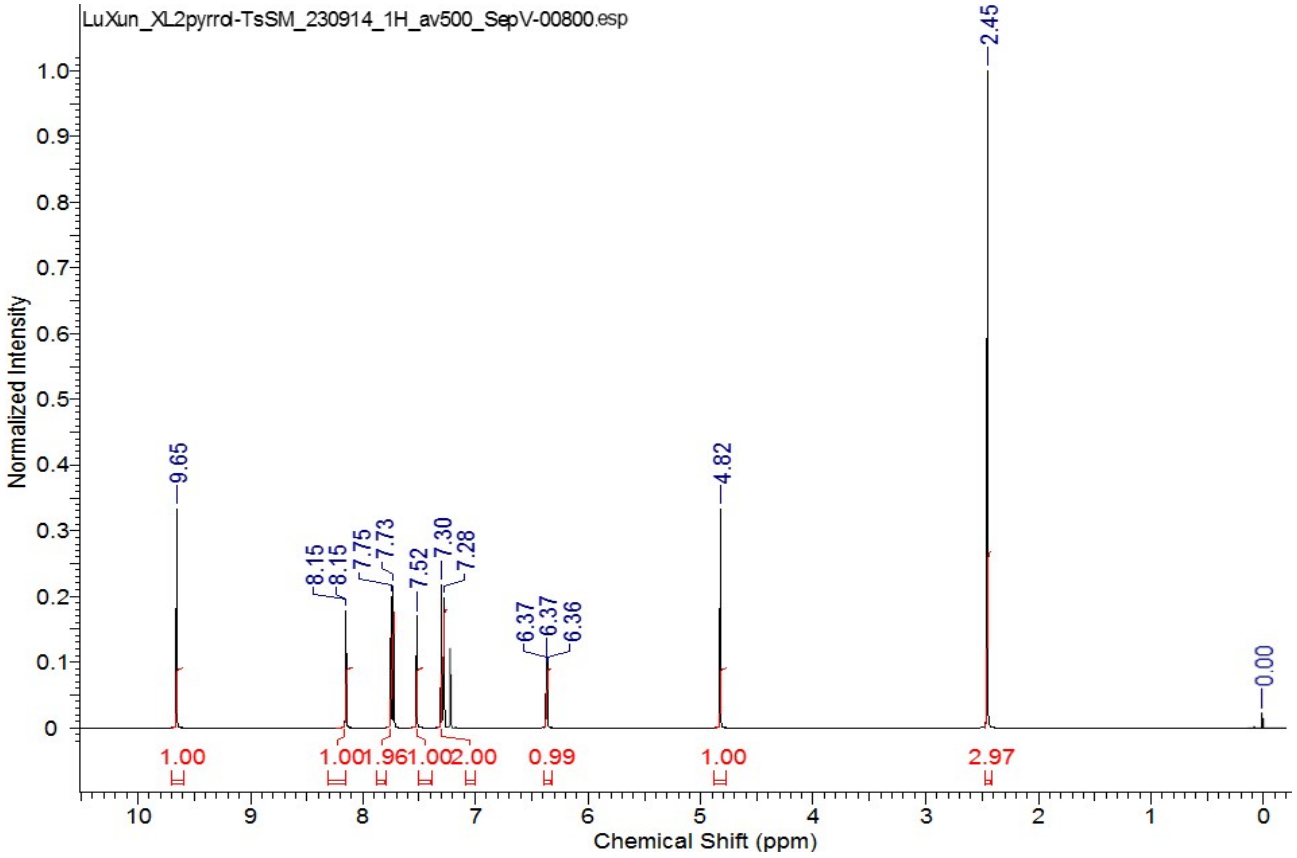
4s

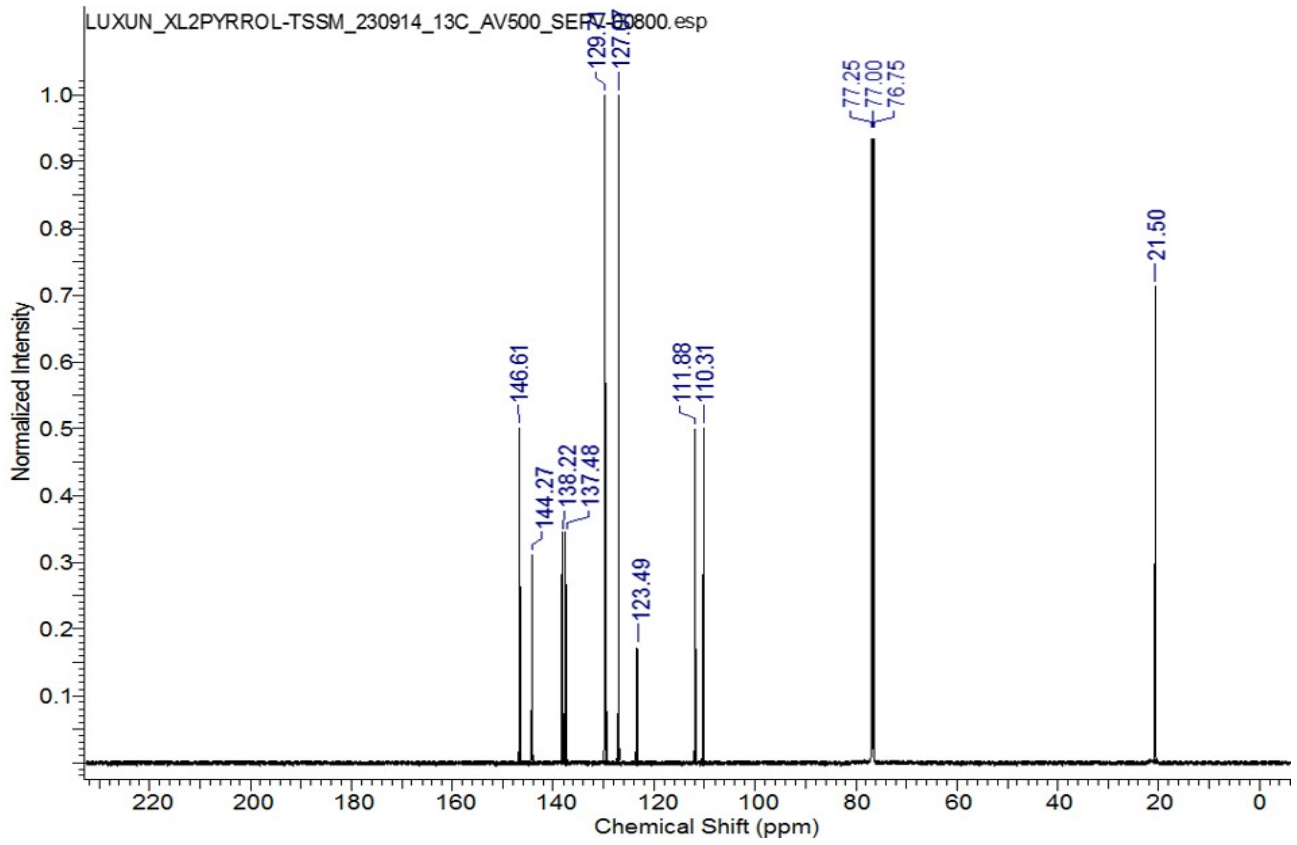

LuXun_XLS-TsSM_170915_1H-13C_av600_SepV-000301.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
9.11
7.87
7.86
7.77
7.77
7.34
7.33
7.20
7.20
2.43
1.00
2.03
2.04
2.09
1.04
3.22

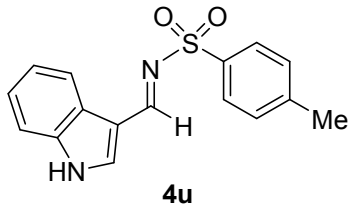

LUXUN_XLS-TSSM_170915_1H-13C_AV600_SepV-000301.011.001.1R.esp
Normalized Intensity
Chemical Shift (ppm)
162.17
144.42
138.94
136.65
135.45
129.46
127.55
77.20
77.00
76.79
21.62


O
O
S
N
H
Me
NH

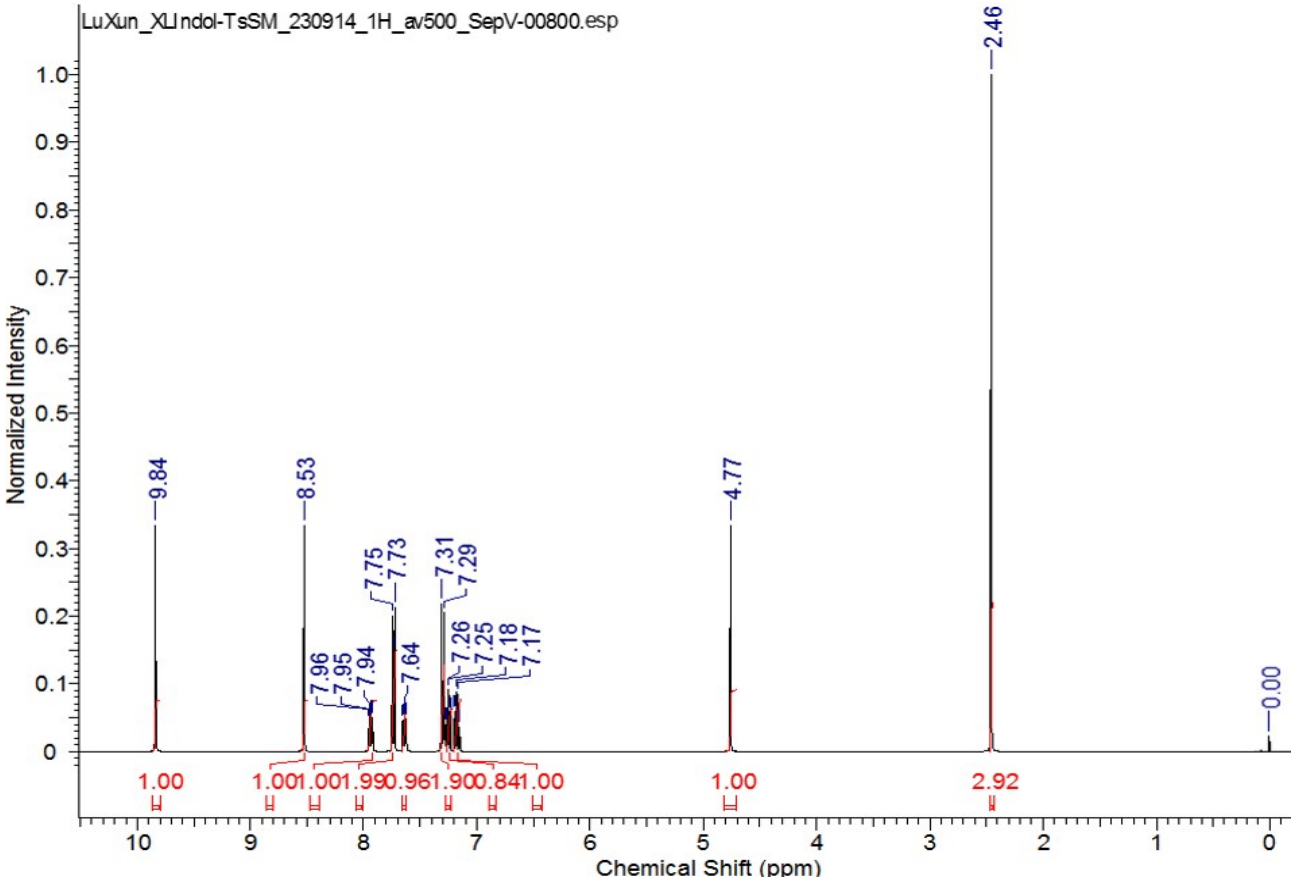
4t

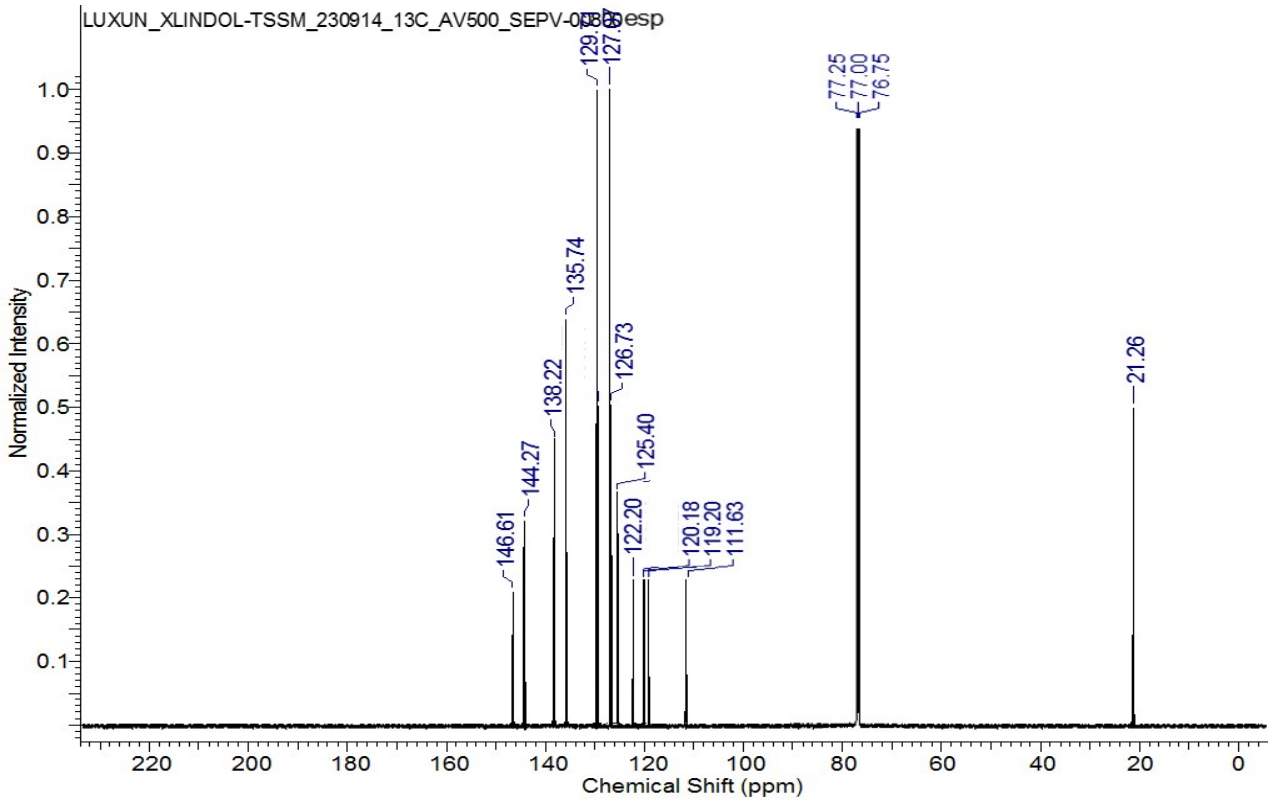

LuXun_XL2pyrrol-TsSM_230914_1H_av500_SepV-00800.esp
Normalized Intensity
Chemical Shift (ppm)
9.65
8.15
8.15
7.75
7.73
7.52
7.30
7.28
6.37
6.37
6.36
4.82
2.45
0.00
1.00
1.00
1.96
1.00
2.00
0.99
1.00
2.97

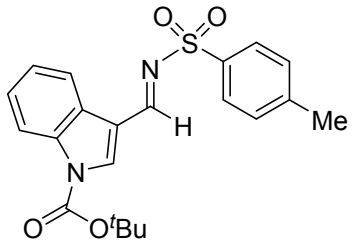

LUXUN_XL2PYRROL-TSSM_230914_13C_AV500_SEPV-00800.esp
Normalized Intensity
Chemical Shift (ppm)
129.47
127.87
77.25
77.00
76.75
146.61
144.27
138.22
137.48
123.49
111.88
110.31
21.50


O
O
S
N
H
Me
HN

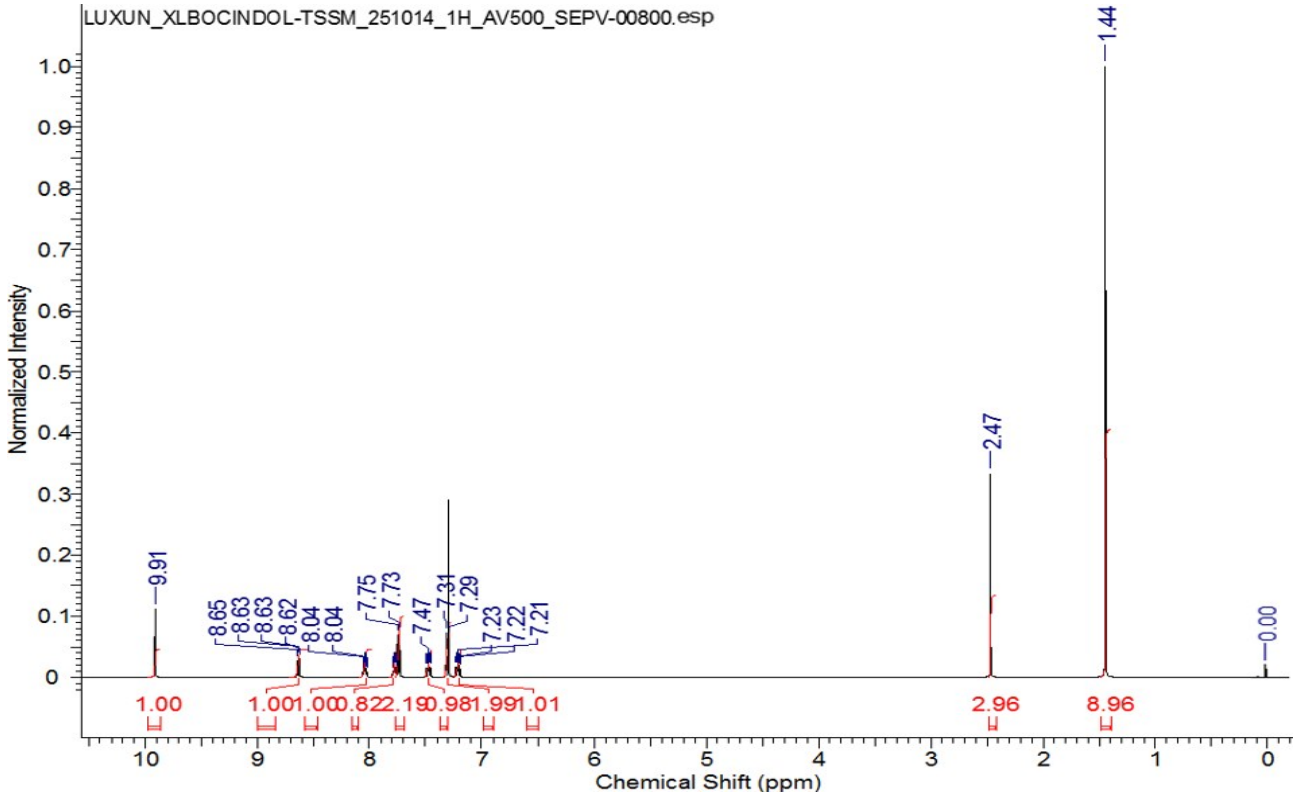
4u

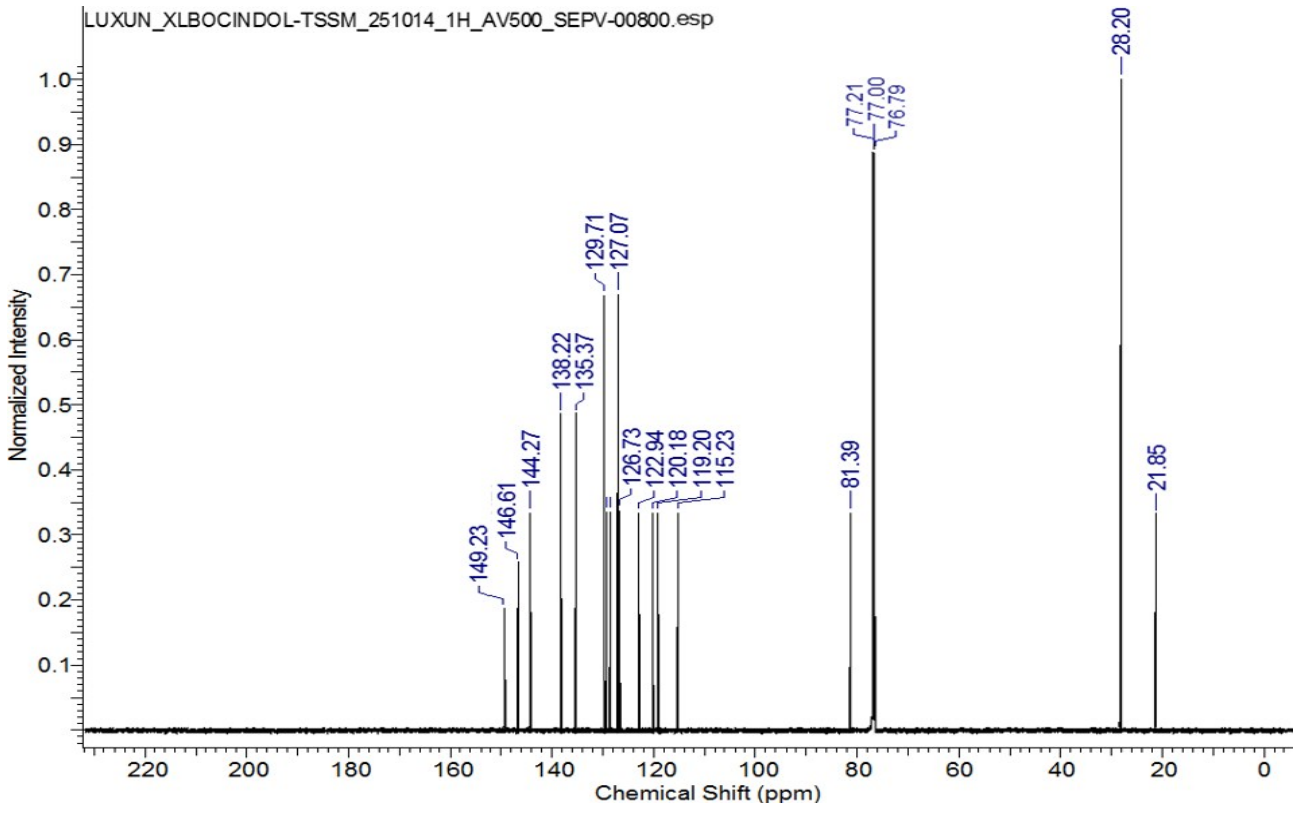

LuXun_XLIndol-TsSM_230914_1H_av500_SepV-00800.esp
Normalized Intensity
Chemical Shift (ppm)
9.84
8.53
7.96
7.95
7.94
7.75
7.73
7.64
7.31
7.29
7.26
7.25
7.18
7.17
4.77
2.46
0.00
1.00
1.00
1.00
1.99
0.96
1.90
0.84
1.00
1.00
2.92

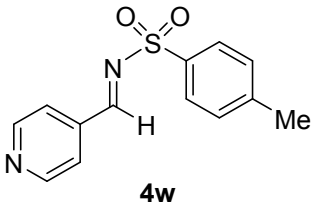

LUXUN_XLINDOL-TSSM_230914_13C_AV500_SEPV-00800.esp
Normalized Intensity
Chemical Shift (ppm)
146.61
144.27
138.22
135.74
129.68
127.68
126.73
125.40
122.20
120.18
119.20
111.63
77.25
77.00
76.75
21.26


O
O
S
N
H
Me
N
O
O
tBu

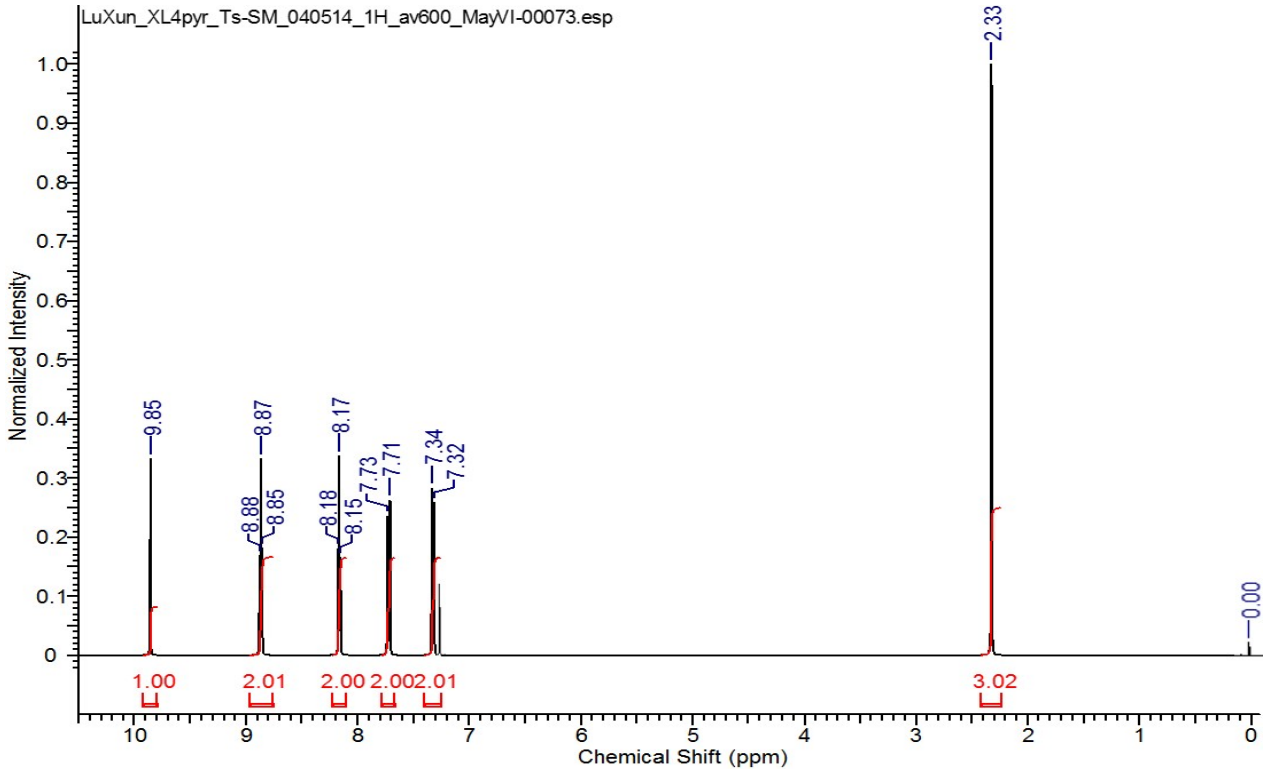
4v

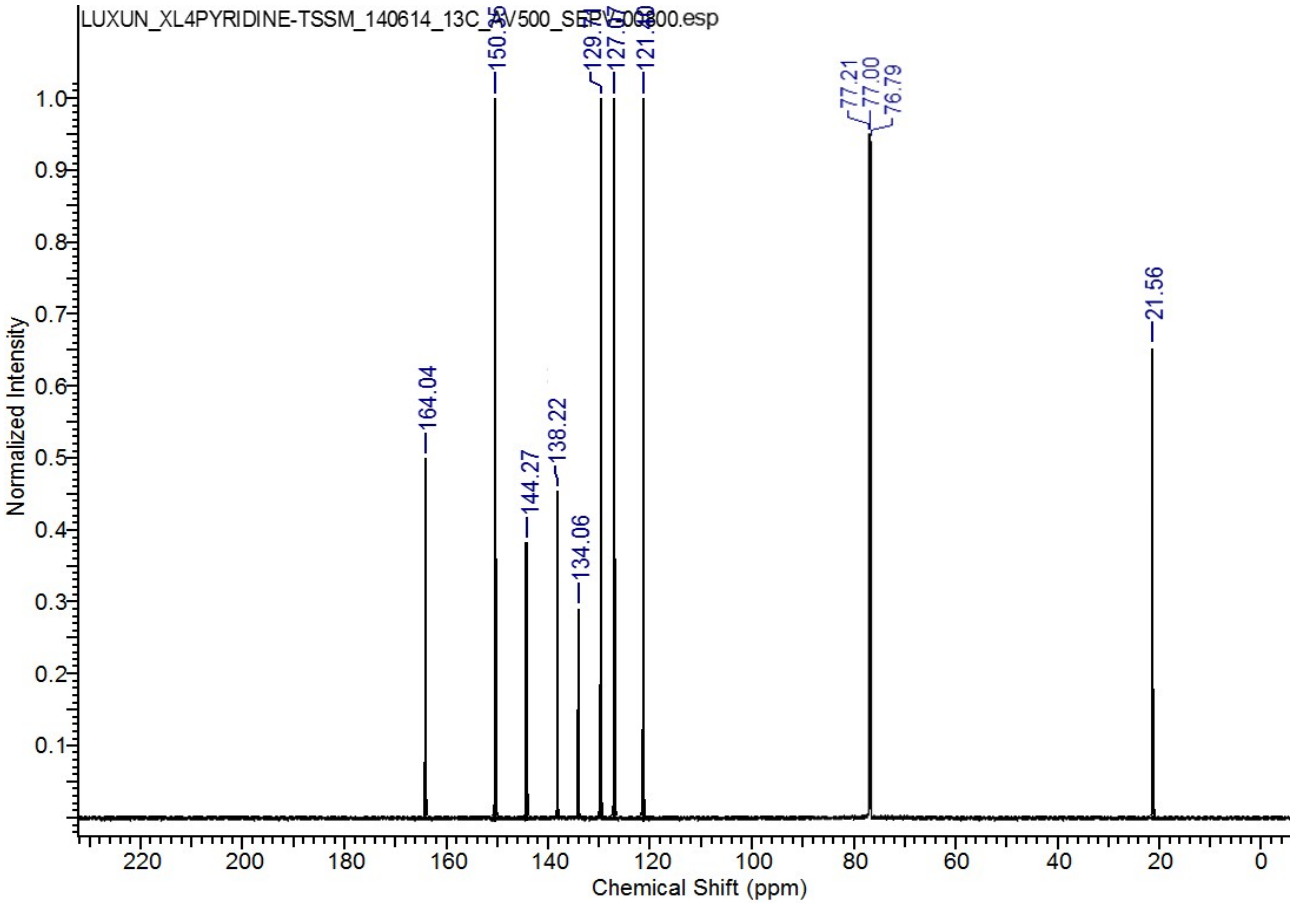

LUXUN_XLBOCINDOL-TSSM_251014_1H_AV500_SEPV-00800.esp
Normalized Intensity
Chemical Shift (ppm)
9.91
8.65
8.63
8.63
8.62
8.04
8.04
7.75
7.73
7.47
7.31
7.29
7.23
7.22
7.21
2.47
1.44
0.00
1.00
1.00
1.00
0.82
2.19
0.98
1.99
1.01
2.96
8.96

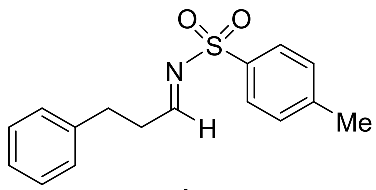

LUXUN_XLBOCINDOL-TSSM_251014_1H_AV500_SEPV-00800.esp
Normalized Intensity
Chemical Shift (ppm)
149.23
146.61
144.27
138.22
135.37
129.71
127.07
126.73
122.94
120.18
119.20
115.23
81.39
77.21
77.00
76.79
28.20
21.85


O
O
S
N
H
Me
N

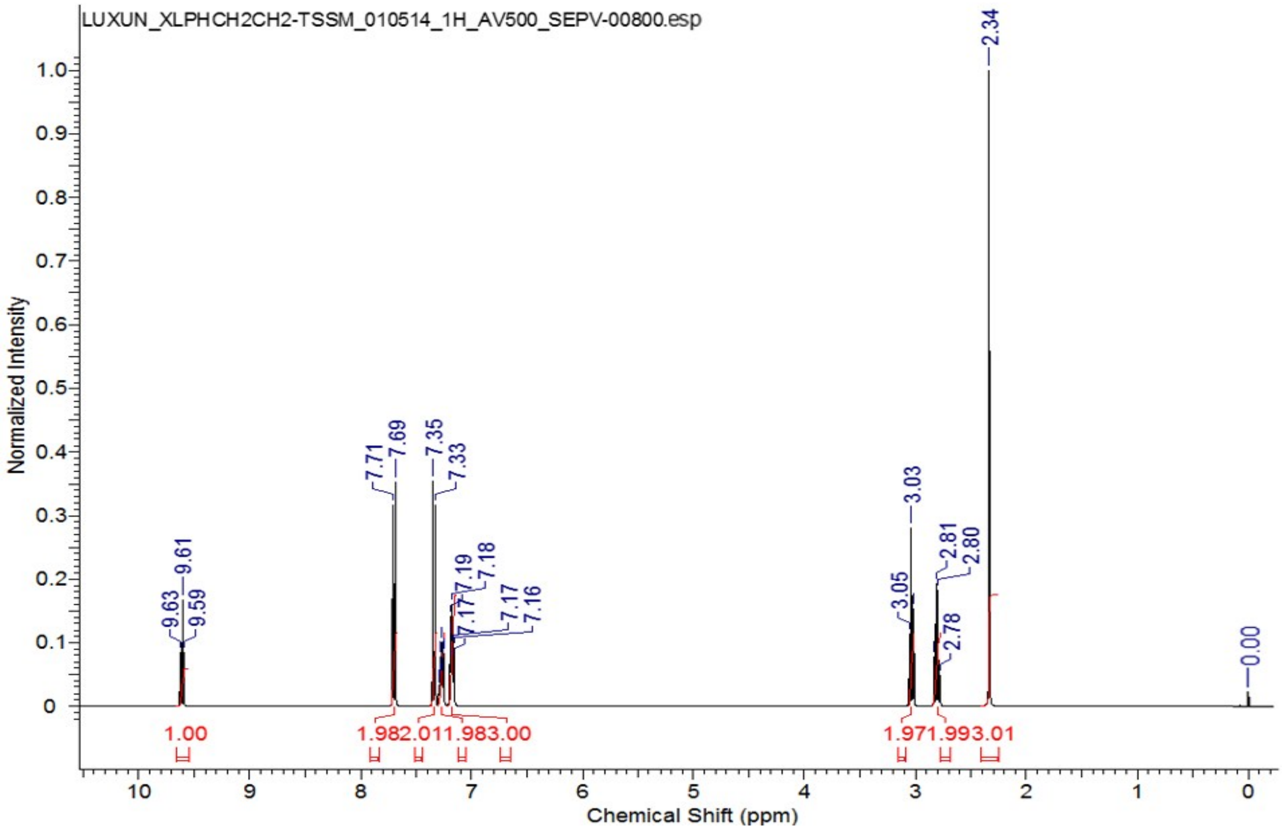
4w

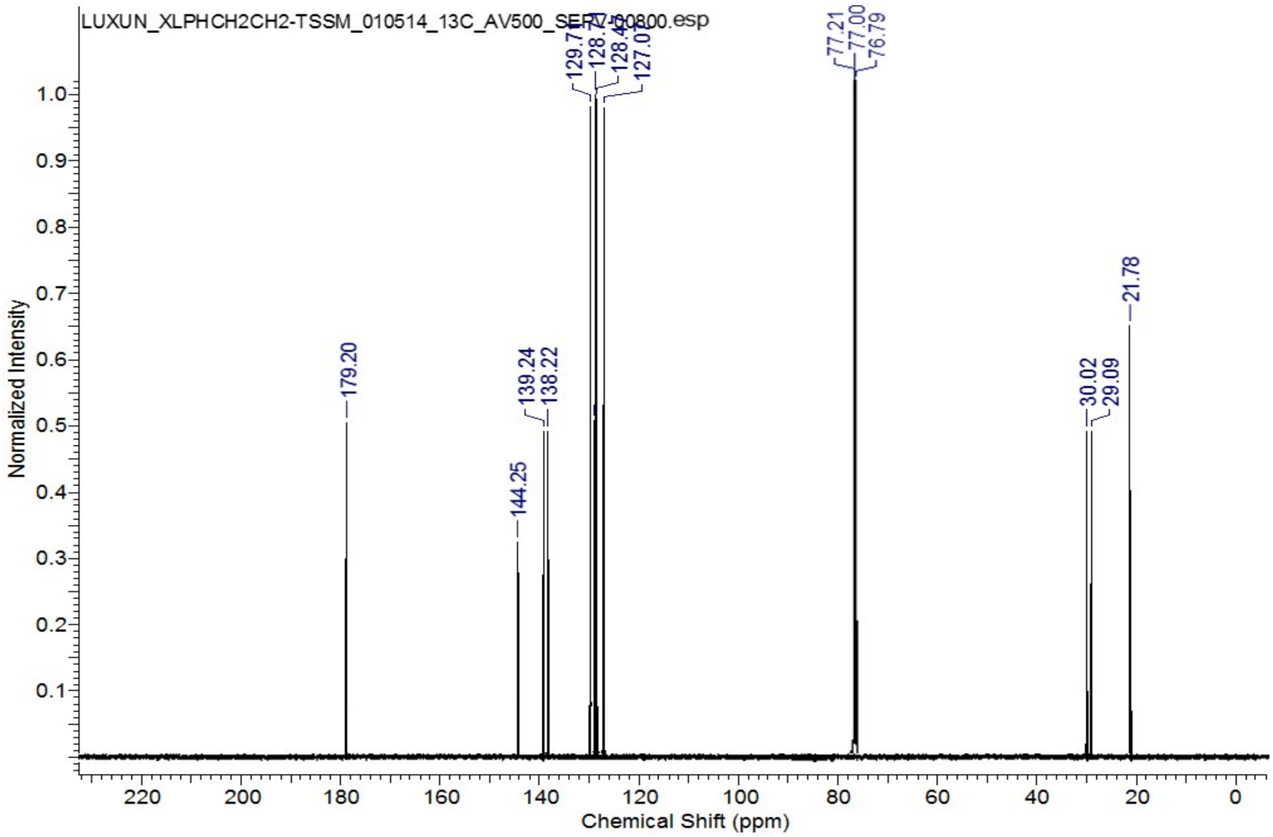

LuXun_XL4pyr_Ts-SM_040514_1H_av600_MayVI-00073.esp
Normalized Intensity
Chemical Shift (ppm)
9.85
8.88
8.87
8.85
8.18
8.17
8.15
7.73
7.71
7.34
7.32
2.33
0.00
1.00
2.01
2.00
2.00
2.01
3.02

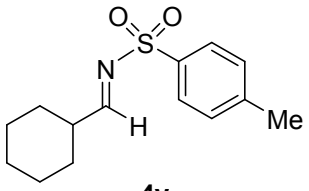

LUXUN_XL4PYRIDINE-TSSM_140614_13C_AV500_SEQ
Normalized Intensity
Chemical Shift (ppm)
164.04
150.35
144.27
138.22
134.06
129.47
127.07
121.40
77.21
77.00
76.79
21.56


O
O
S
N
H
Me

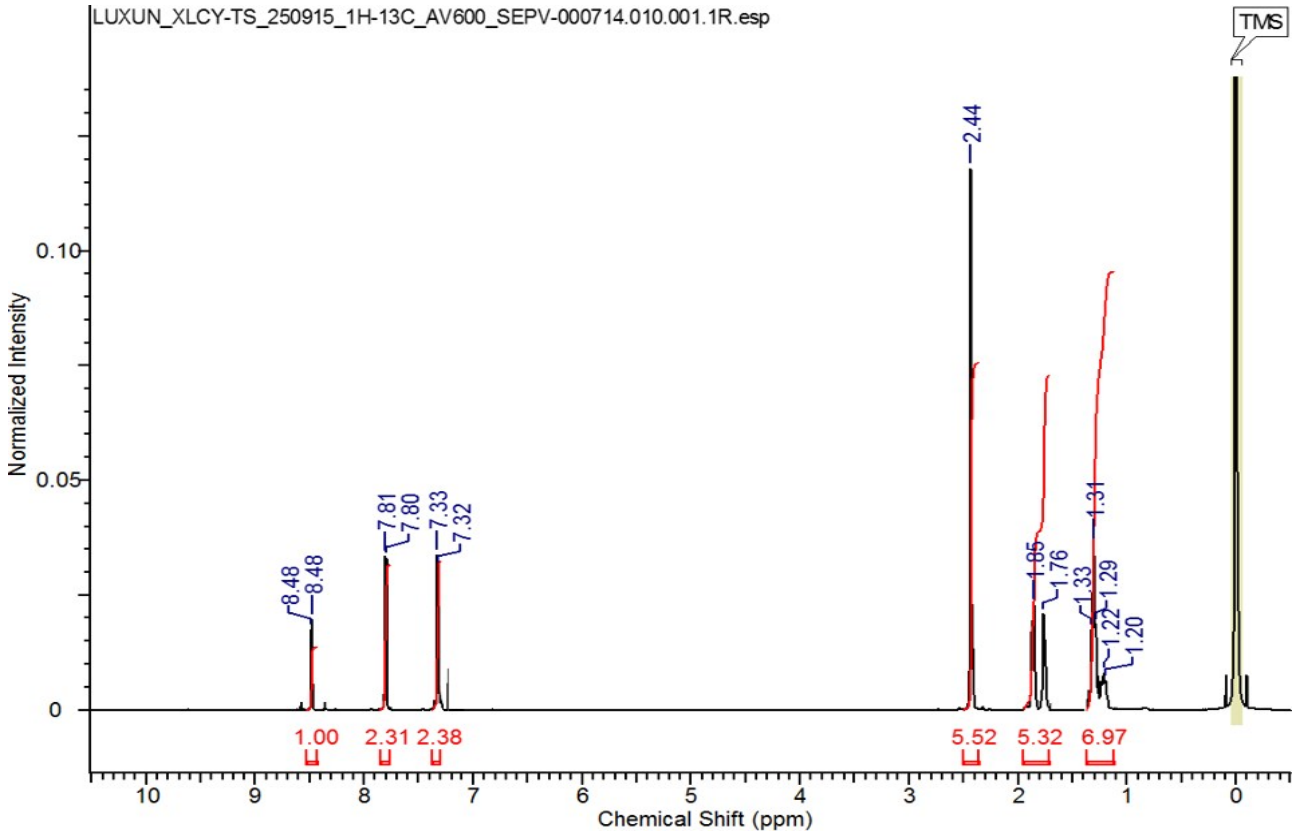
4x

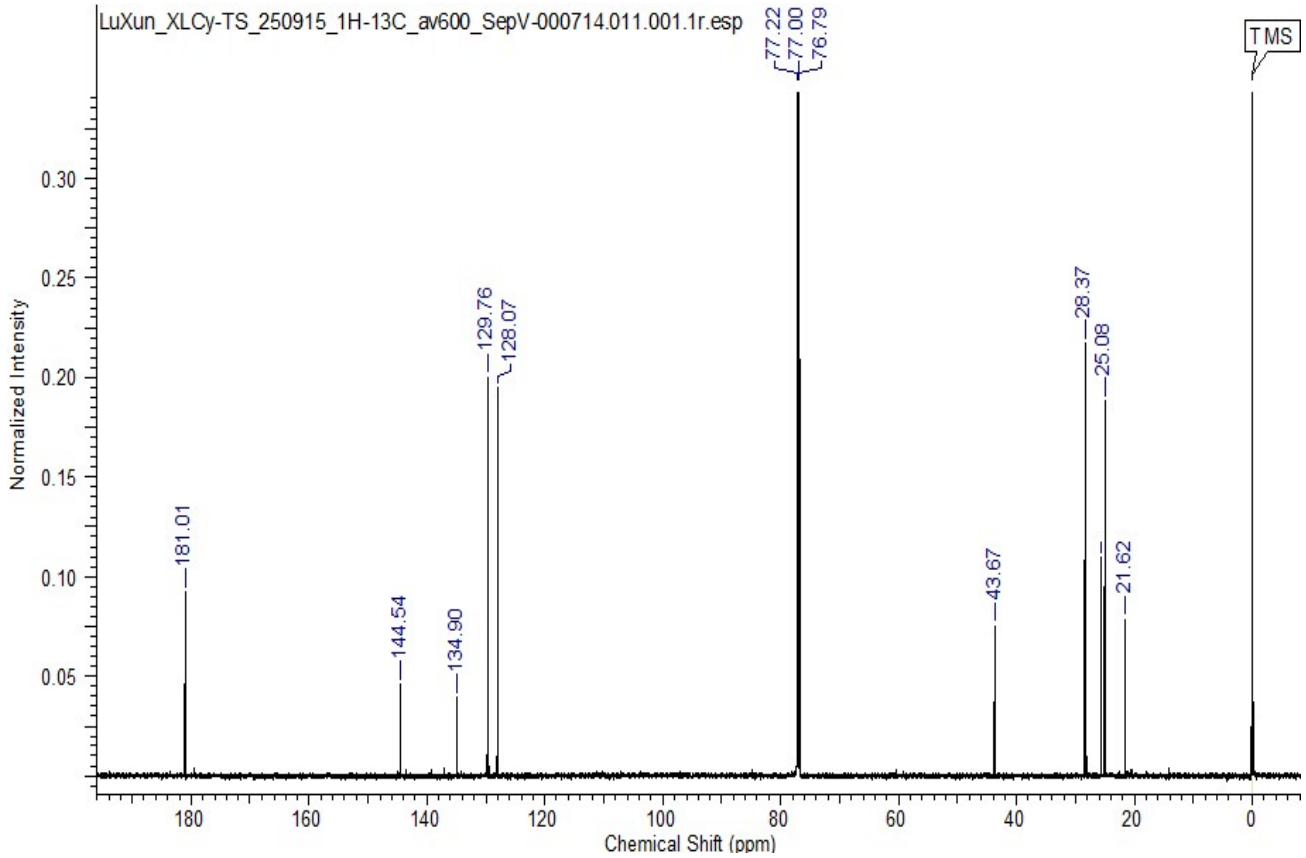

LUXUN_XLPHCH2CH2-TSSM_010514_1H_AV500_SEPV-00800.esp
Normalized Intensity
Chemical Shift (ppm)

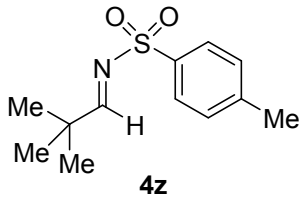

LUXUN_XLPHCH2CH2-TSSM_010514_13C_AV500_SEPV-00800.esp
Normalized Intensity
Chemical Shift (ppm)


O
O
S
N
H
Me

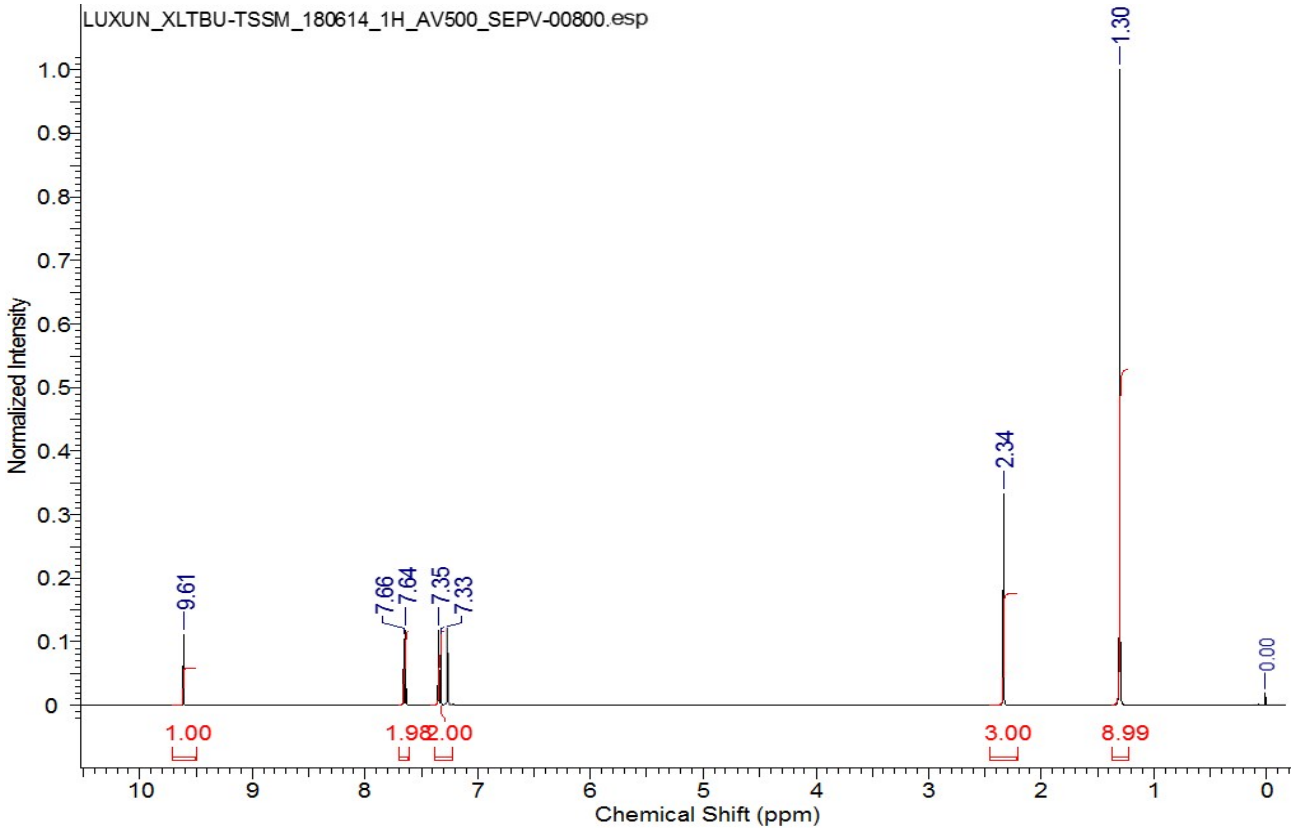
4y

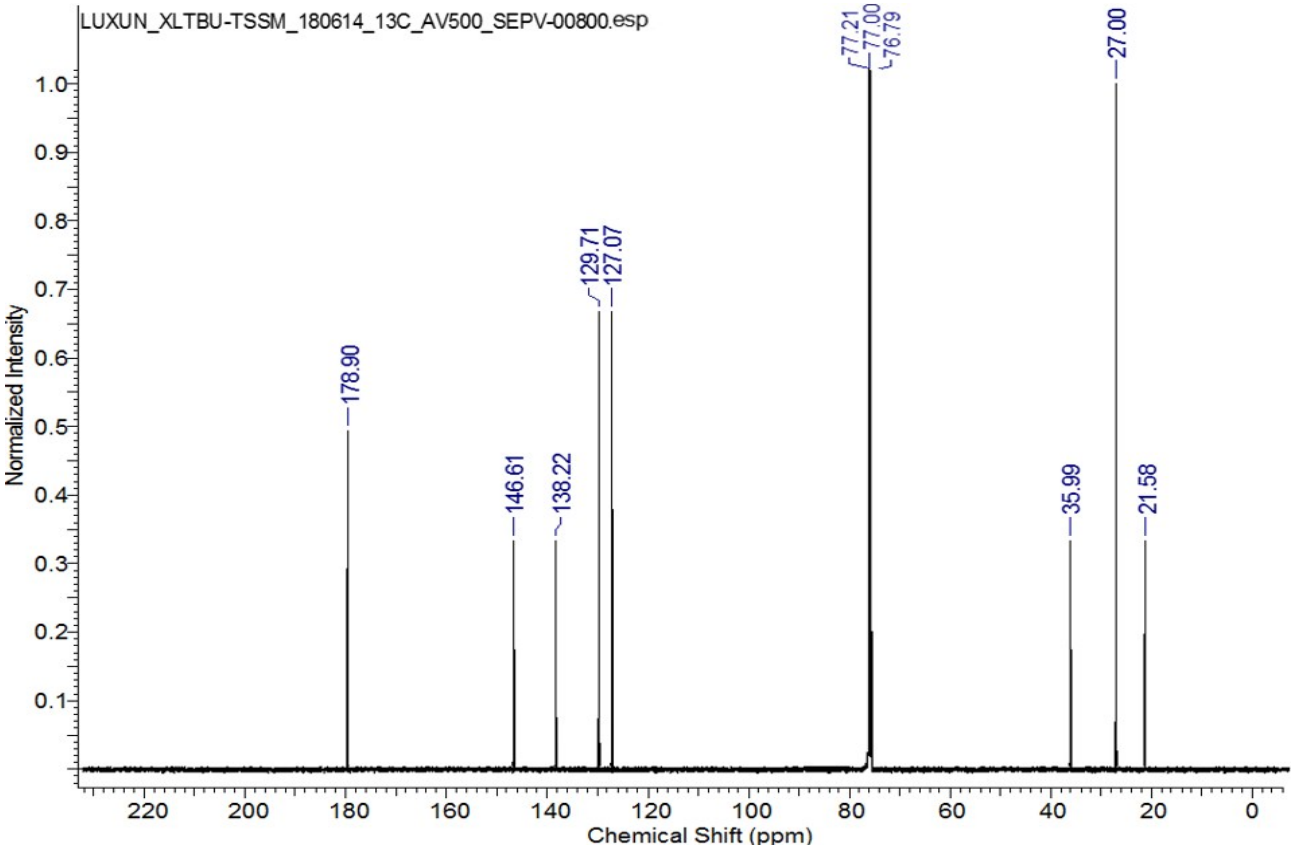

LUXUN_XLCY-TS_250915_1H-13C_AV600_SEPV-000714.010.001.1R.esp
TMS
2.44
7.81
7.80
7.33
7.32
8.48
8.48
1.85
1.76
1.33
1.31
1.29
1.22
1.20
1.00
2.31
2.38
5.52
5.32
6.97
Normalized Intensity
Chemical Shift (ppm)

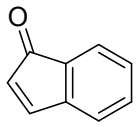

LuXun_XLCy-TS_250915_1H-13C_av600_SepV-000714.011.001.1r.esp
77.22
77.00
76.79
TMS
129.76
128.07
28.37
25.08
181.01
144.54
134.90
43.67
21.62
Normalized Intensity
Chemical Shift (ppm)


O
O
S
N
H
Me
Me
Me
Me

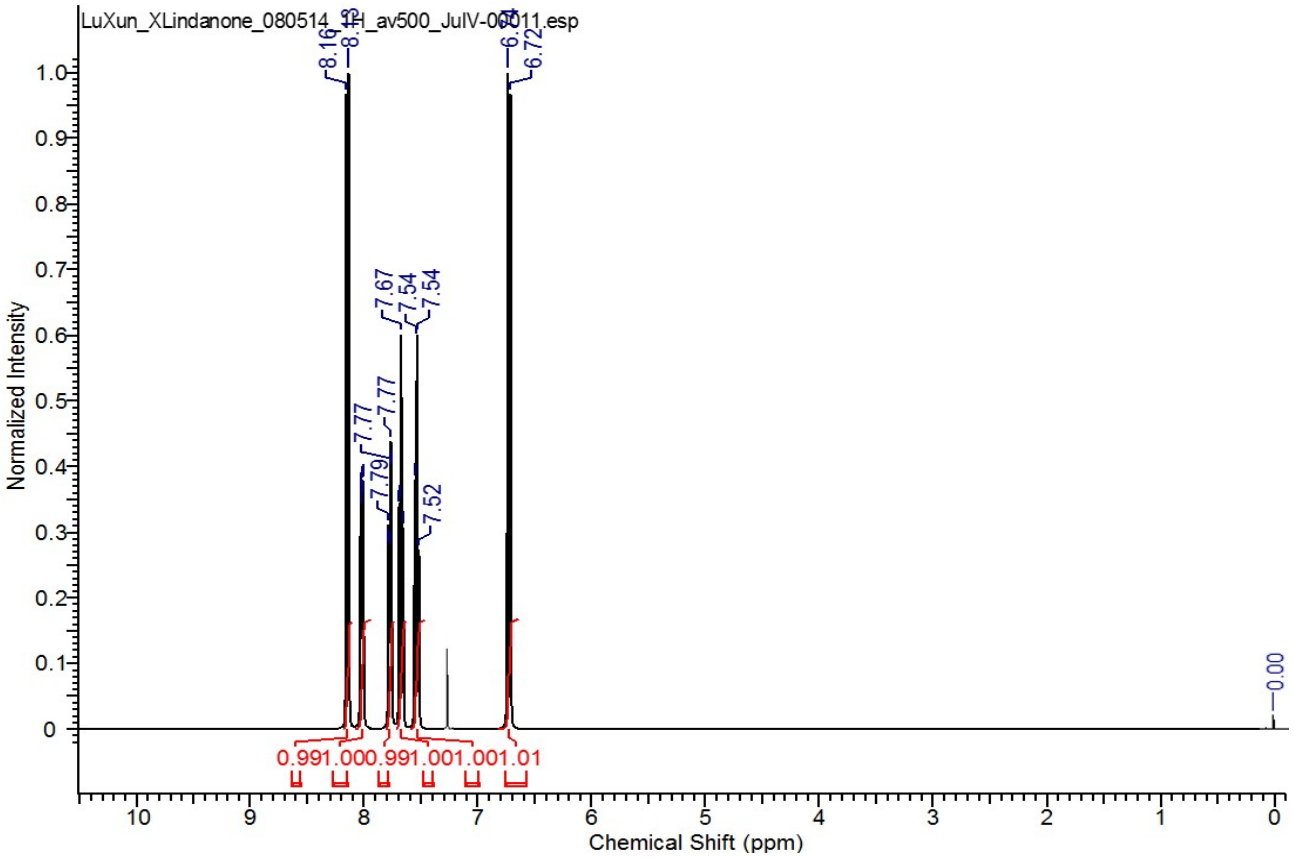
4z

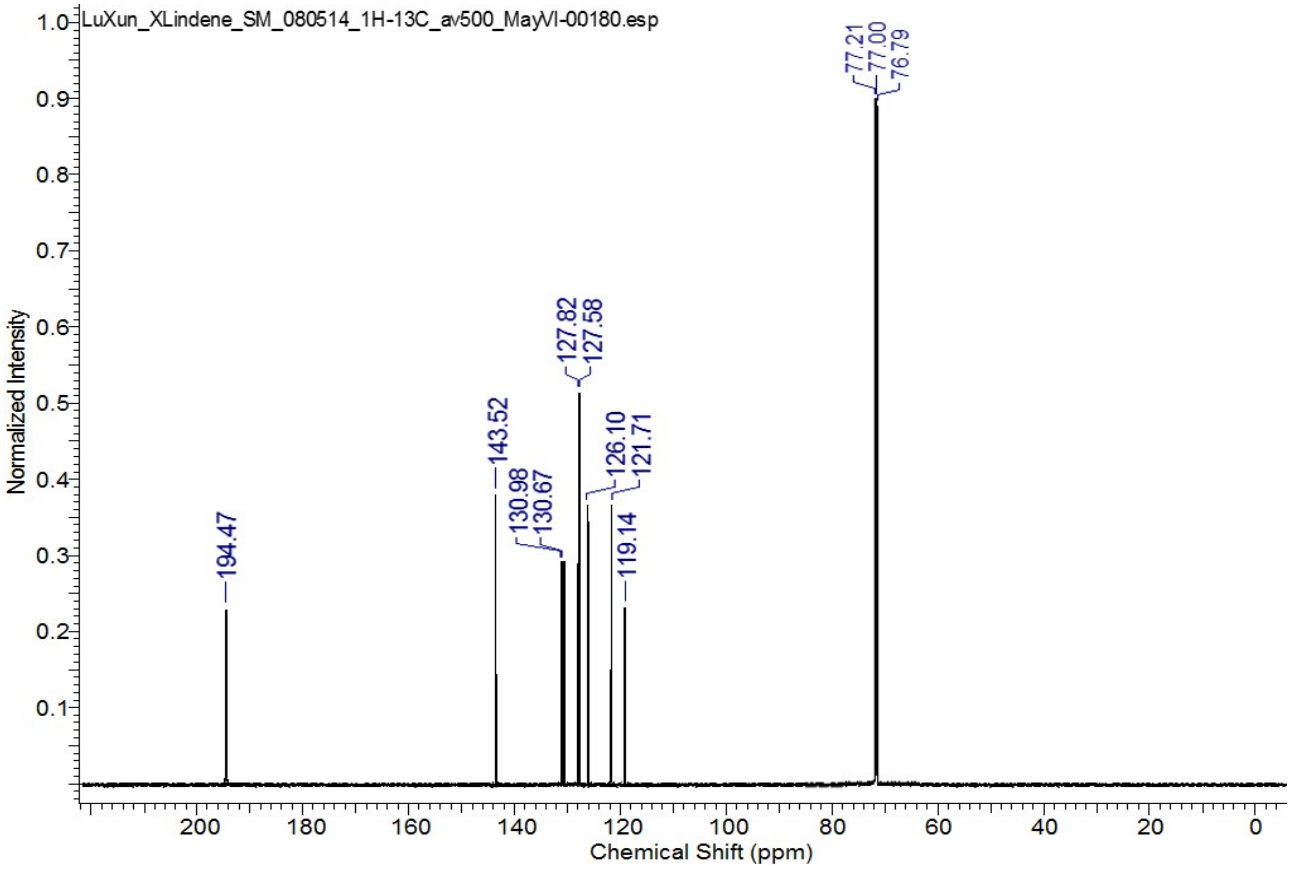

LUXUN_XLTBU-TSSM_180614_1H_AV500_SEPV-00800.esp
Normalized Intensity
Chemical Shift (ppm)
9.61
7.66
7.64
7.35
7.33
2.34
1.30
0.00
1.00
1.98
2.00
3.00
8.99

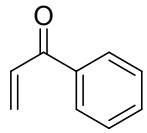

LUXUN_XLTBU-TSSM_180614_13C_AV500_SEPV-00800.esp
Normalized Intensity
Chemical Shift (ppm)
178.90
146.61
138.22
129.71
127.07
77.21
77.00
76.79
35.99
27.00
21.58



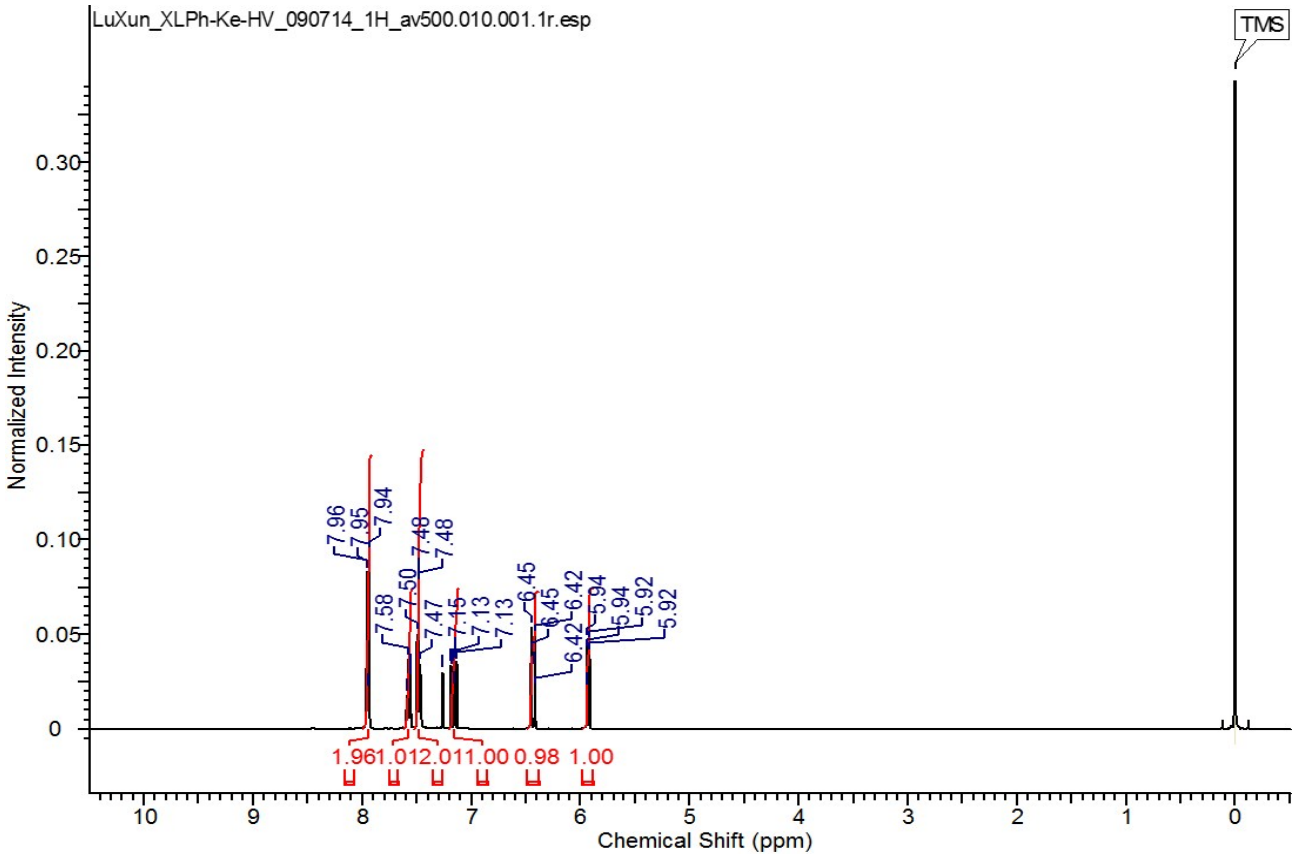
5b

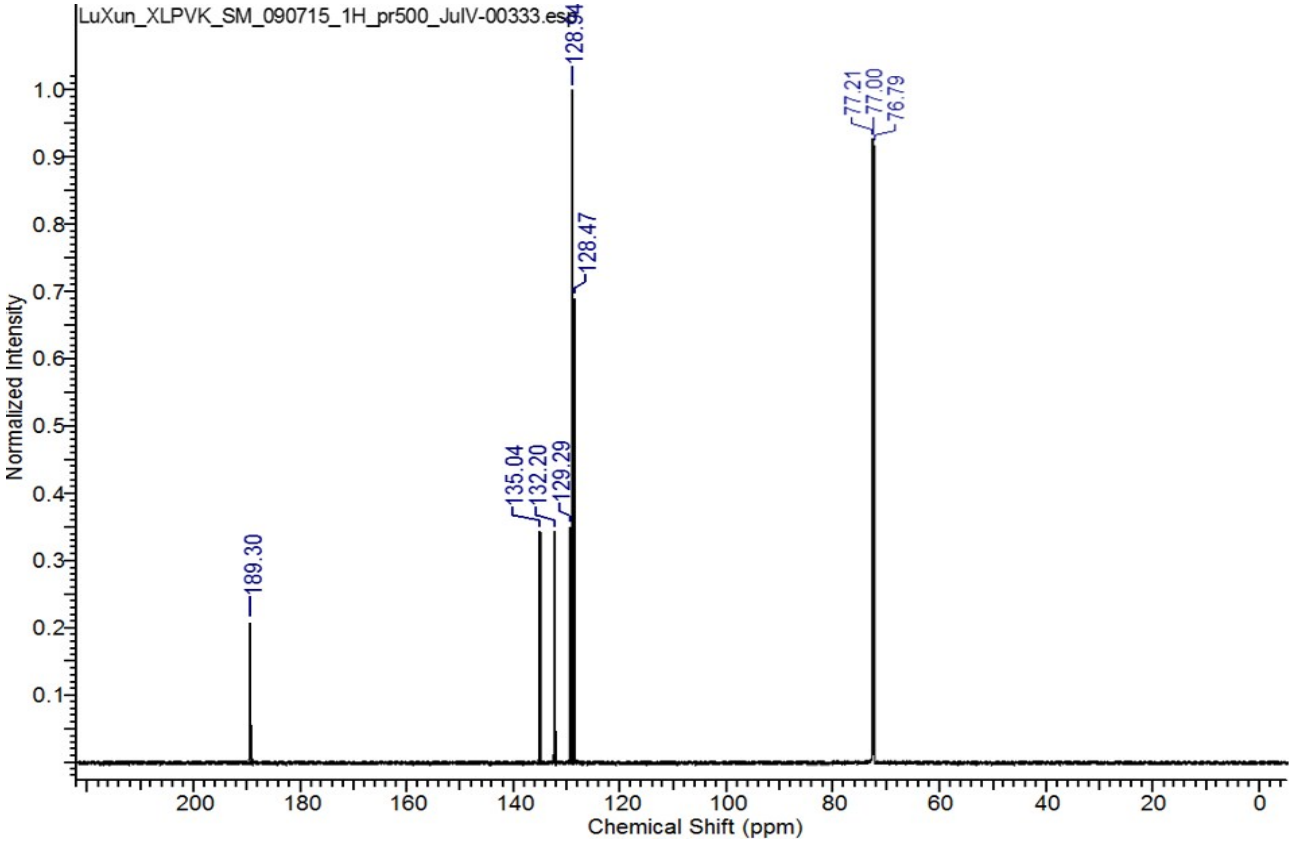

LuXun_XLindanone_080514_1H_av500_JulV-00011.esp
8.19
8.18
6.74
6.72
7.67
7.54
7.54
7.77
7.77
7.79
7.52
0.00
0.99 1.00 0.99 1.00 1.00 1.01
Normalized Intensity
Chemical Shift (ppm)

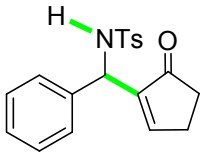

LuXun_XLindene_SM_080514_1H-13C_av500_MayVI-00180.esp
77.21
77.00
76.79
127.82
127.58
143.52
130.98
130.67
126.10
121.71
119.14
194.47
Normalized Intensity
Chemical Shift (ppm)



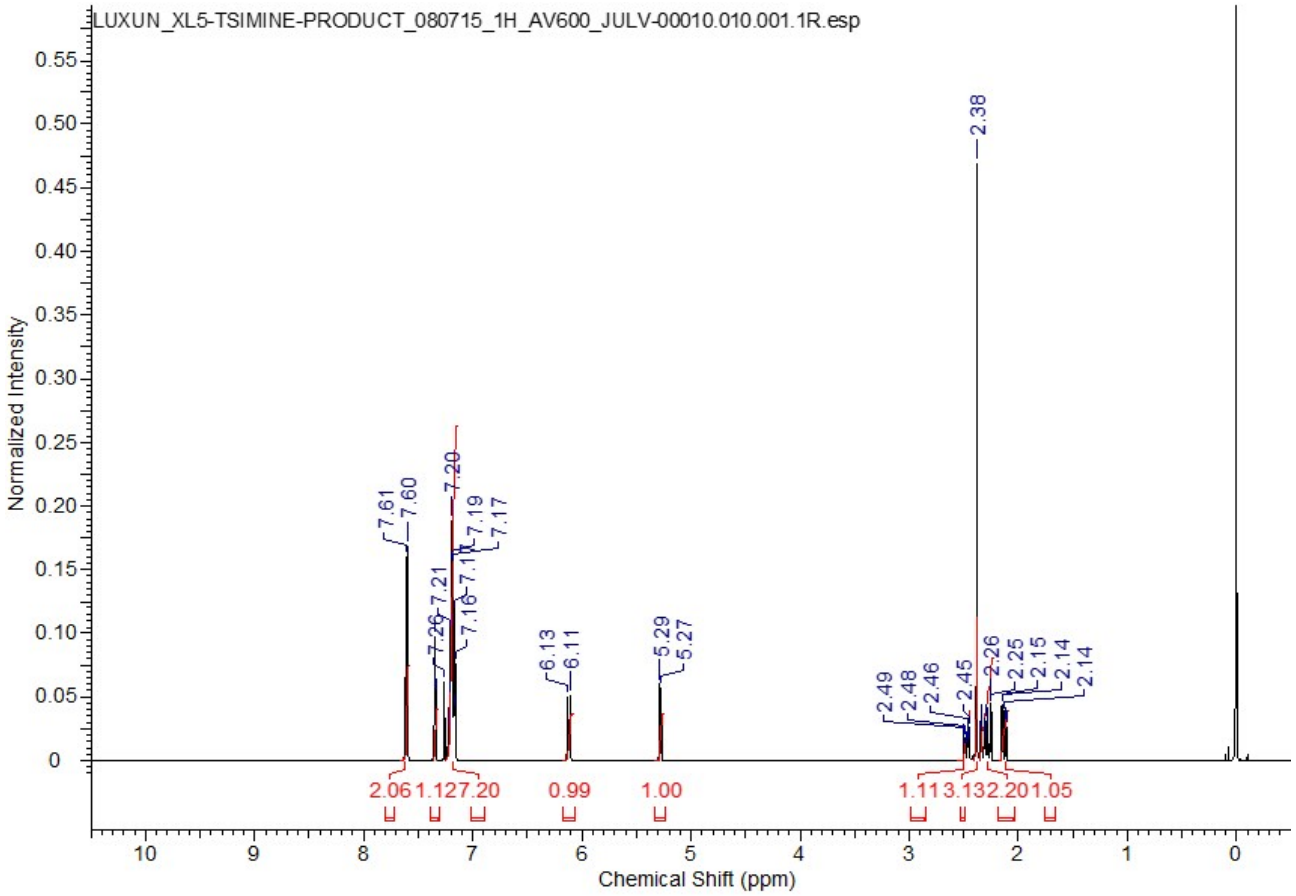
5e

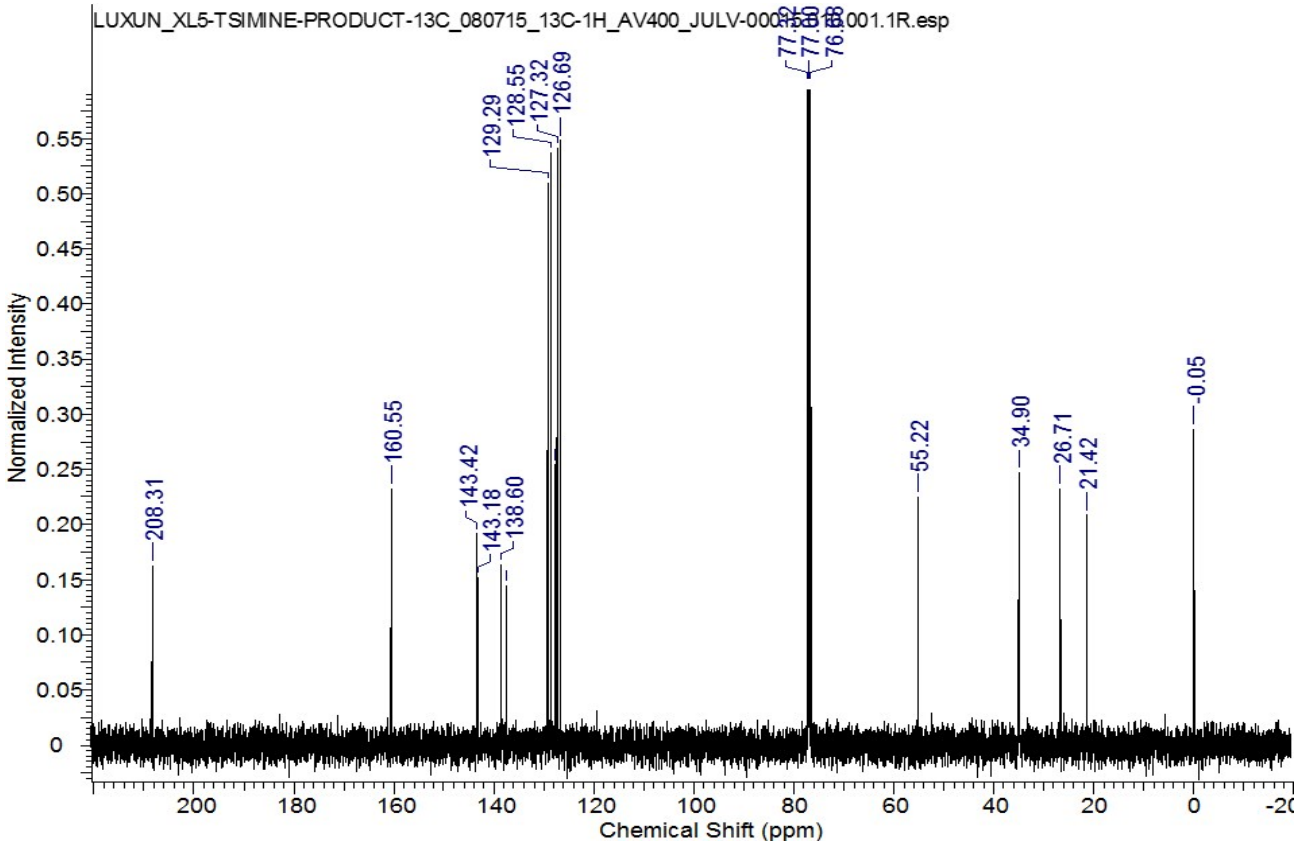

LuXun_XLPh-Ke-HV_090714_1H_av500.010.001.1r.esp
TMS
Normalized Intensity
Chemical Shift (ppm)
7.96
7.95
7.94
7.58
7.50
7.48
7.48
7.47
7.45
7.13
7.13
6.45
6.45
6.42
6.42
5.94
5.94
5.92
5.92
1.96 1.01 2.01 1.00 0.98 1.00

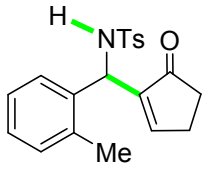

LuXun_XLPVK_SM_090715_1H_pr500_JulV-00333.esp
Normalized Intensity
Chemical Shift (ppm)
189.30
135.04
132.20
129.29
128.94
128.47
77.21
77.00
76.79


H
NTs
O

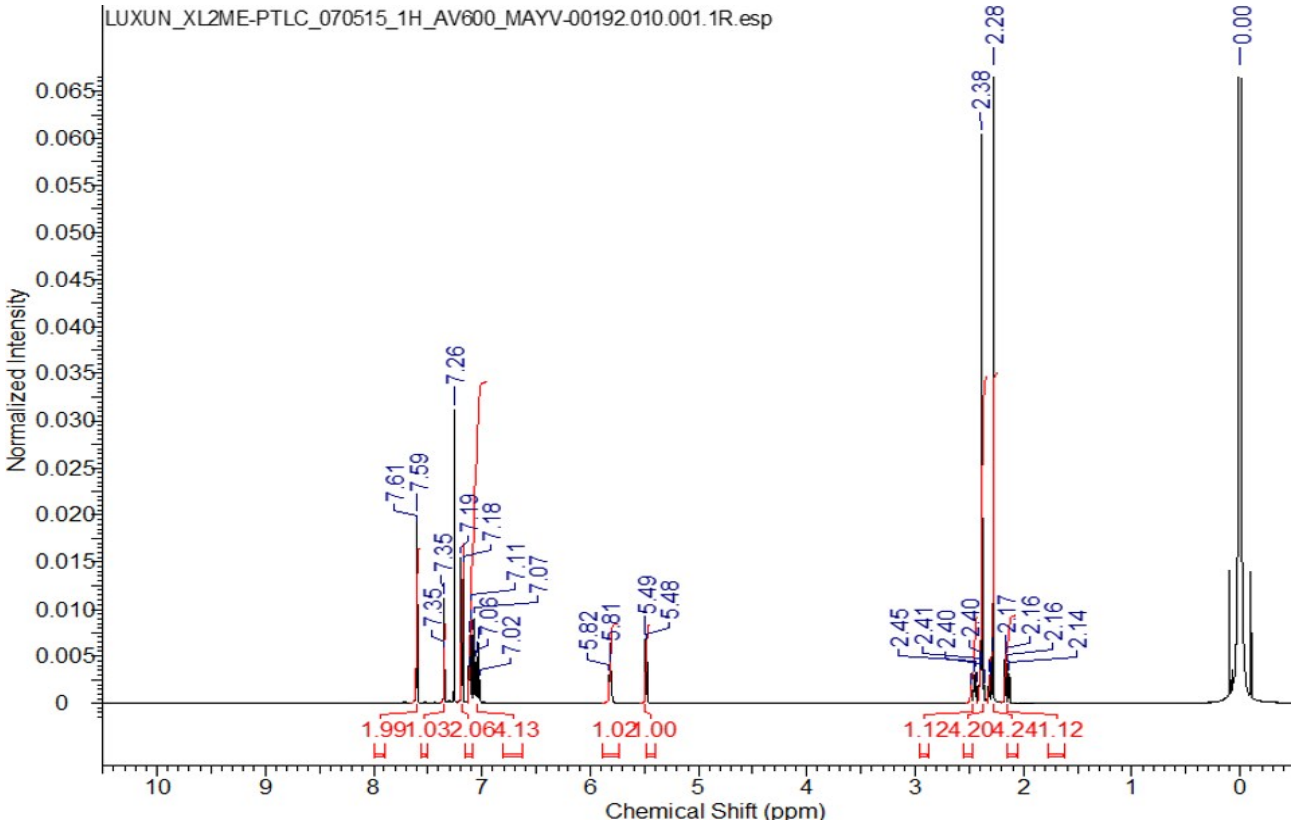
6a

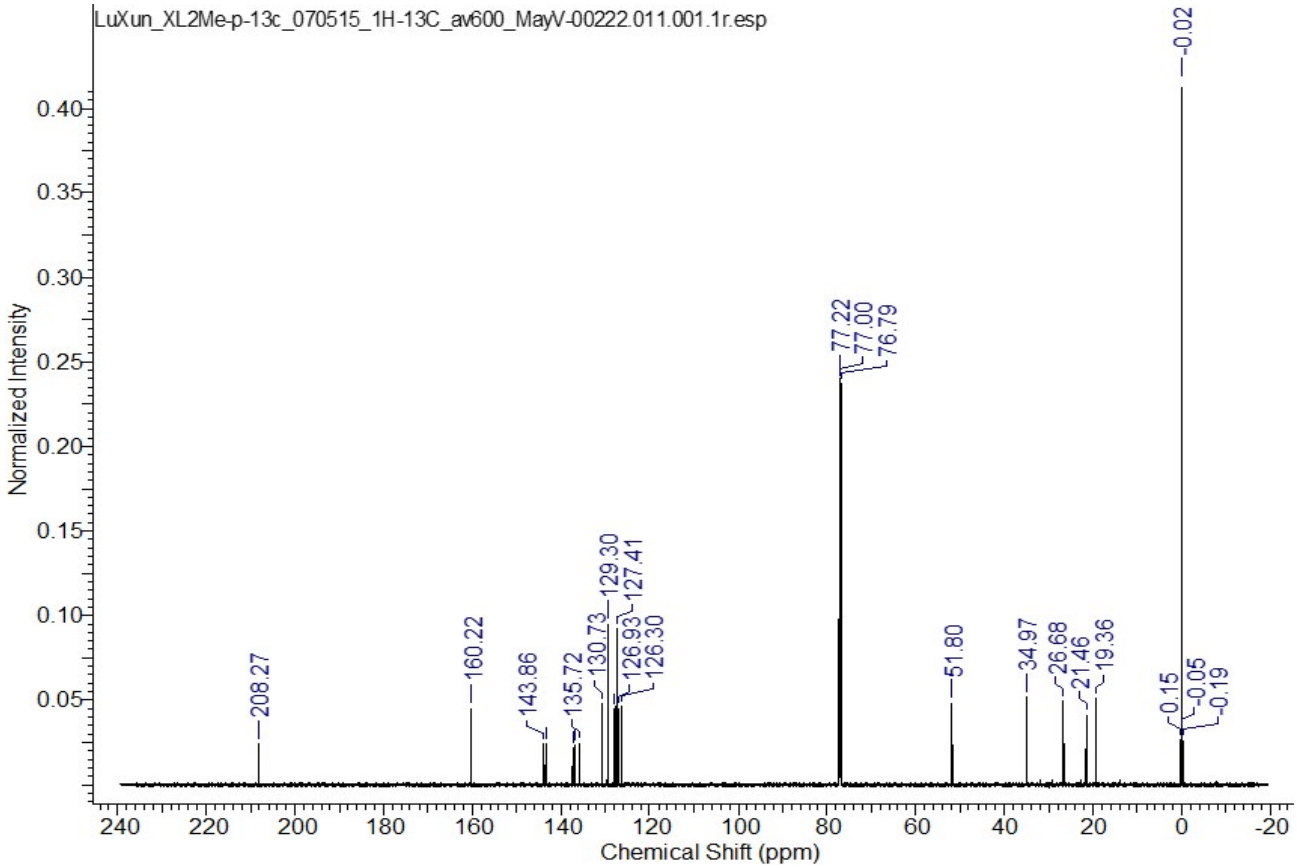

LUXUN_XL5-TSIMINE-PRODUCT_080715_1H_AV600_JULV-00010.010.001.1R.esp
Normalized Intensity
Chemical Shift (ppm)
2.38
7.61
7.60
7.20
7.19
7.17
7.21
7.16
6.13
6.11
5.29
5.27
2.49
2.48
2.46
2.45
2.26
2.25
2.15
2.14
2.06
1.12
7.20
0.99
1.00
1.11
3.13
2.20
1.05

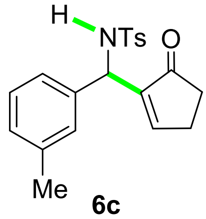

LUXUN_XL5-TSIMINE-PRODUCT-13C_080715_13C-1H_AV400_JULV-00045
001.1R.esp
Normalized Intensity
Chemical Shift (ppm)
129.29
128.55
127.32
126.69
208.31
160.55
143.42
143.18
138.60
55.22
34.90
26.71
21.42
-0.05


H
NTs
O
Me

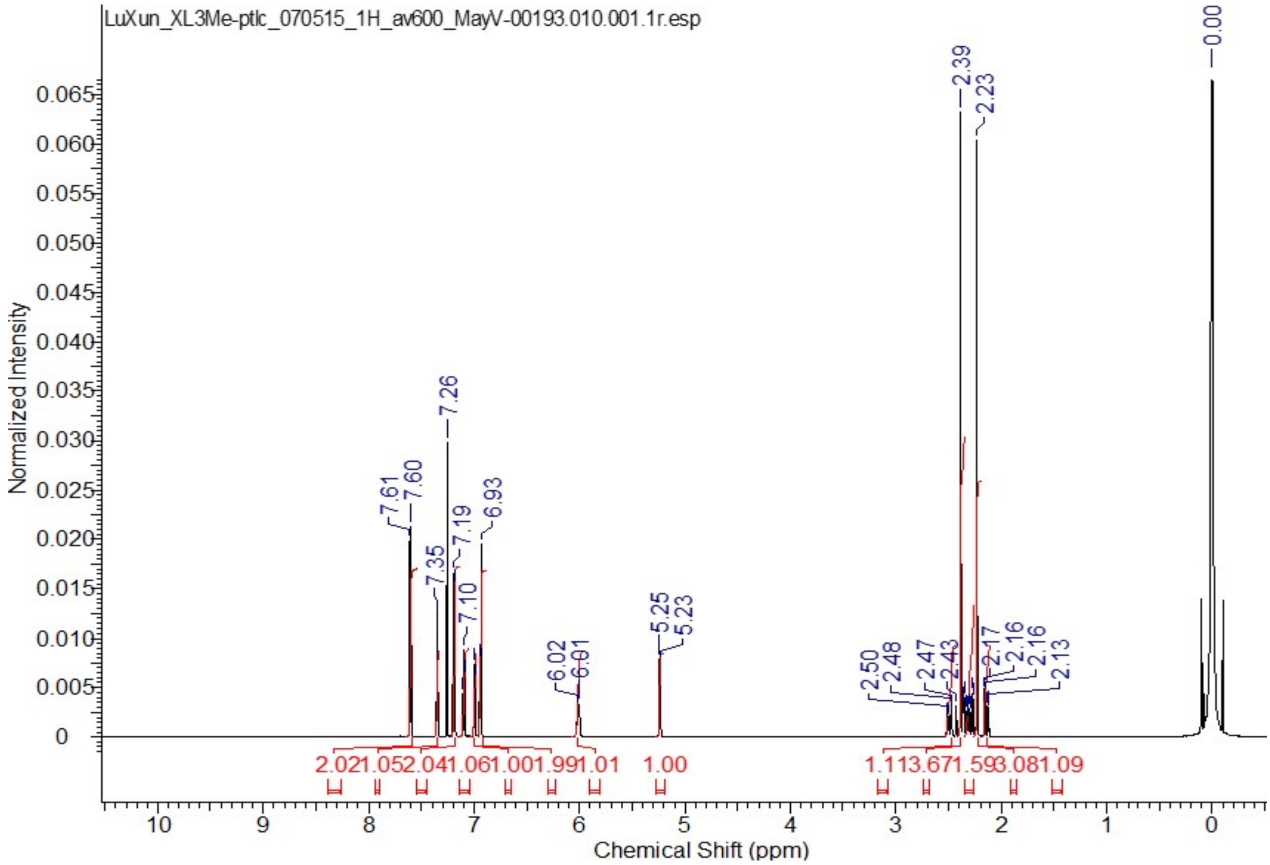
6b

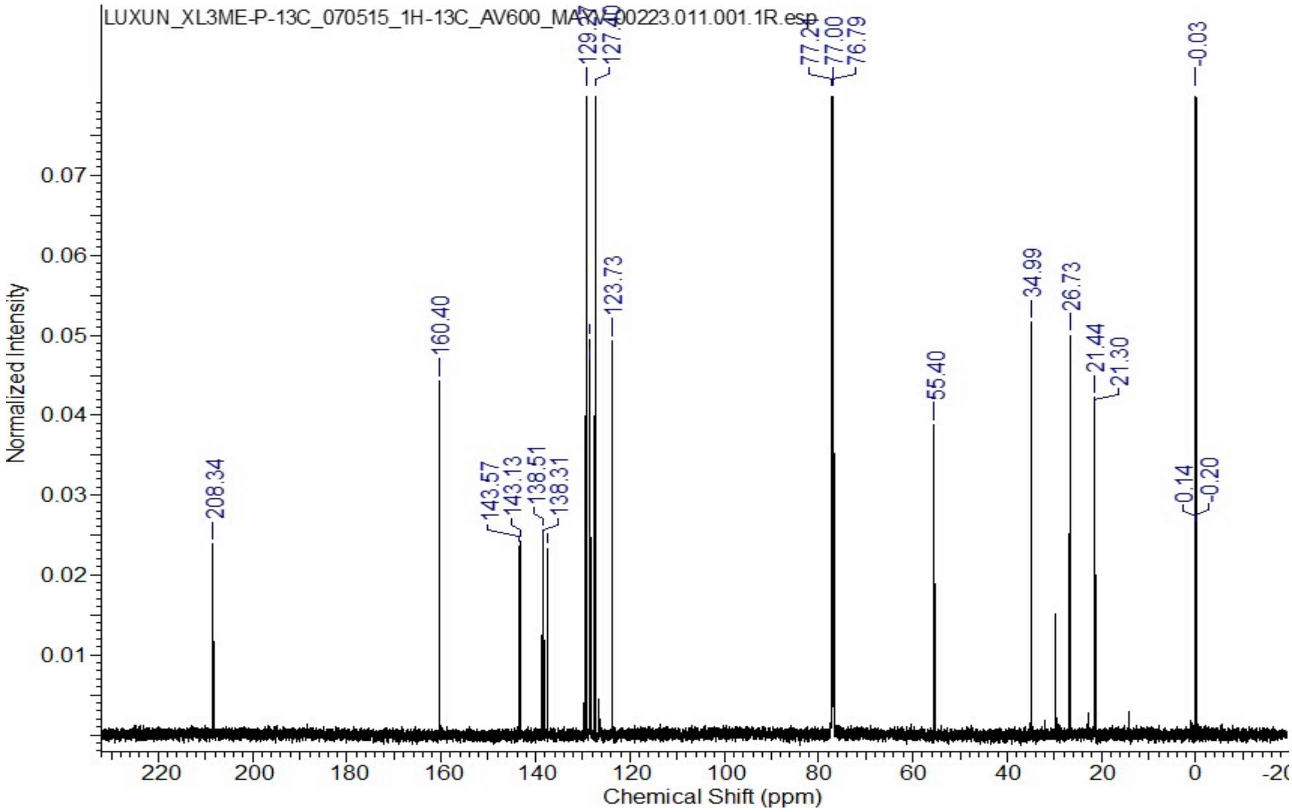

LUXUN_XL2ME-PTLC_070515_1H_AV600_MAYV-00192.010.001.1R.esp
Normalized Intensity
Chemical Shift (ppm)
7.61
7.59
7.35
7.35
7.26
7.19
7.18
7.11
7.07
7.06
7.02
5.82
5.81
5.49
5.48
2.45
2.41
2.40
2.40
2.38
2.28
2.17
2.16
2.16
2.14
0.00
1.99
1.03
2.06
4.13
1.02
1.00
1.12
4.20
4.24
1.12

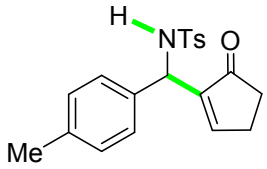

LuXun_XL2Me-p-13c_070515_1H-13C_av600_MayV-00222.011.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
208.27
160.22
143.86
135.72
130.73
129.30
127.41
126.93
126.30
77.22
77.00
76.79
51.80
34.97
26.68
21.46
19.36
0.15
-0.02
-0.05
-0.19


H
NTs
O
Me

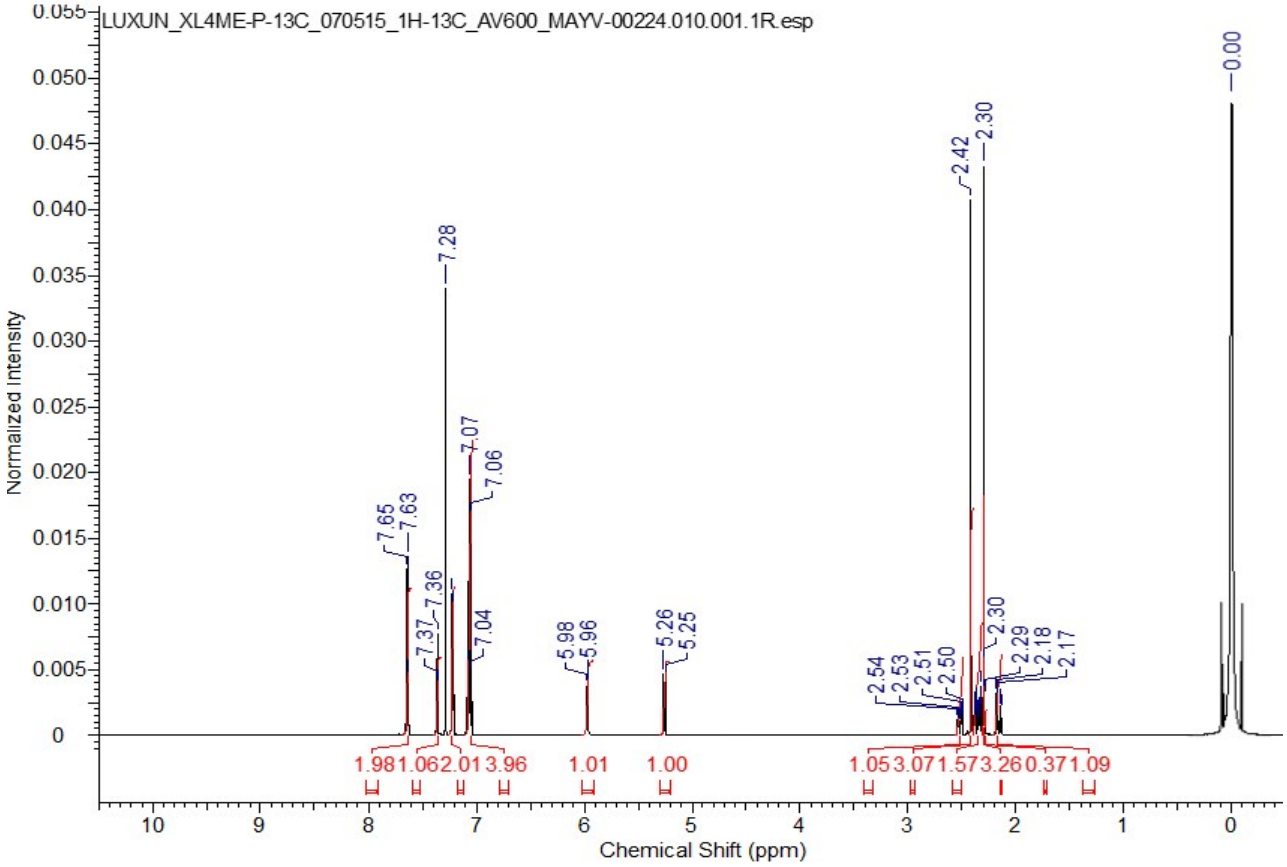
6c

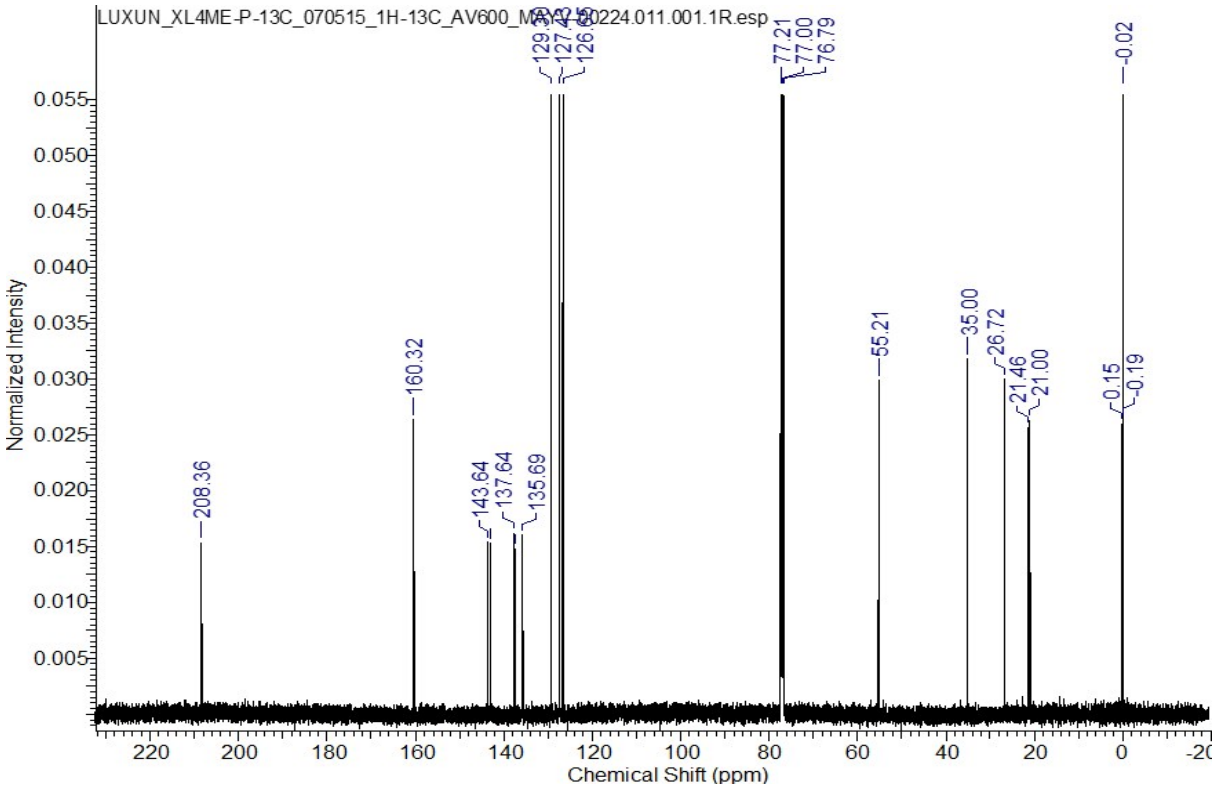

LuXun_XL3Me-ptlc_070515_1H_av600_MayV-00193.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
7.61
7.60
7.35
7.26
7.19
7.10
6.93
6.02
6.01
5.25
5.23
2.50
2.48
2.47
2.43
2.39
2.23
2.17
2.16
2.16
2.13
0.00
2.02
1.05
2.04
1.06
1.00
1.99
1.01
1.00
1.11
3.67
1.59
3.08
1.09

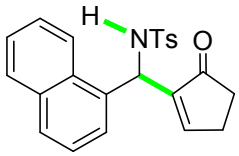

LUXUN_XL3ME-P-13C_070515_1H-13C_AV600_MAYV-00223.011.001.1R.esp
Normalized Intensity
Chemical Shift (ppm)
208.34
160.40
143.57
143.13
138.51
138.31
123.73
77.24
77.00
76.79
55.40
34.99
26.73
21.44
21.30
-0.03
0.14
-0.20


H
NTs
O
Me

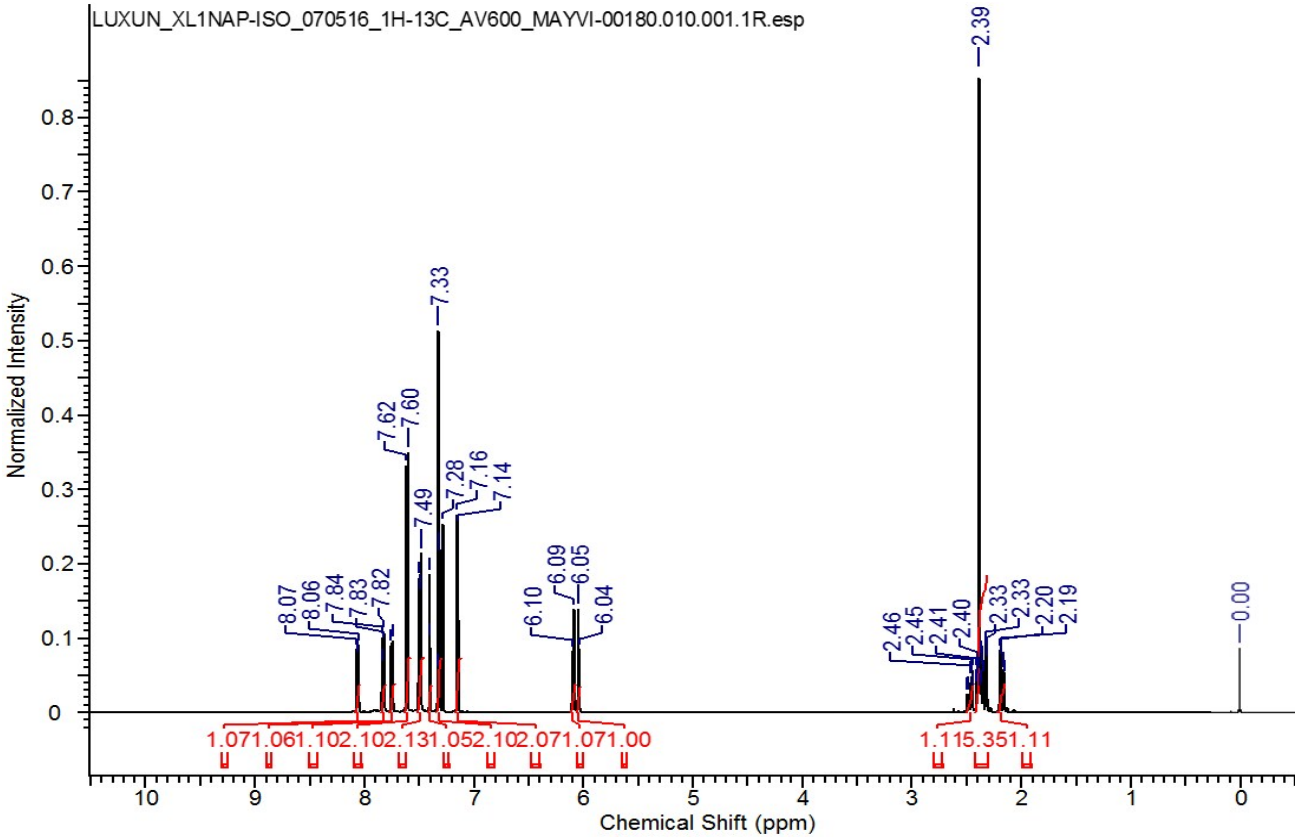
6d

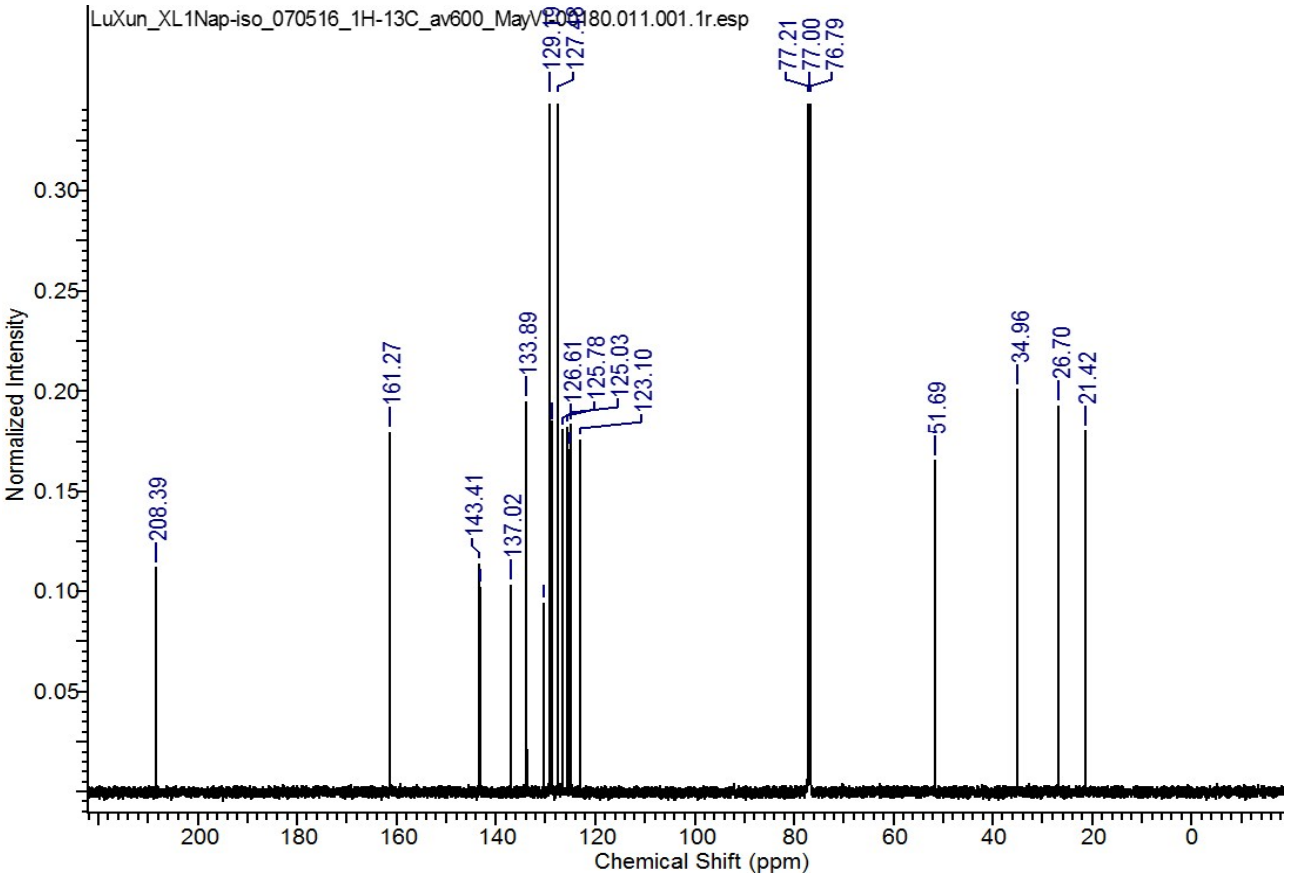

LUXUN_XL4ME-P-13C_070515_1H-13C_AV600_MAYV-00224.010.001.1R.esp
Normalized Intensity
Chemical Shift (ppm)
0.00
2.42
2.30
7.28
7.07
7.06
7.65
7.63
7.36
7.37
7.04
5.98
5.96
5.26
5.25
2.54
2.53
2.51
2.50
2.30
2.29
2.18
2.17
1.98
1.06
2.01
3.96
1.01
1.00
1.05
3.07
1.57
3.26
0.37
1.09

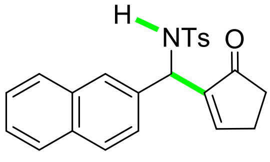

LUXUN_XL4ME-P-13C_070515_1H-13C_AV600_MAYV-00224.011.001.1R.esp
Normalized Intensity
Chemical Shift (ppm)
77.21
77.00
76.79
-0.02
208.36
160.32
143.64
137.64
135.69
55.21
35.00
26.72
21.46
21.00
0.15
0.19


H
NTs
O

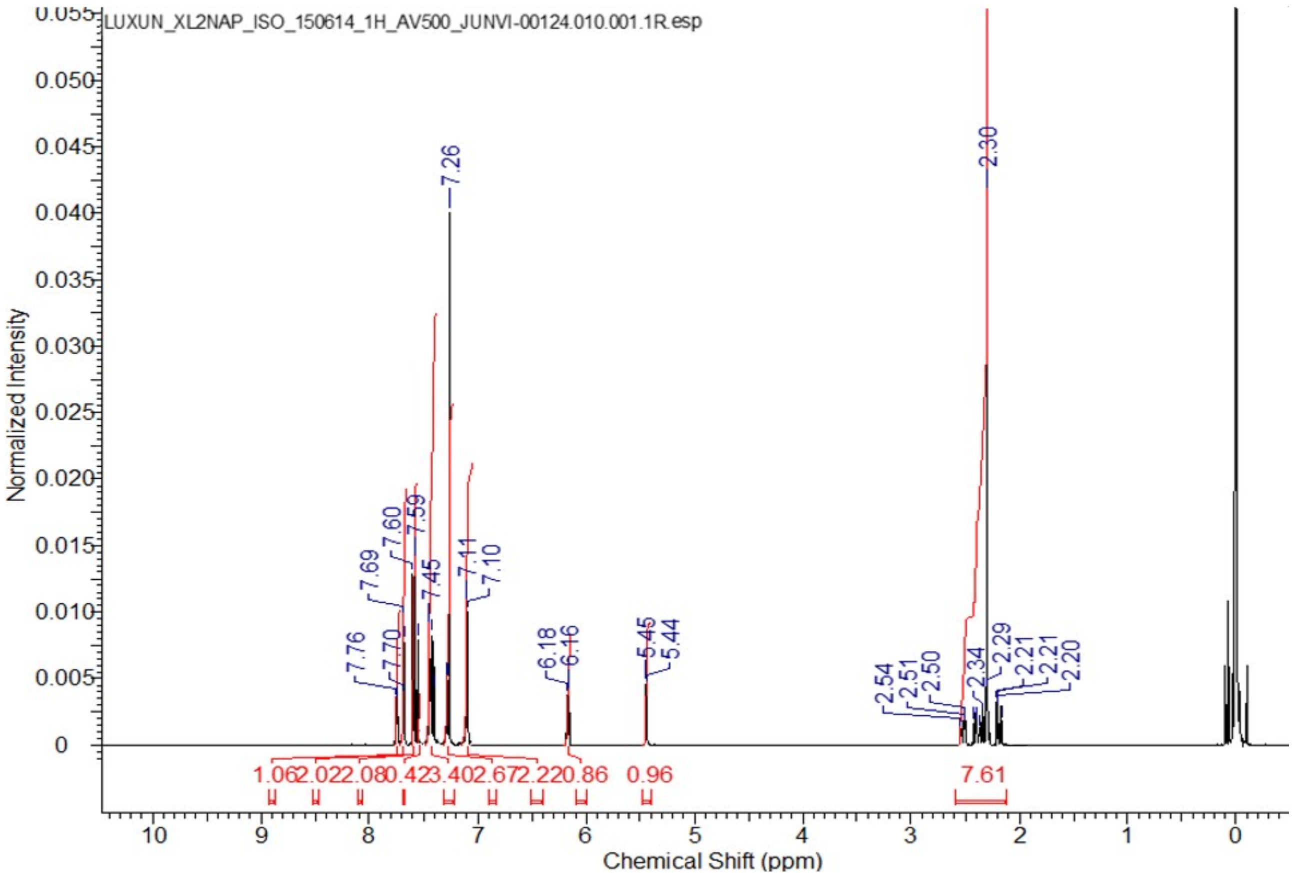
6e

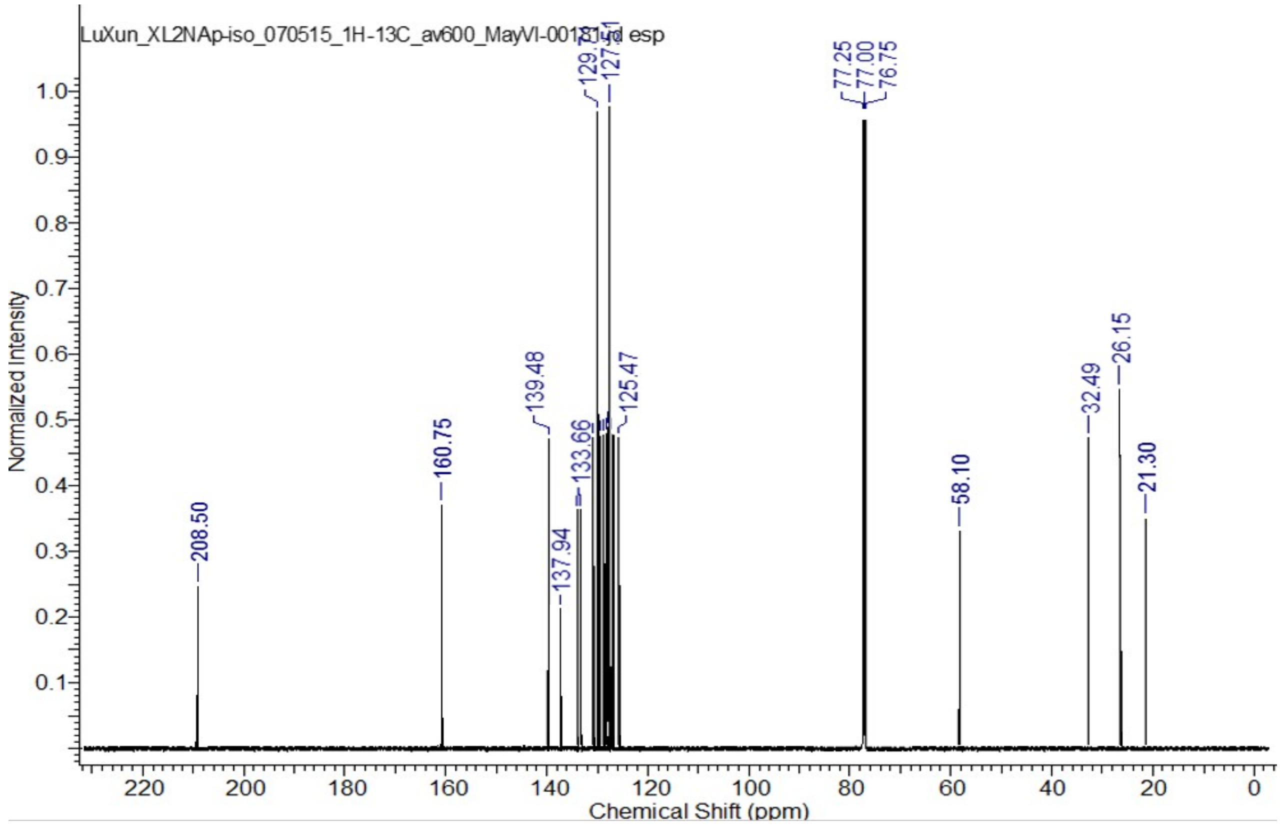

LUXUN_XL1NAP-ISO_070516_1H-13C_AV600_MAYVI-00180.010.001.1R.esp
Normalized Intensity
Chemical Shift (ppm)
2.39
7.33
7.62
7.60
7.49
7.28
7.16
7.14
8.07
8.06
7.84
7.83
7.82
6.10
6.09
6.05
6.04
2.46
2.45
2.41
2.40
2.33
2.33
2.20
2.19
0.00
1.071.061.102.102.131.052.102.071.071.00
1.115.351.11

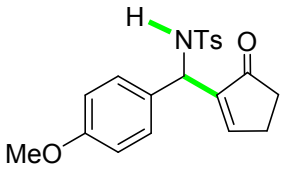

LuXun_XL1Nap-iso_070516_1H-13C_av600_MayVI-00180.011.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
77.21
77.00
76.79
129.
127.
208.39
161.27
143.41
137.02
133.89
126.61
125.78
125.03
123.10
51.69
34.96
26.70
21.42



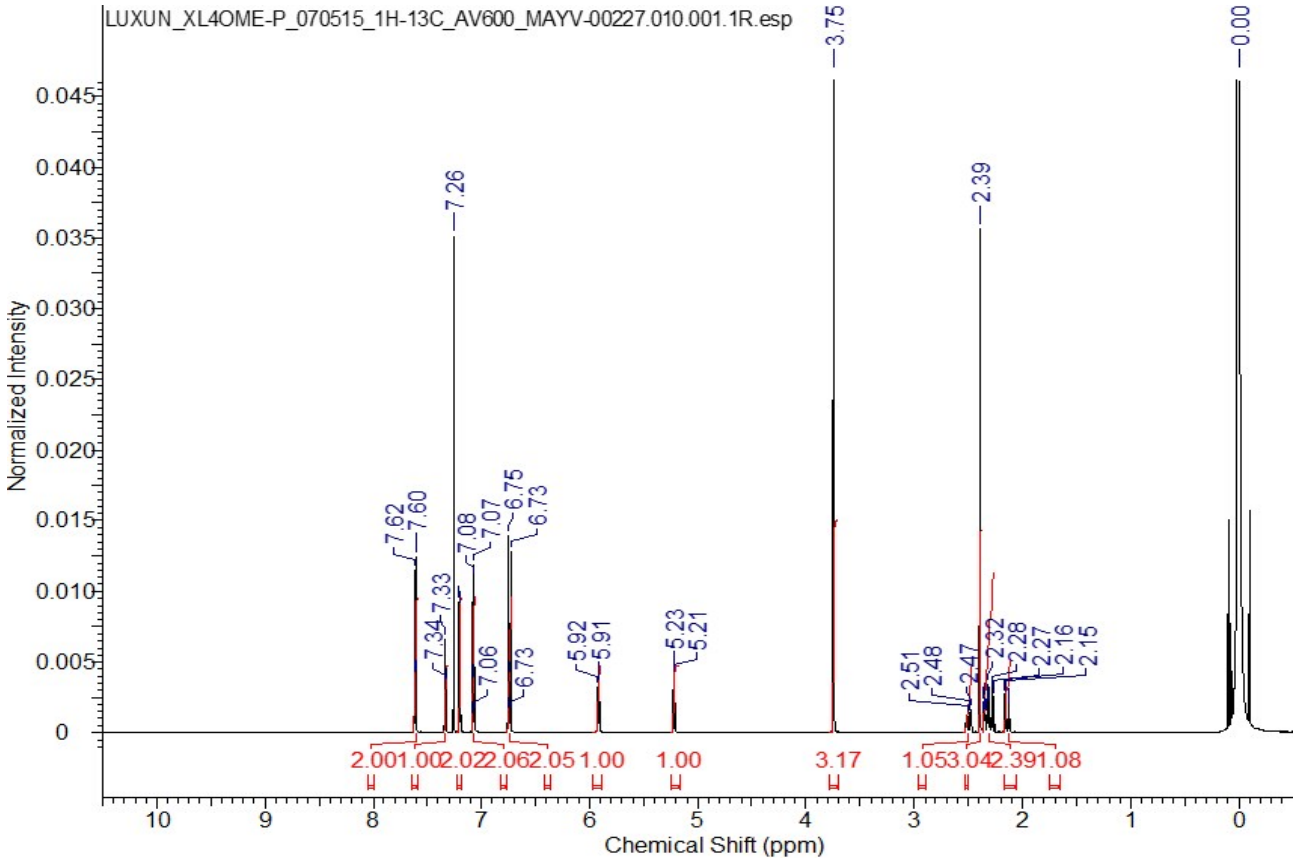
6f

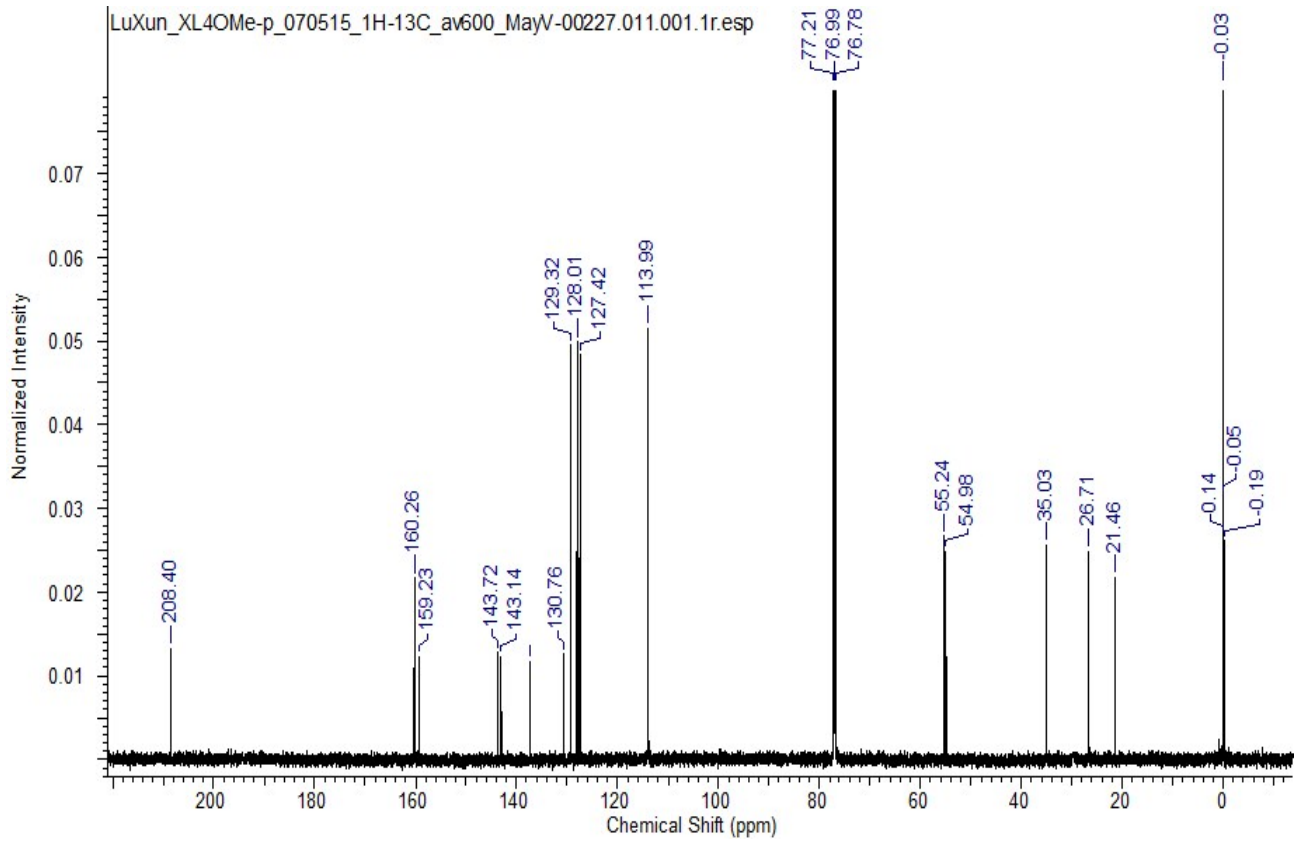

LUXUN_XL2NAP_ISO_150614_1H_AV500_JUNVI-00124.010.001.1R.esp
Normalized Intensity
Chemical Shift (ppm)
7.26
2.30

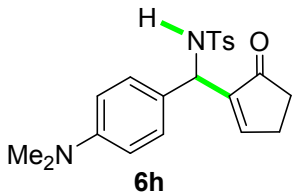

Normalized Intensity
Chemical Shift (ppm)
208.50
160.75
139.48
137.94
133.66
125.47
77.25
77.00
76.75
58.10
32.49
26.15
21.30


H
NTs
O
MeO

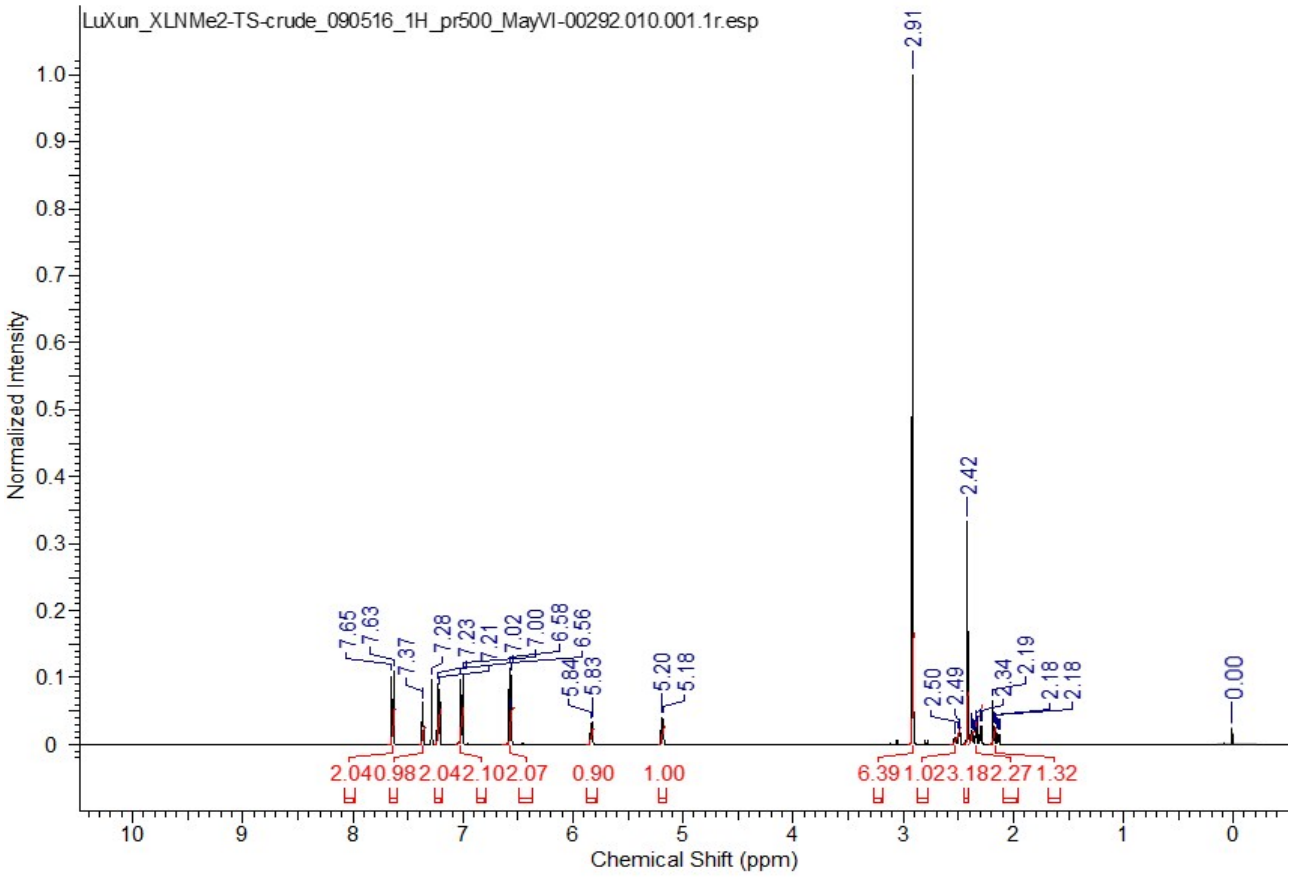
6g

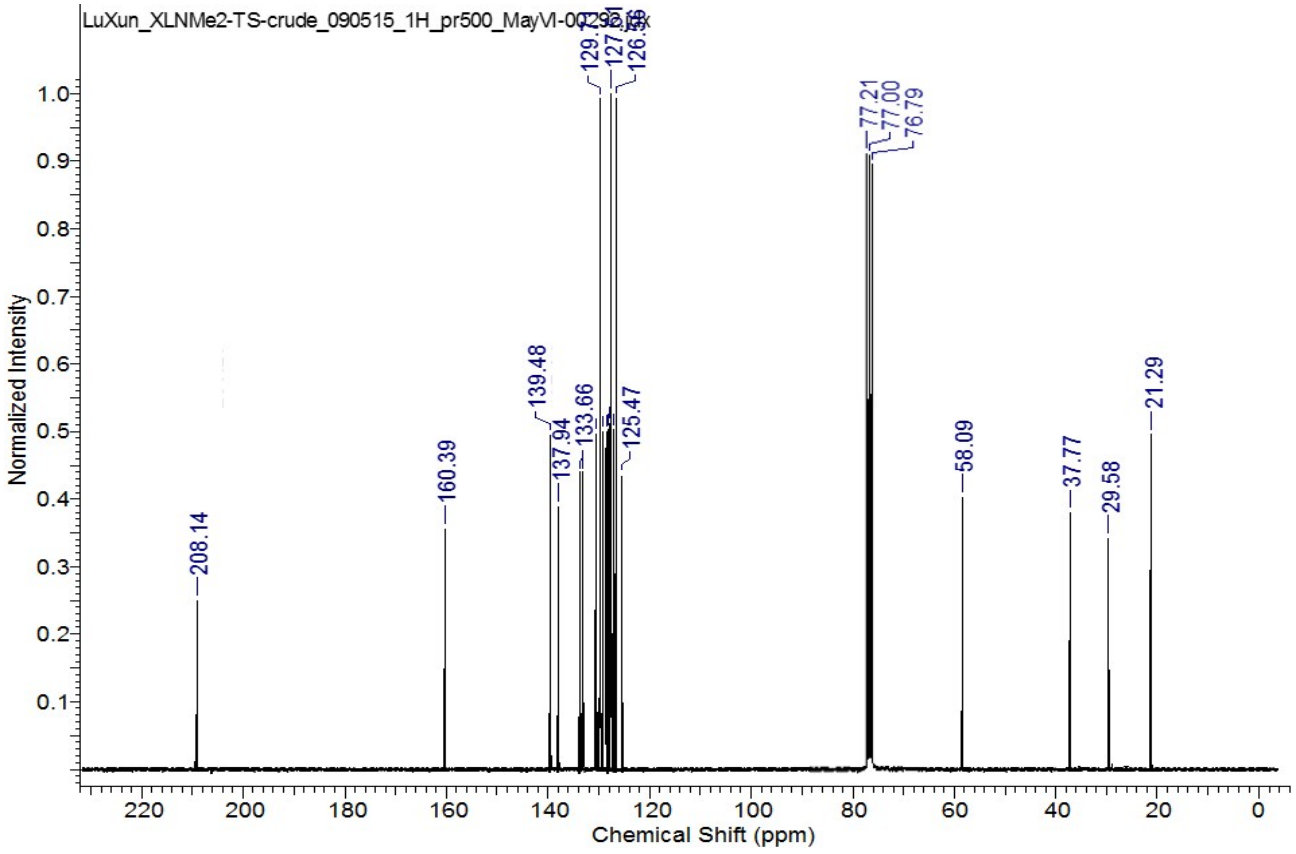

LUXUN_XL4OME-P_070515_1H-13C_AV600_MAYV-00227.010.001.1R.esp
Normalized Intensity
Chemical Shift (ppm)
7.62
7.60
7.34
7.33
7.26
7.08
7.07
7.06
6.75
6.73
6.73
5.92
5.91
5.23
5.21
3.75
2.51
2.48
2.47
2.39
2.32
2.28
2.27
2.16
2.15
0.00
2.00
1.00
2.02
2.06
2.05
1.00
1.00
3.17
1.05
3.04
2.39
1.08

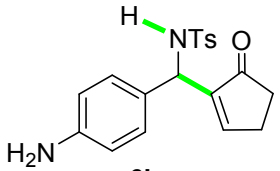

LuXun_XL4OMe-p_070515_1H-13C_av600_MayV-00227.011.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
208.40
160.26
159.23
143.72
143.14
130.76
129.32
128.01
127.42
113.99
77.21
76.99
76.78
55.24
54.98
35.03
26.71
21.46
0.14
0.05
0.03
0.19


H
NTs
O
Me2N

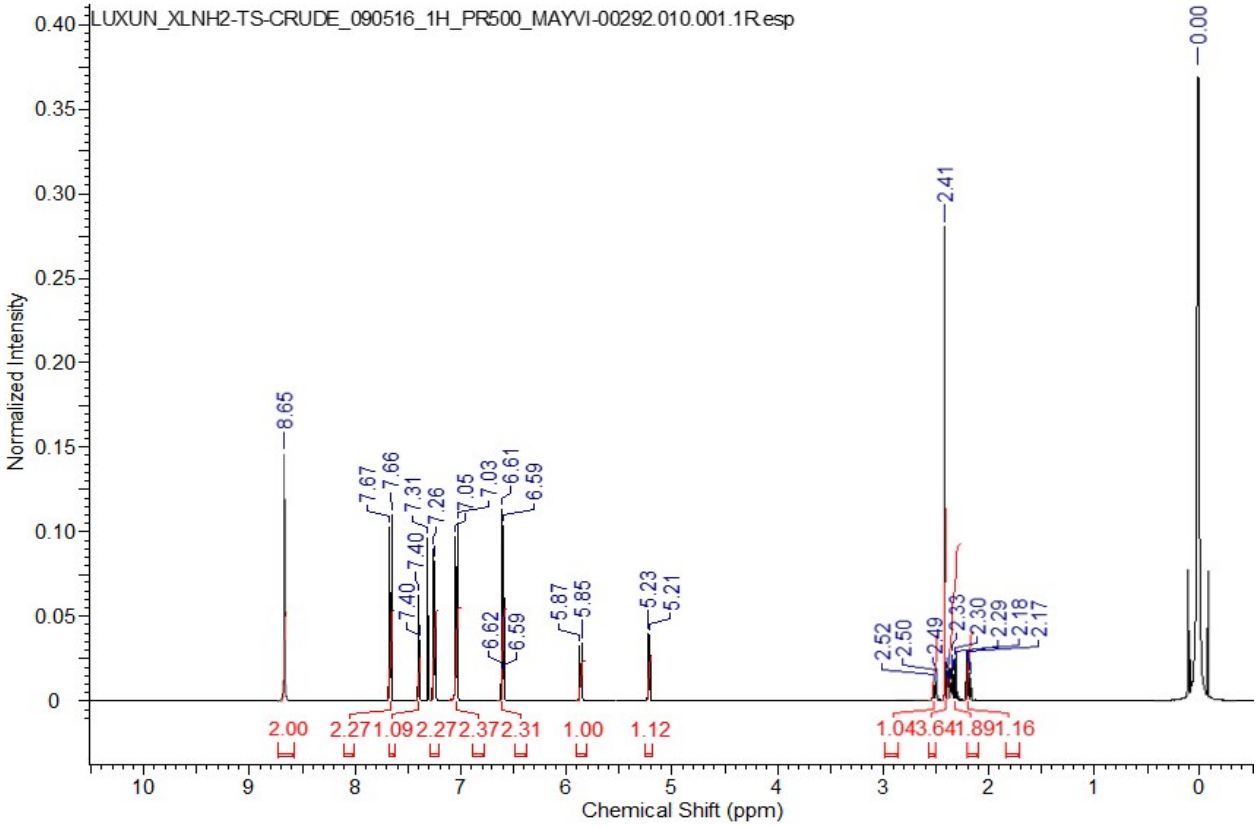
6h

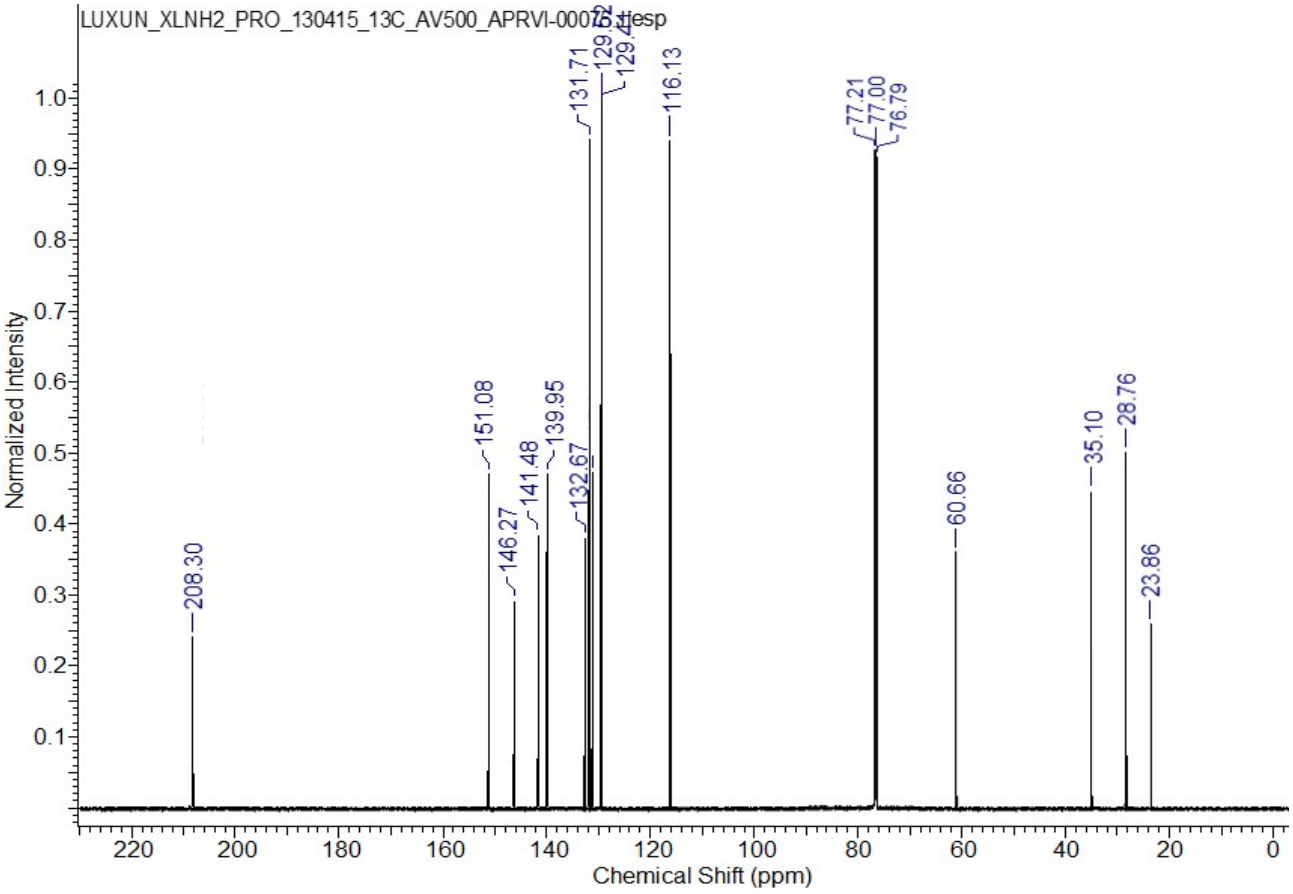

LuXun_XLNMe2-TS-crude_090516_1H_pr500_MayVI-00292.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
2.91
2.42
7.65
7.63
7.37
7.28
7.23
7.21
7.02
7.00
6.58
6.56
5.84
5.83
5.20
5.18
2.50
2.49
2.34
2.19
2.18
2.18
0.00
2.04
0.98
2.04
2.10
2.07
0.90
1.00
6.39
1.02
3.18
2.27
1.32

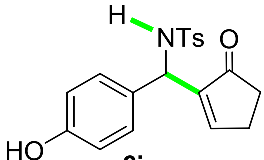

LuXun_XLNMe2-TS-crude_090515_1H_pr500_MayVI-00292.xx
Normalized Intensity
Chemical Shift (ppm)
208.14
160.39
139.48
137.94
133.66
125.47
77.21
77.00
76.79
58.09
37.77
29.58
21.29


H
NTs
O
H_2N

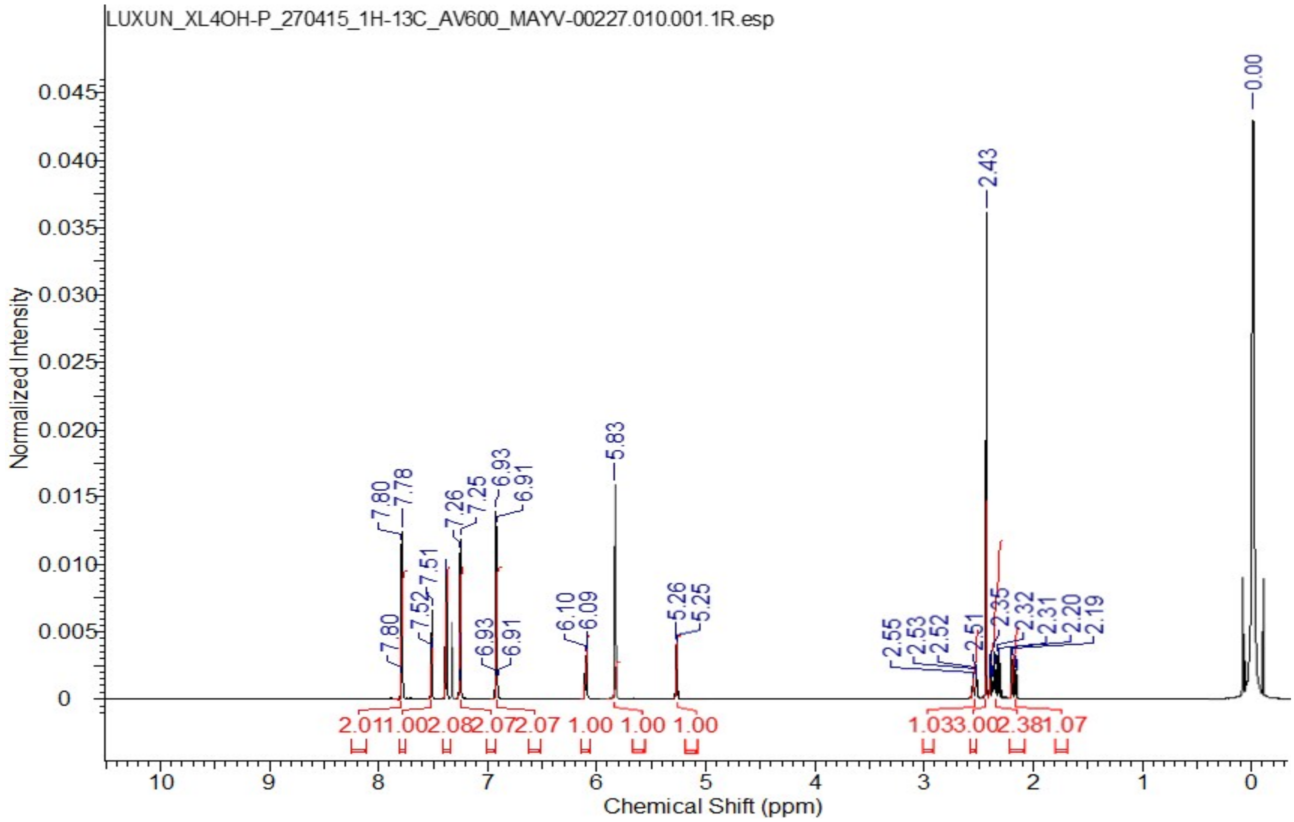
6i

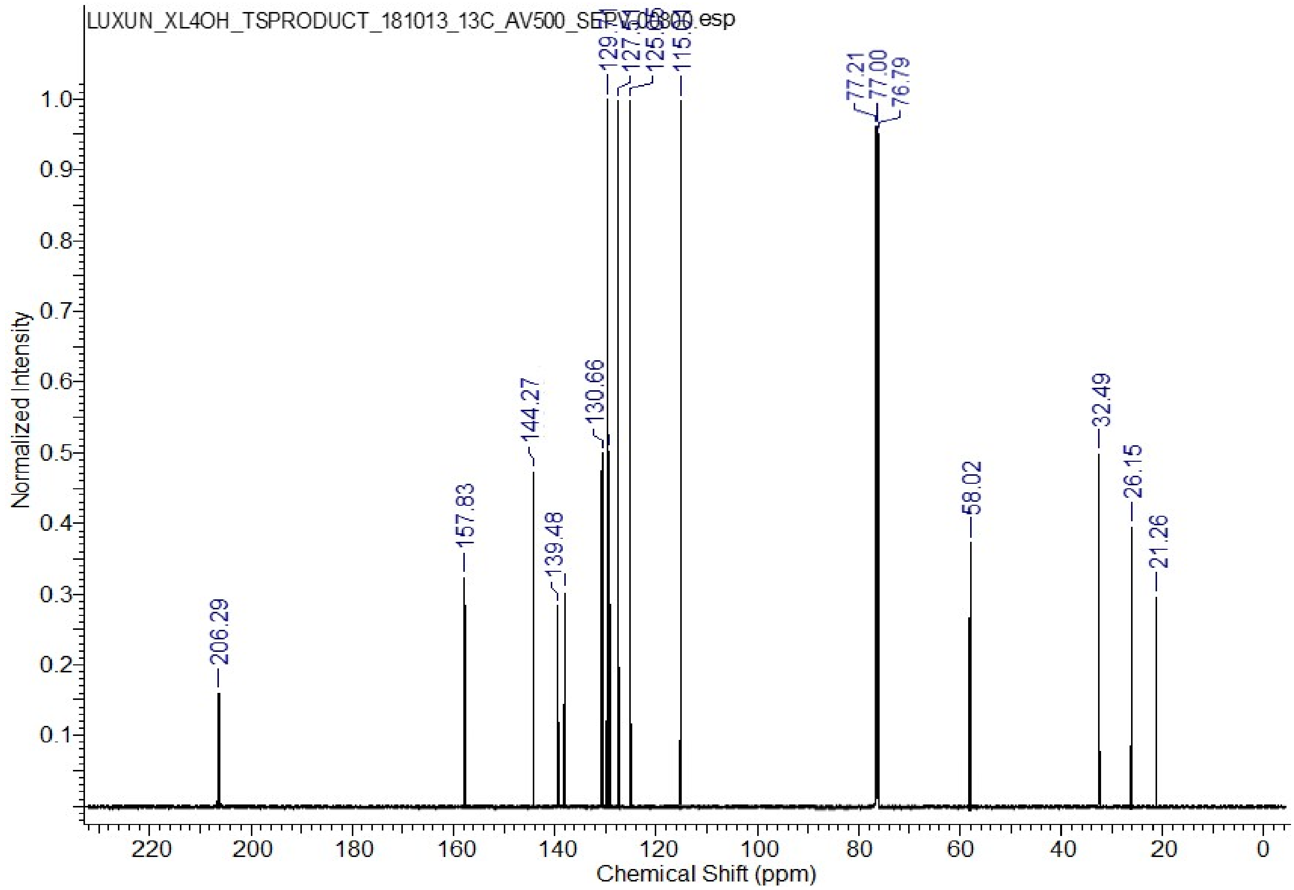

LUXUN_XLNH2-TS-CRUDE_090516_1H_PR500_MAYVI-00292.010.001.1R.esp
Normalized Intensity
Chemical Shift (ppm)
8.65
7.67
7.66
7.40
7.40
7.31
7.26
7.05
7.03
6.62
6.61
6.59
6.59
5.87
5.85
5.23
5.21
2.52
2.50
2.49
2.33
2.30
2.29
2.18
2.17
0.00
2.41
2.00
2.27
1.09
2.27
2.37
2.31
1.00
1.12
1.04
3.64
1.89
1.16

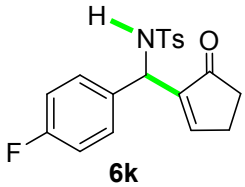

LUXUN_XLNH2_PRO_130415_13C_AV500_APRVI-00076.1.esp
Normalized Intensity
Chemical Shift (ppm)
208.30
151.08
146.27
141.48
139.95
132.67
131.71
129.62
129.41
116.13
77.21
77.00
76.79
60.66
35.10
28.76
23.86


H
NTs
O
HO

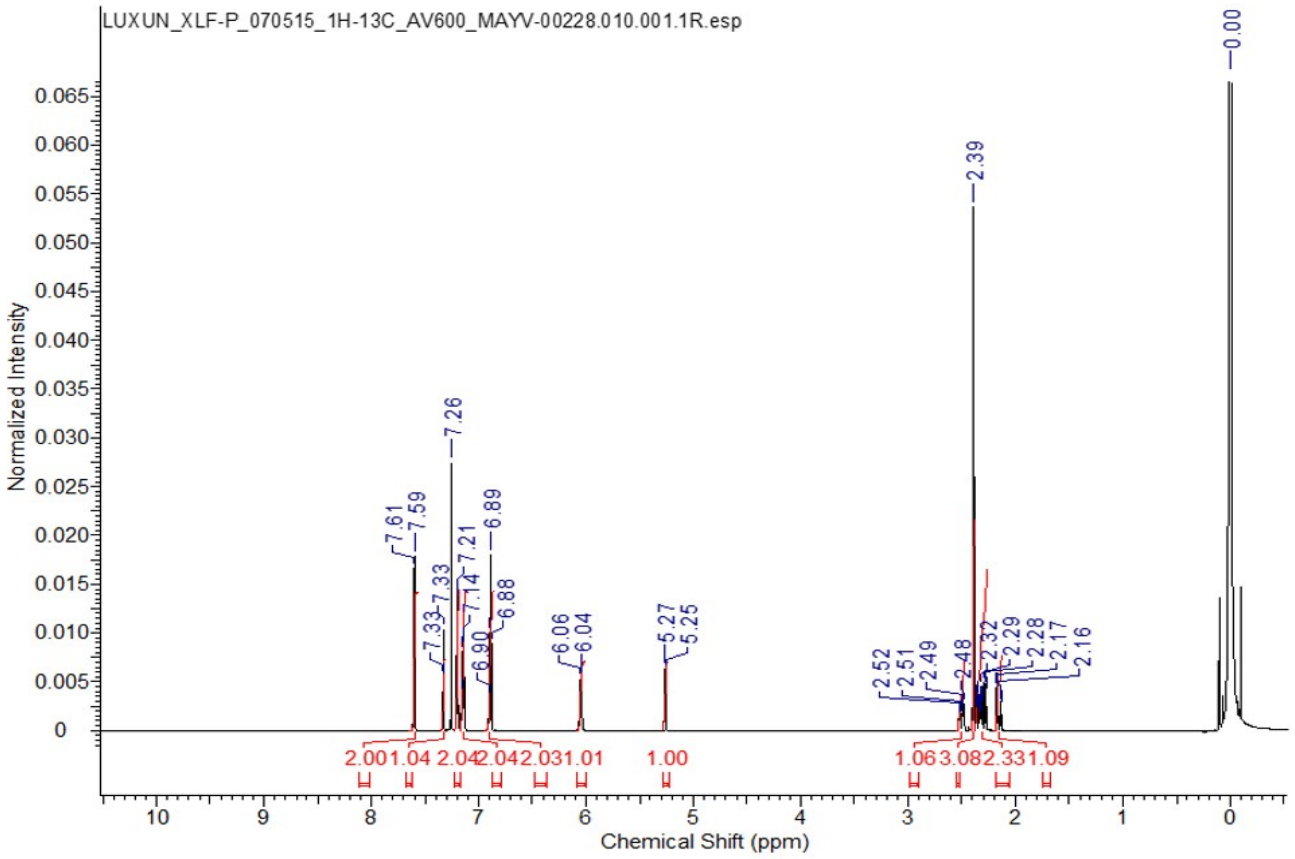
6j

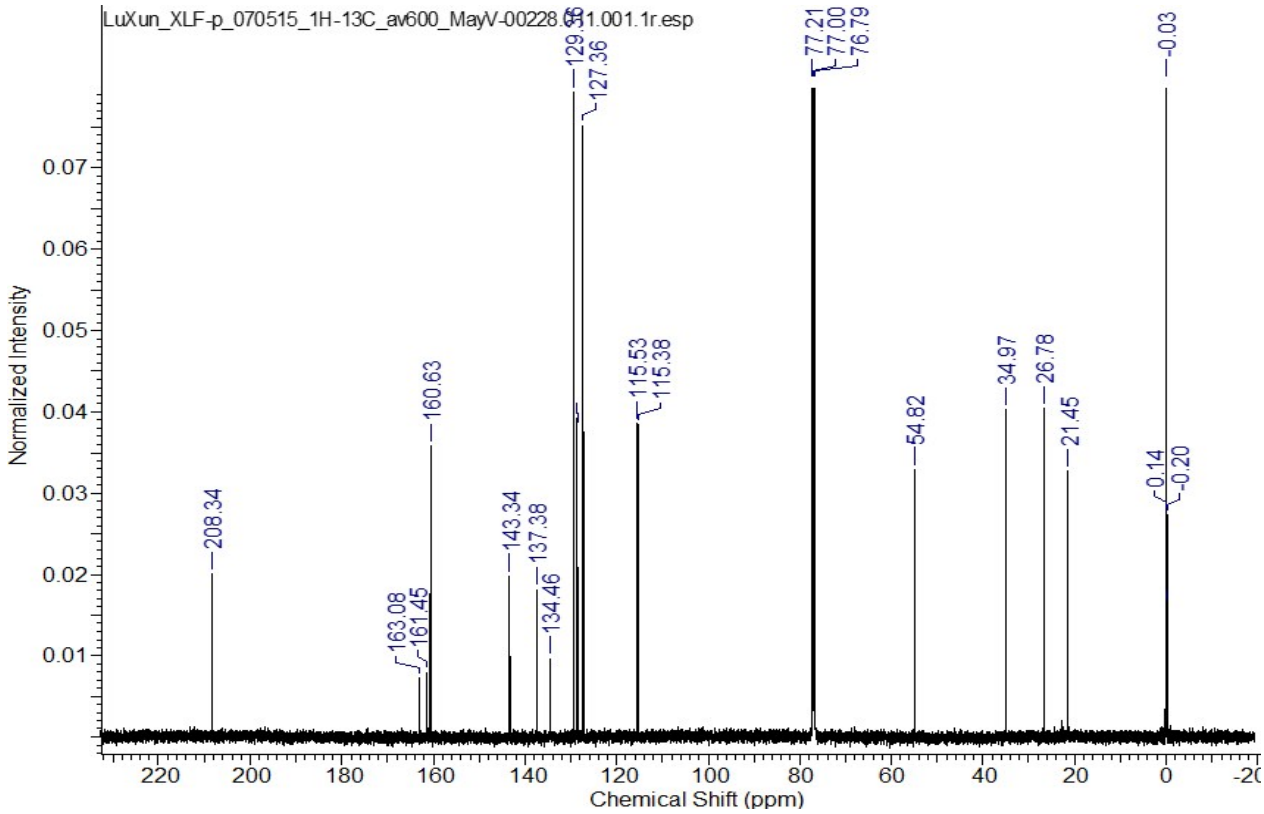

LUXUN_XL4OH-P_270415_1H-13C_AV600_MAYV-00227.010.001.1R.esp
Normalized Intensity
Chemical Shift (ppm)

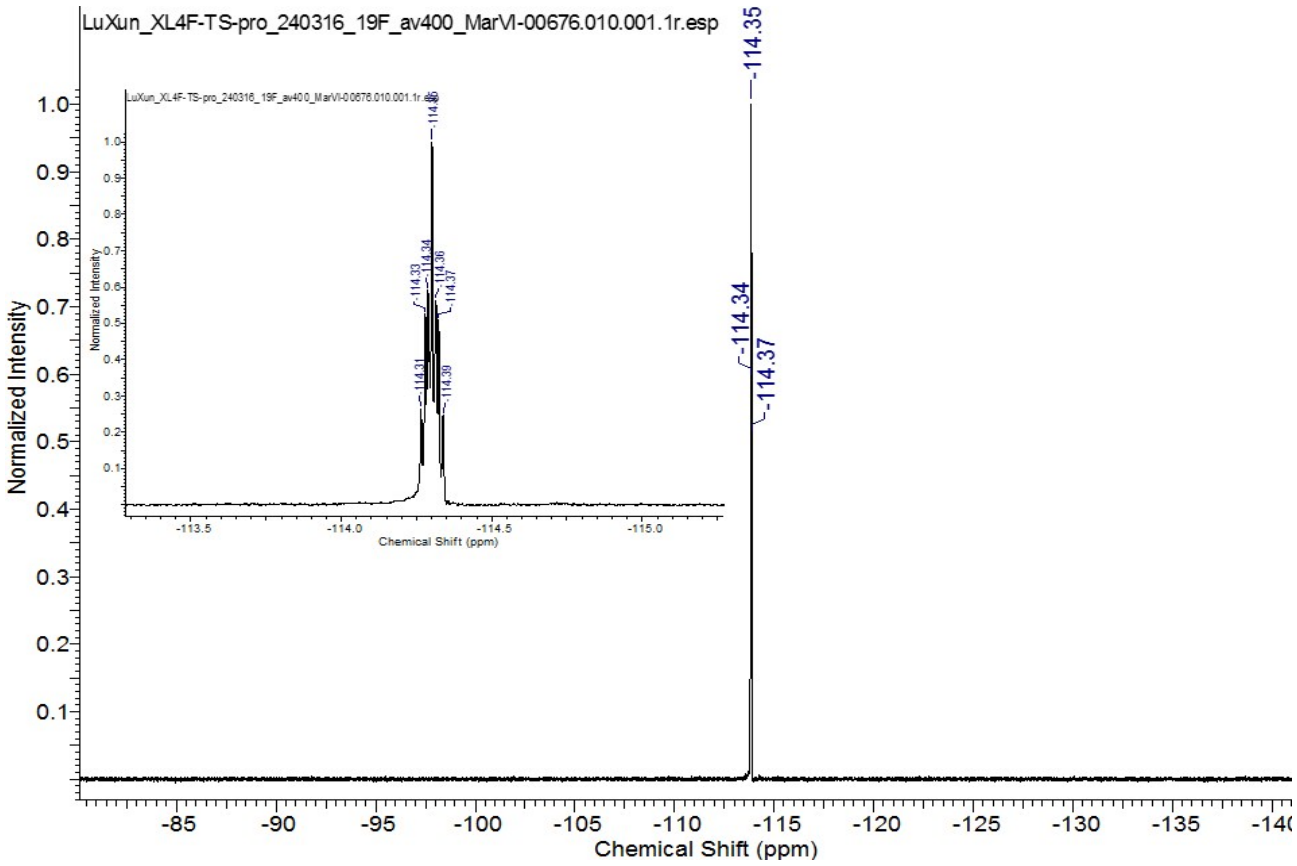

LUXUN_XL4OH_TSPRODUCT_181013_13C_AV500_SEPV-08000.esp
Normalized Intensity
Chemical Shift (ppm)

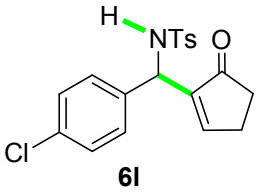

H
NTs
O
F

6k

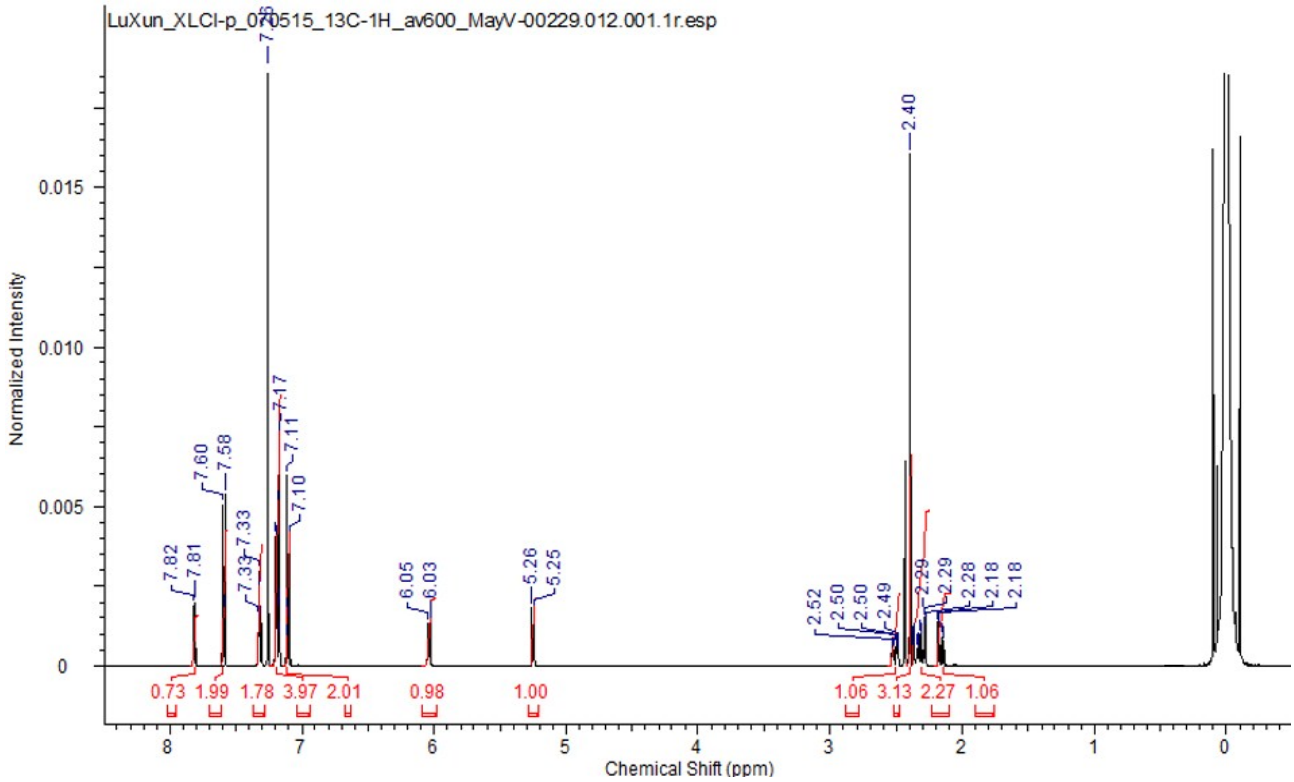

LUXUN_XLF-P_070515_1H-13C_AV600_MAYV-00228.010.001.1R.esp
Normalized Intensity
Chemical Shift (ppm)
0.00
2.39
7.61
7.59
7.26
7.33
7.33
7.21
7.14
6.89
6.88
6.90
6.06
6.04
5.27
5.25
2.52
2.51
2.49
2.48
2.32
2.29
2.28
2.17
2.16
2.001.04 2.04 2.04 2.03 1.01
1.00
1.06 3.08 2.33 1.09

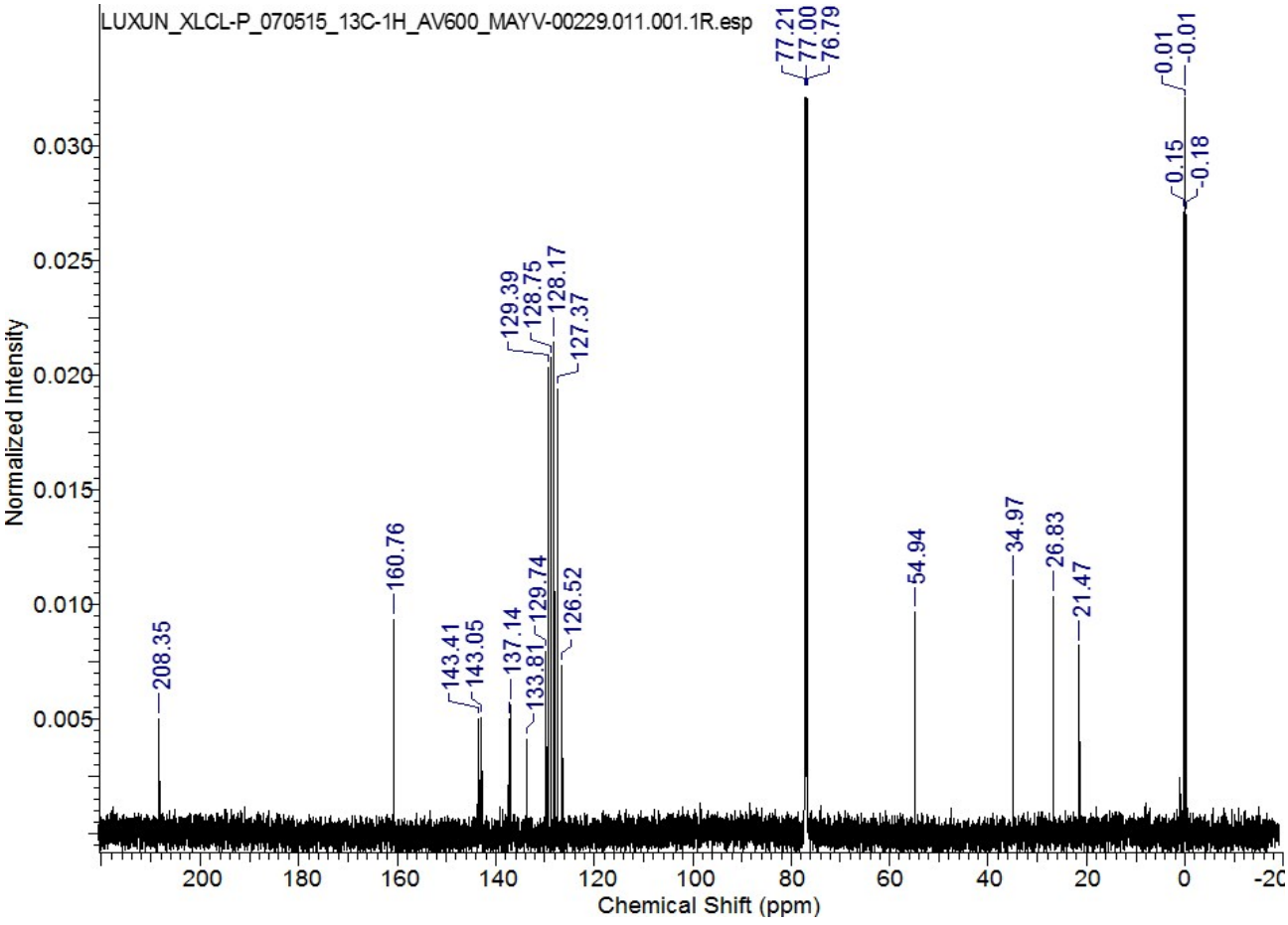

LuXun_XLF-p_070515_1H-13C_av600_MayV-00228.011.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
77.21
77.00
76.79
129.36
127.36
-0.03
160.63
115.53
115.38
54.82
34.97
26.78
21.45
208.34
143.34
137.38
134.46
163.08
161.45
0.14
0.20

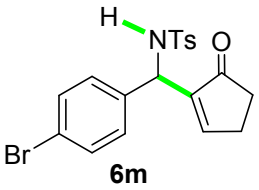

LuXun_XL4F-TS-pro_240316_19F_av400_MarVI-00676.010.001.1r.esp
-114.35
-114.34
-114.37
Normalized Intensity
Chemical Shift (ppm)
-114.33
-114.34
-114.36
-114.37
-114.31
-114.39
-113.5
-114.0
-114.5
-115.0


H
NTs
O
Cl

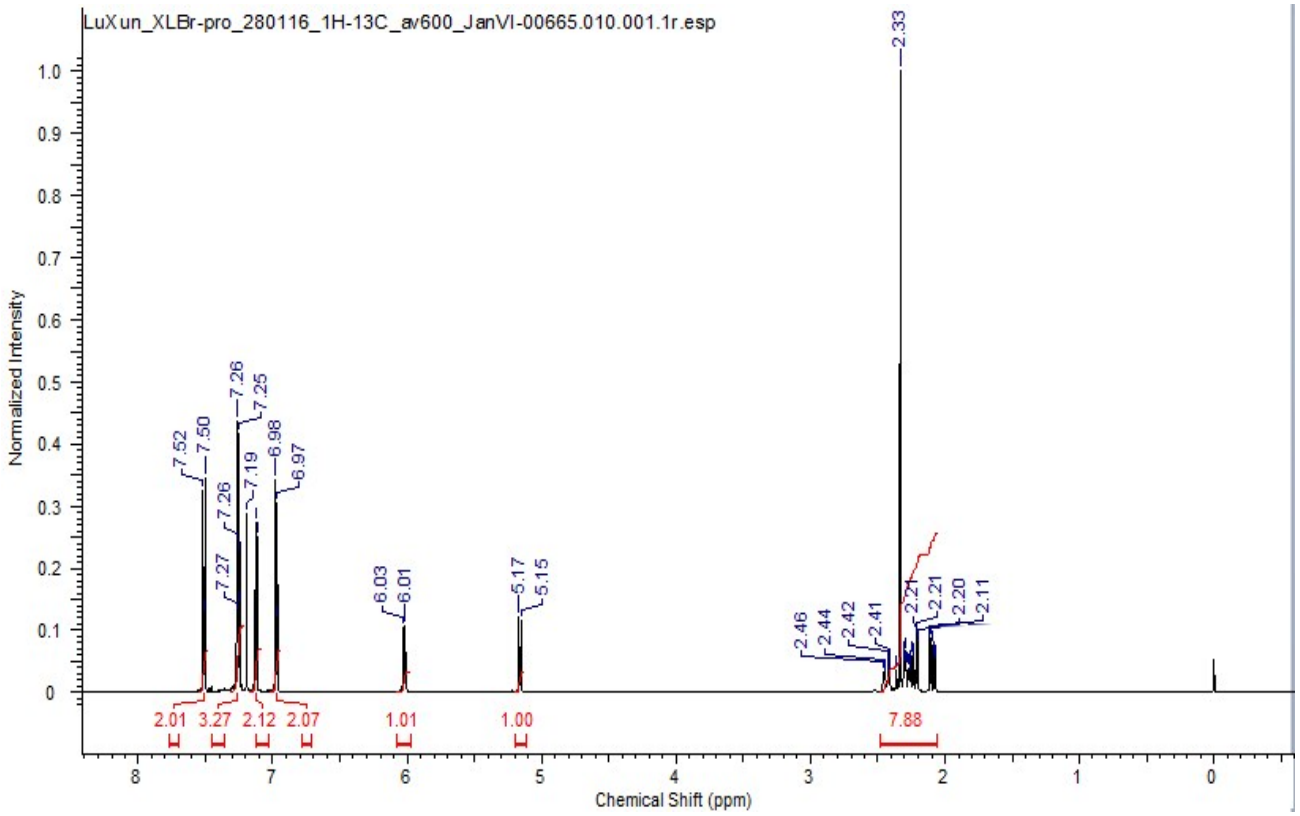
6l

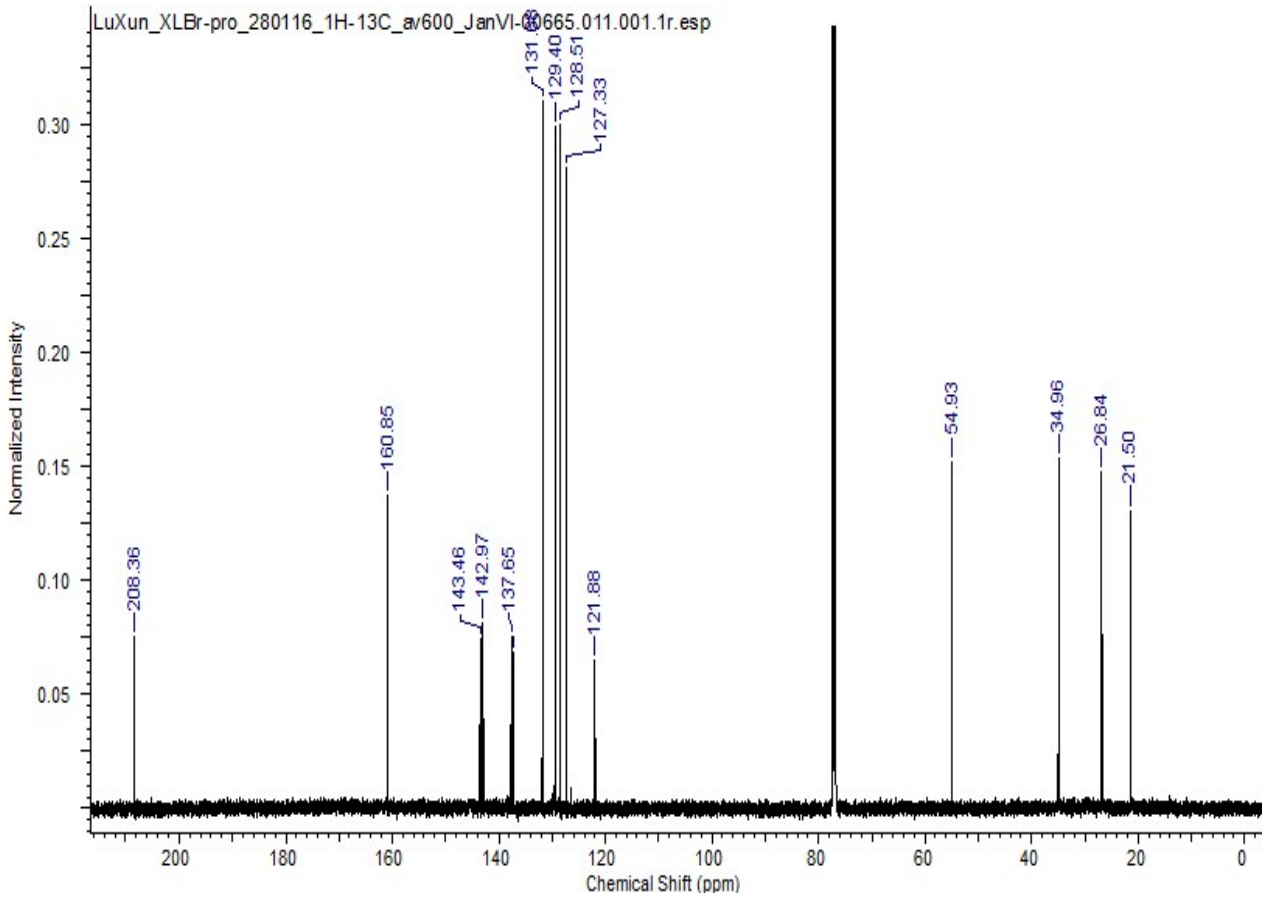

LuXun_XLCl-p_070515_13C-1H_av600_MayV-00229.012.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
7.82
7.81
7.60
7.58
7.33
7.33
7.26
7.17
7.11
7.10
6.05
6.03
5.26
5.25
2.52
2.50
2.50
2.49
2.40
2.29
2.29
2.28
2.18
2.18
0.73
1.99
1.78
3.97
2.01
0.98
1.00
1.06
3.13
2.27
1.06

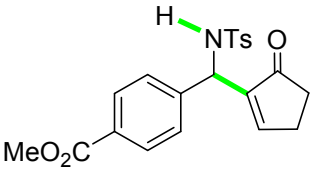

LUXUN_XLCL-P_070515_13C-1H_AV600_MAYV-00229.011.001.1R.esp
Normalized Intensity
Chemical Shift (ppm)
208.35
160.76
143.41
143.05
137.14
133.81
129.74
129.39
128.75
128.17
127.37
126.52
77.21
77.00
76.79
54.94
34.97
26.83
21.47
0.01
-0.01
0.15
-0.18


H
NTs
O
Br

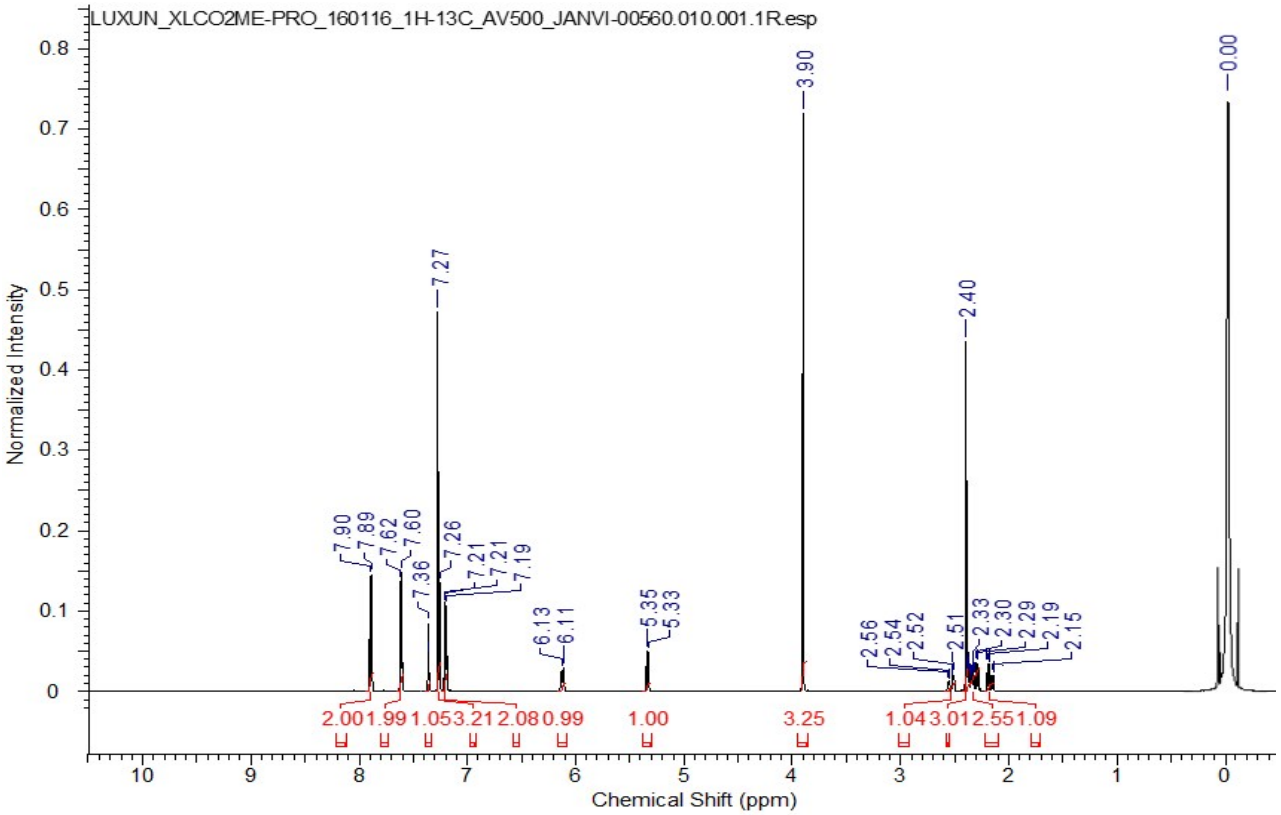
6m

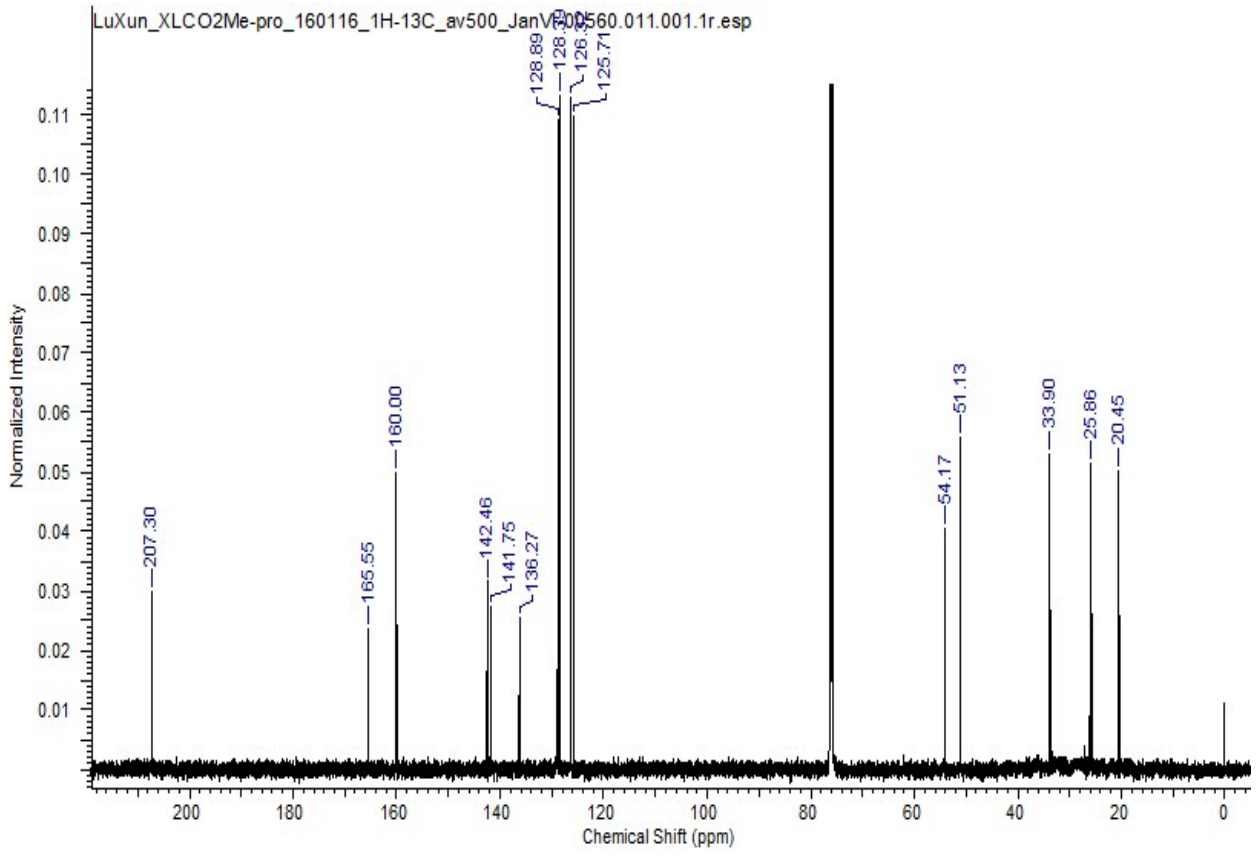

LuXun_XLBr-pro_280116_1H-13C_av600_JanVI-00665.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
2.33
7.52
7.50
7.26
7.25
6.98
6.97
7.26
7.19
7.27
6.03
6.01
5.17
5.15
2.46
2.44
2.42
2.41
2.21
2.21
2.20
2.11
2.01
3.27
2.12
2.07
1.01
1.00
7.88

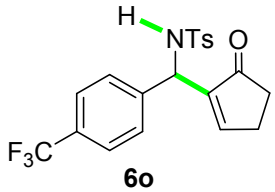

LuXun_XLBr-pro_280116_1H-13C_av600_JanVI-00665.011.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
131.68
129.40
128.51
127.33
208.36
160.85
143.46
142.97
137.65
121.88
54.93
34.96
26.84
21.50


H
NTs
O
MeO2C

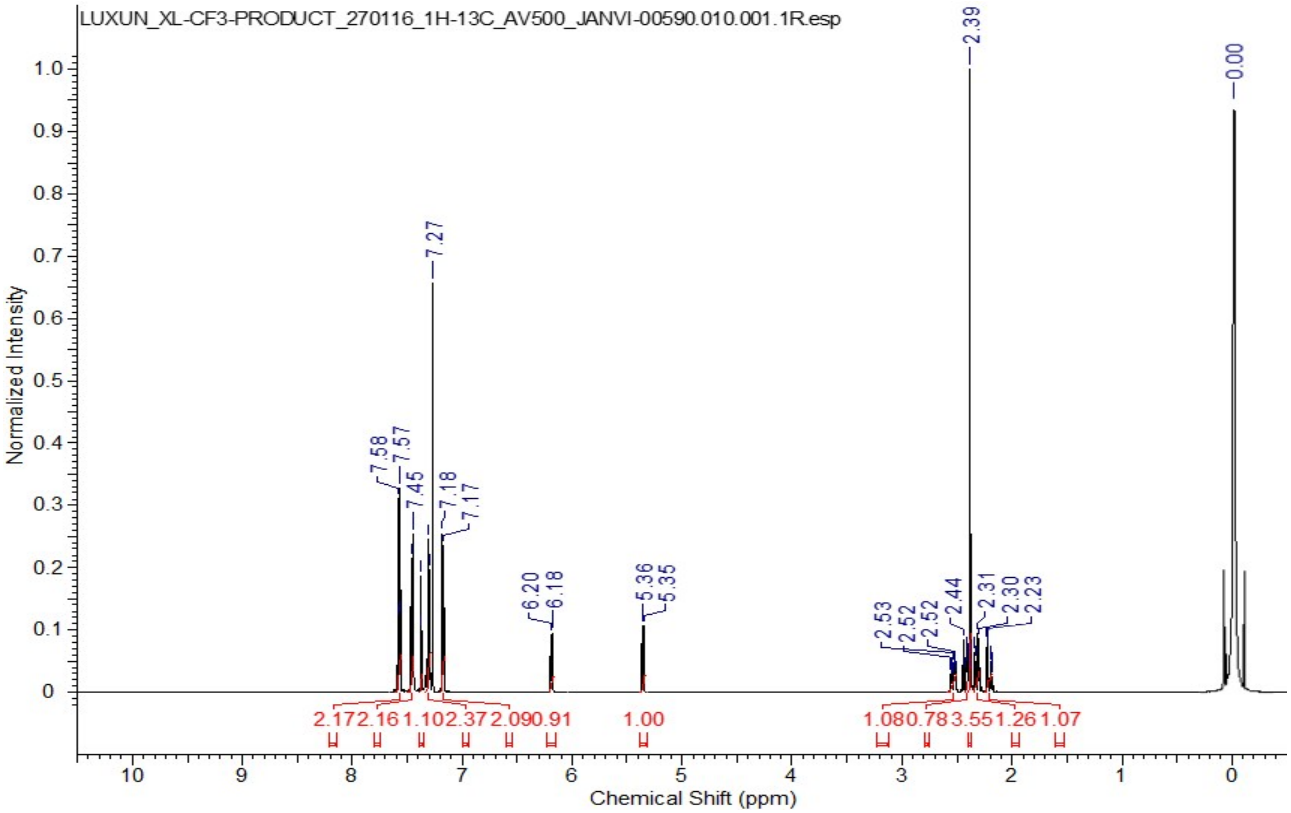
6n

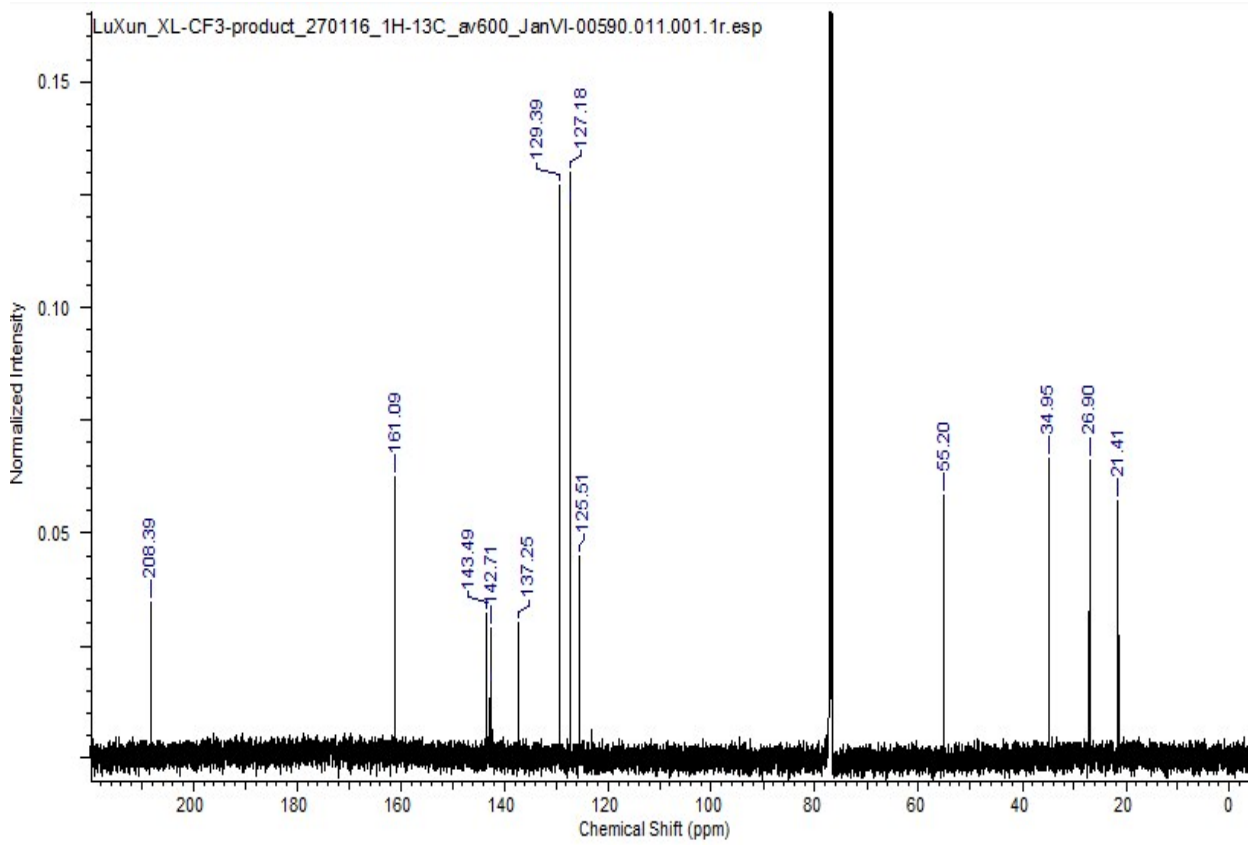

LUXUN_XLCO2ME-PRO_160116_1H-13C_AV500_JANVI-00560.010.001.1R.esp
Normalized Intensity
Chemical Shift (ppm)
7.90
7.89
7.62
7.60
7.36
7.27
7.26
7.21
7.21
7.19
6.13
6.11
5.35
5.33
3.90
2.56
2.54
2.52
2.51
2.40
2.33
2.30
2.29
2.19
2.15
0.00
2.00 1.99 1.05 3.21 2.08 0.99 1.00 3.25 1.04 3.01 2.55 1.09

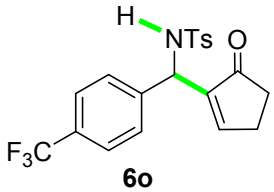

LuXun_XLCO2Me-pro_160116_1H-13C_av500_JanVI-00560.011.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
207.30
165.55
160.00
142.46
141.75
136.27
128.89
128.30
126.35
125.71
54.17
51.13
33.90
25.86
20.45


H
NTs
O
F3C

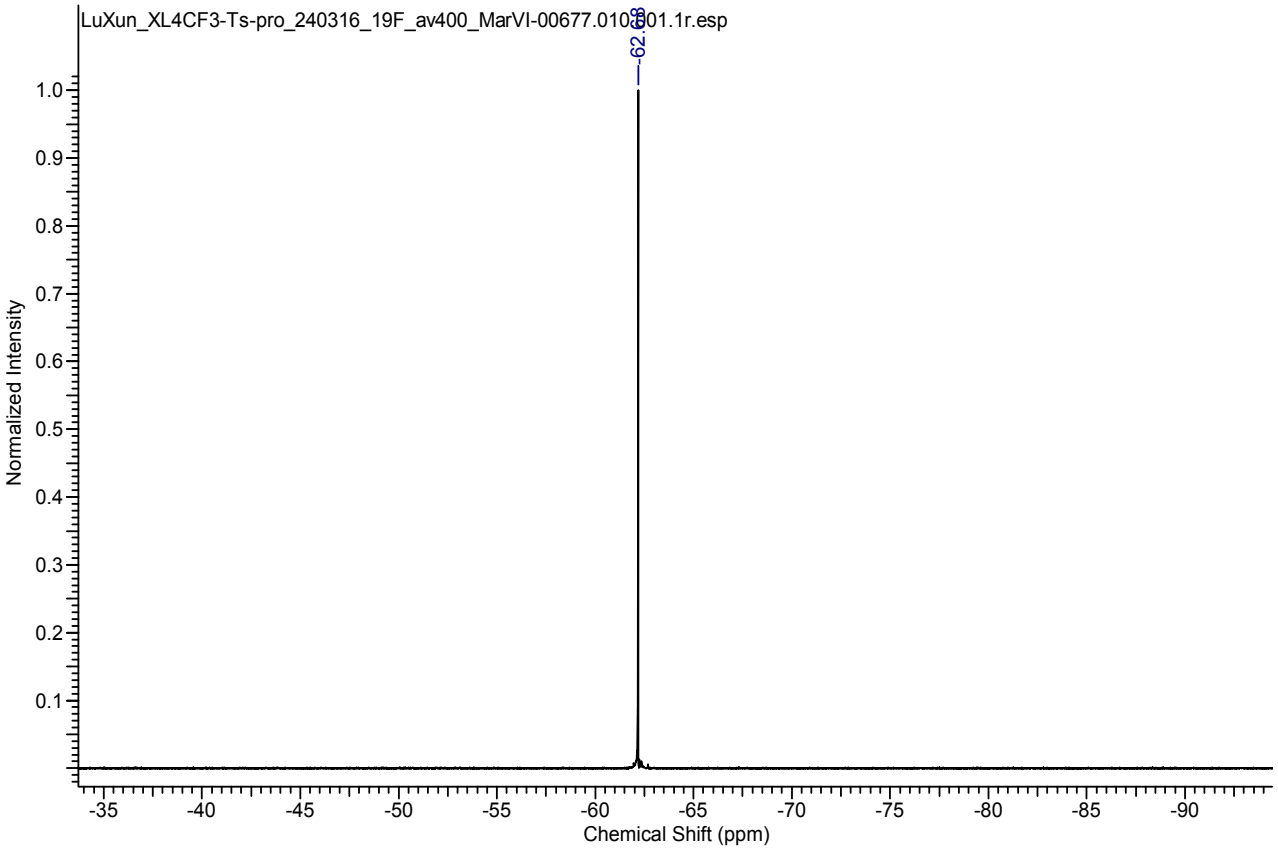
6o

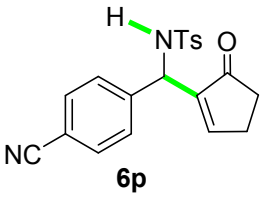

LUXUN_XL-CF3-PRODUCT_270116_1H-13C_AV500_JANVI-00590.010.001.1R.esp
Normalized Intensity
Chemical Shift (ppm)
7.58
7.57
7.45
7.27
7.18
7.17
6.20
6.18
5.36
5.35
2.53
2.52
2.52
2.44
2.31
2.30
2.23
2.39
0.00
2.17
2.16
1.10
2.37
2.09
0.91
1.00
1.08
0.78
3.55
1.26
1.07


LuXun_XL-CF3-product_270116_1H-13C_av600_JanVI-00590.011.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
208.39
161.09
143.49
142.71
137.25
129.39
127.18
125.51
55.20
34.95
26.90
21.41

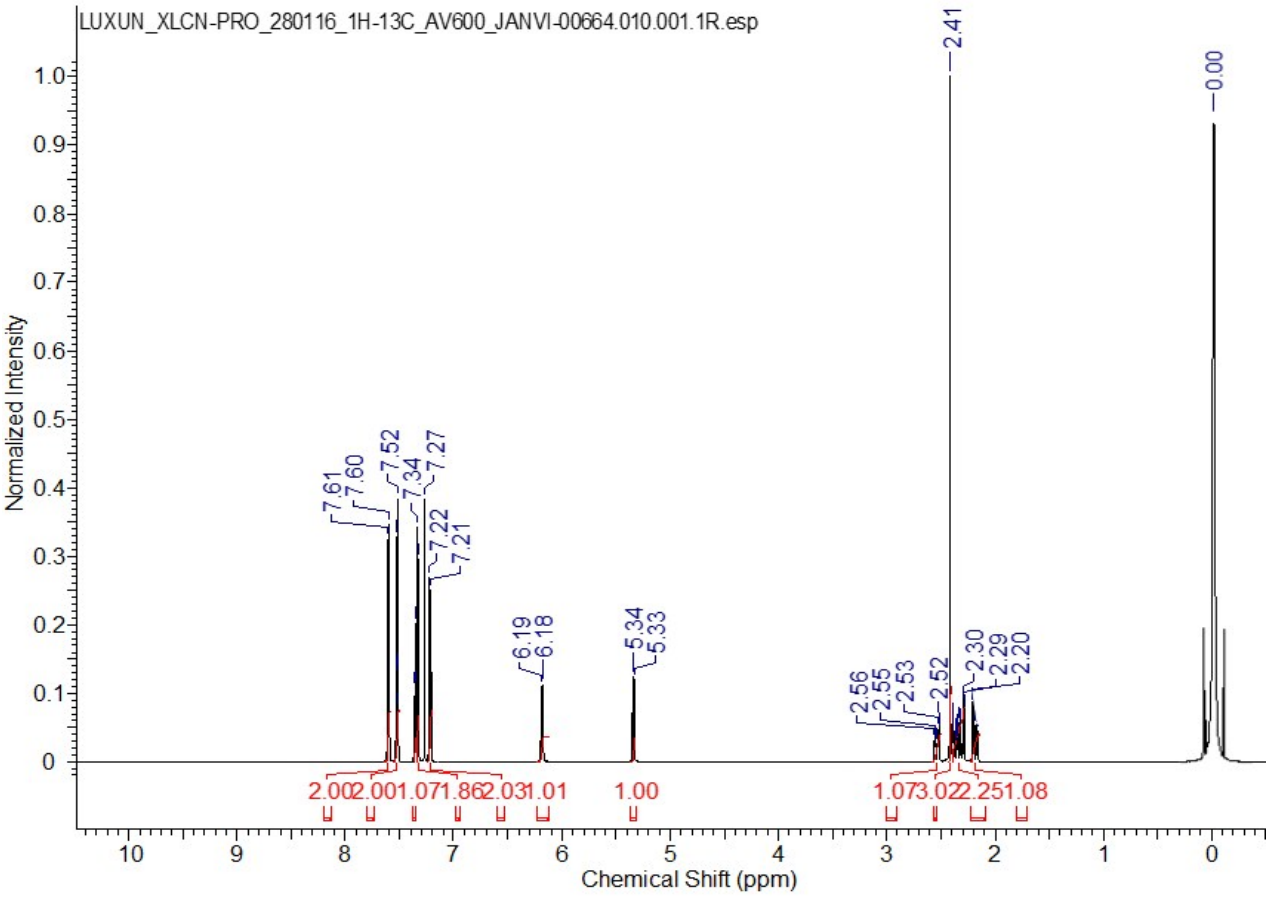

H
NTs
O
F3C

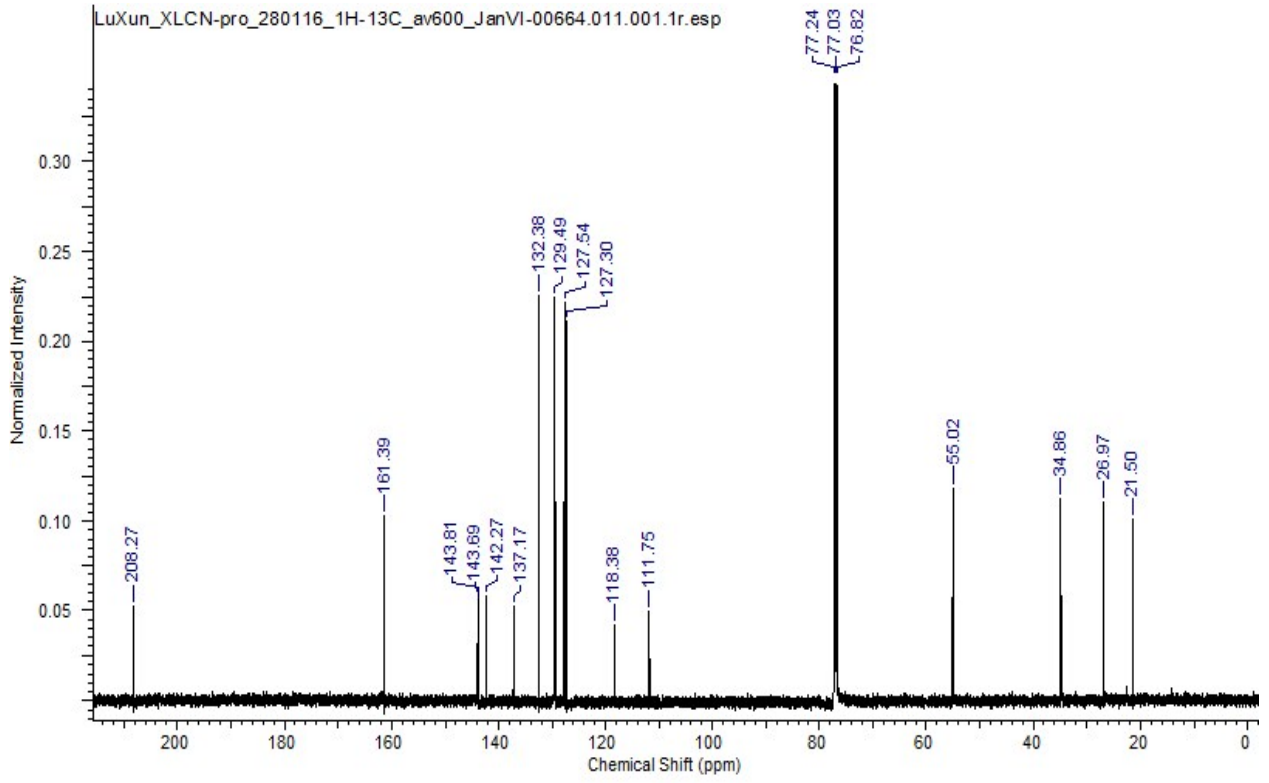
6o

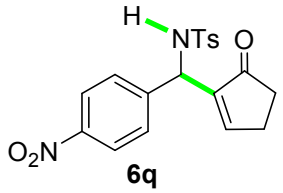

LuXun_XL4CF3-Ts-pro_240316_19F_av400_MarVI-00677.010001.1r.esp
-62.68
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
Chemical Shift (ppm)


H
NTs
O
NC

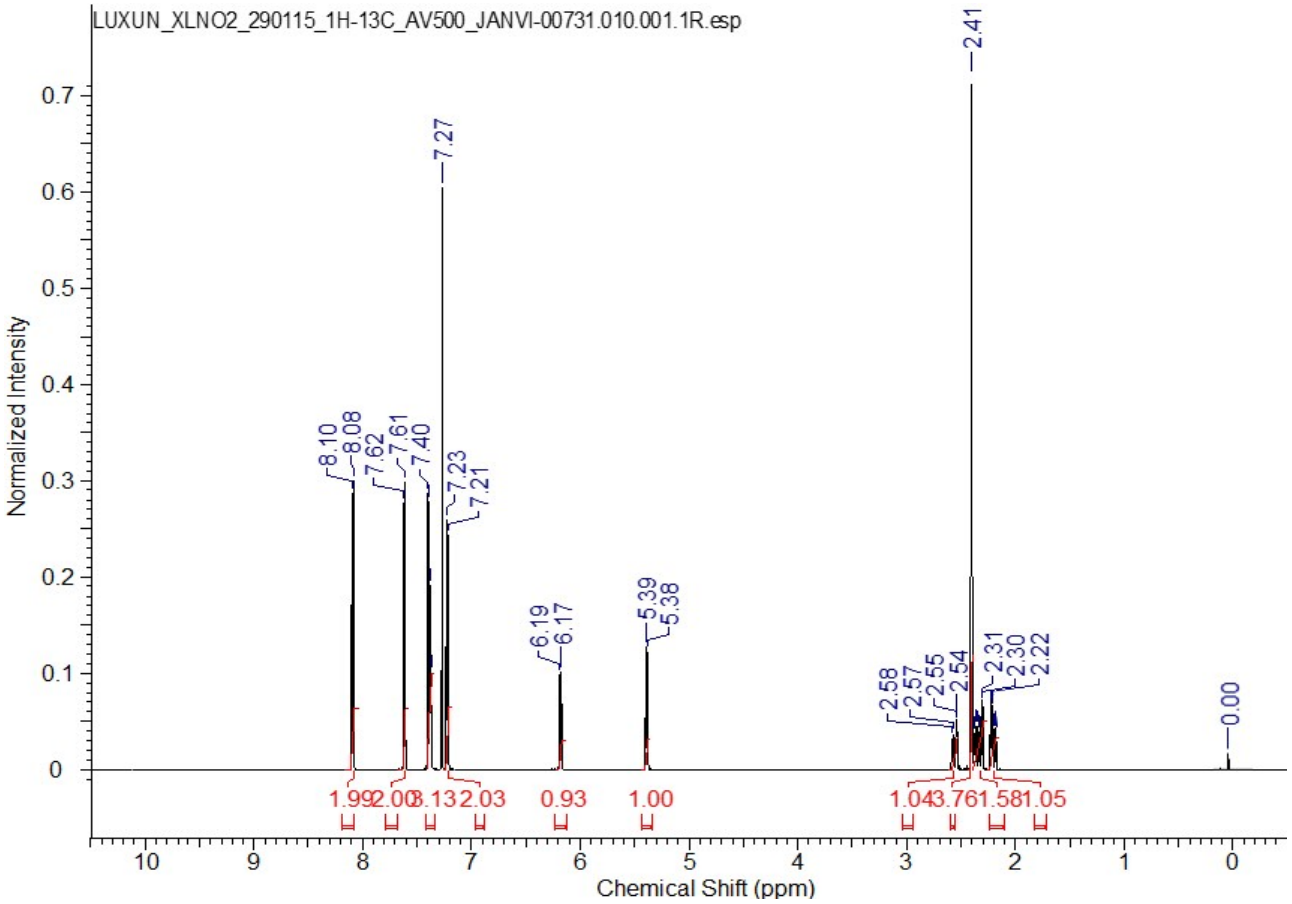
6p

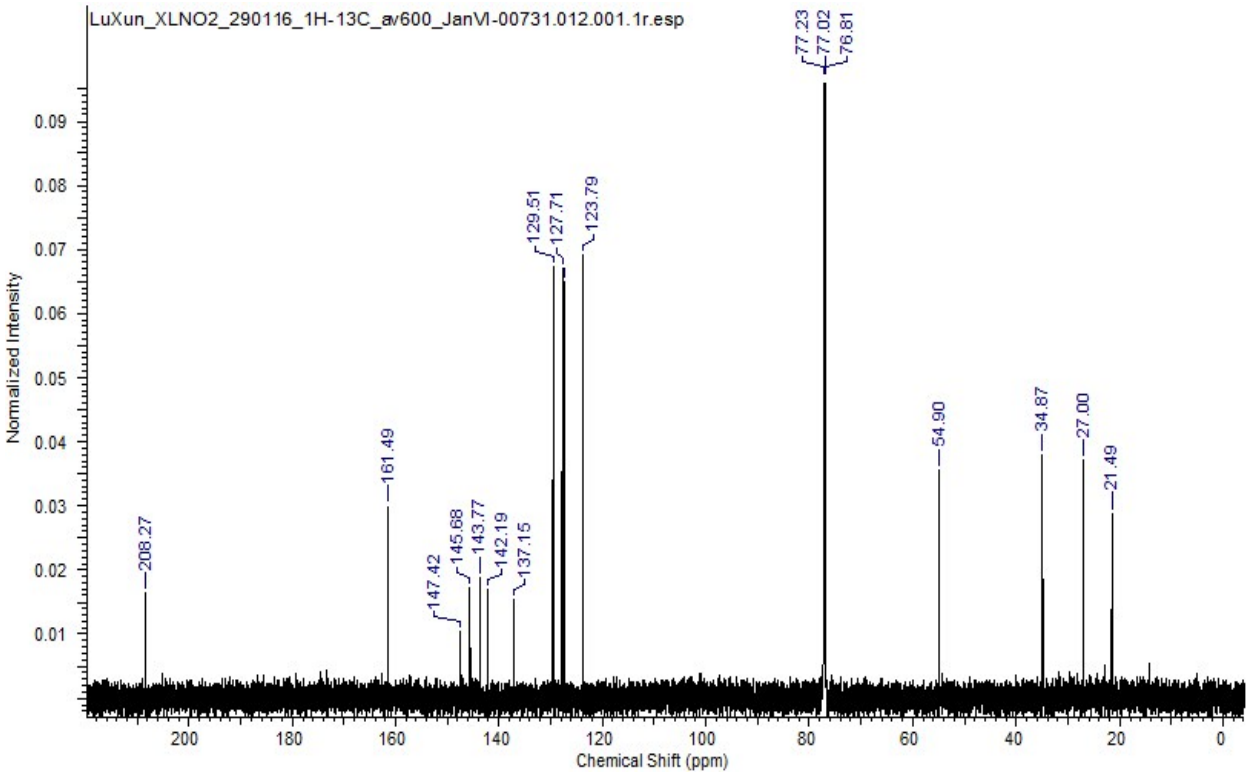

LUXUN_XLCN-PRO_280116_1H-13C_AV600_JANVI-00664.010.001.1R.esp
Normalized Intensity
Chemical Shift (ppm)
7.61
7.60
7.52
7.34
7.27
7.22
7.21
6.19
6.18
5.34
5.33
2.56
2.55
2.53
2.52
2.30
2.29
2.20
2.41
0.00
2.00
2.00
1.07
1.86
2.03
1.01
1.00
1.07
3.02
2.25
1.08

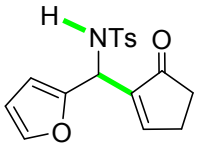

LuXun_XLCN-pro_280116_1H-13C_av600_JanVI-00664.011.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
77.24
77.03
76.82
132.38
129.49
127.54
127.30
208.27
161.39
143.81
143.69
142.27
137.17
118.38
111.75
55.02
34.86
26.97
21.50


H
NTs
O
O2N

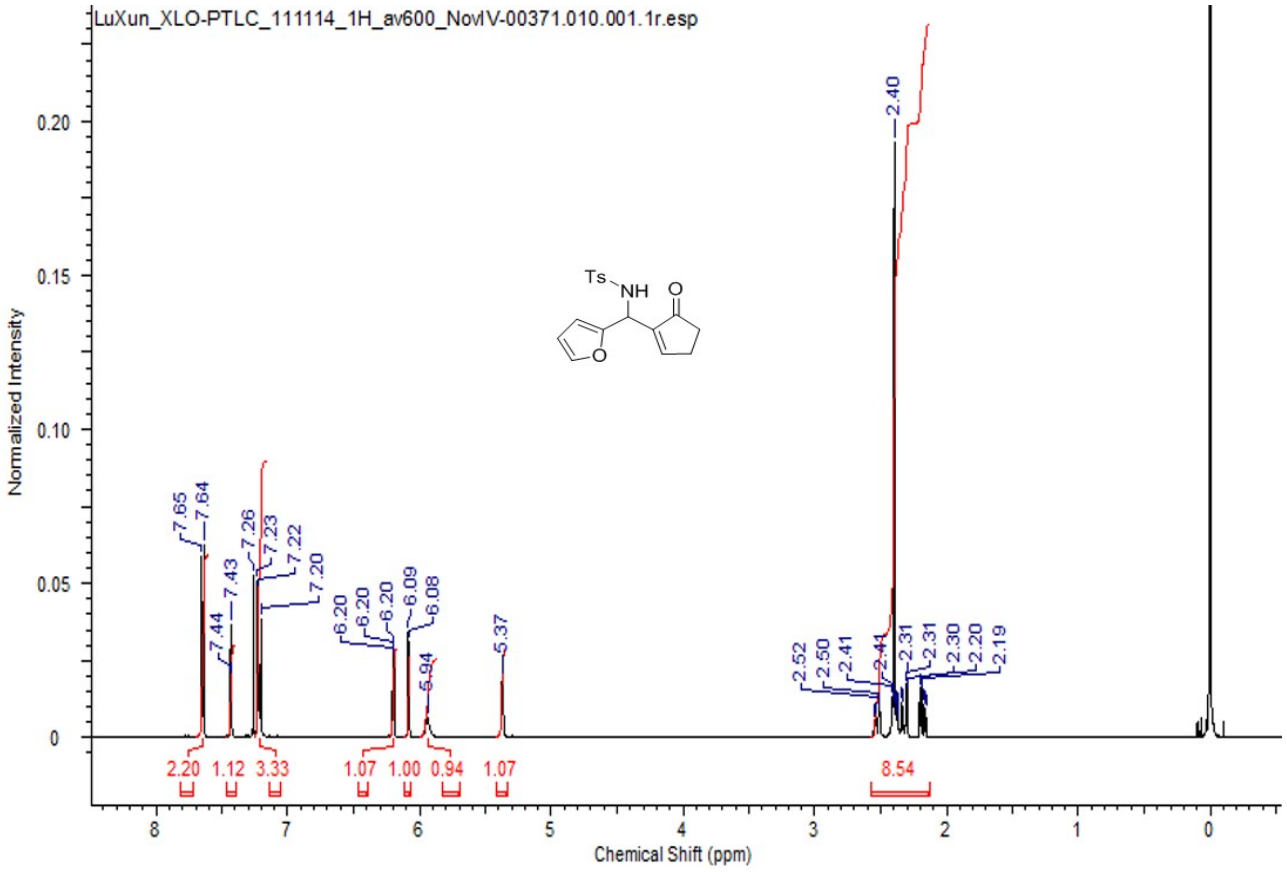
6q

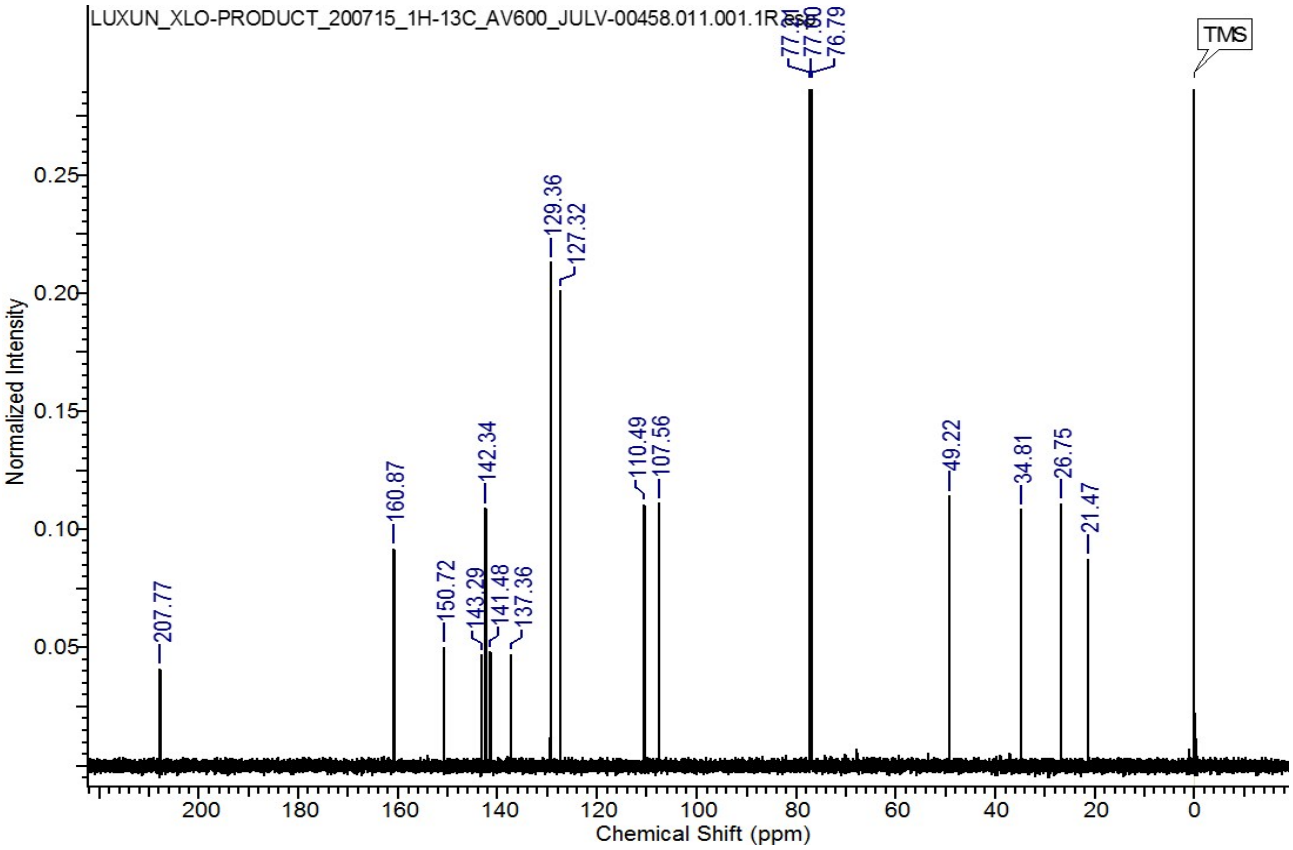

LUXUN_XLNO2_290115_1H-13C_AV500_JANVI-00731.010.001.1R.esp
Normalized Intensity
Chemical Shift (ppm)
8.10
8.08
7.62
7.61
7.40
7.27
7.23
7.21
6.19
6.17
5.39
5.38
2.58
2.57
2.55
2.54
2.41
2.31
2.30
2.22
0.00
1.99
2.00
3.13
2.03
0.93
1.00
1.04
3.76
1.58
1.05

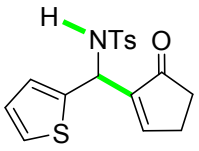

LuXun_XLNO2_290116_1H-13C_av600_JanVI-00731.012.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
208.27
161.49
147.42
145.68
143.77
142.19
137.15
129.51
127.71
123.79
77.23
77.02
76.81
54.90
34.87
27.00
21.49


H
NTs
O
O

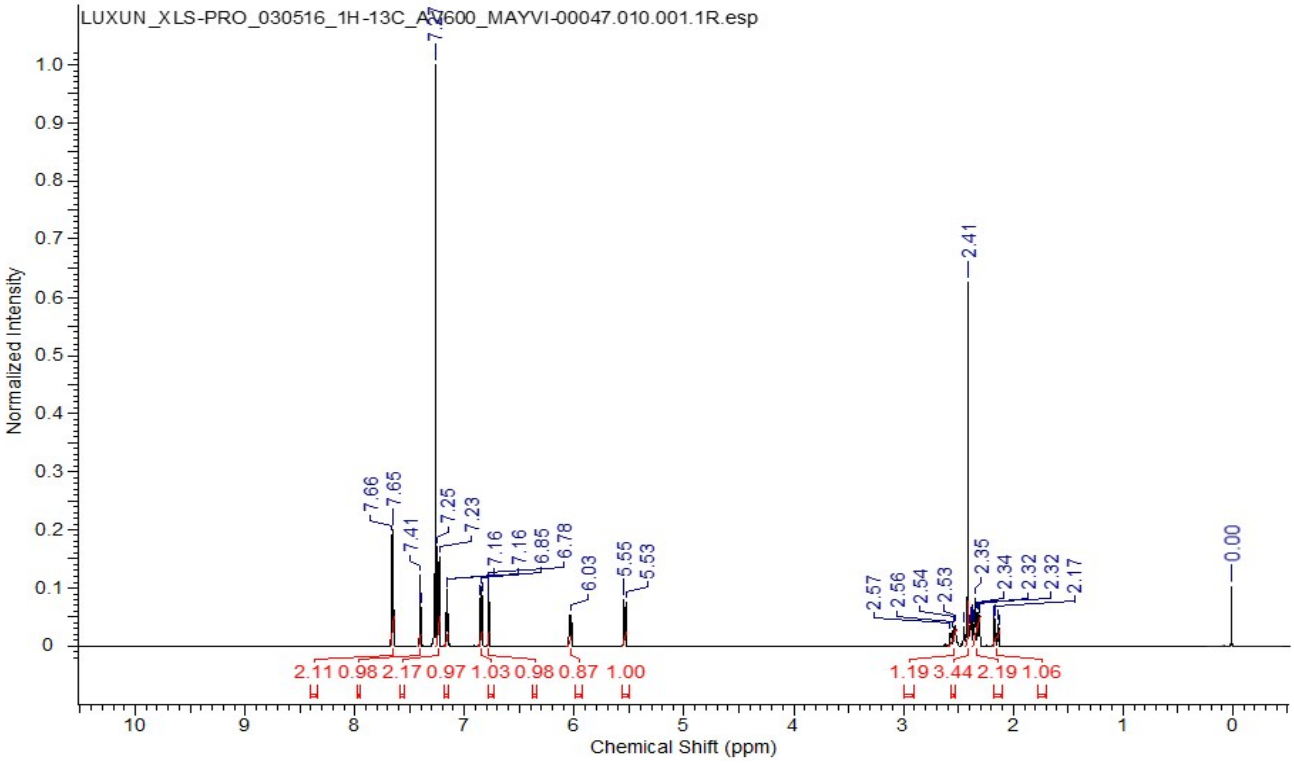
6r

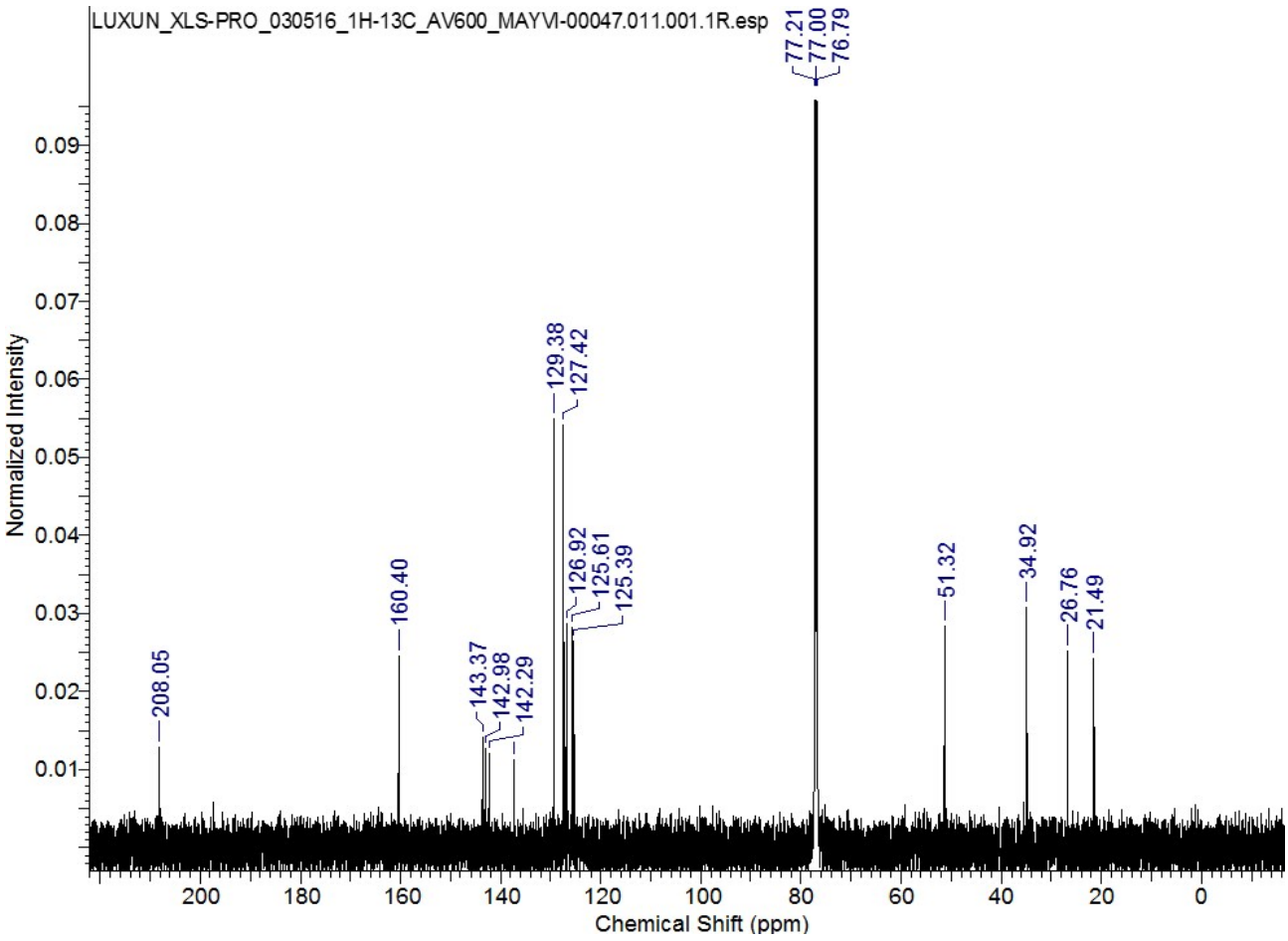

LuXun_XLO-PTLC_111114_1H_av600_NovIV-00371.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
Ts
NH
O
O
7.65
7.64
7.44
7.43
7.26
7.23
7.22
7.20
6.20
6.20
6.20
6.09
6.08
5.94
5.37
2.52
2.50
2.41
2.41
2.40
2.31
2.31
2.30
2.20
2.19
2.20
1.12
3.33
1.07
1.00
0.94
1.07
8.54

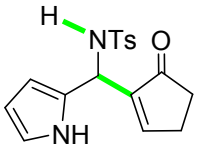

LUXUN_XLO-PRODUCT_200715_1H-13C_AV600_JULV-00458.011.001.1R.esp
Normalized Intensity
Chemical Shift (ppm)
TMS
77.41
77.00
76.79
129.36
127.32
110.49
107.56
49.22
34.81
26.75
21.47
207.77
160.87
150.72
143.29
142.34
141.48
137.36


H
NTs
O
S

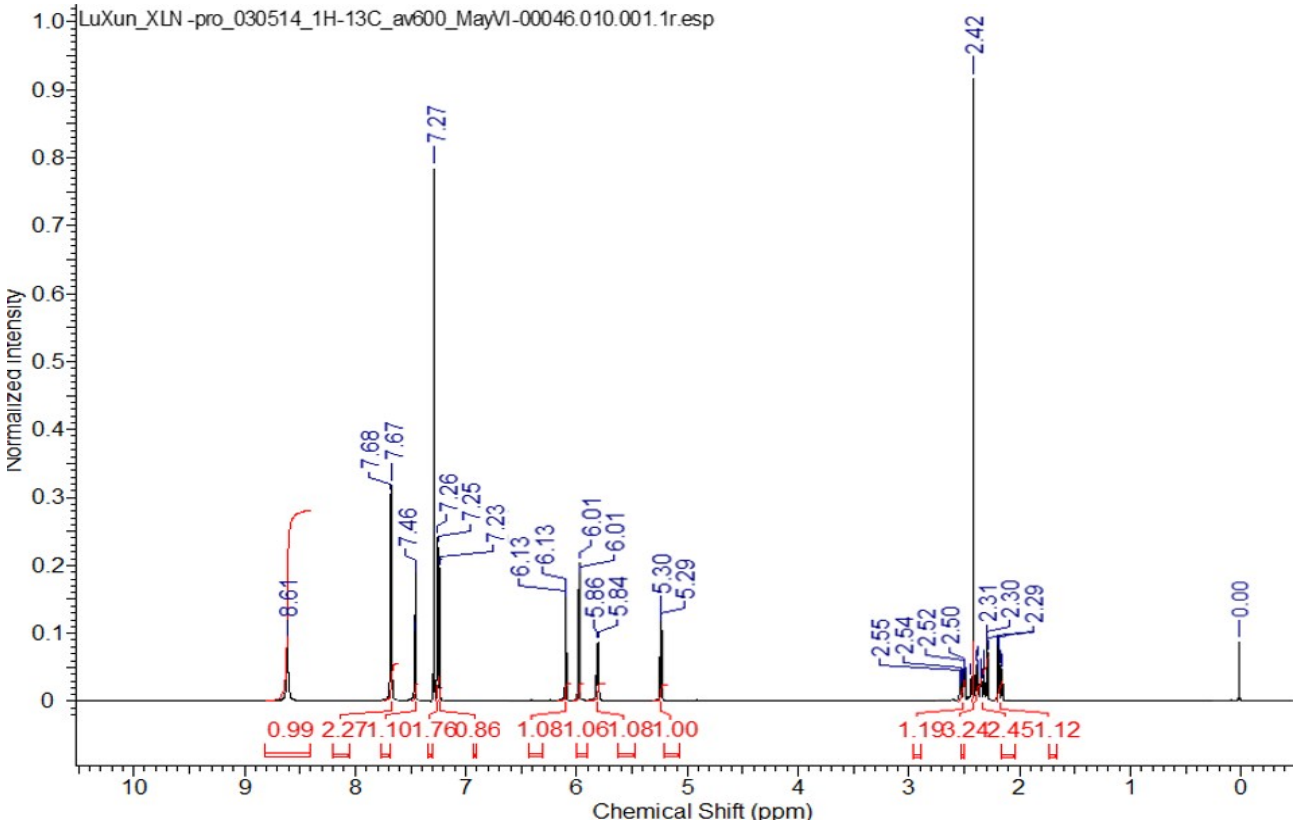
6s

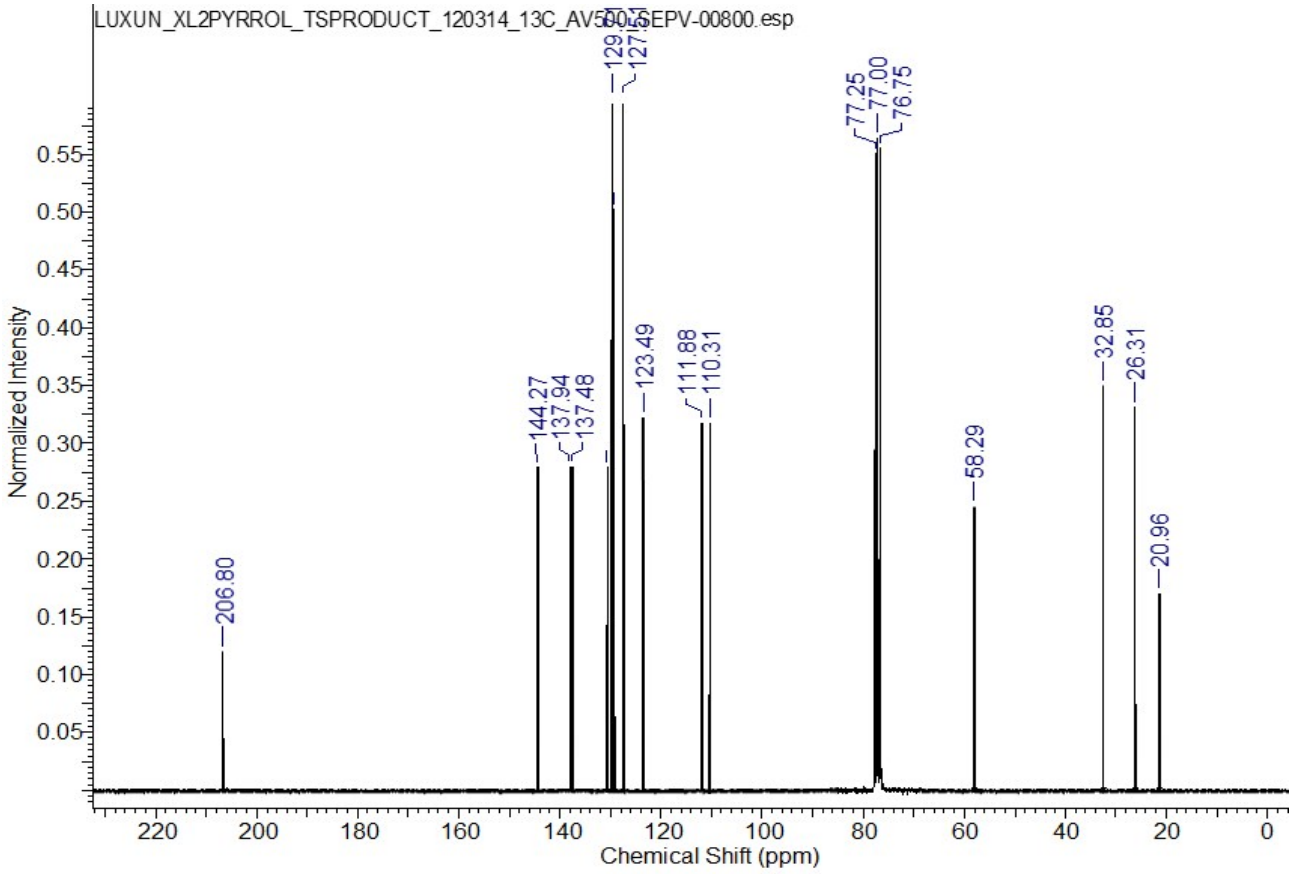

LUXUN_XLS-PRO_030516_1H-13C_AV600_MAYVI-00047.010.001.1R.esp
Normalized Intensity
Chemical Shift (ppm)
7.66
7.65
7.41
7.25
7.23
7.16
7.16
6.85
6.78
6.03
5.55
5.53
2.57
2.56
2.54
2.53
2.41
2.35
2.34
2.32
2.32
2.17
0.00
2.11 0.98 2.17 0.97 1.03 0.98 0.87 1.00
1.19 3.44 2.19 1.06

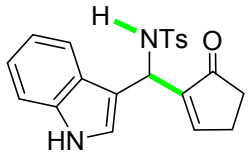

LUXUN_XLS-PRO_030516_1H-13C_AV600_MAYVI-00047.011.001.1R.esp
Normalized Intensity
Chemical Shift (ppm)
77.21
77.00
76.79
208.05
160.40
143.37
142.98
142.29
129.38
127.42
126.92
125.61
125.39
51.32
34.92
26.76
21.49


H
NTs
O
NH

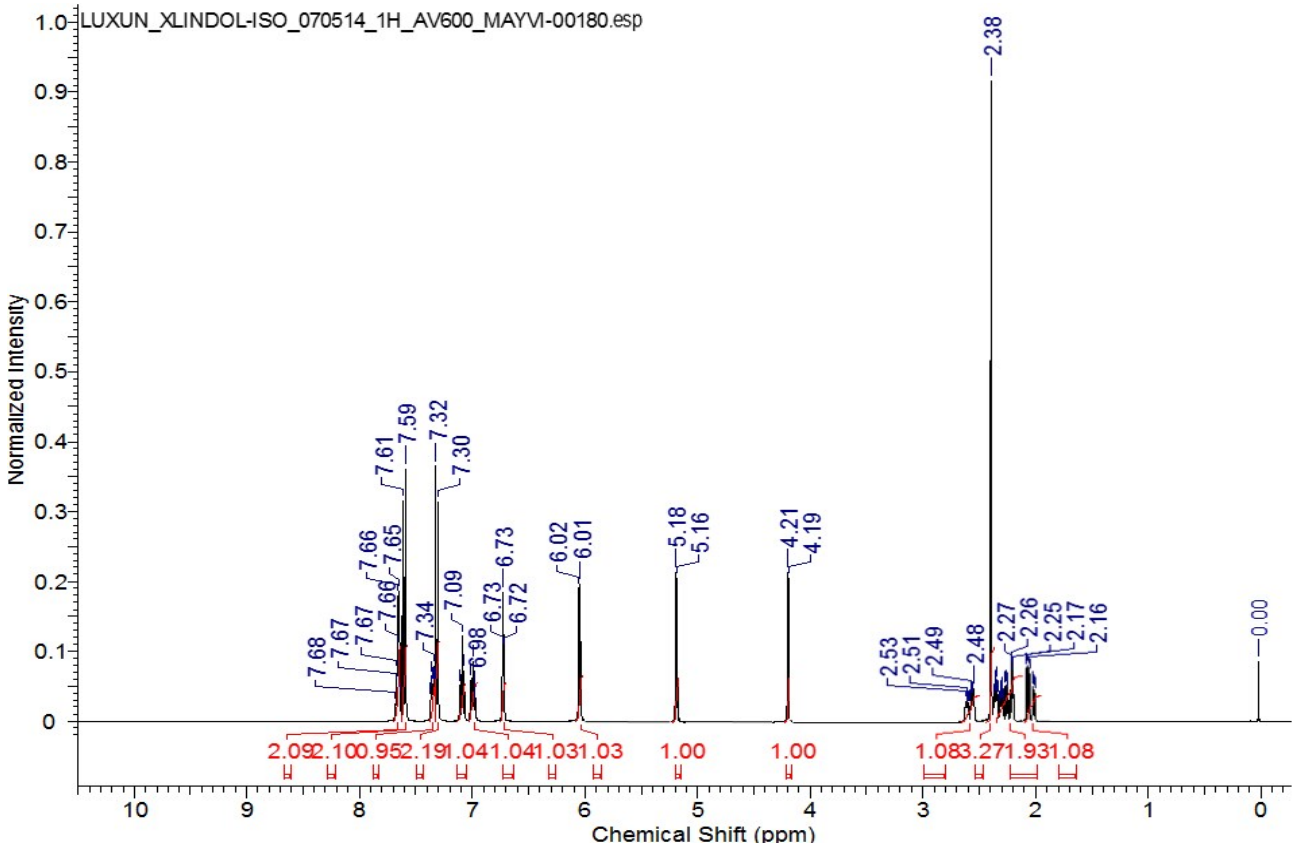
6t

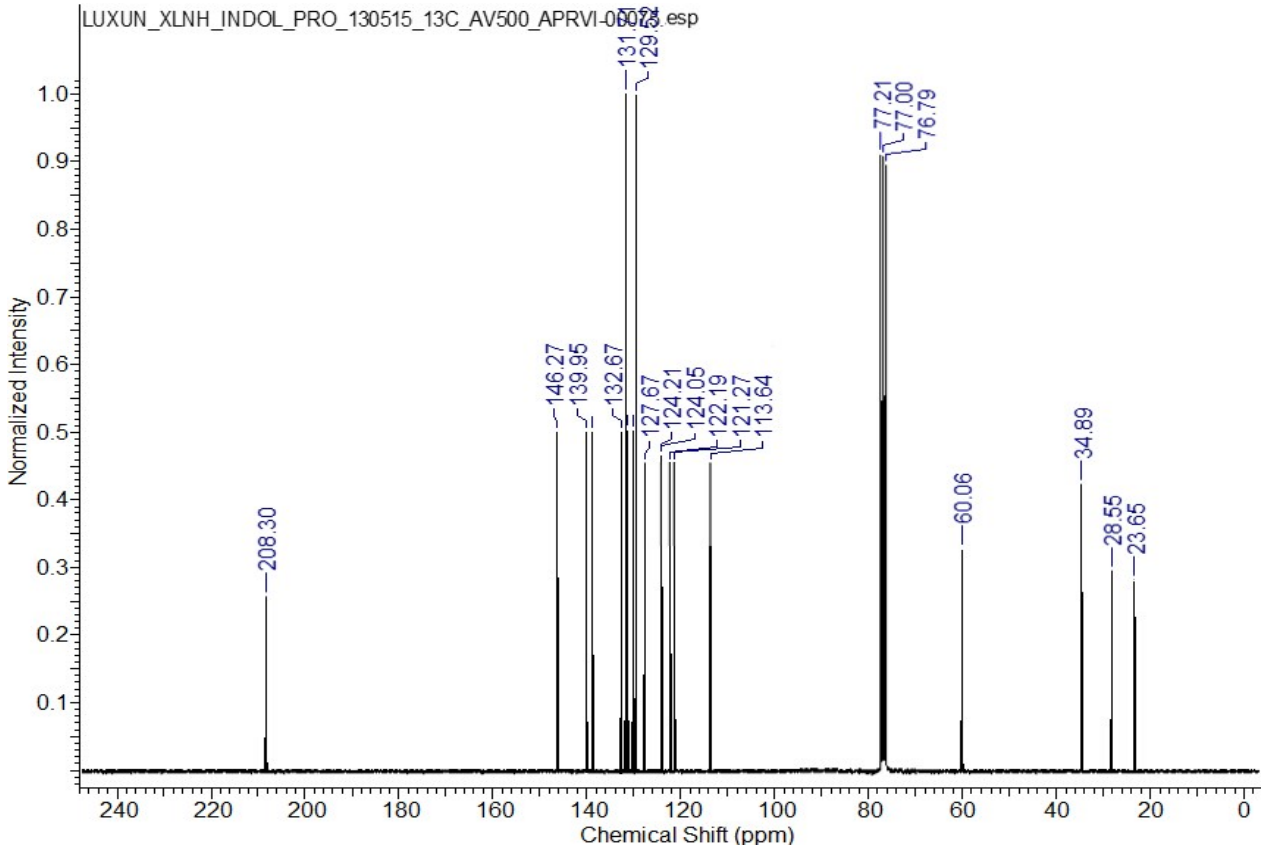

LuXun_XLN -pro_030514_1H-13C_av600_MayVI-00046.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
9.61
7.68
7.67
7.46
7.27
7.26
7.25
7.23
6.13
6.13
6.01
6.01
5.86
5.84
5.30
5.29
2.55
2.54
2.52
2.50
2.42
2.31
2.30
2.29
0.00
0.99 2.27 1.10 1.76 0.86 1.08 1.06 1.08 1.00 1.19 3.24 2.45 1.12

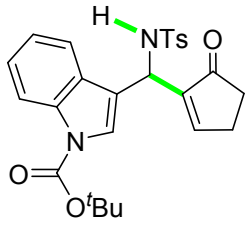

LUXUN_XL2PYRROL_TSPRODUCT_120314_13C_AV500_SEPV-00800.esp
Normalized Intensity
Chemical Shift (ppm)
206.80
144.27
137.94
137.48
129.
127.
123.49
111.88
110.31
77.25
77.00
76.75
58.29
32.85
26.31
20.96


H
NTs
O
HN

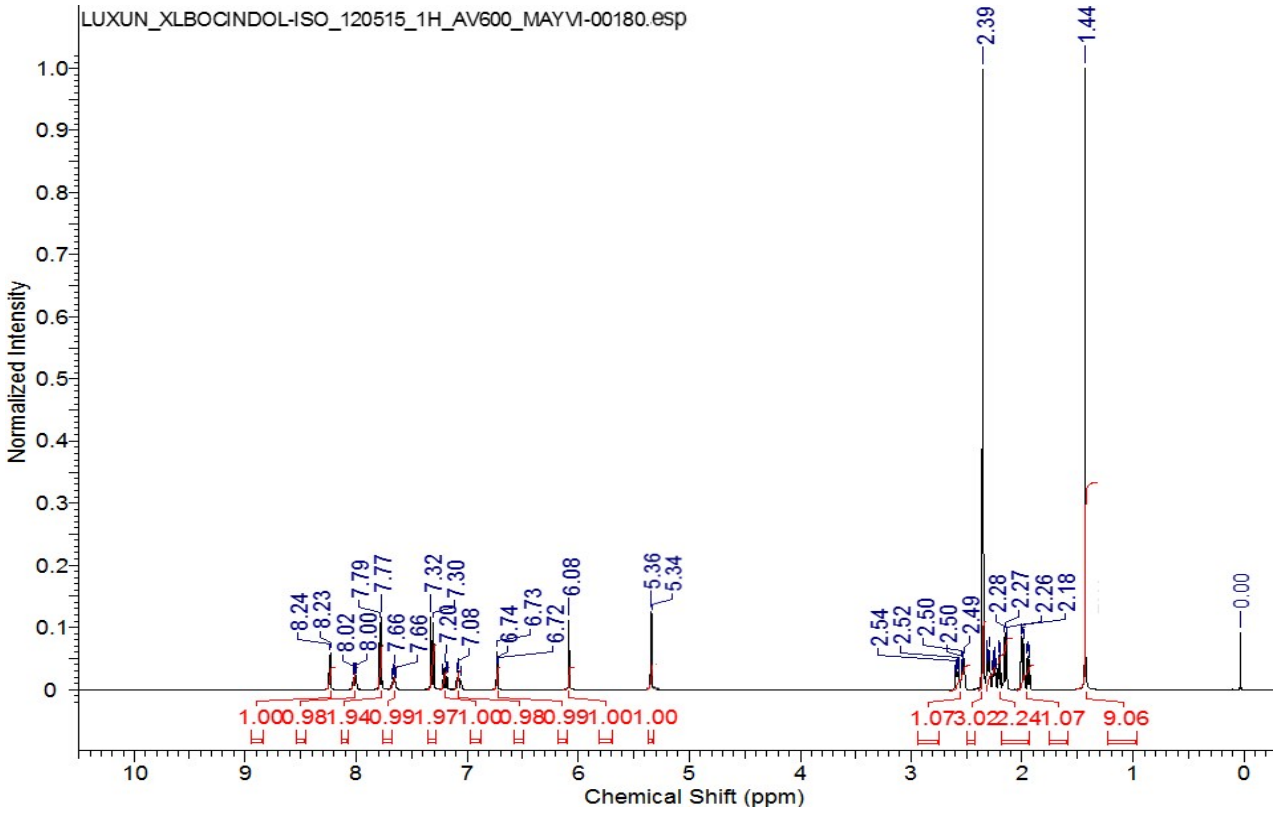
6u

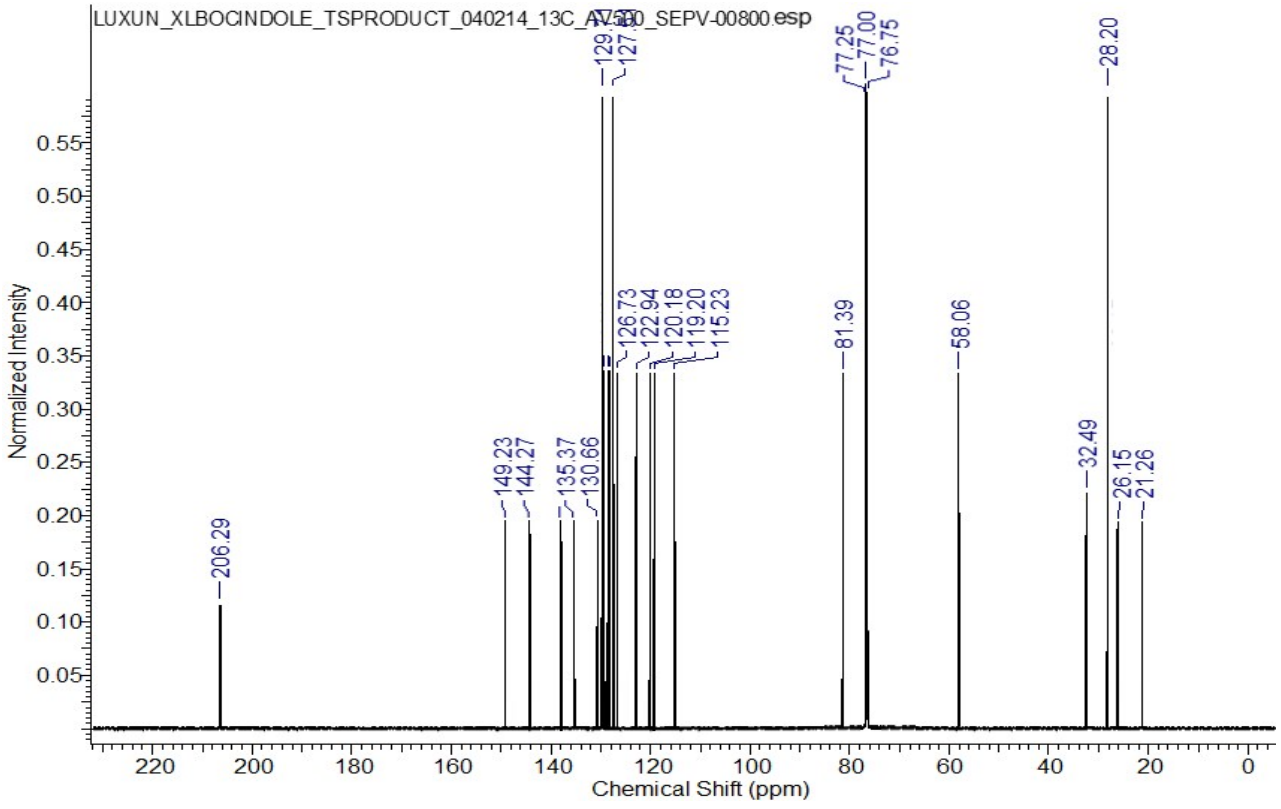

LUXUN_XLINDOL-ISO_070514_1H_AV600_MAYVI-00180.esp
Normalized Intensity
Chemical Shift (ppm)
2.38
7.61
7.59
7.32
7.30
7.66
7.65
7.68
7.67
7.67
7.66
7.34
7.09
6.98
6.73
6.72
6.73
6.02
6.01
5.18
5.16
4.21
4.19
2.53
2.51
2.49
2.48
2.27
2.26
2.25
2.17
2.16
0.00
2.09
2.10
0.95
2.19
1.04
1.04
1.03
1.03
1.00
1.00
1.08
3.27
1.93
1.08

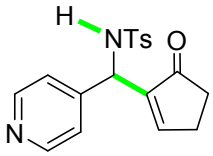

LUXUN_XLNH_INDOL_PRO_130515_13C_AV500_APRVI-00074.esp
Normalized Intensity
Chemical Shift (ppm)
131.74
129.53
77.21
77.00
76.79
146.27
139.95
132.67
127.67
124.21
124.05
122.19
121.27
113.64
208.30
60.06
34.89
28.55
23.65


H
NTs
O
N
O
O
tBu

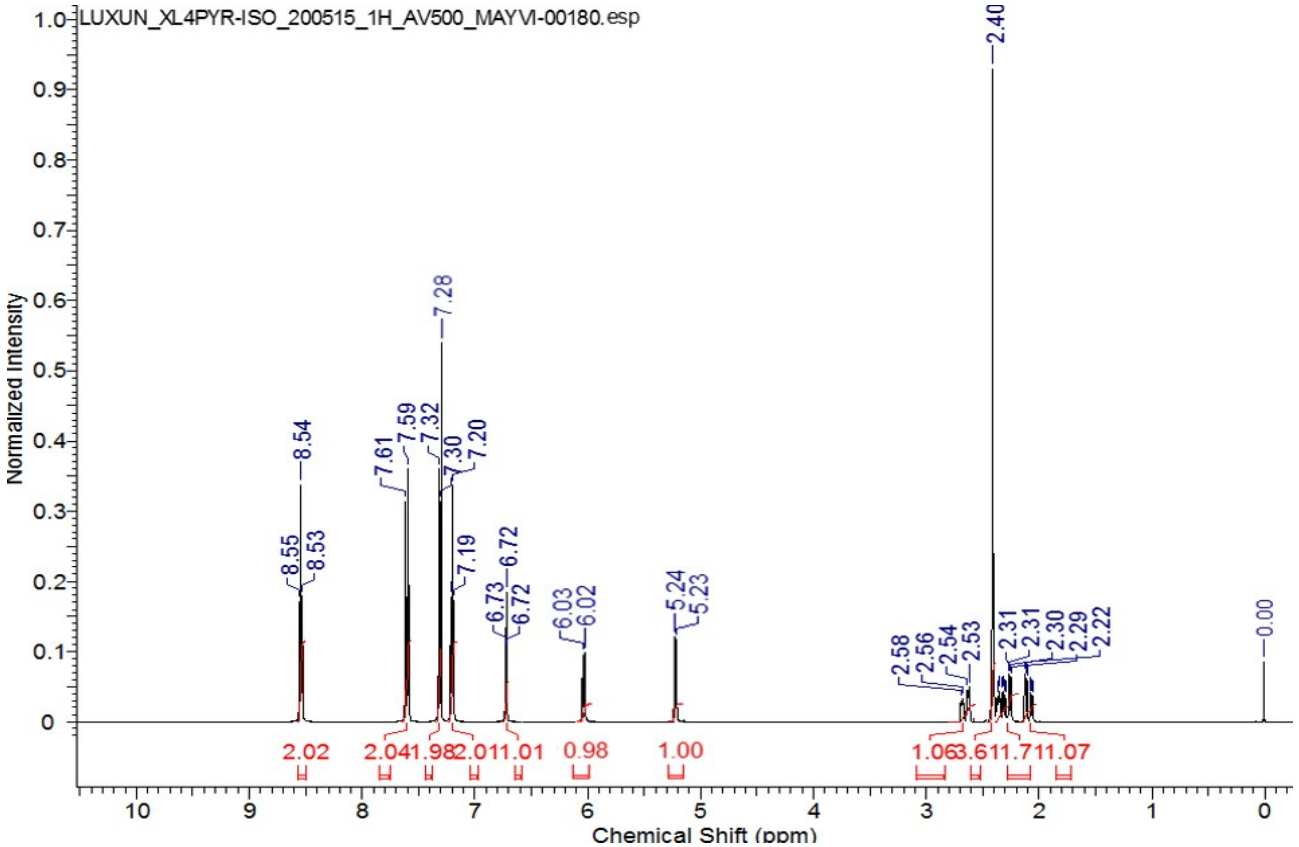
6v

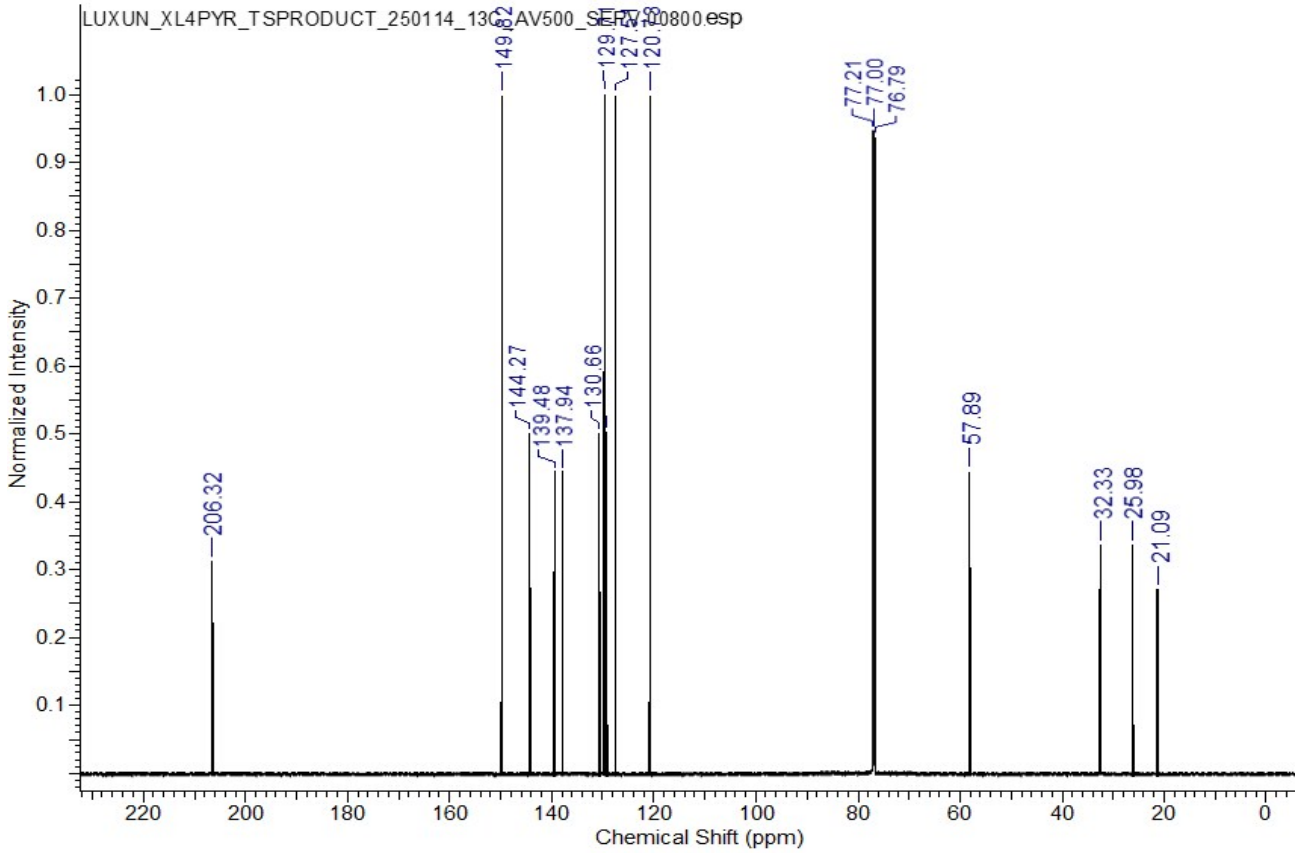

LUXUN_XLBOCINDOL-ISO_120515_1H_AV600_MAYVI-00180.esp
Normalized Intensity
Chemical Shift (ppm)
8.24
8.23
8.02
8.00
7.79
7.77
7.66
7.66
7.32
7.30
7.20
7.08
6.74
6.73
6.72
6.08
5.36
5.34
2.54
2.52
2.50
2.50
2.49
2.28
2.27
2.26
2.18
2.39
1.44
0.00
1.00 0.98 1.94 0.99 1.97 1.00 0.98 0.99 1.00 1.00
1.07 3.02 2.24 1.07 9.06

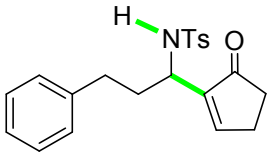

LUXUN_XLBOCINDOLE_TSPRODUCT_040214_13C_AV600_SEPV-00800.esp
Normalized Intensity
Chemical Shift (ppm)
206.29
149.23
144.27
135.37
130.66
129.
127.
126.73
122.94
120.18
119.20
115.23
77.25
77.00
76.75
81.39
58.06
32.49
28.20
26.15
21.26


H
NTs
O
N

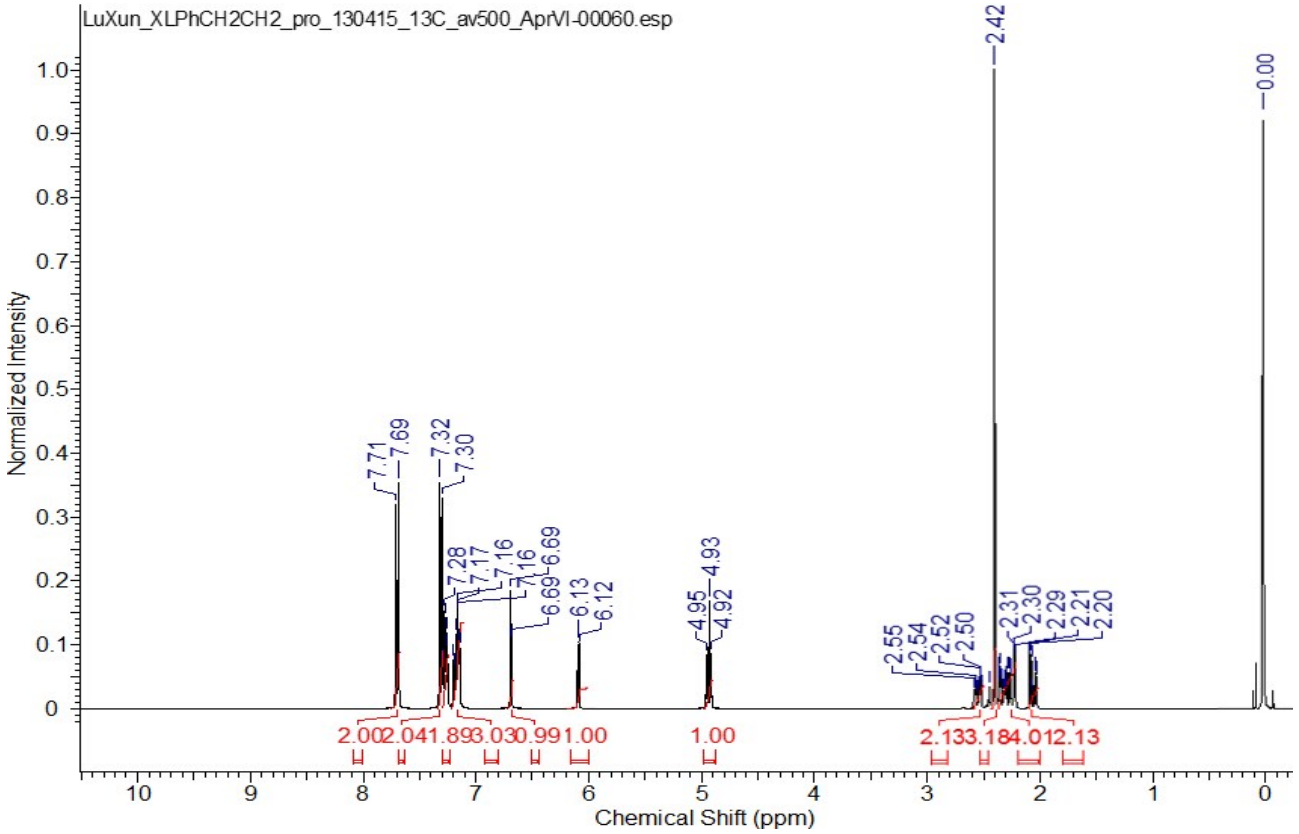
6w

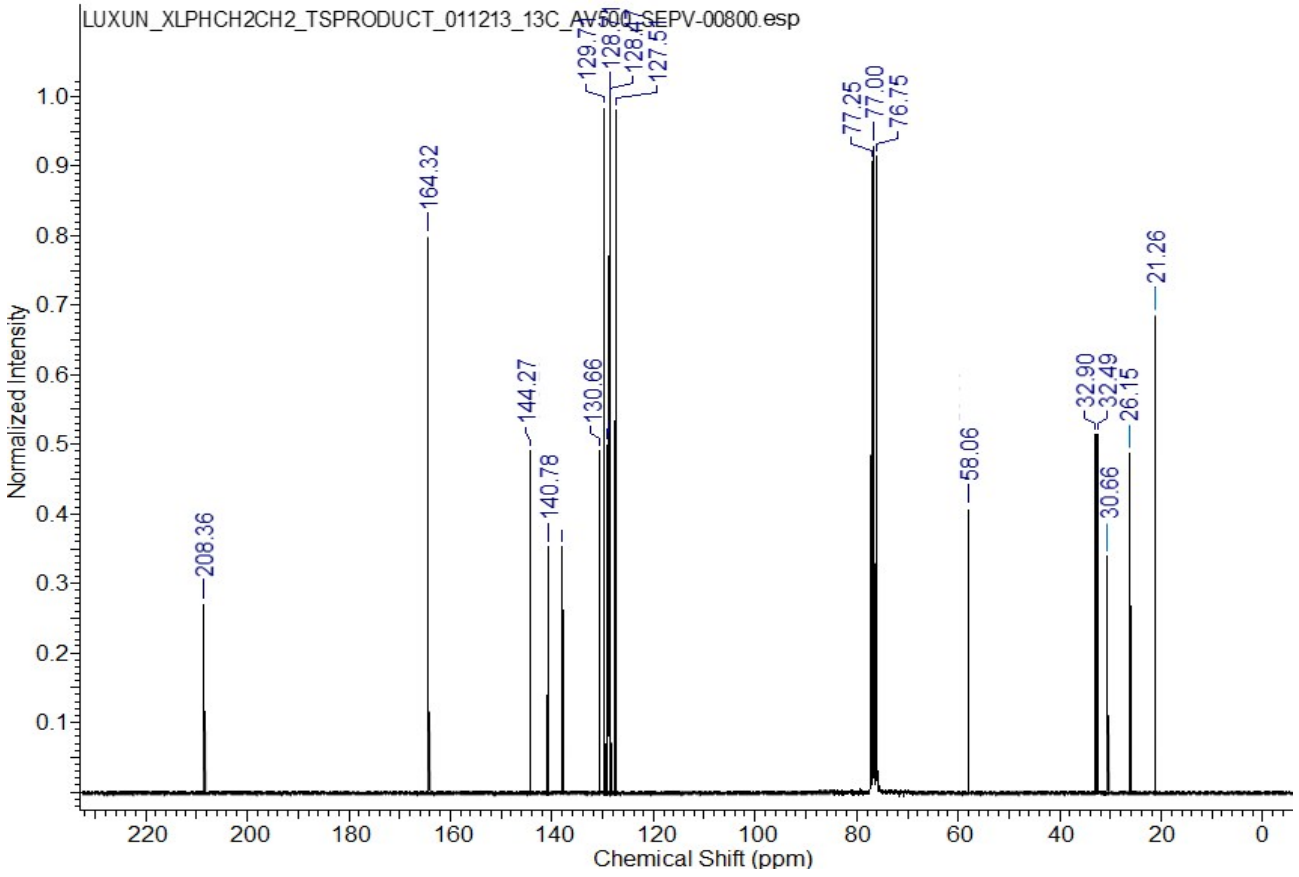

LUXUN_XL4PYR-ISO_200515_1H_AV500_MAYVI-00180.esp
Normalized Intensity
Chemical Shift (ppm)
8.55
8.53
8.54
7.61
7.59
7.32
7.28
7.30
7.20
7.19
6.73
6.72
6.72
6.03
6.02
5.24
5.23
2.58
2.56
2.54
2.53
2.40
2.31
2.31
2.30
2.29
2.22
0.00
2.02
2.04
1.98
2.01
1.01
0.98
1.00
1.06
3.61
1.71
1.07

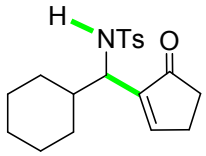

LUXUN_XL4PYR_TSPRODUCT_250114_13C_AV500_SERV-20800.esp
Normalized Intensity
Chemical Shift (ppm)
206.32
144.27
139.48
137.94
130.66
77.21
77.00
76.79
57.89
32.33
25.98
21.09


H
NTs
O

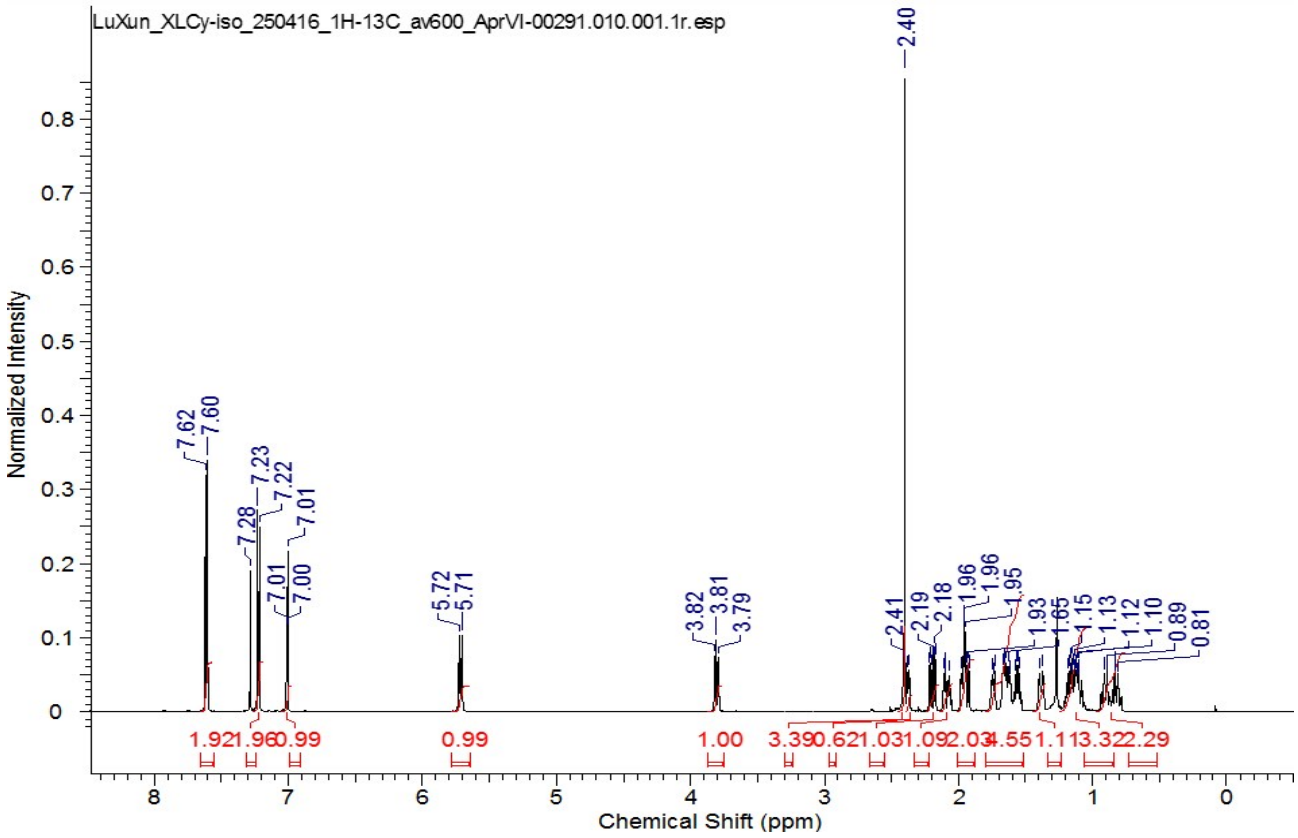
6x

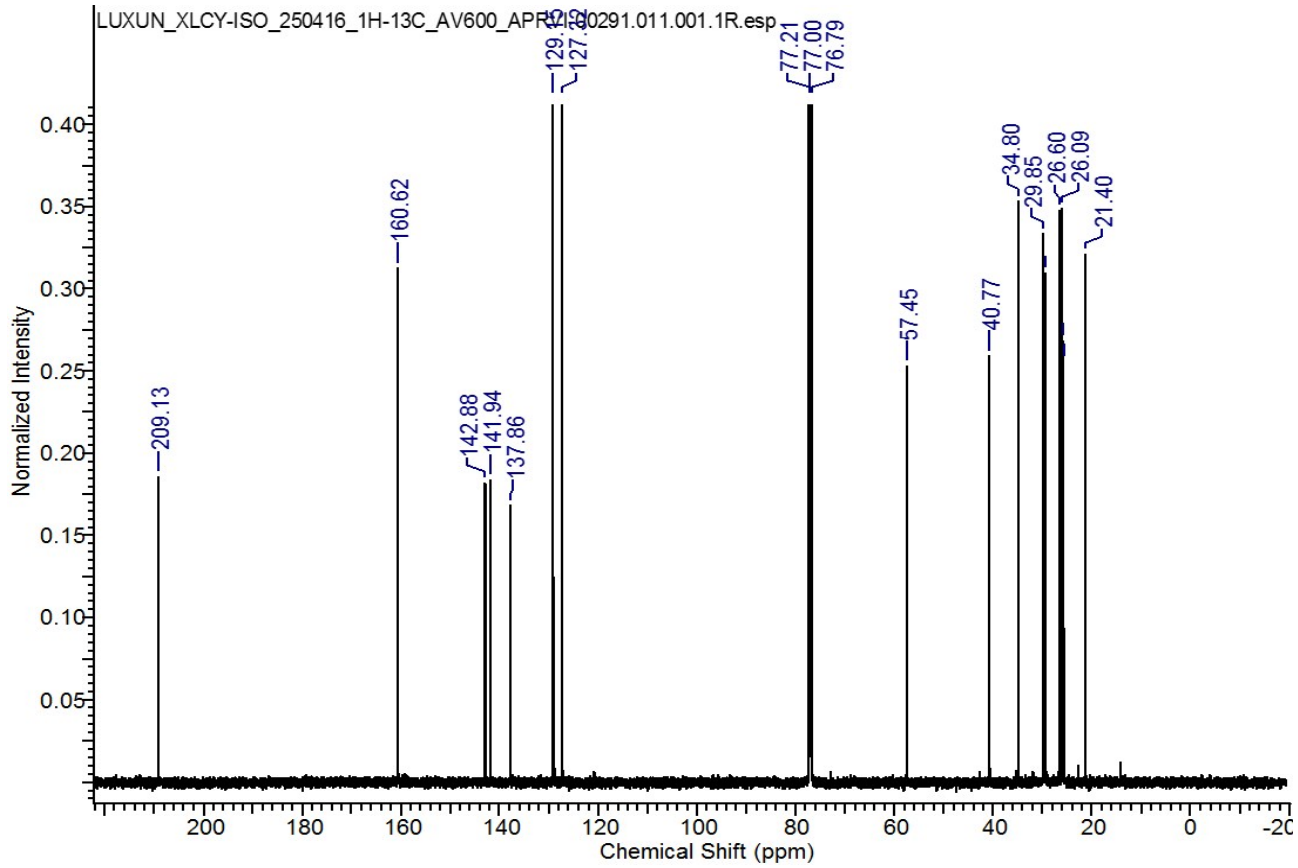

LuXun_XLPhCH2CH2_pro_130415_13C_av500_AprVI-00060.esp
Normalized Intensity
Chemical Shift (ppm)
2.42
0.00
7.71
7.69
7.32
7.30
7.28
7.17
7.16
6.69
6.13
6.12
4.95
4.93
4.92
2.55
2.54
2.52
2.50
2.31
2.30
2.29
2.21
2.20
2.00
2.04
1.89
3.03
0.99
1.00
1.00
2.13
3.18
4.01
2.13


LUXUN_XLPHCH2CH2_TSPRODUCT_011213_13C_AV500_SEPV-00800.esp
Normalized Intensity
Chemical Shift (ppm)
164.32
144.27
140.78
130.66
129.7
128.5
128.4
127.5
77.25
77.00
76.75
58.06
32.90
32.49
30.66
26.15
21.26
208.36


H
NTs
O

6y


LuXun_XLCy-iso_250416_1H-13C_av600_AprVI-00291.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
2.40
7.62
7.60
7.23
7.22
7.28
7.01
7.01
7.00
5.72
5.71
3.82
3.81
3.79
2.41
2.19
2.18
1.96
1.96
1.95
1.93
1.65
1.15
1.13
1.12
1.10
0.89
0.81
1.92
1.96
0.99
0.99
1.00
3.39
0.62
1.03
1.09
2.03
4.55
1.11
3.32
2.29


LUXUN_XLCY-ISO_250416_1H-13C_AV600_APR
Normalized Intensity
Chemical Shift (ppm)
209.13
160.62
142.88
141.94
137.86
129.12
127.40
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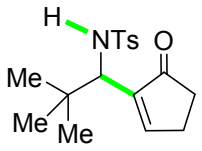
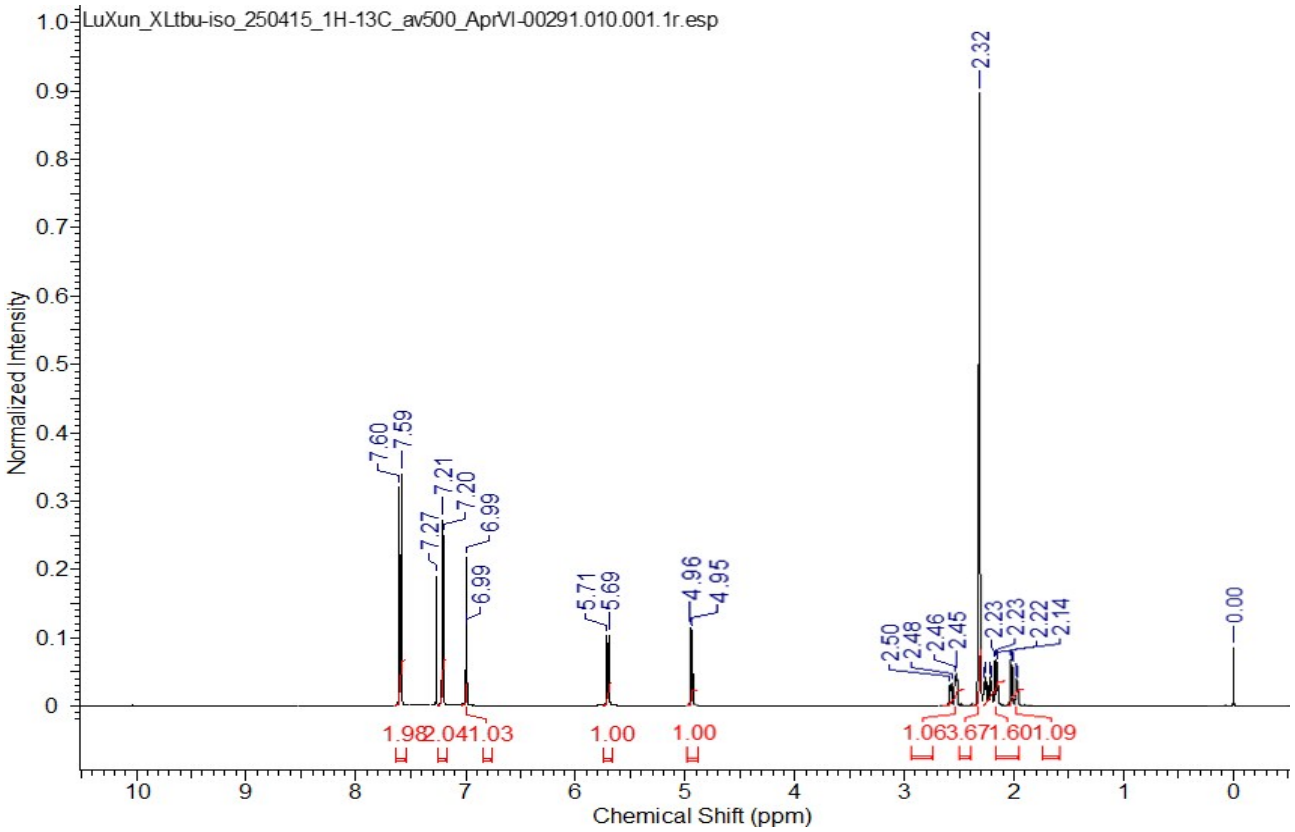
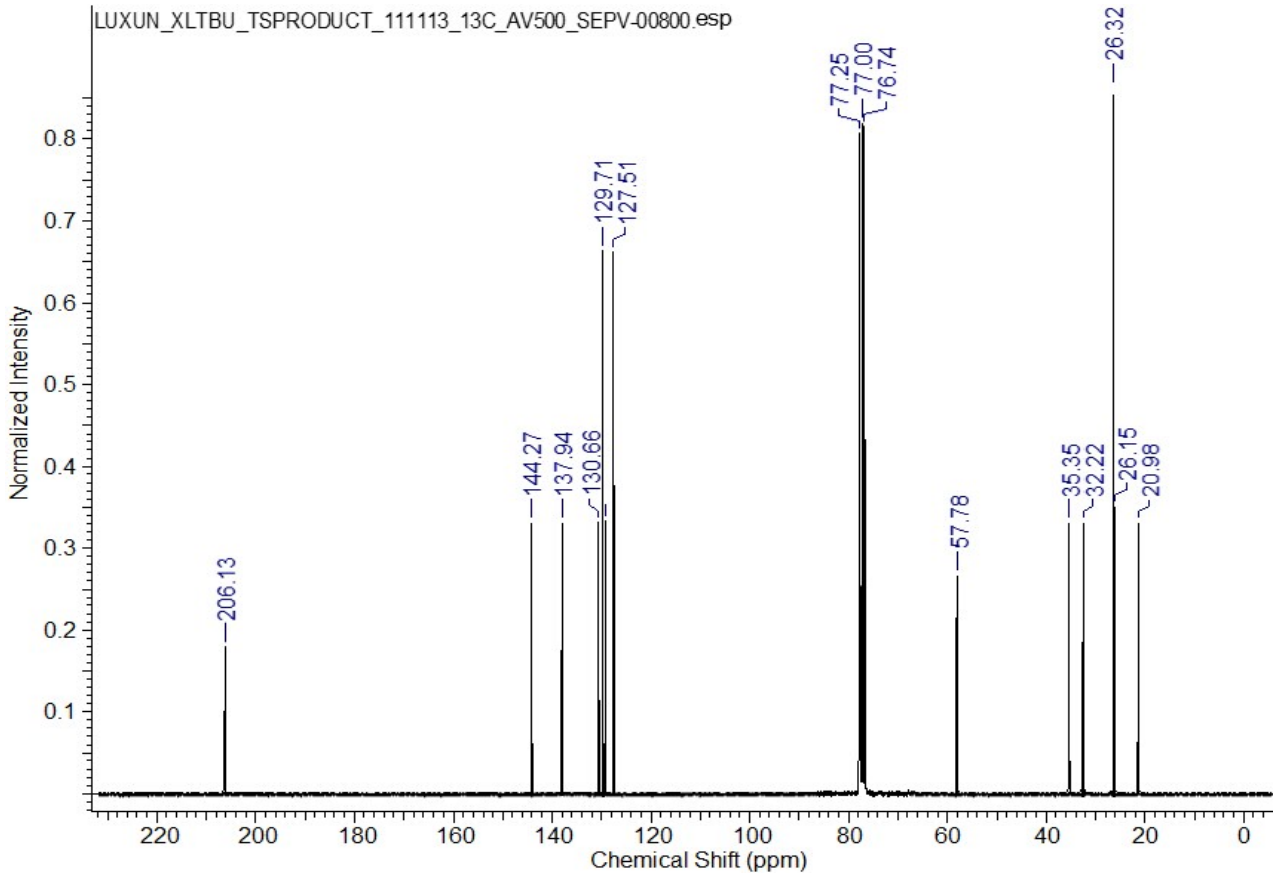
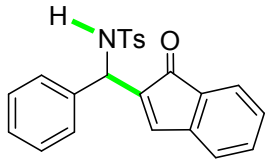
77.00
76.79
57.45
40.77
34.80
29.85
26.60
26.09
21.40


H
NTs
O
Me
Me
Me

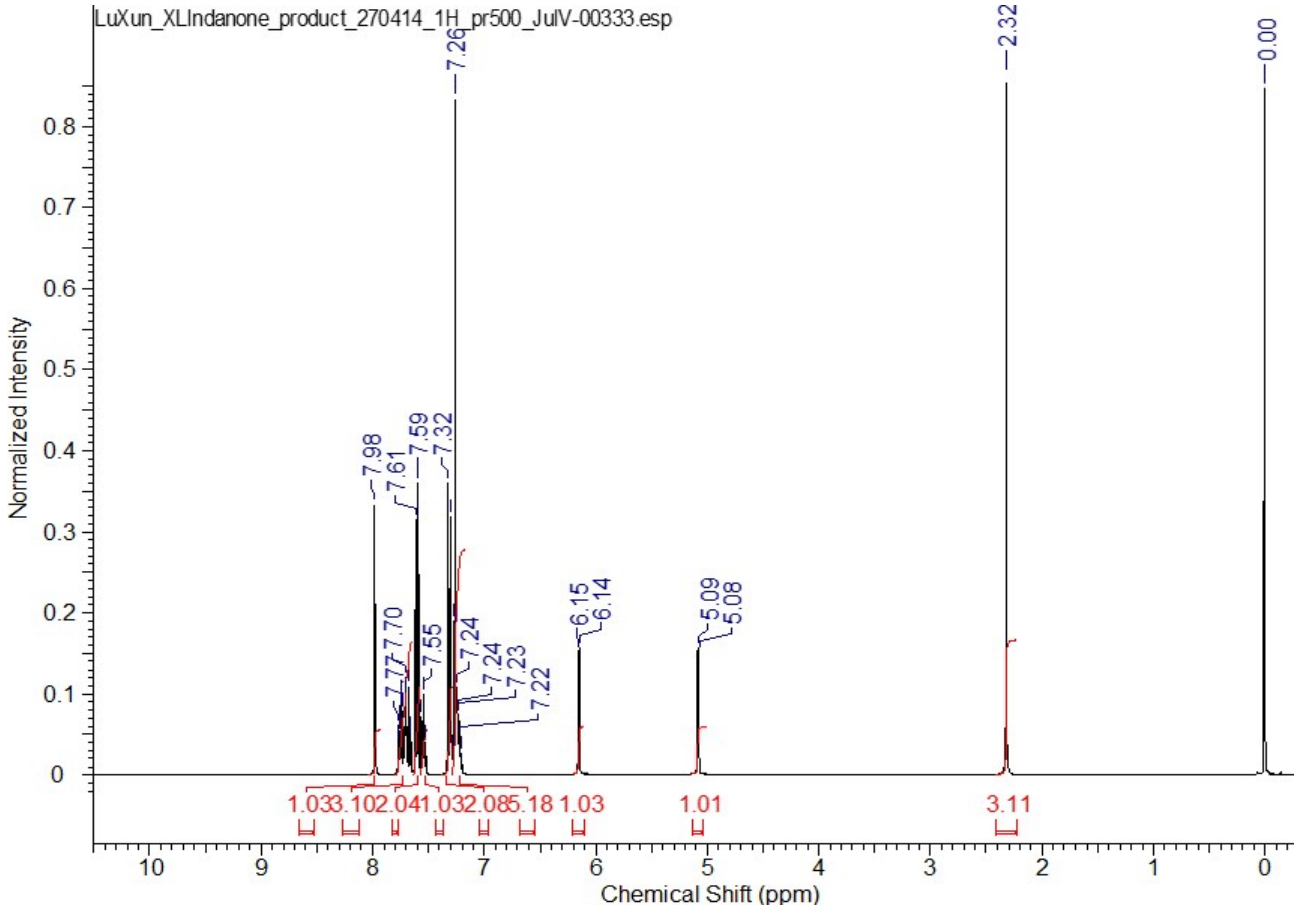
6z

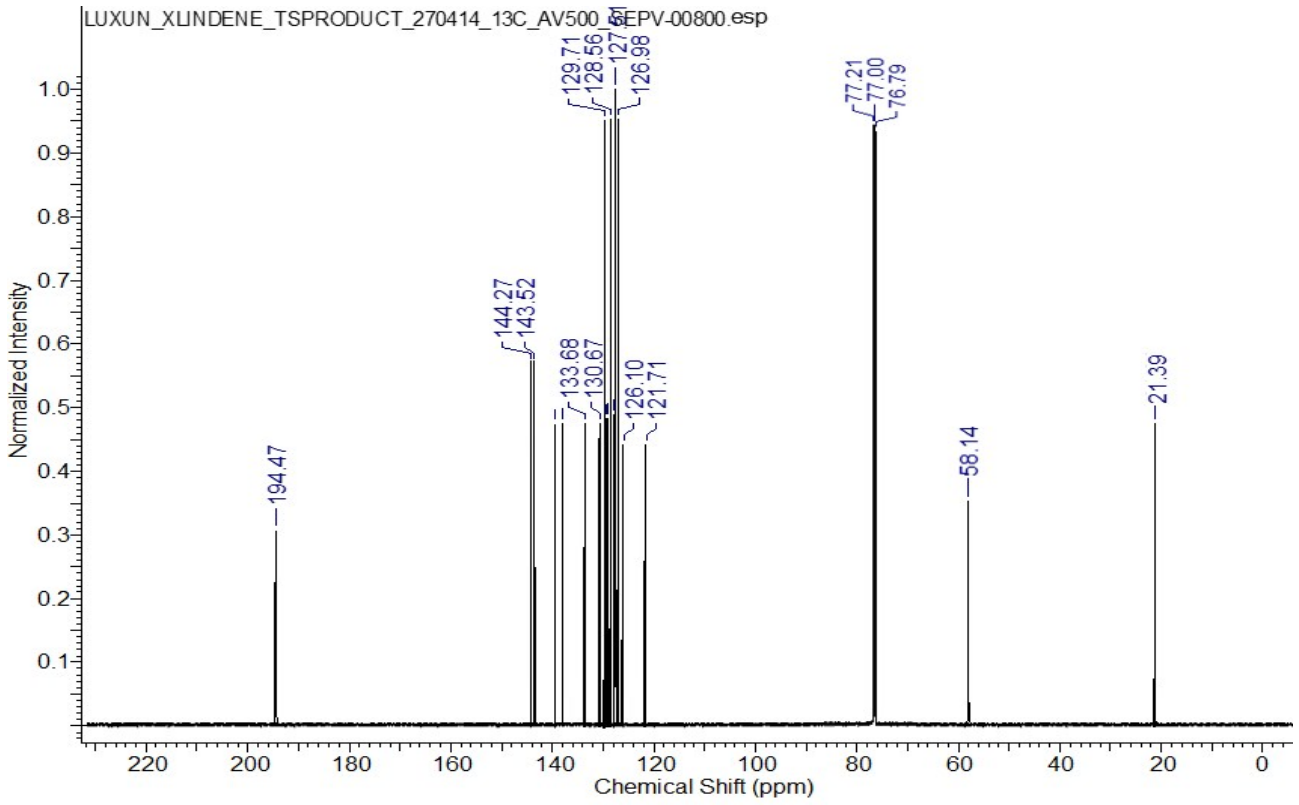

LuXun_XLtbu-iso_250415_1H-13C_av500_AprVI-00291.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
7.60
7.59
7.27
7.21
7.20
6.99
6.99
5.71
5.69
4.96
4.95
2.50
2.48
2.46
2.45
2.32
2.23
2.23
2.22
2.14
0.00
1.98
2.04
1.03
1.00
1.00
1.06
3.67
1.60
1.09

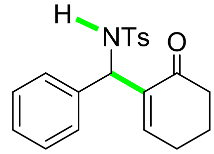

LUXUN_XLTBU_TSPRODUCT_111113_13C_AV500_SEPV-00800.esp
Normalized Intensity
Chemical Shift (ppm)
206.13
144.27
137.94
130.66
129.71
127.51
77.25
77.00
76.74
57.78
35.35
32.22
26.32
26.15
20.98


H
NTs
O

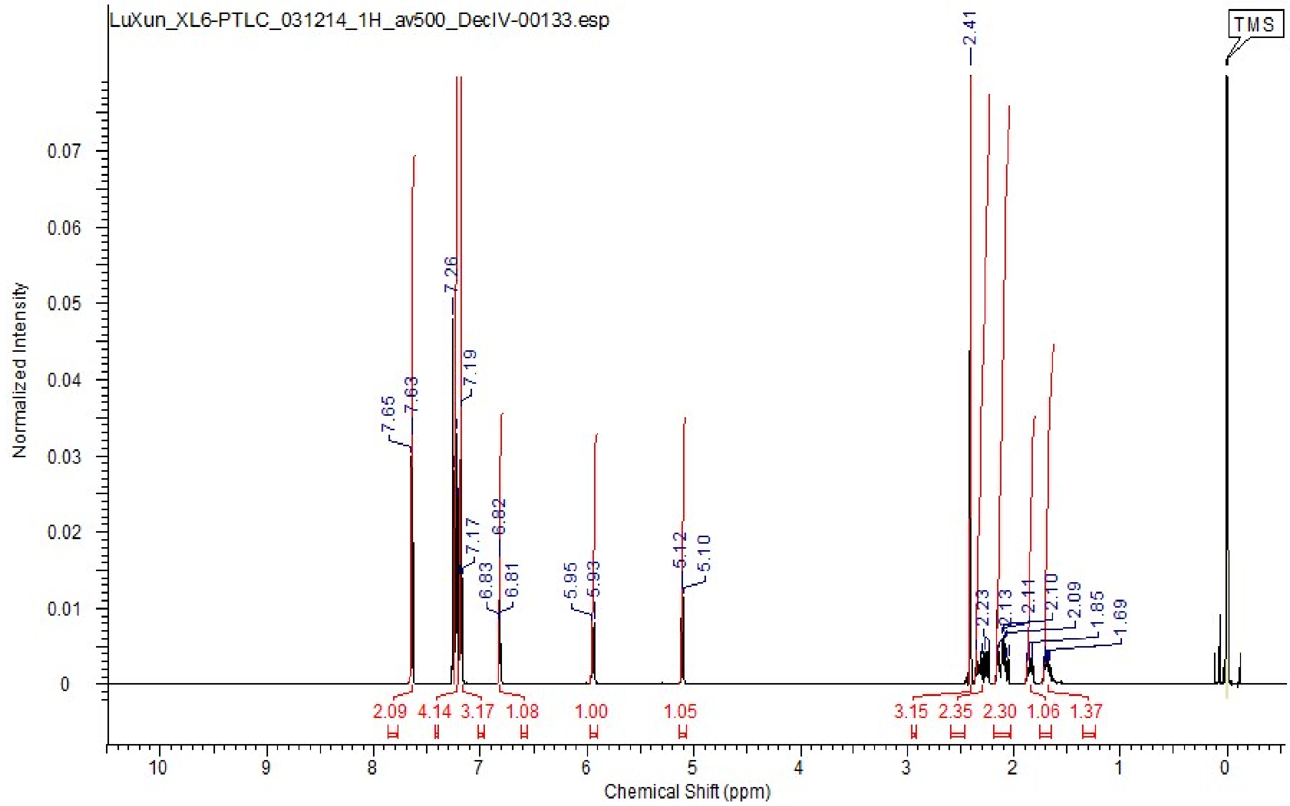
6ab

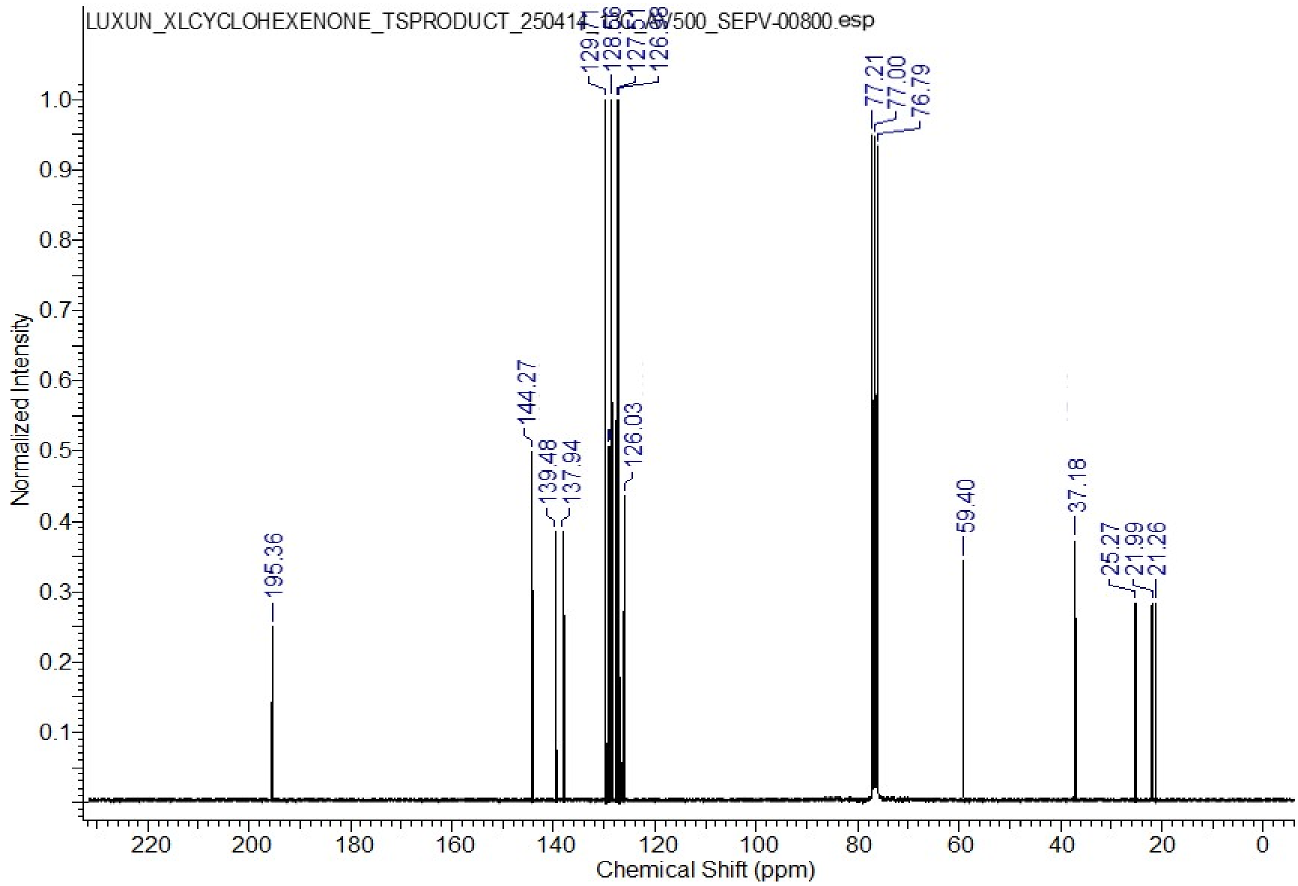

LuXun_XLIndanone_product_270414_1H_pr500_JulV-00333.esp
Normalized Intensity
Chemical Shift (ppm)
7.98
7.61
7.59
7.32
7.26
7.77
7.70
7.55
7.24
7.24
7.23
7.22
6.15
6.14
5.09
5.08
2.32
0.00
1.03
3.10
2.04
1.03
2.08
5.18
1.03
1.01
3.11

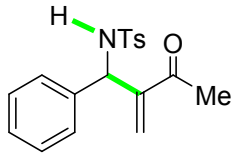

LUXUN_XLINDENE_TSPRODUCT_270414_13C_AV500_6EPV-00800.esp
Normalized Intensity
Chemical Shift (ppm)
194.47
144.27
143.52
133.68
130.67
129.71
128.56
127.61
126.98
126.10
121.71
77.21
77.00
76.79
58.14
21.39


H
NTs
O

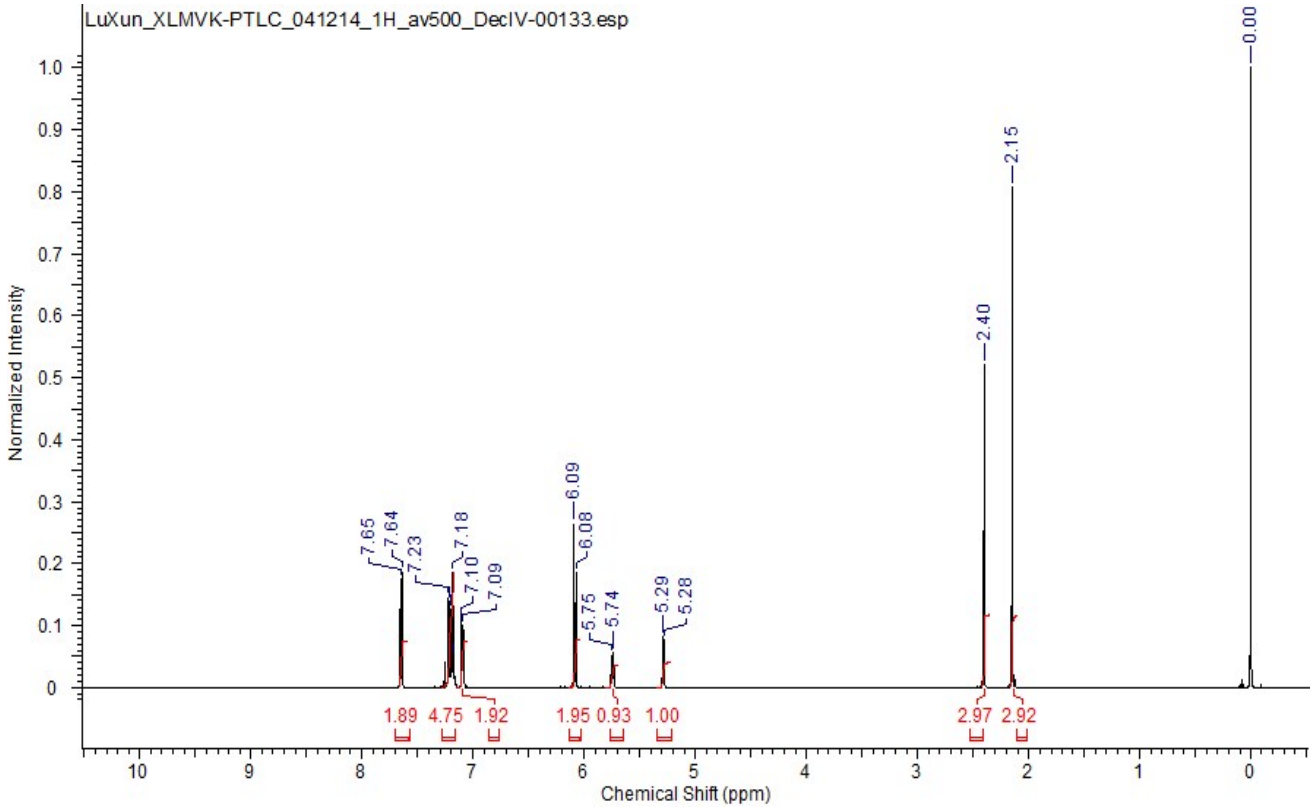
6ac

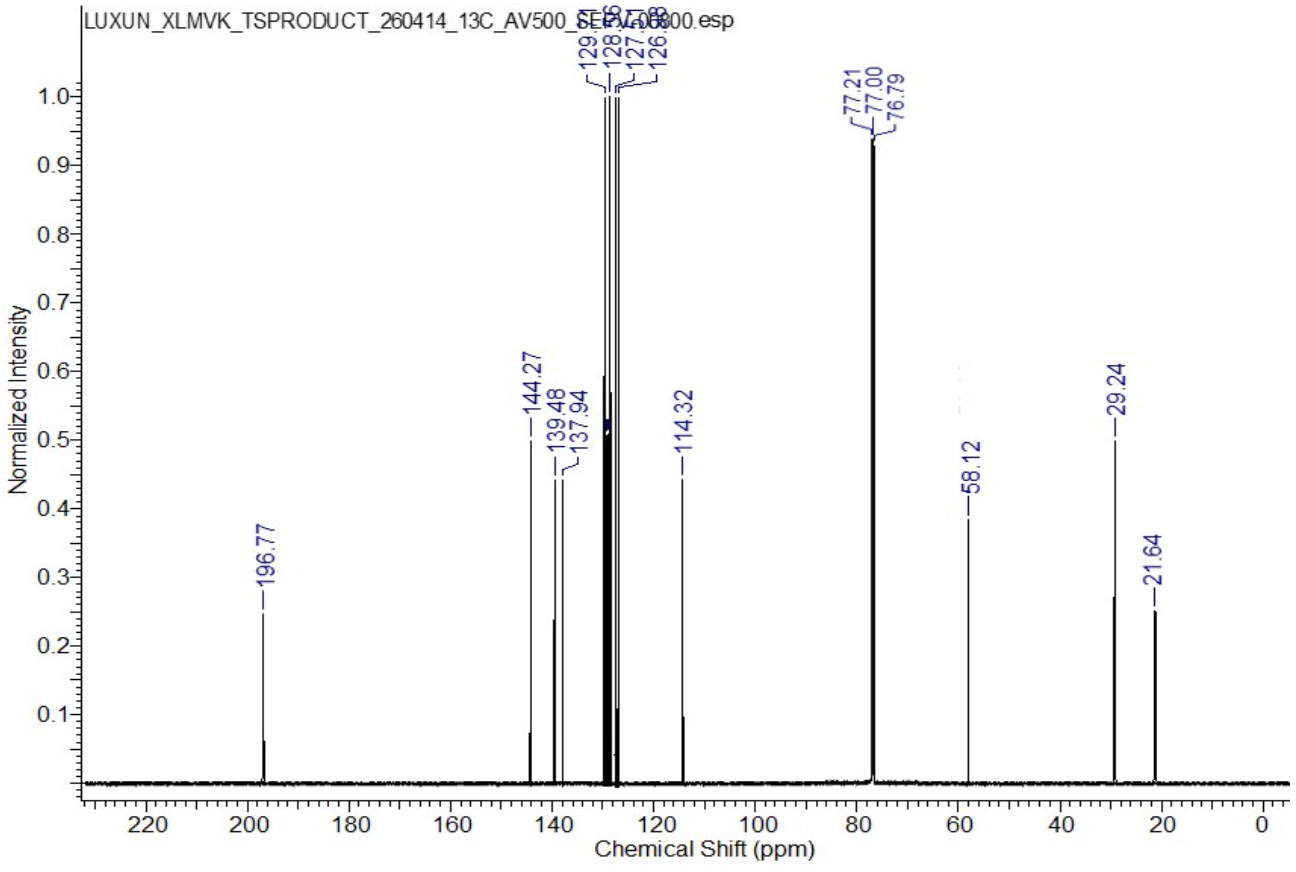

LuXun_XL6-PTLC_031214_1H_av500_DecIV-00133.esp
TMS
Normalized Intensity
Chemical Shift (ppm)

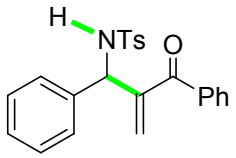

Normalized Intensity
195.36
144.27
139.48
137.94
126.03
77.21
77.00
76.79
59.40
37.18
25.27
21.99
21.26
Chemical Shift (ppm)


H
NTs
O
Me

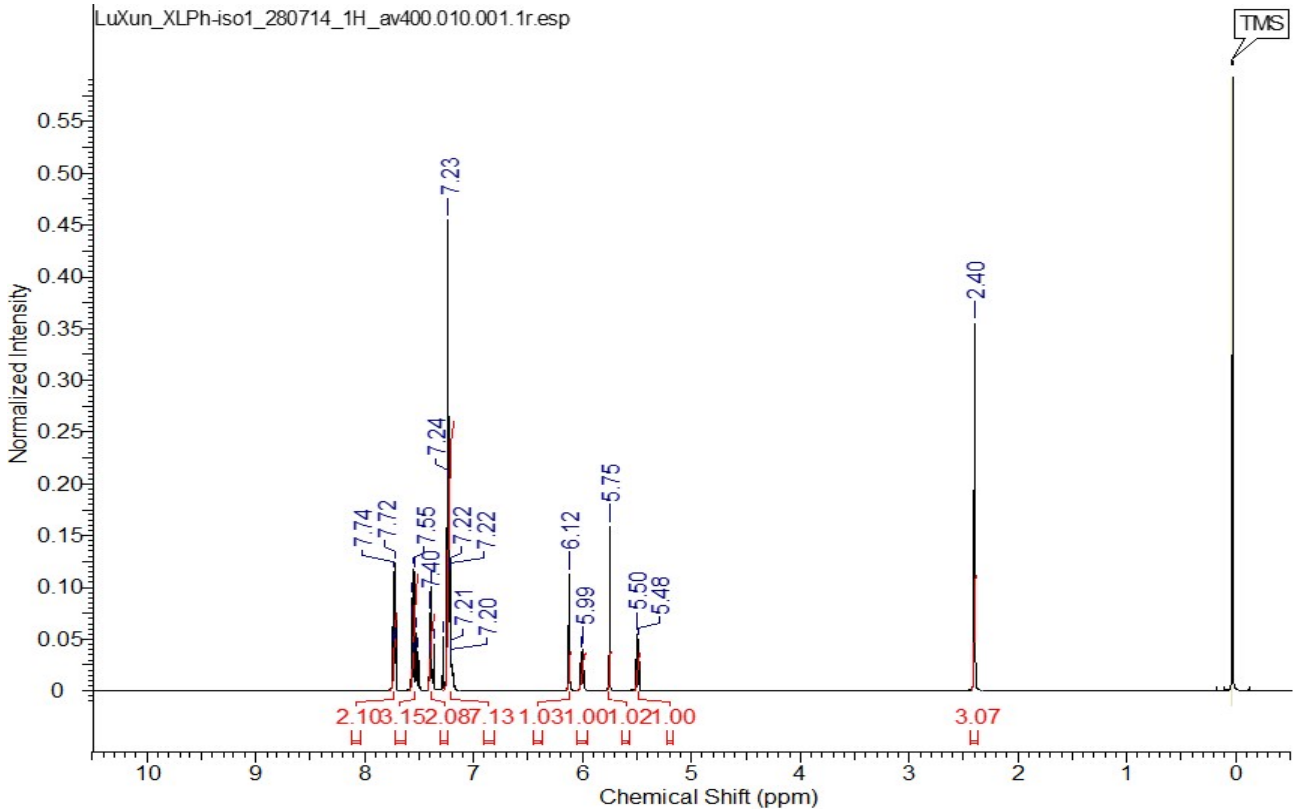
6ad

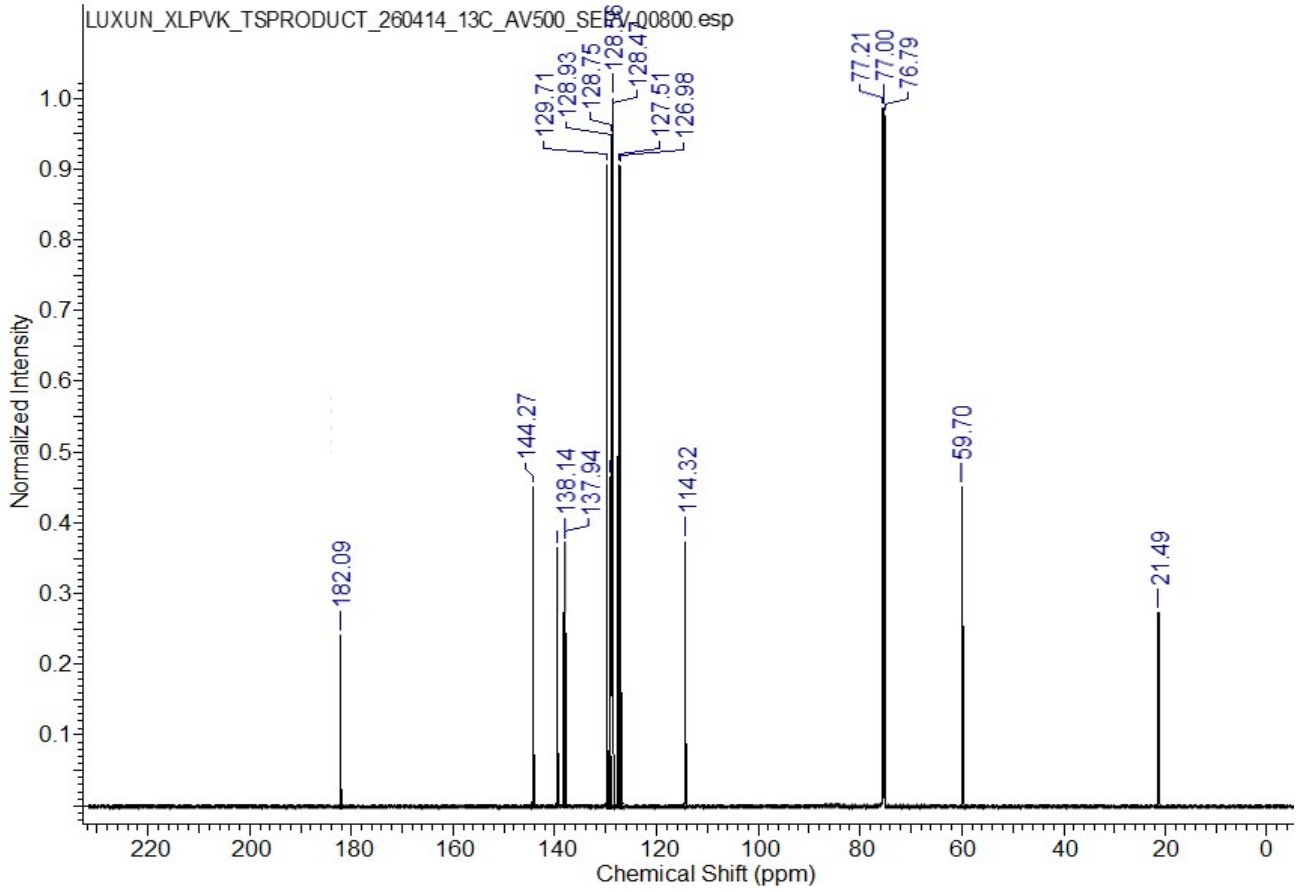

LuXun_XLMVK-PTLC_041214_1H_av500_DecIV-00133.esp
Normalized Intensity
Chemical Shift (ppm)
7.65
7.64
7.23
7.18
7.10
7.09
6.09
6.08
5.75
5.74
5.29
5.28
2.40
2.15
0.00
1.89
4.75
1.92
1.95
0.93
1.00
2.97
2.92

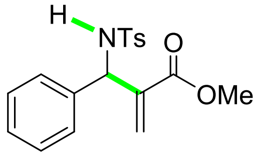

LUXUN_XLMVK_TSPRODUCT_260414_13C_AV500
Normalized Intensity
Chemical Shift (ppm)
196.77
144.27
139.48
137.94
114.32
77.21
77.00
76.79
58.12
29.24
21.64


H
NTs
O
Ph

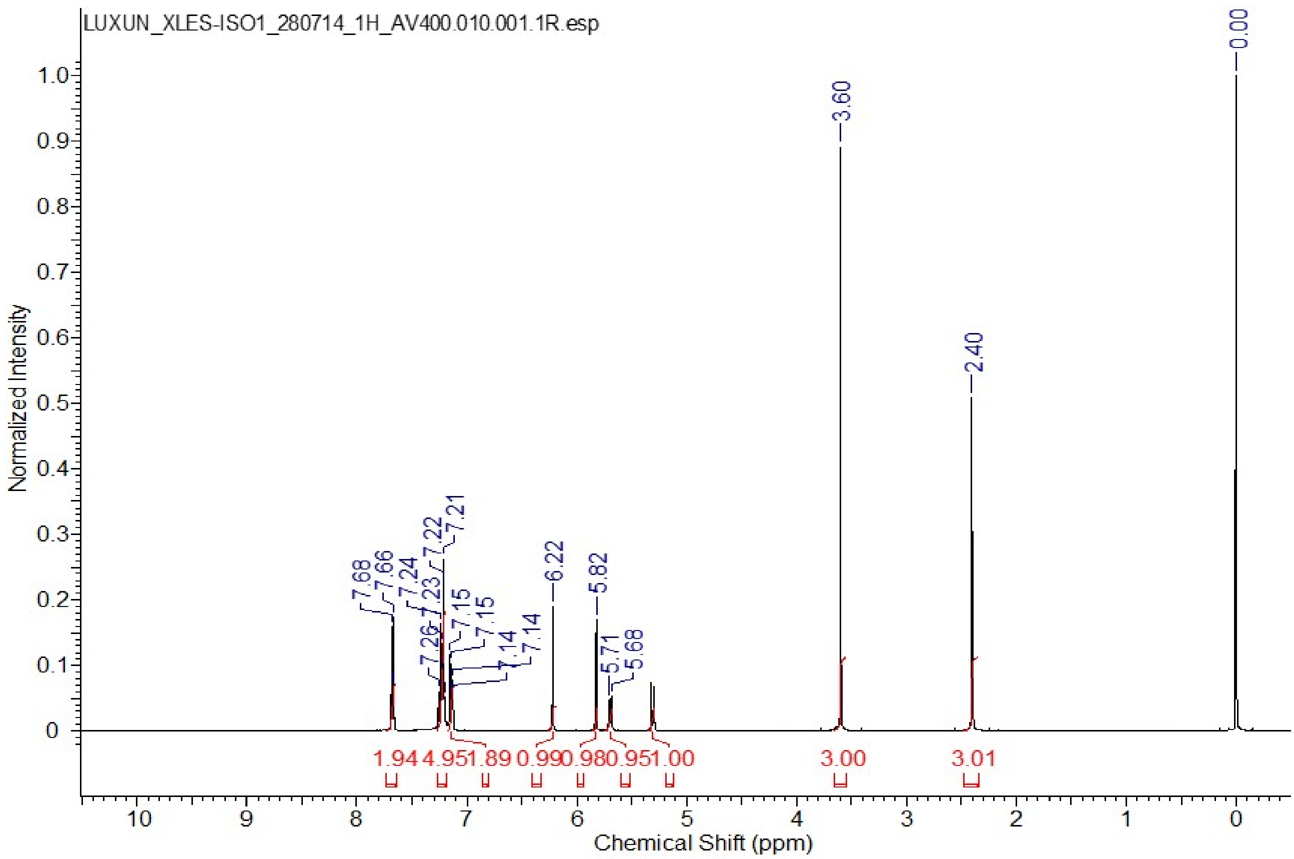
6ae

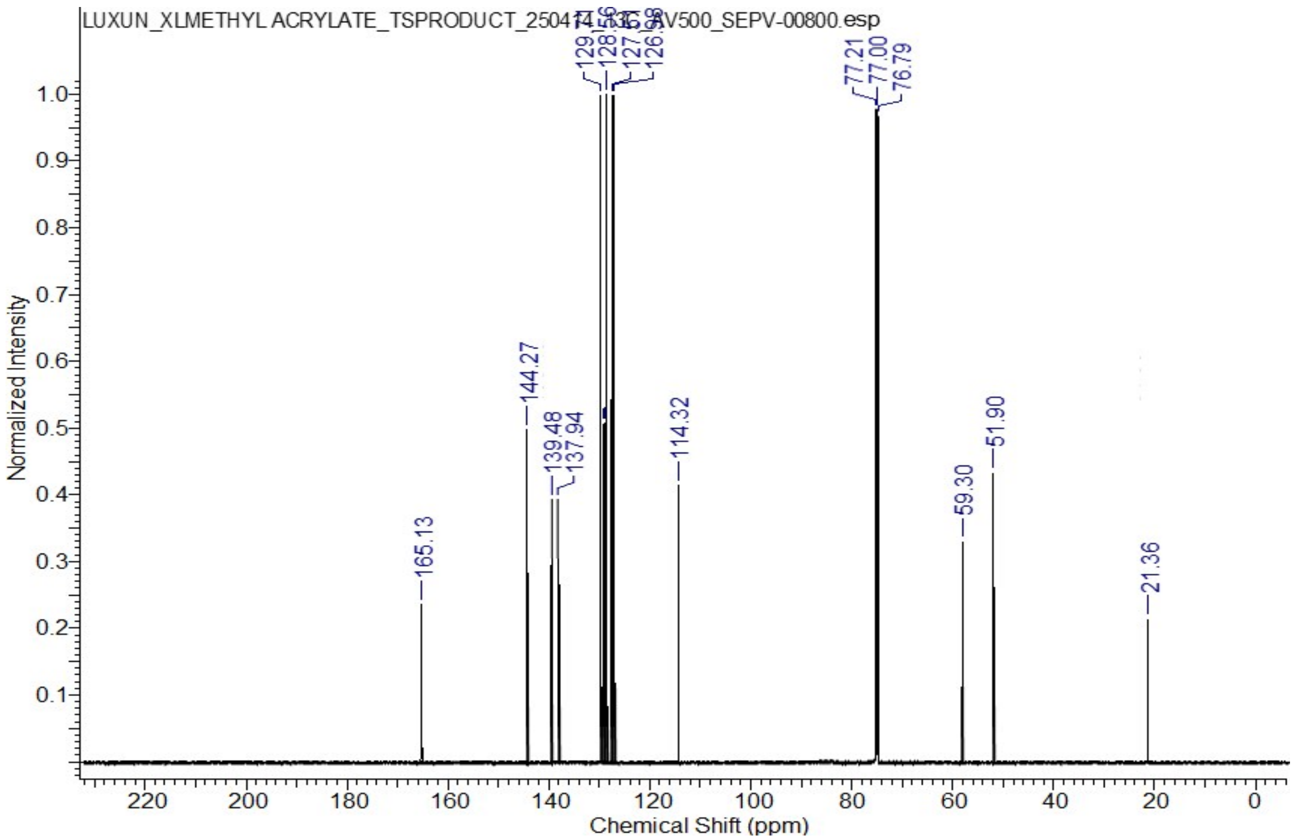

LuXun_XLPh-iso1_280714_1H_av400.010.001.1r.esp
TMS
Normalized Intensity
Chemical Shift (ppm)
7.74
7.72
7.55
7.40
7.24
7.23
7.22
7.22
7.21
7.20
6.12
5.99
5.75
5.50
5.48
2.40
2.10
3.15
2.08
7.13
1.03
1.00
1.02
1.00
3.07

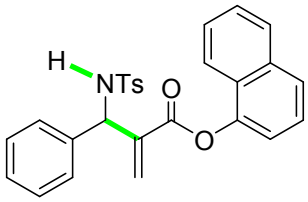

LUXUN_XLPVK_TSPRODUCT_260414_13C_AV500_SEEV_00800.esp
Normalized Intensity
Chemical Shift (ppm)
182.09
144.27
138.14
137.94
129.71
128.93
128.75
128.47
127.51
126.98
114.32
77.21
77.00
76.79
59.70
21.49



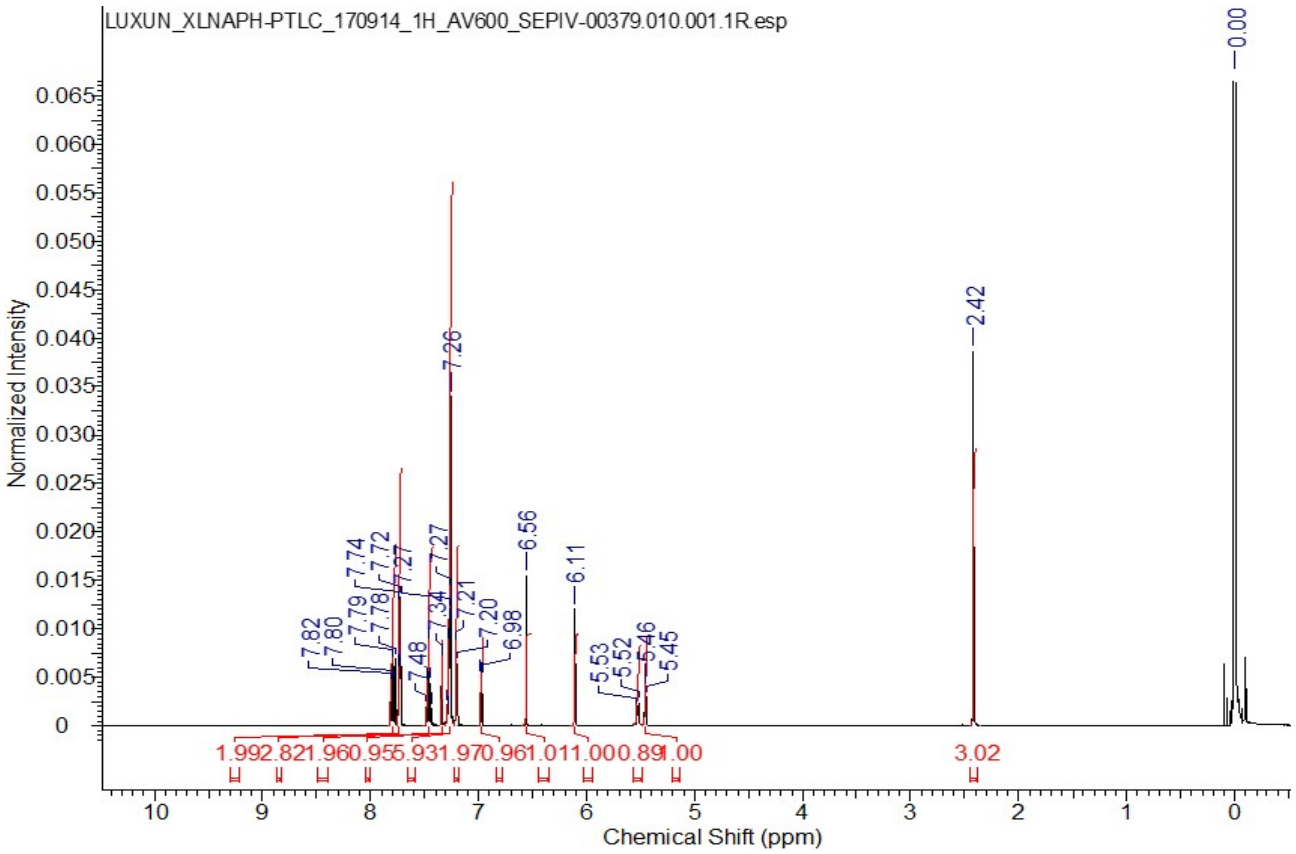
6af

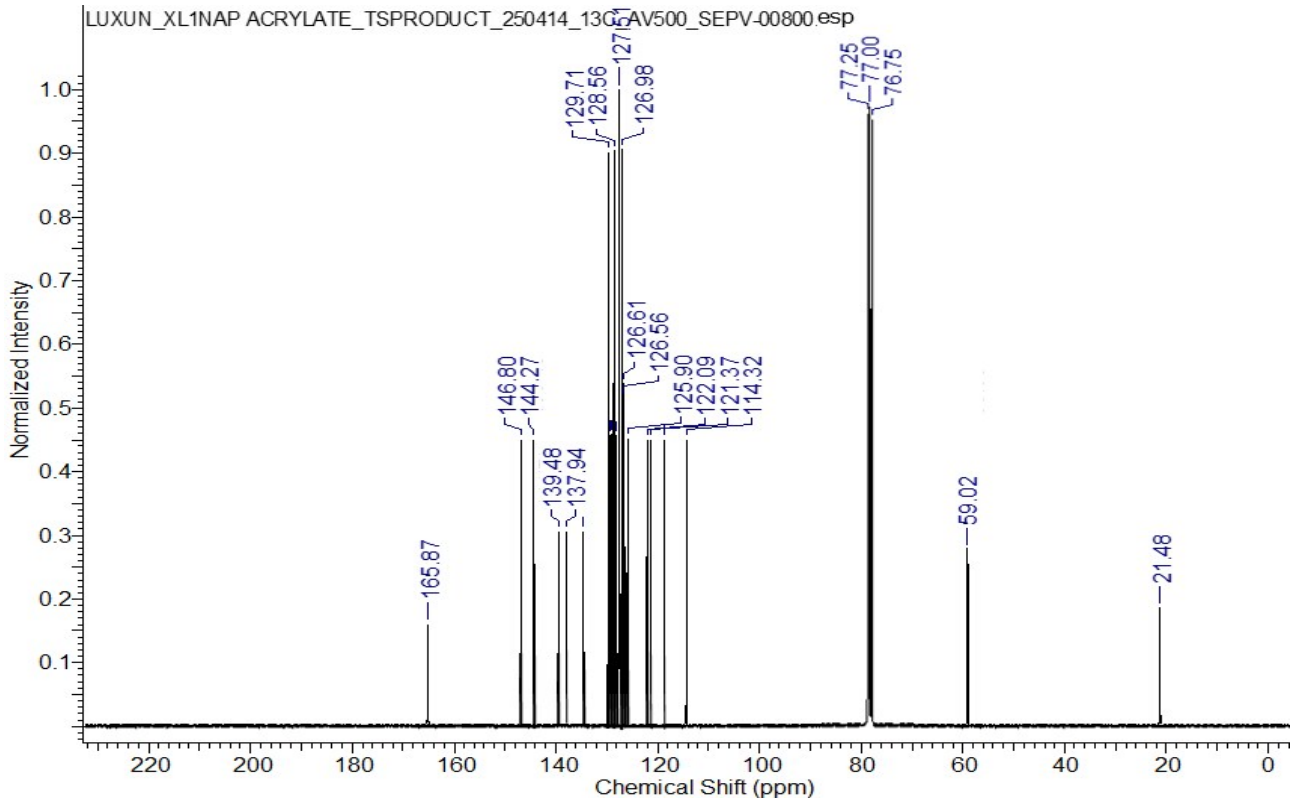

LUXUN_XLES-ISO1_280714_1H_AV400.010.001.1R.esp
Normalized Intensity
Chemical Shift (ppm)
7.68
7.66
7.24
7.23
7.22
7.21
7.26
7.15
7.15
7.14
7.14
6.22
5.82
5.71
5.68
3.60
2.40
0.00
1.94
4.95
1.89
0.99
0.98
0.95
1.00
3.00
3.01

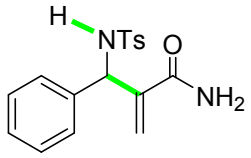

Normalized Intensity
Chemical Shift (ppm)
165.13
144.27
139.48
137.94
114.32
77.21
77.00
76.79
59.30
51.90
21.36


H
NTs
O
O

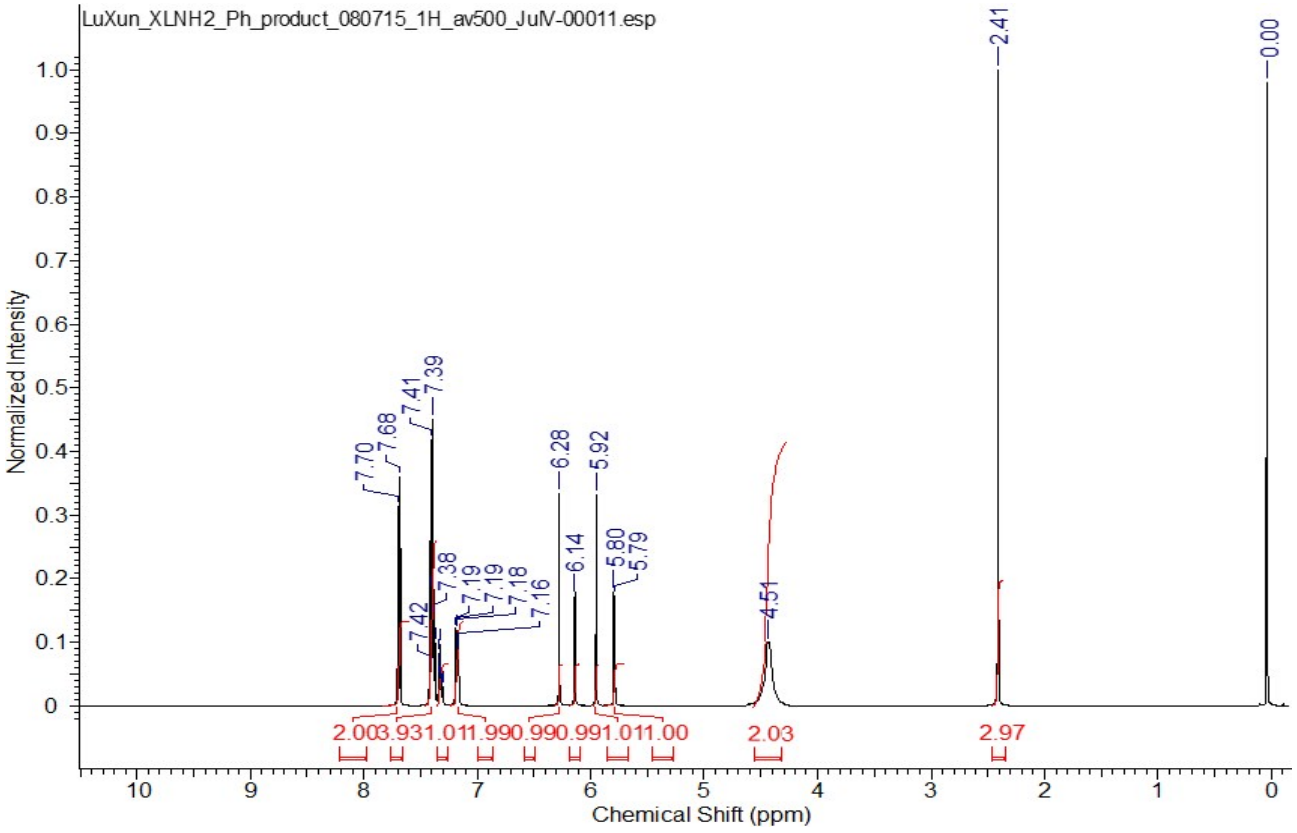
6ag

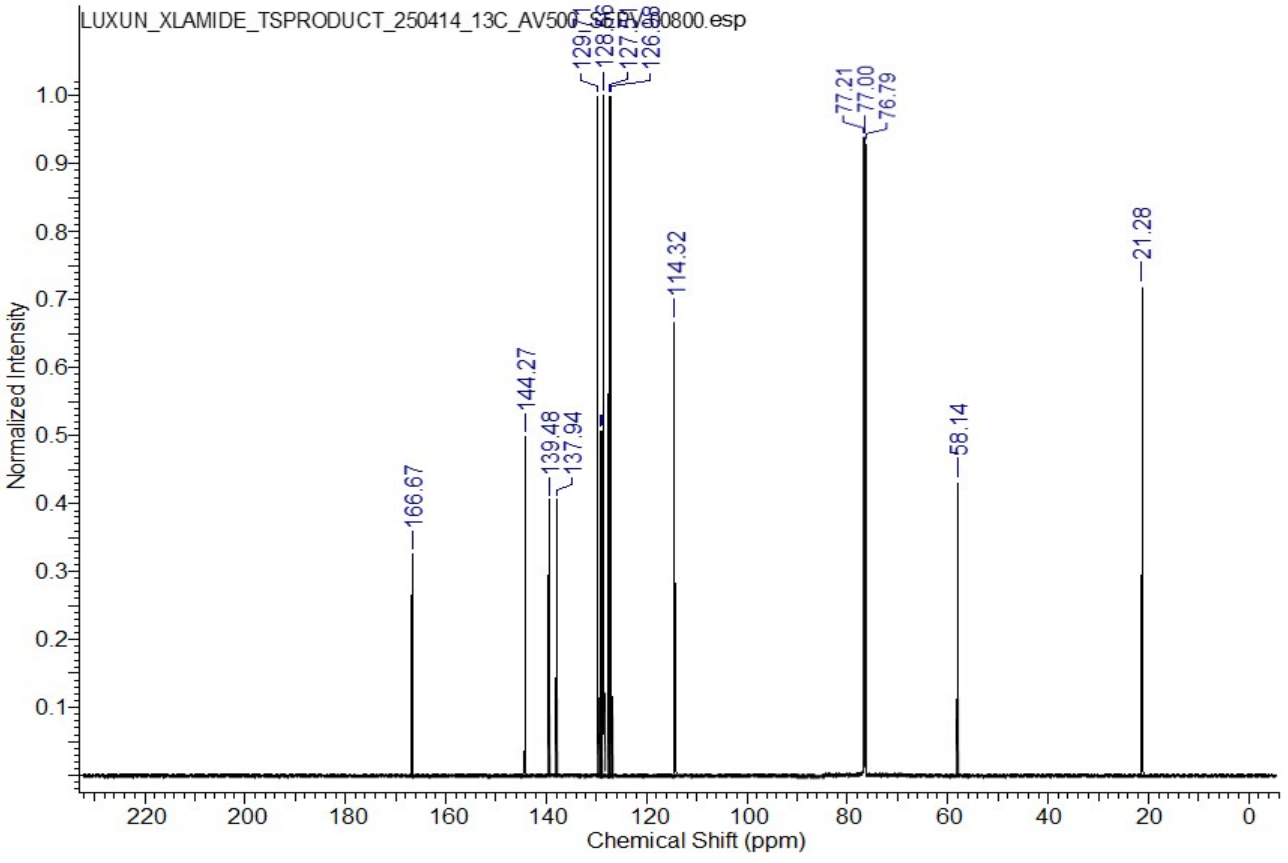

LUXUN_XLNAPH-PTLC_170914_1H_AV600_SEPIV-00379.010.001.1R.esp
Normalized Intensity
Chemical Shift (ppm)
0.00
2.42
7.26
6.56
6.11
1.99 2.82 1.96 0.95 5.93 1.97 0.96 1.01 1.00 0.89 1.00
3.02

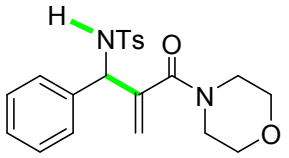

LUXUN_XL1NAP ACRYLATE_TSPRODUCT_250414_13C_AV500_SEPV-00800.esp
Normalized Intensity
Chemical Shift (ppm)
165.87
146.80
144.27
139.48
137.94
129.71
128.56
127.51
126.98
126.61
126.56
125.90
122.09
121.37
114.32
77.25
77.00
76.75
59.02
21.48


H
NTs
O
NH2

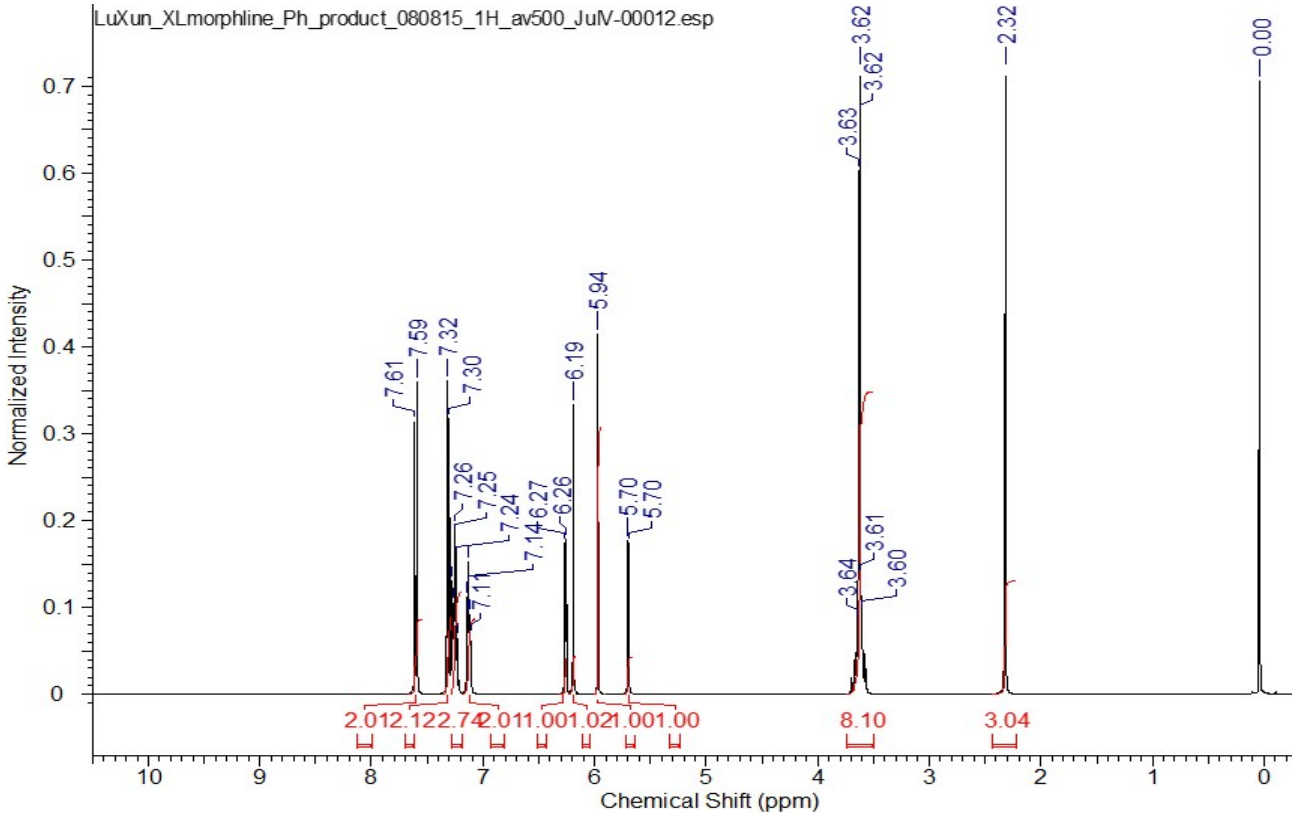
6ah

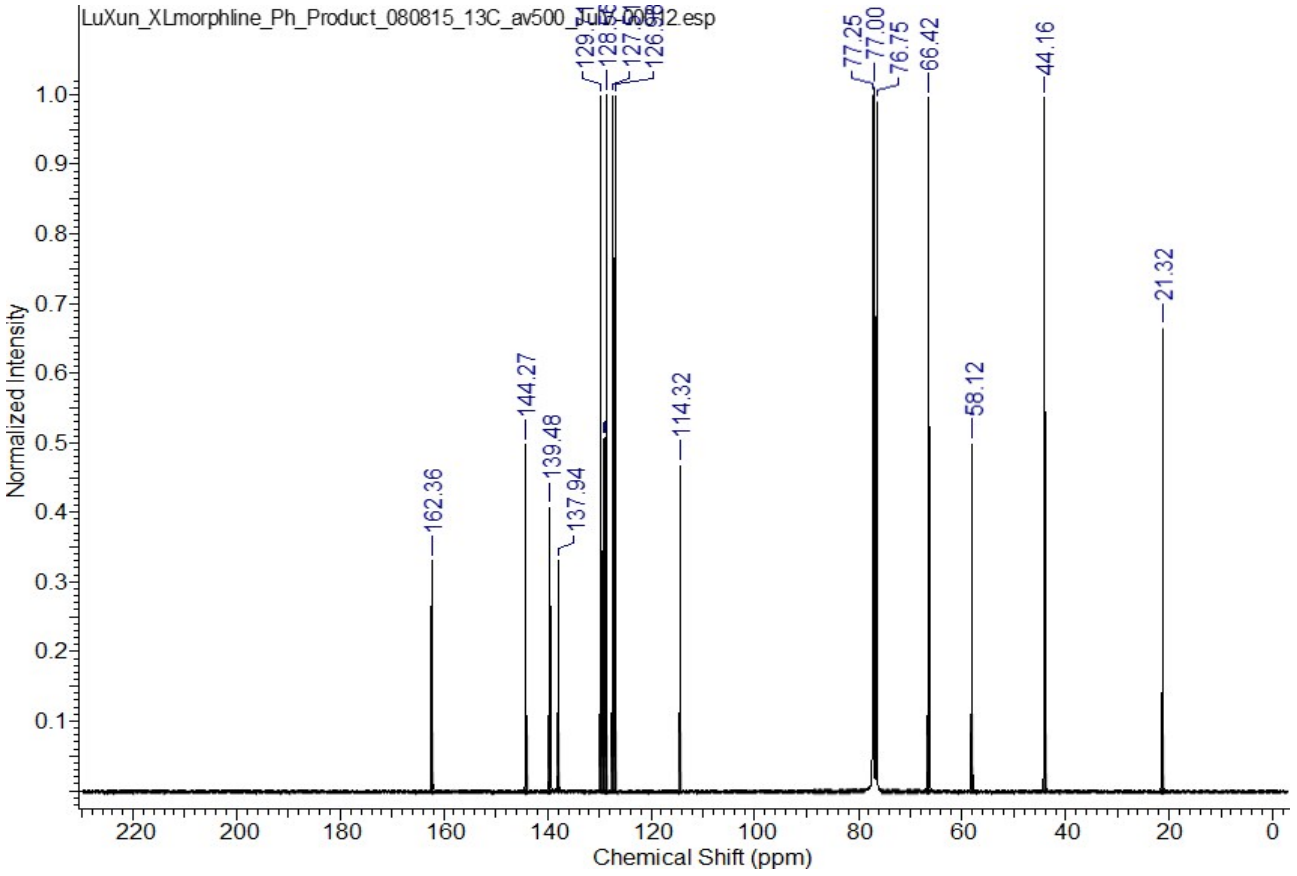

LuXun_XLNH2_Ph_product_080715_1H_av500_JulV-00011.esp
Normalized Intensity
Chemical Shift (ppm)
7.70
7.68
7.41
7.39
7.42
7.38
7.19
7.19
7.18
7.16
6.28
6.14
5.92
5.80
5.79
4.51
2.41
0.00
2.00
3.93
1.01
1.99
0.99
0.99
1.01
1.00
2.03
2.97

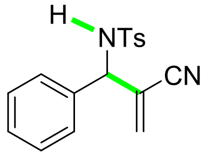

LUXUN_XLAMIDE_TSPRODUCT_250414_13C_AV500
Normalized Intensity
Chemical Shift (ppm)
166.67
144.27
139.48
137.94
114.32
77.21
77.00
76.79
58.14
21.28


H
NTs
O
N
O

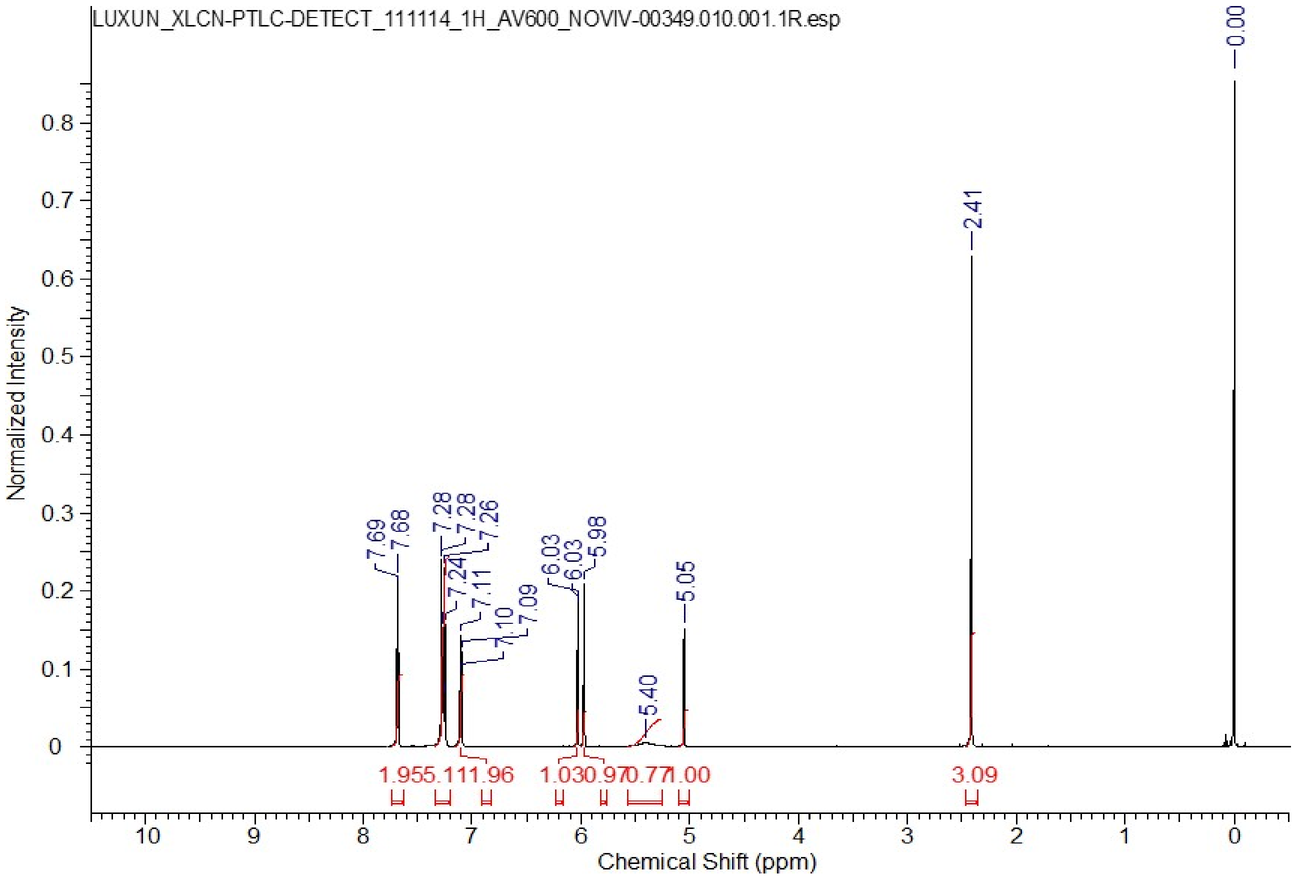
6ai

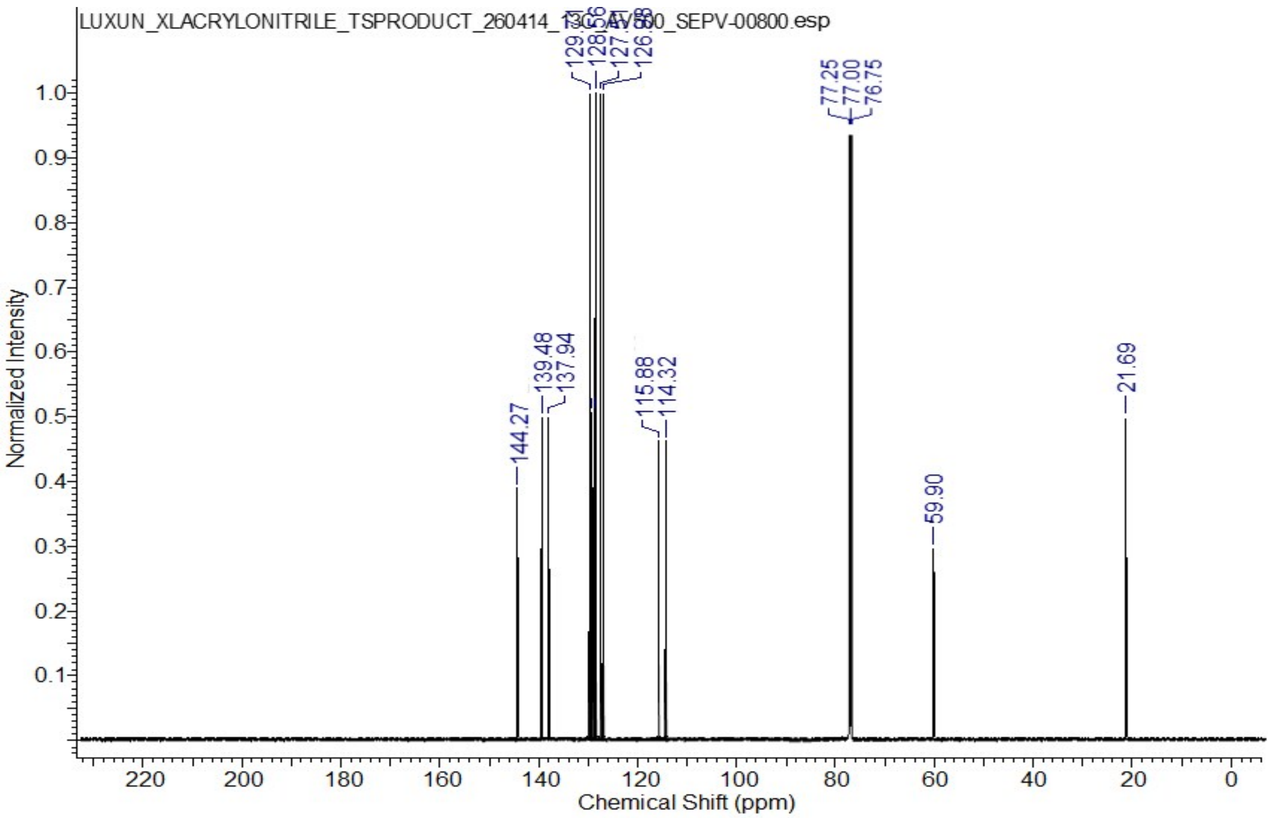

LuXun_XLmorphline_Ph_product_080815_1H_av500_JulV-00012.esp
Normalized Intensity
Chemical Shift (ppm)
7.61
7.59
7.32
7.30
7.26
7.25
7.24
7.14
6.27
6.26
7.11
6.19
5.94
5.70
5.70
3.64
3.63
3.62
3.62
3.61
3.60
2.32
0.00
2.01
2.12
2.74
2.01
1.00
1.02
1.00
1.00
8.10
3.04

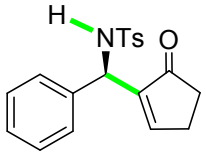

LuXun_XLmorphline_Ph_Product_080815_13C_av500_JulV-00012.esp
Normalized Intensity
Chemical Shift (ppm)
162.36
144.27
139.48
137.94
114.32
77.25
77.00
76.75
66.42
58.12
44.16
21.32


H
NTs
CN

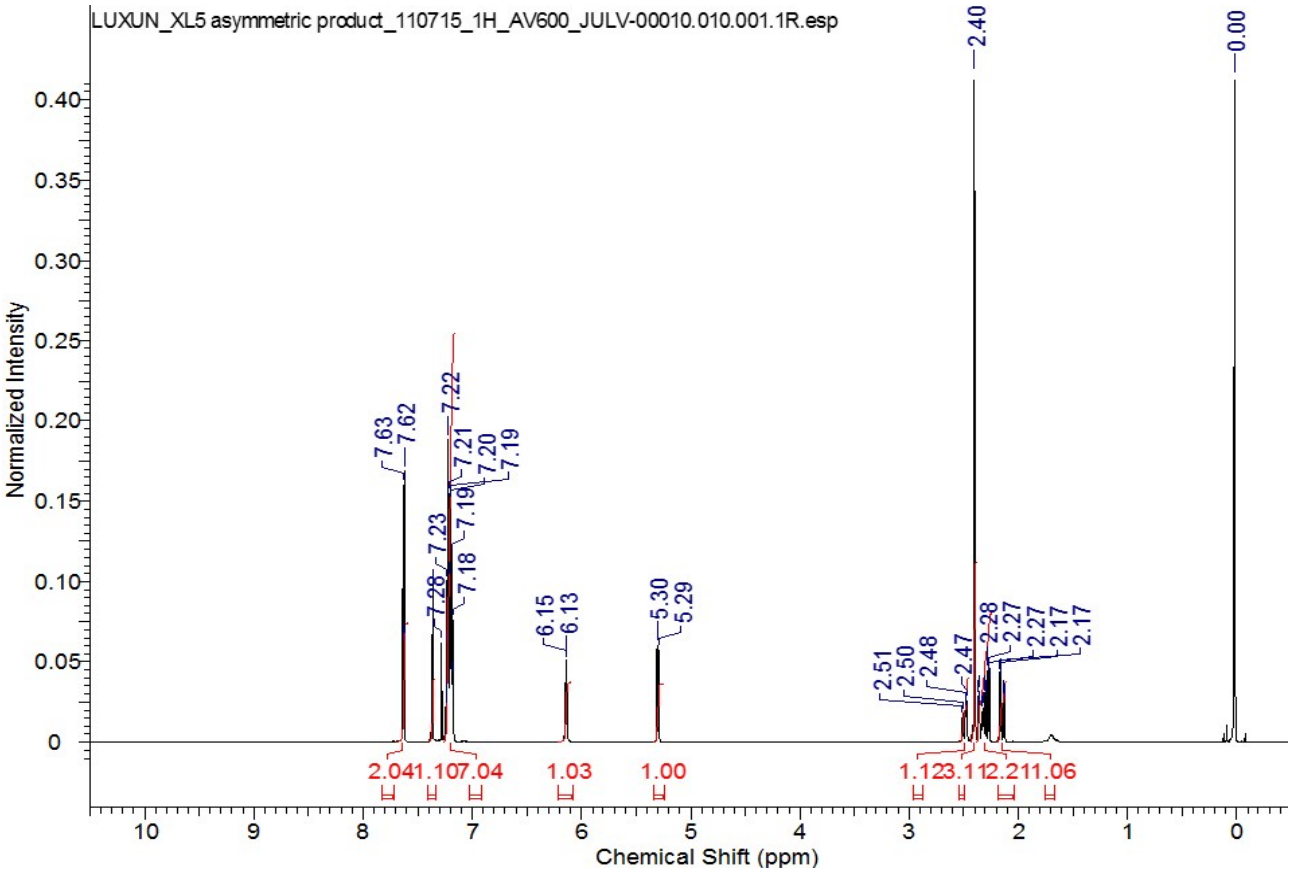
6aj

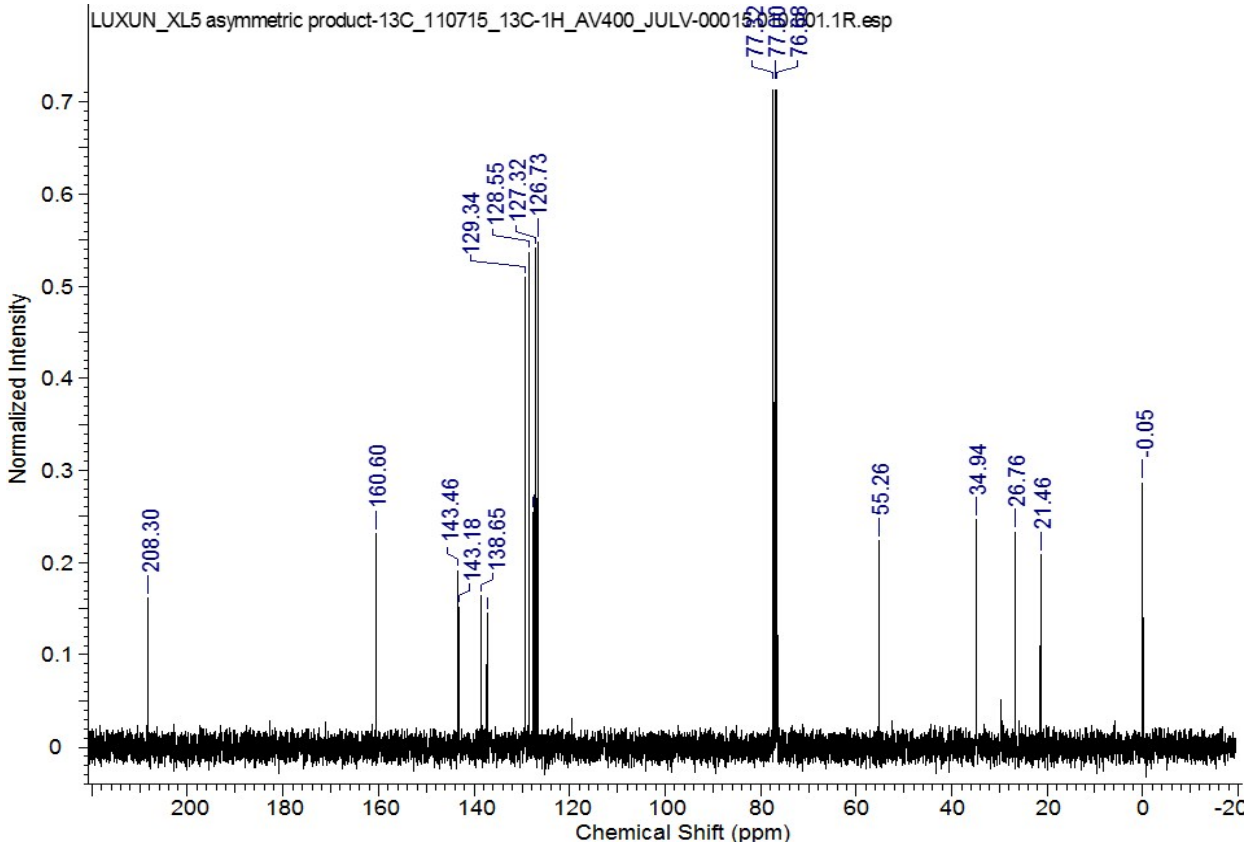

LUXUN_XLCN-PTLC-DETECT_111114_1H_AV600_NOVIV-00349.010.001.1R.esp
Normalized Intensity
Chemical Shift (ppm)
7.69
7.68
7.28
7.28
7.28
7.26
7.24
7.11
7.10
7.09
6.03
6.03
5.98
5.40
5.05
2.41
0.00
1.95
5.11
1.96
1.03
0.97
0.77
1.00
3.09


LUXUN_XLACRYLONITRILE_TSPRODUCT_260414_13C_AV600_SEPV-00800.esp
Normalized Intensity
Chemical Shift (ppm)
144.27
139.48
137.94
115.88
114.32
77.25
77.00
76.75
59.90
21.69


H
NTs
O

(*R*)-**6a**


LUXUN_XL5 asymmetric product_110715_1H_AV600_JULV-00010.010.001.1R.esp
Normalized Intensity
Chemical Shift (ppm)
2.40
0.00
7.63
7.62
7.22
7.21
7.20
7.19
7.23
7.19
7.18
7.28
6.15
6.13
5.30
5.29
2.51
2.50
2.48
2.47
2.28
2.27
2.27
2.17
2.17
2.04
1.10
7.04
1.03
1.00
1.12
3.11
2.21
1.06


LUXUN_XL5 asymmetric product-13C_110715_13C-1H_AV400_JULV-00015.010.001.1R.esp
Normalized Intensity
Chemical Shift (ppm)
77.32
77.00
76.68
129.34
128.55
127.32
126.73
208.30
160.60
143.46
143.18
138.65
55.26
34.94
26.76
21.46
-0.05

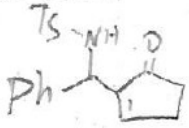
7 Copies of HPLC Charts

SHIMADZU LabSolutions

Analysis Report

IB Hex:iPrOH = 80:20 0.5mL/min

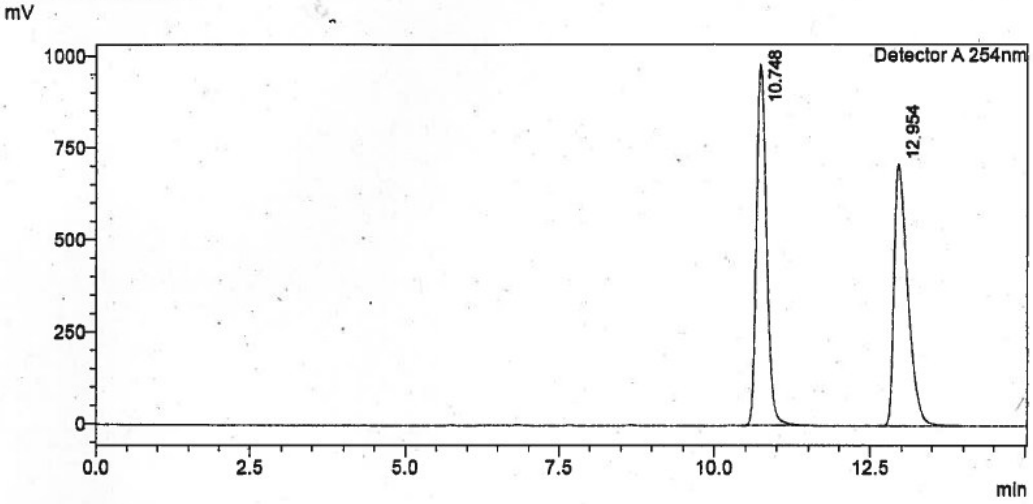
racemic



<Sample Information>

Sample Name	: XLrac_80_20		
Sample ID	:		
Data Filename	: XLrac_80_20.lcd		
Method Filename	: 10min_wash.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 24/06/2014 10:00:51	Acquired by	: System Administrator
Date Processed	: 24/06/2014 10:27:49	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Mark	Name	Area%
1	10.748	10780289	979690	M		49.651
2	12.954	10931896	709817	M		50.349
Total		21712185	1689507			100.000

C:\LabSolutions\Data\XL\XunLu single runs\XLrac_80_20.lcd

SHIMADZU LabSolutions

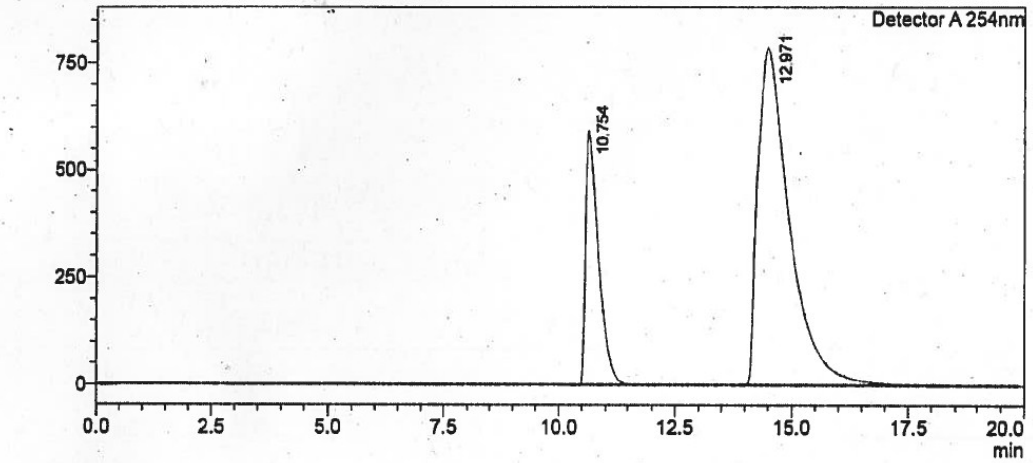
Analysis Report

IB Hex : iPrOH = 80:20. 0.8 ml/min
asymmetric

<Sample Information>

Sample Name	: XLasy8_80_20		
Sample ID	:		
Data Filename	: XLasy8_80_20.lcd		
Method Filename	: 10min_wash.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 24/06/2014 10:34:46	Acquired by	: System Administrator
Date Processed	: 24/06/2014 10:54:15	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Mark	Name	Area%
1	10.754	529381	24443	M		32.440
2	12.971	1102476	28675	M		67.560
Total		1631857	53118			100.000

35-1 free

C:\LabSolutions\Data\XL\XunLu single runs\XLasy8_80_20.lcd