

Palladium-Catalyzed Divergent Cycloisomerization of 1,6-Enynes Controlled by Functional Groups for the Synthesis of Pyrroles, Cyclopentenes, and Tetrahydropyridines

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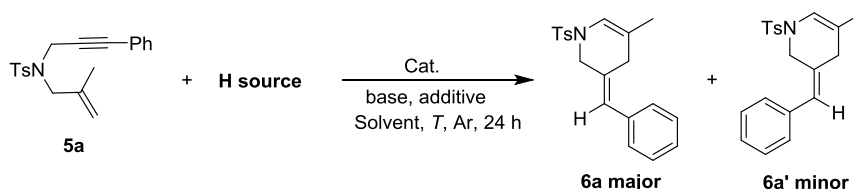
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I. General Remarks: Column chromatography was carried out on silica gel. Unless noted ^1H NMR spectra were recorded on 400 MHz in CDCl_3 , ^{13}C NMR spectra were recorded on 100 MHz in CDCl_3 , ^{19}F NMR spectra were recorded on 376 MHz in CDCl_3 . IR spectra were recorded on an FT-IR spectrometer and only major peaks are reported in cm^{-1} . Melting points were determined on a microscopic apparatus and were uncorrected. All new products were further characterized by HRMS (high resolution mass spectra), high resolution mass spectrometry (HRMS) spectra was obtained on a microTOF-Q instrument equipped with an ESI source; copies of their ^1H NMR and ^{13}C NMR spectra are provided. All reagents were used as received unless otherwise stated. Glucose, D-Mannitol, Fructose, Sucrose, B_2Pin_2 , $\text{Pd}(\text{tBu}_3\text{P})_2$, and common used solvents were purchased from Sigma-Aldrich. All reagents or catalysts were directly used from purchased without further purification.

II. Optimization conditions for the synthesis of products 6

Table S1. Screening of reaction conditions^[a]



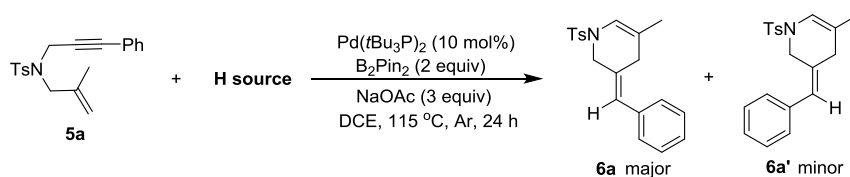
| Entry | Catalyst (mol%) | Solvent (mL) | Base (equiv.) | H source (equiv.) | Additive (equiv.) | Yield(%) (E/Z) |
|-------|--|---------------|-------------------------------|-------------------|-------------------|----------------|
| 1 | $\text{Pd}(\text{tBu}_3\text{P})_2$ (10) | DCE (1.0) | NaOAc (3.0) | Glucose (3.0) | | 60 (1.2:1) |
| 2 | $\text{Pd}(\text{tBu}_3\text{P})_2$ (10) | DCE (1.0) | NaOAc (2.0) | Glucose (3.0) | | <5 |
| 3 | $\text{Pd}(\text{tBu}_3\text{P})_2$ (10) | DCE (1.0) | KOAc (3.0) | Glucose (3.0) | | 58 (4.0:1) |
| 4 | $\text{Pd}(\text{tBu}_3\text{P})_2$ (10) | DCE (1.0) | NaOH (3.0) | Glucose (3.0) | | <5 |
| 5 | $\text{Pd}(\text{tBu}_3\text{P})_2$ (10) | DCE (1.0) | K_2CO_3 (3.0) | Glucose (3.0) | | 15 (3.3:1) |
| 6 | $\text{Pd}(\text{tBu}_3\text{P})_2$ (10) | DMF (1.0) | NaOAc (3.0) | Glucose (3.0) | | <5 |
| 7 | $\text{Pd}(\text{tBu}_3\text{P})_2$ (10) | Toluene (1.0) | NaOAc (3.0) | Glucose (3.0) | | <5 |
| 8 | $\text{Pd}(\text{tBu}_3\text{P})_2$ (10) | PhCl (1.0) | NaOAc (3.0) | Glucose (3.0) | | <5 |
| 9 | $\text{Pd}(\text{tBu}_3\text{P})_2$ (10) | DCE (1.0) | NaOAc (3.0) | Glucose (2.0) | | <5 |
| 10 | $\text{Pd}(\text{tBu}_3\text{P})_2$ (10) | DCE (1.0) | NaOAc (3.0) | Glucose (1.2) | | 0 |
| 11 | $\text{Pd}(\text{tBu}_3\text{P})_2$ (10) | DCE (1.0) | NaOAc (3.0) | Sucrose (3.0) | | 58 (1.2:1) |

| | | | | | | |
|----------------------|---|------------------|--------------------|--------------------------|---|-------------------|
| 12 | Pd(<i>t</i> Bu ₃ P) ₂ (10) | DCE (1.0) | NaOAc (3.0) | D-Mannitol (3.0) | | 70.6 (2.0:1) |
| 13 | Pd(<i>t</i> Bu ₃ P) ₂ (10)/ X-phos (12.5%) | DCE (1.0) | NaOAc (3.0) | Glucose (3.0) | | 25 (1.8:1) |
| 14 | Pd(<i>t</i> Bu ₃ P) ₂ (10)/ Dppe (12.5%) | DCE (1.0) | NaOAc (3.0) | Glucose (3.0) | | <5 |
| 15 | Pd(<i>t</i> Bu ₃ P) ₂ (10)/ Dppp (12.5%) | DCE (1.0) | NaOAc (3.0) | Glucose (3.0) | | <5 |
| 16 | [RuCl ₂ (<i>p</i> -cym ene)] ₂ (5) | DCE (1.0) | NaOAc (3.0) | Glucose (3.0) | | 14 (2.0:1) |
| 17 | [Cp* <i>RhCl</i>] ₂ (5) | DCE (1.0) | NaOAc (3.0) | Glucose (3.0) | | <5 |
| 18 | Pd(<i>t</i>Bu₃P)₂ (10) | DCE (1.0) | NaOAc (3.0) | Glucose (3.0) | B₂Pin₂ (2.0) | 57 (1.2:1) |
| 19 | Pd(<i>t</i>Bu₃P)₂ (10) | DCE (1.0) | NaOAc (4.0) | Glucose (4.0) | B₂Pin₂ (2.0) | 71 (1.4:1) |
| 20 | Pd(<i>t</i>Bu₃P)₂ (10) | DCE (2.0) | NaOAc (3.0) | Glucose (3.0) | B₂Pin₂ (2.0) | 69 (2.6:1) |
| 21 | Pd(<i>t</i> Bu ₃ P) ₂ (10) | DCE (1.0) | NaOAc (4.0) | Glucose (3.0) | PhB(OH) ₂ (4.0) | 55 (1.6:1) |
| 22 | Pd(<i>t</i> Bu ₃ P) ₂ (10) | DCE (1.0) | NaOAc (4.0) | Glucose (4.0) | PhB(OH) ₂ (4.0) | 24 (3.0:1) |
| 23 | Pd(<i>t</i> Bu ₃ P) ₂ (10) | DCE (1.0) | NaOAc (3.0) | Glucose (3.0) | DIPEA | <5 |
| 24 ^[b] | Pd(<i>t</i> Bu ₃ P) ₂ (10) | DCE (1.0) | NaOAc (3.0) | Glucose (3.0) | | 65 (1.2:1) |
| 25 ^[b] | Pd(<i>t</i> Bu ₃ P) ₂ (10) | DCE (2.0) | NaOAc (3.0) | Glucose (3.0) | | 64 (3.0:1) |
| 26 ^[b, c] | Pd(<i>t</i> Bu ₃ P) ₂ (10) | DCE (2.0) | NaOAc (3.0) | Glucose (3.0) | | 63 (3.0:1) |
| 27 | Pd(<i>t</i> Bu ₃ P) ₂ (10) | DCE (1.0) | NaOAc (3.0) | Glucose (4.0) | | 53 (1.6:1) |
| 28 ^[d] | Pd(<i>t</i> Bu ₃ P) ₂ (10) | DCE (1.0) | NaOAc (3.0) | Glucose (3.0) | | 38 (1.6:1) |
| 29 ^[d] | Pd(<i>t</i> Bu ₃ P) ₂ (10) | DCE (1.5) | NaOAc (3.0) | Glucose (3.0) | | 35 (2.0:1) |
| 30 | Pd(<i>t</i> Bu ₃ P) ₂ (10) | DCE (1.0) | NaOAc (3.0) | HCOOH (3.0) | | 35 (1.4:1) |
| 31 | Pd(<i>t</i> Bu ₃ P) ₂ (10) | DCE (1.0) | NaOAc (3.0) | <i>i</i> PrOH (3.0) | | <5 |

[a] **5a** (0.1 mmol), H source (0.3 mmol), Pd(*t*Bu₃P)₂ (10 mol%), NaOAc (0.3 mmol), DCE (1 mL),

at 115 °C for 24 h. [b] The reaction temperature is 130 °C. [c] 36 h. [d] The solvent is ultra-dry.

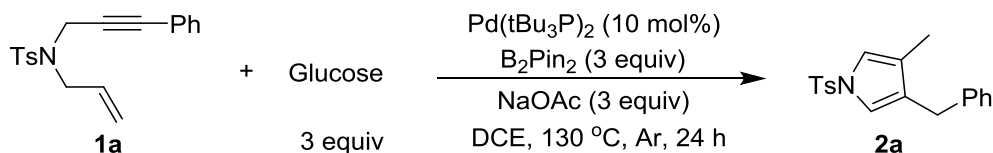
Table S2. Screening of H sources^[a]



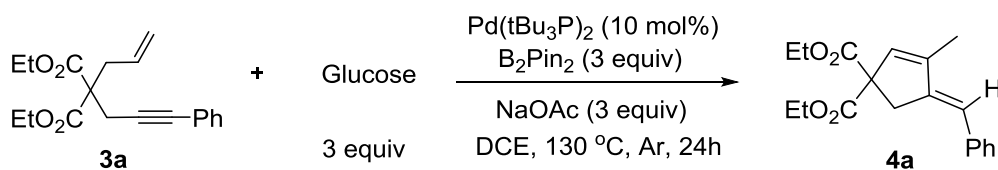
| Entry | H source | pKa (25 °C) | Yield(%) (E/Z) |
|-------------------|------------------------------------|-------------|----------------|
| 1 | H ₂ O | 14 (15.7) | 51 (1.5:1) |
| 2 | CH ₃ CH ₂ OH | 15.24±0.10 | 49 (1.1:1) |
| 3 | Glycerol | 13.68±0.20 | 50 (1.1:1) |
| 4 | CH ₃ COOH | 4.79±0.10 | 53 (1.25:1) |
| 5 | NH ₄ Cl | 9.26±0.20 | 52 (1.3:1) |
| 6 | Glucose | 12.45±0.20 | 69 (2.6:1) |
| 7 | Gluconolactone | 12.13±0.70 | 67.6 (3.6:1) |
| 8 | D-Mannitol | 13.14±0.20 | 70.6 (2.0:1) |
| 9 | Fructose | 11.52±0.70 | 70 (3.1:1) |
| 10 ^[b] | Sucrose | 12.81±0.70 | 58 (1.2:1) |
| 11 | <i>i</i> PrOH | 15.31±0.20 | 53 (1.6:1) |
| 12 ^[b] | HCOOH | 3.74±0.10 | 35 (1.4:1) |

[a] **5a** (0.1 mmol), H source (0.3 mmol), B₂Pin₂ (0.2 mmol), Pd(*t*Bu₃P)₂ (10 mol%), NaOAc (0.3 mmol), DCE (2 mL), at 115 °C for 24 h. [b] Without B₂Pin₂.

III General Procedure for the synthesis of products **2**, **4**, **6**

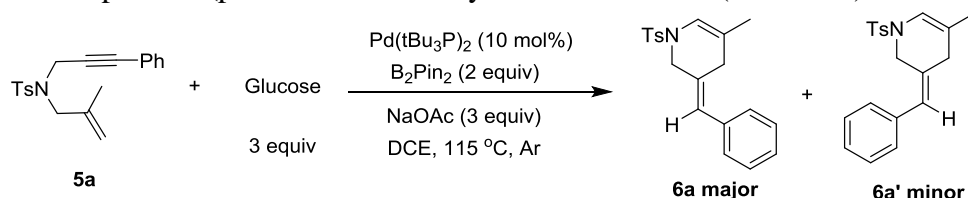


The mixture of N-allyl-4-methyl-N-(3-phenylprop-2-yn-1-yl)benzenesulfonamide **1a** (0.10 mmol) and Glucose (0.30 mmol), B₂Pin₂ (0.30 mmol), Pd(*t*Bu₃P)₂ (0.010 mmol), NaOAc (0.30 mmol) were combined in DCE (2.0 mL) at 130 °C for 24 h under argon atmosphere. After the reaction, 6 mL water was added to quench the reaction, and the resulting mixture was extracted twice with ethyl acetate (2×10 mL). The combined organic extracts were washed with brine (10 mL), dried over Na₂SO₄ and concentrated. Purification of the crude product by flash column chromatography afforded the product (petroleum ether/ethyl acetate as eluent (20:1-10:1)).



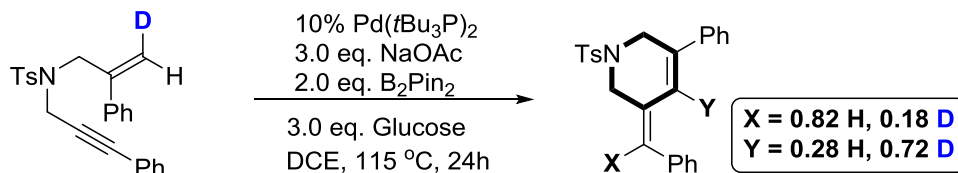
The mixture of diethyl 2-allyl-2-(3-phenylprop-2-yn-1-yl)malonate **3a** (0.10 mmol) and Glucose (0.30 mmol), B₂Pin₂ (0.30 mmol), Pd(*t*Bu₃P)₂ (0.010 mmol), NaOAc

(0.30 mmol) were combined in DCE (2.0 mL) at 130 °C for 24 h under argon atmosphere. After the reaction, 6 mL water was added to quench the reaction, and the resulting mixture was extracted twice with ethyl acetate (2×10 mL). The combined organic extracts were washed with brine (10 mL), dried over Na₂SO₄ and concentrated. Purification of the crude product by flash column chromatography afforded the product (petroleum ether/ethyl acetate as eluent (20:1-10:1)).

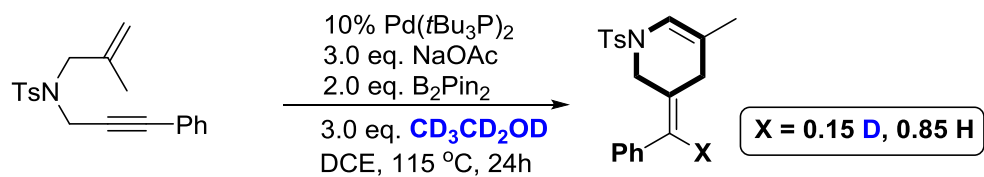
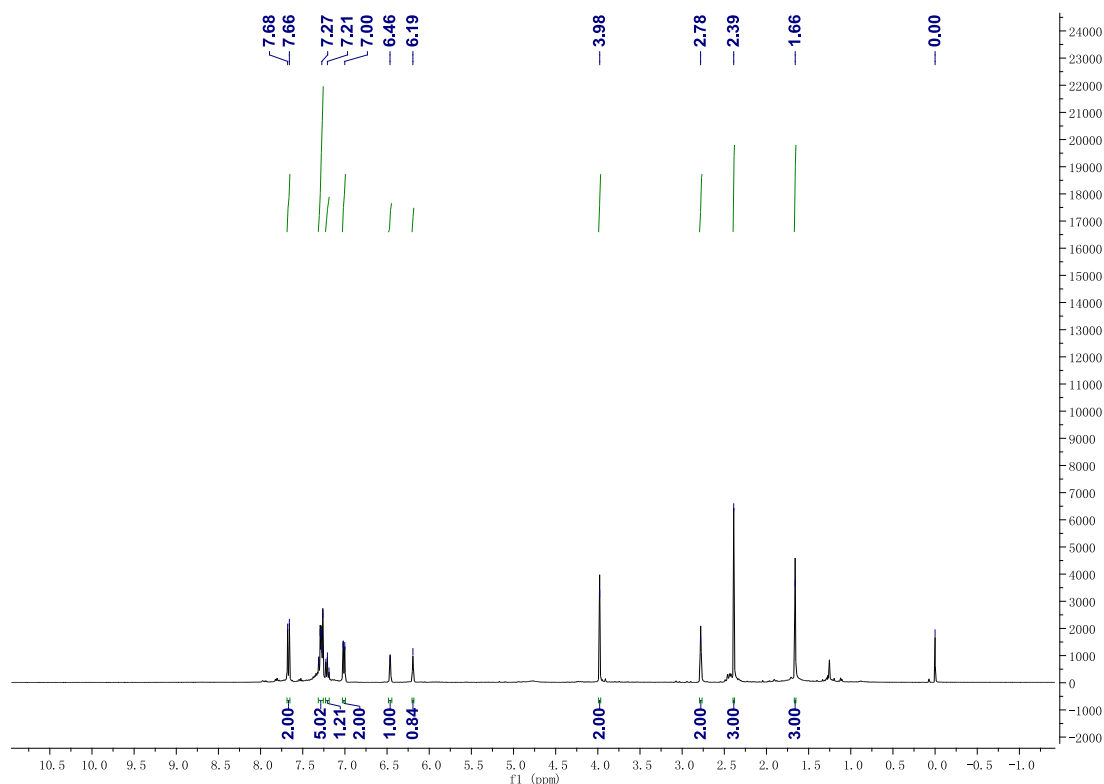


The mixture of 4-methyl-N-(2-methylallyl)-N-(3-phenylprop-2-yn-1-yl)-benzenesulfonamide **5a** (0.20 mmol) and Glucose (0.60 mmol), B₂Pin₂ (0.40 mmol), Pd(*t*Bu₃P)₂ (10 mol%), NaOAc (0.60 mmol) were combined in DCE (2.0 mL) at 115 °C for 24 h under argon atmosphere. After the reaction, 6 mL water was added to quench the reaction, and the resulting mixture was extracted twice with ethyl acetate (2×10 mL). The combined organic extracts were washed with brine (10 mL), dried over Na₂SO₄ and concentrated. Purification of the crude product by flash column chromatography afforded the product (petroleum ether/ethyl acetate as eluent (20:1-10:1)).

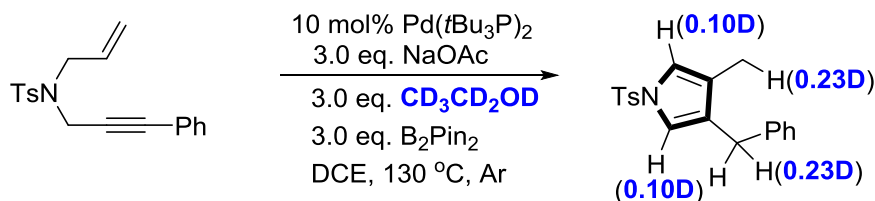
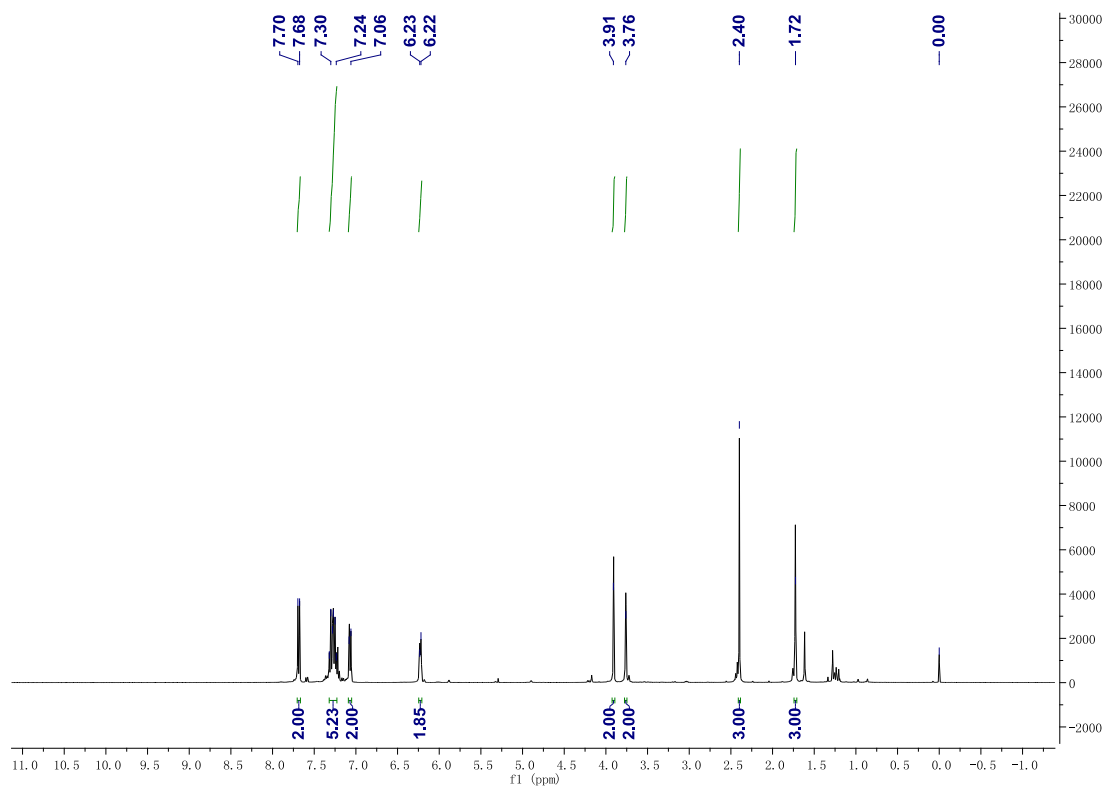
IV. Deuterium labeling experiments and crossover experiment:



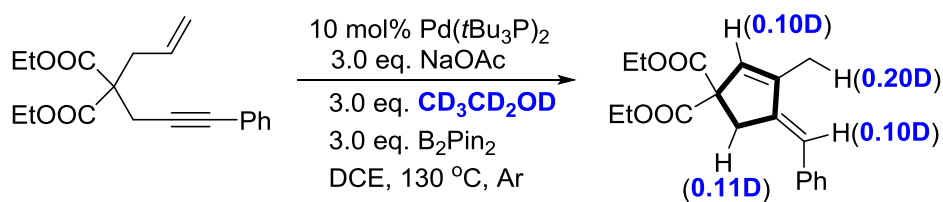
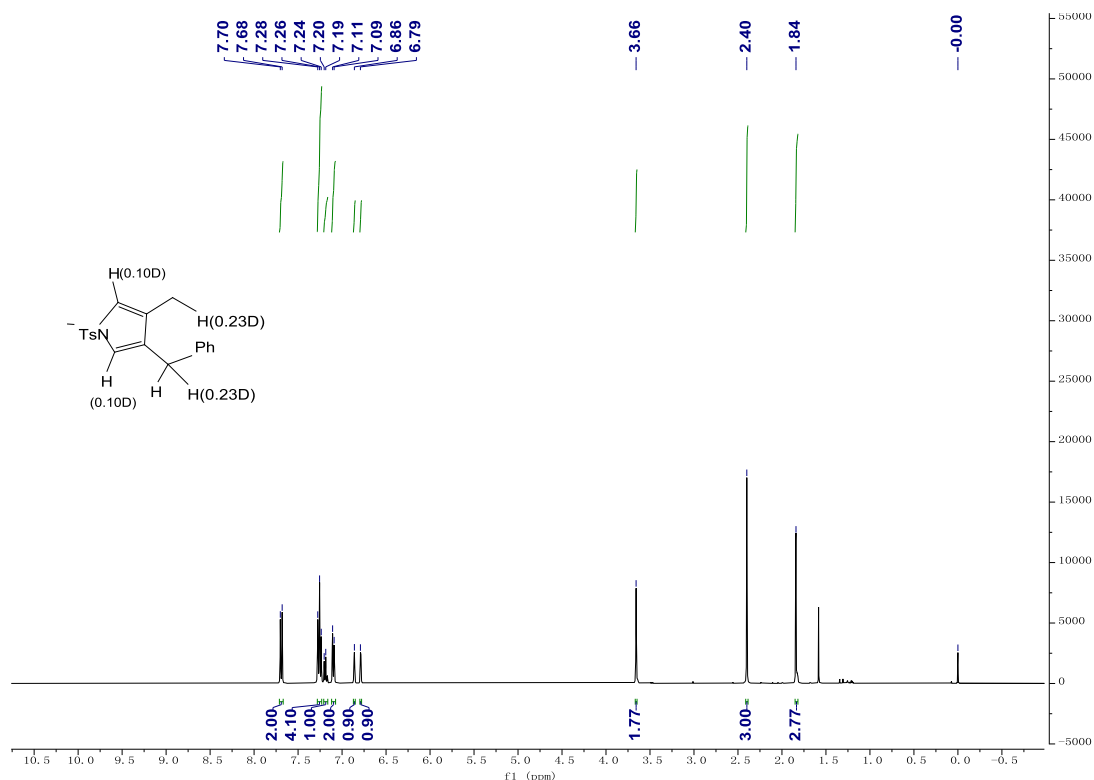
The mixture of (Z)-4-methyl-N-(2-phenylallyl-3-d)-N-(3-phenylprop-2-yn-1-yl)-benzenesulfonamide (0.20 mmol) and Glucose (0.30 mmol), B₂Pin₂ (0.40 mmol), Pd(*t*Bu₃P)₂ (0.020 mmol), NaOAc (0.60 mmol) were combined in DCE (3.0 mL) at 115 °C for 24 h under argon atmosphere. After the reaction, 6 mL water was added to quench the reaction, and the resulting mixture was extracted twice with ethyl acetate (2×10 mL). The combined organic extracts were washed with brine (10 mL), dried over Na₂SO₄ and concentrated. Purification of the crude product by flash column chromatography afforded the product (petroleum ether/ethyl acetate as eluent (20:1-10:1)).



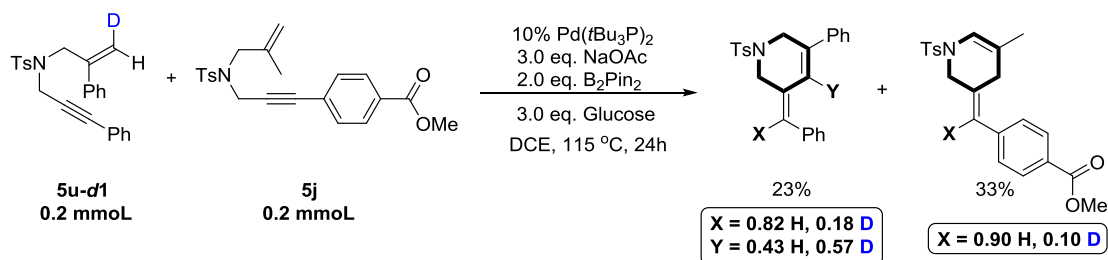
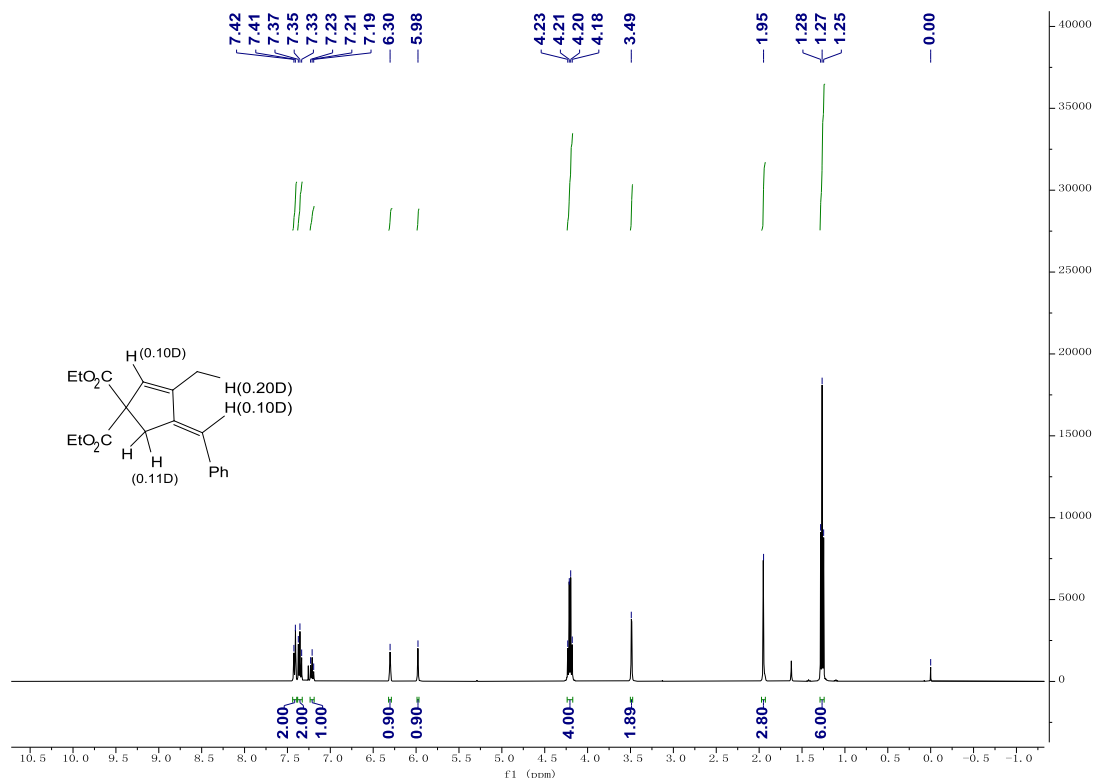
The mixture of 4-methyl-N-(2-methylallyl)-N-(3-phenylprop-2-yn-1-yl)-benzenesulfonamide (0.20 mmol) and C_2D_5OD (0.60 mmol), B_2Pin_2 (0.40 mmol), $Pd(tBu_3P)_2$ (0.020 mmol), $NaOAc$ (0.60 mmol) were combined in DCE (3.0 mL) at 115 °C for 24 h under argon atmosphere. After the reaction, 6 mL water was added to quench the reaction, and the resulting mixture was extracted twice with ethyl acetate (2×10 mL). The combined organic extracts were washed with brine (10 mL), dried over Na_2SO_4 and concentrated. Purification of the crude product by flash column chromatography afforded the product (petroleum ether/ethyl acetate as eluent (20:1-10:1)).



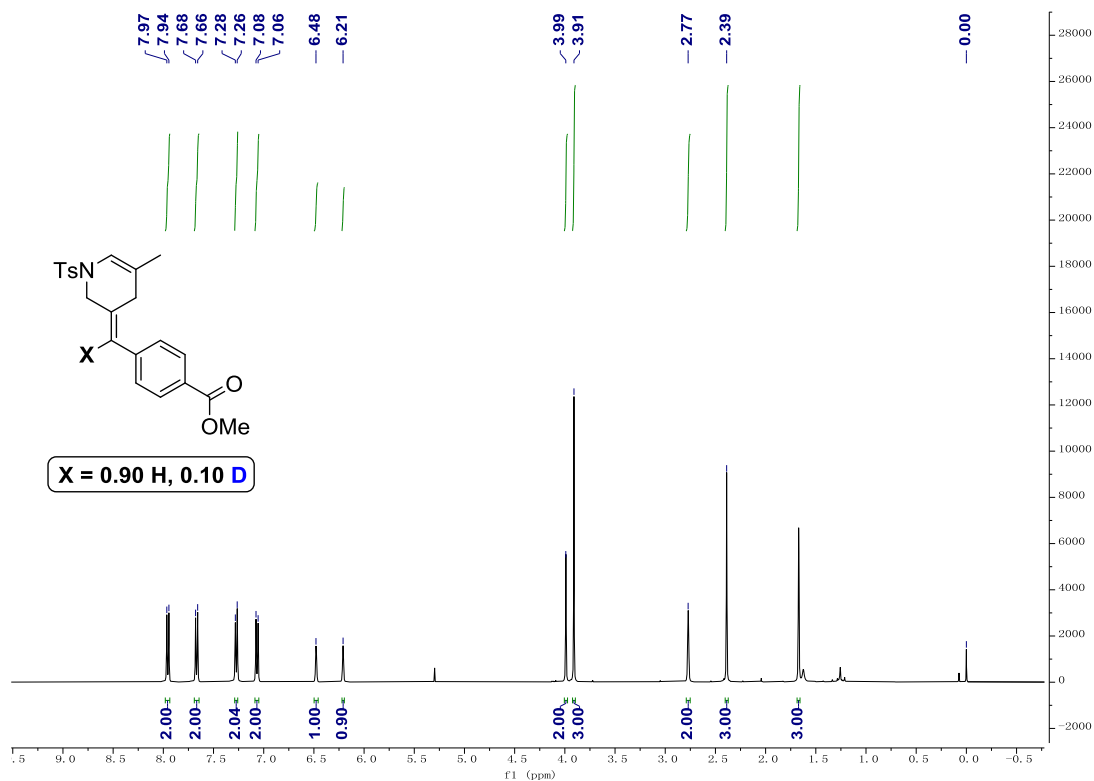
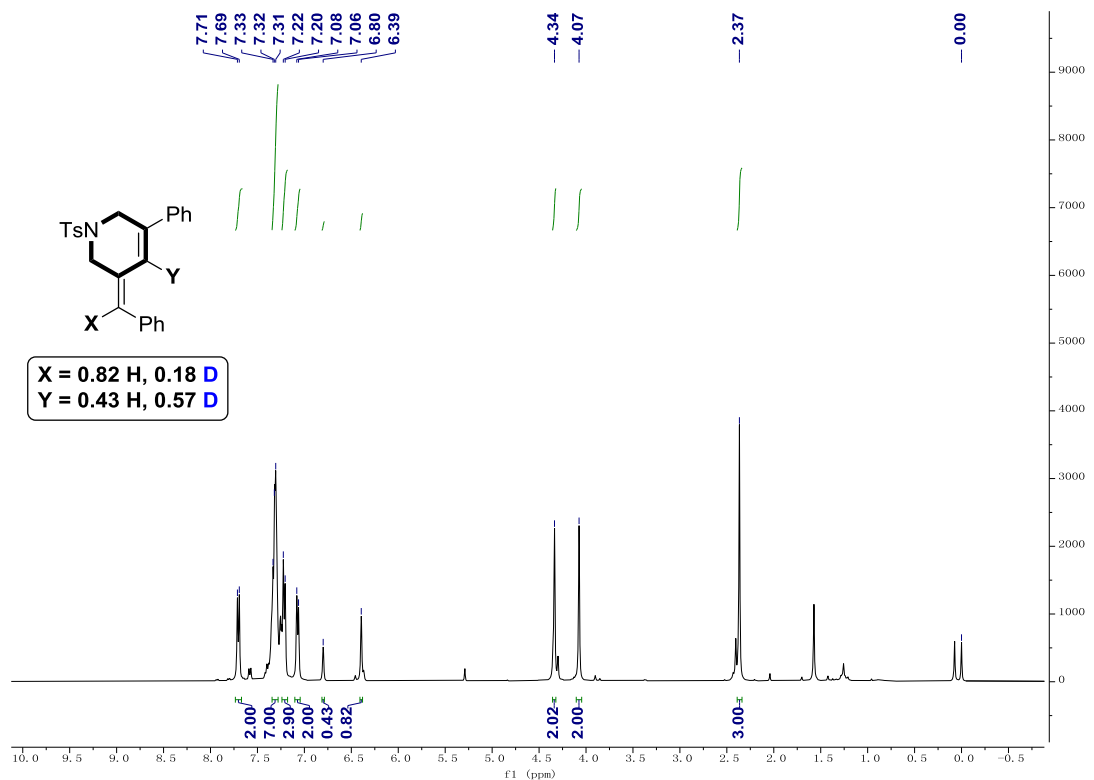
The mixture of N-allyl-4-methyl-N-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (0.10 mmol) and $\text{C}_2\text{D}_5\text{OD}$ (0.30 mmol), B_2Pin_2 (0.30 mmol), $\text{Pd}(t\text{Bu}_3\text{P})_2$ (0.010 mmol), NaOAc (0.30 mmol) were combined in DCE (2.0 mL) at 130 °C for 24 h under argon atmosphere. After the reaction, 6 mL water was added to quench the reaction, and the resulting mixture was extracted twice with ethyl acetate (2×10 mL). The combined organic extracts were washed with brine (10 mL), dried over Na_2SO_4 and concentrated. Purification of the crude product by flash column chromatography afforded the product (petroleum ether/ethyl acetate as eluent (20:1-10:1)).



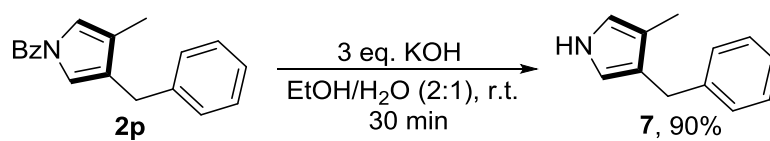
The mixture of diethyl 2-allyl-2-(3-phenylprop-2-yn-1-yl)malonate (0.10 mmol) and C₂D₅OD (0.30 mmol), B₂Pin₂ (0.30 mmol), Pd(*t*Bu₃P)₂ (0.010 mmol), NaOAc (0.30 mmol) were combined in DCE (2.0 mL) at 130 °C for 24 h under argon atmosphere. After the reaction, 6 mL water was added to quench the reaction, and the resulting mixture was extracted twice with ethyl acetate (2×10 mL). The combined organic extracts were washed with brine (10 mL), dried over Na₂SO₄ and concentrated. Purification of the crude product by flash column chromatography afforded the product (petroleum ether/ethyl acetate as eluent (20:1-10:1)).



The mixture of **5u-d1** (0.20 mmol) and **5j** (0.20 mmol), Glucose (0.12 mmol), B₂Pin₂ (0.80 mmol), Pd(*t*Bu₃P)₂ (0.04 mmol), NaOAc (0.12 mmol) were combined in DCE (6.0 mL) at 115 °C for 24 h under argon atmosphere. After the reaction, 10 mL water was added to quench the reaction, and the resulting mixture was extracted twice with ethyl acetate (2×15 mL). The combined organic extracts were washed with brine (15mL), dried over Na₂SO₄ and concentrated. Purification of the crude product by flash column chromatography afforded the product (petroleum ether/ethyl acetate as eluent (30:1-10:1)).

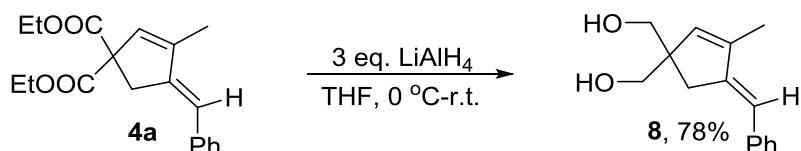


V. Further transformation of products 2 and 4



To a stirred of (3-benzyl-4-methyl-1H-pyrrol-1-yl)(phenyl)methanone (55.0 mg, 0.20

mmol) in EtOH (2.0 mL) and H₂O (1.0 mL) was added KOH (33.6 mg, 0.60 mmol). The solution is stirred for 30 min at room temperature and monitored by thin layer chromatography. After consumption of the starting material, the reaction is then diluted with water (6 mL) and extracted with CH₂Cl₂ (2×10 mL). The organic layer is washed with saturated aqueous NaHCO₃, saturated aqueous brine, then dried over Na₂SO₄ and concentrated. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate =10:1) provided 3-benzyl-4-methyl-1H-pyrrole (31.0 mg, 90%) as a colorless liquid.



diethyl (E)-4-benzylidene-3-methylcyclopent-2-ene-1,1-dicarboxylate (47 mg, 0.15 mmol) in dry THF (2.0 mL) was added dropwise to a solution of LiAlH₄ (1 M in THF, 0.45 mL) at 0 °C. The reaction mixture was stirred at room temperature for 2 h. After cooling to 0 °C, EtOAc (3.0 mL) was added, and the resulting solution was poured into 1 M HCl (5 mL). After separation of the layers, the water layer was extracted with EtOAc (2×10 mL). The combined organic layers were washed with saturated NaCl solution (10 mL), dried over Na₂SO₄, and filtered. The solvent was removed under reduced pressure, purification by column chromatography on silica gel (petroleum ether/ethyl acetate =3:1) provided (3-benzyl-4-methylcyclopenta-2,4-diene-1,1-diyl)dimethanol (27.0 mg, 78%) as a white solid.

VI. X-ray Crystal Diffraction Data for 2m, 4i, (E)-6a

Datablock: 20200911_x2b_0ma_a_a ((E)-6a, CCDC 2035068)

Bond precision: C-C = 0.0048 Å

Wavelength = 0.71073

Cell: a=10.8820(6) b=13.2681(7) c=13.7729(7)
 alpha=71.004(2) beta=78.844(2) gamma=78.236(2)

Temperature: 293 K

| | Calculated | Reported |
|------------------------|--|--|
| Volume | 1823.35(17) | 1823.35(17) |
| Space group | P -1 | P -1 |
| Hall group | -P 1 | -P 1 |
| Moiety formula | C ₂₀ H ₂₁ N O ₂ S | 2(C ₂₀ H ₂₁ N O ₂ S) |
| Sum formula | C ₂₀ H ₂₁ N O ₂ S | C ₄₀ H ₄₂ N ₂ O ₄ S ₂ |
| Mr | 339.44 | 678.87 |
| Dx, g cm ⁻³ | 1.237 | 1.237 |
| Z | 4 | 2 |
| Mu (mm ⁻¹) | 0.189 | 0.189 |
| F000 | 720.0 | 720.0 |
| F000' | 720.78 | |
| h,k,lmax | 13,16,16 | 13,16,16 |
| Nref | 6986 | 6622 |

Tmin,Tmax

0.668,0.745

Tmin'

Correction method= # Reported T Limits: Tmin=0.668 Tmax=0.745

AbsCorr = MULTI-SCAN

Data completeness= 0.948

Theta(max)= 25.765

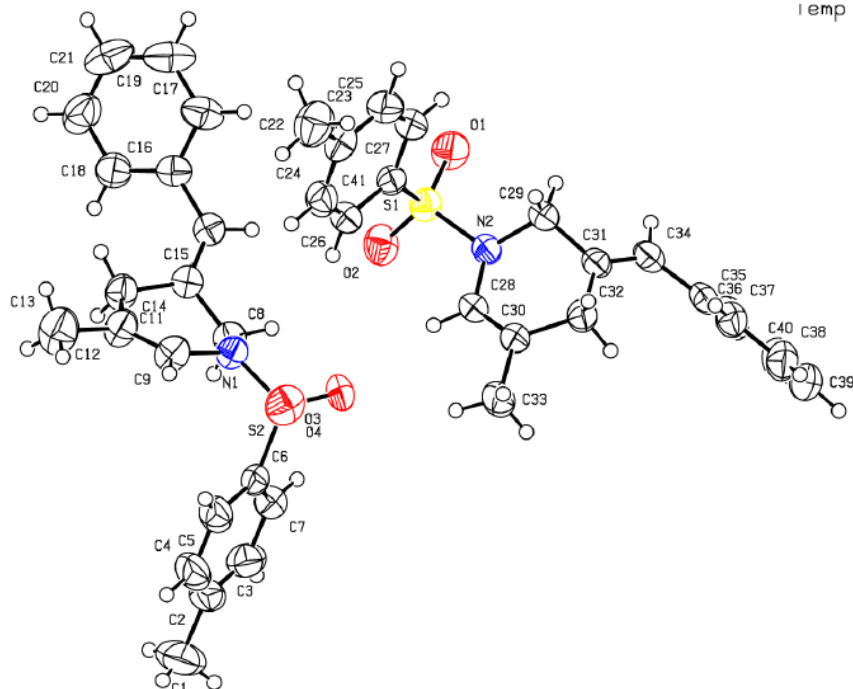
R(reflections)= 0.0574(5122)

wR2(reflections)= 0.1500(6622)

S = 1.052

Npar= 437

Temp



Datablock: 20200930_x3_0m_a (2m, CCDC 2035069)

Bond precision: C-C = 0.0035 Å

Wavelength=0.71073

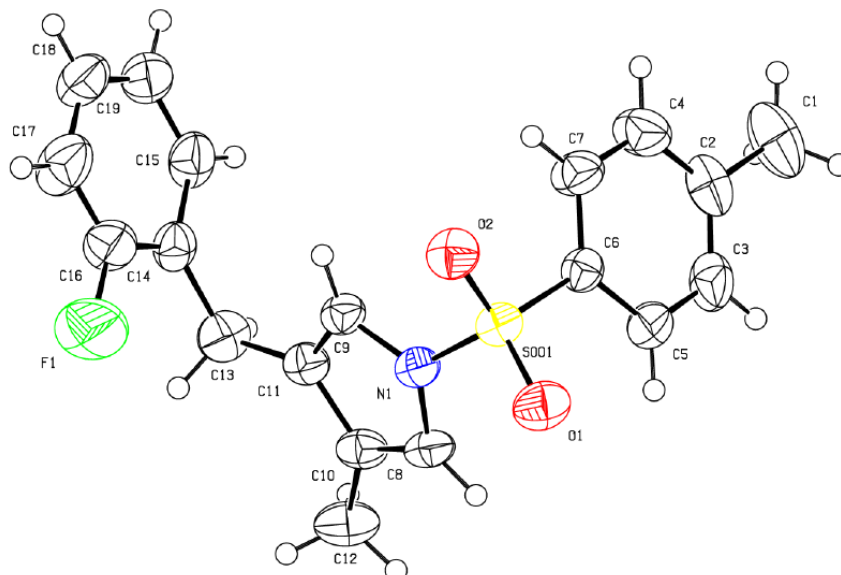
Cell: a=10.955(4) b=10.995(4) c=14.499(5)

alpha=90 beta=101.851(15) gamma=90

Temperature: 297 K

| | Calculated | Reported |
|----------------|------------------|------------------|
| Volume | 1709.2(11) | 1709.3(10) |
| Space group | P 21/n | P 1 21/n 1 |
| Hall group | -P 2yn | -P 2yn |
| Moiety formula | C19 H18 F N O2 S | C19 H18 F N O2 S |
| Sum formula | C19 H18 F N O2 S | C19 H18 F N O2 S |
| Mr | 343.40 | 343.40 |
| Dx,g cm-3 | 1.334 | 1.334 |
| Z | 4 | 4 |
| Mu (mm-1) | 0.210 | 0.210 |
| F000 | 720.0 | 720.0 |
| F000' | 720.83 | |
| h,k,lmax | 14,14,18 | 14,14,18 |
| Nref | 3891 | 3872 |

Tmin,Tmax 0.680,0.746
 Tmin'
 Correction method= # Reported T Limits: Tmin=0.680 Tmax=0.746
 AbsCorr = MULTI-SCAN
 Data completeness= 0.995 Theta(max)= 27.403
 R(reflections)= 0.0536(2752) wR2(reflections)= 0.1338(3872)
 S = 1.060 Npar= 219



Datablock: 1 (4i, CCDC2045080)

Bond precision: C-C = 0.0033 Å

Cell: a=8.5832(9) b=11.1549(12)
 alpha=65.477(2) beta=86.417(2)

Wavelength=0.71073
 c=11.2505(12)
 gamma=88.804(2)

Temperature: 296 K

| | Calculated | Reported |
|------------------------|--|--|
| Volume | 978.08(18) | 978.08(18) |
| Space group | P -1 | P -1 |
| Hall group | -P 1 | -P 1 |
| Moiety formula | C ₂₁ H ₂₄ O ₅ | ? |
| Sum formula | C ₂₁ H ₂₄ O ₅ | C ₂₁ H ₂₄ O ₅ |
| Mr | 356.40 | 356.40 |
| Dx,g cm ⁻³ | 1.210 | 1.210 |
| Z | 2 | 2 |
| Mu (mm ⁻¹) | 0.086 | 0.086 |
| F000 | 380.0 | 380.0 |
| F000' | 380.20 | |
| h,k,lmax | 10,13,13 | 10,13,13 |
| Nref | 3449 | 3418 |
| Tmin,Tmax | 0.978, | 0.983 |
| Tmin' | 0.978 | |

Correction method= Not given

Data completeness= 0.991

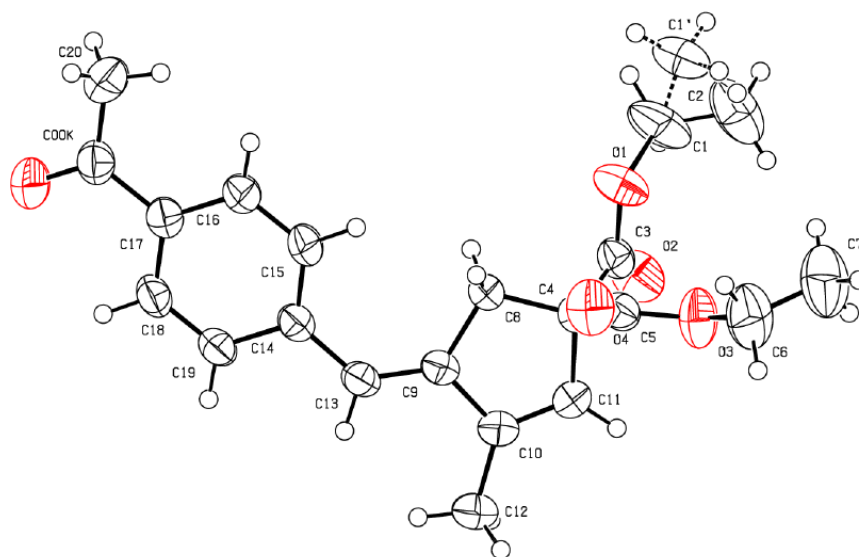
R(reflections)= 0.0591(2725)

S = 1.034

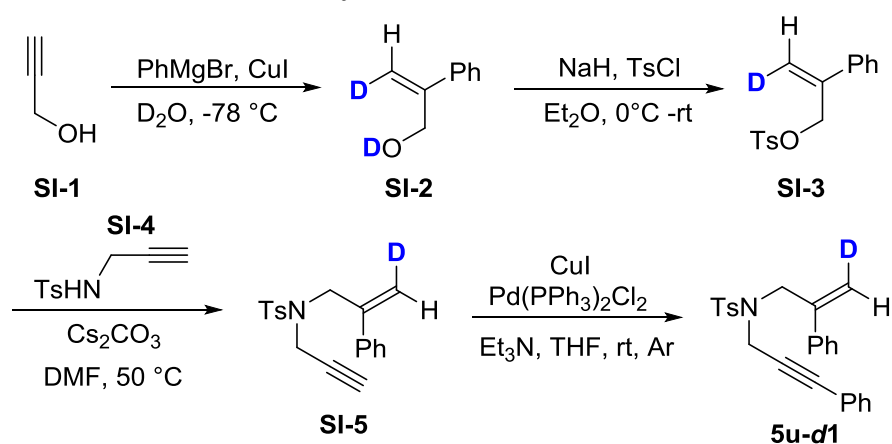
Npar= 246

Theta(max)= 24.998

wR2(reflections)= 0.1868(3418)



VII. General Procedure for the synthesis of 5u-d1



General Procedure:

Preparation of SI-2: To a solution of propargyl alcohol **SI-1** (1.12 g, 20 mmol) in dry THF (40 mL) was vacuum purged three times, backfilling with N₂. CuI (0.38 g, 2.0 mmol) was added under stirring and N₂ atmosphere. The suspension was cooled to -78 °C. Then a solution of PhMgBr (9.05 g, 50 mmol) in 60 mL THF was added dropwise by constant pressure funnel under vigorous stirring. The resulting mixture held at -78 °C for 1 h. Then it was warmed to room temperature and stirred for 18 h. The mixture was cooled to -78 °C again and quenched slowly with D₂O (4.0 g, 200 mmol). After the suspension was warmed to room temperature, dilute HCl solution (1 N, 150 mL) was added and the aqueous layer was extracted with EtOAc (3 × 50 mL). The combined organic layers were washed brine (30 mL), dried with Na₂SO₄, and concentrated in vacuo. Purification by column chromatography (PE: EA=5:1) afforded the **SI-2** as a yellow liquid (2.67 g, 19.6 mmol, 98% yield).

Preparation of SI-3: To a suspension of NaH (Purity is 60%) (1.08 g, 27 mmol) in 15

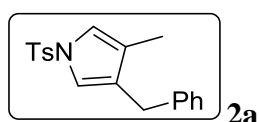
mL Et₂O was added **SI-2** (2.45 g, 18 mmol) under N₂ atmosphere. The mixture was stirred for 30 min at room temperature and then cooled to 0 °C. A solution of TsCl (3.43 g, 18 mmol) in 15 mL Et₂O was added dropwise. The resulting mixture was warmed to room temperature and stirred for 1 h. Then the solution was quenched with a saturated aqueous solution of NH₄Cl (30 mL). The aqueous layer was extracted with Et₂O (3×10 mL). The combined organic layers were washed with brine (25 mL), dried with Na₂SO₄, and concentrated in vacuo to afford the crude product **SI-3** as a yellow solid (3.12 g, 10.8 mmol, 60% yield), which was used without further purification.

Preparation of SI-5: To a solution of **SI-3** (2.89 g, 10 mmol) in 15 mL DMF was added **SI-4** (4.18 g, 20 mmol) and Cs₂CO₃ (9.78 g, 30 mmol). The mixture was heated to 50 °C and stirred for 5 h. The reaction was quenched with a saturated aqueous solution of NH₄Cl (30 mL), the aqueous layer was extracted with EtOAc (20 mL). The combined organic layers were washed with brine (3×30 mL), dried with Na₂SO₄, and evaporated. The crude product was purified by column chromatography (PE: EA=2:1) to give the **SI-5** (2.54 g, 7.8 mmol, 78% yield) as a yellow solid.

Preparation of 5u-d1: Under the protection of argon. To a solution of iodobenzene (1.7 g, 8.4 mmol), Pd(PPh₃)₂Cl₂ (0.098 g, 0.14 mmol), CuI (0.053 g, 0.28 mmol) in Et₃N (10 mL) and THF (8 mL) were added dropwise **SI-5** (2.28 g, 7 mmol). The resulting mixture was stirred overnight at room temperature until the completion of the reaction (monitoring by TLC). The mixture was quenched with HCl and extracted with EtOAc (2×15 mL), washed with brine (10 mL), dried over Na₂SO₄, and concentrated under vacuo. The crude residue was purified by flash chromatography (PE: EA=6:1) to provide **5u-d1** (2.3 g, 5.7 mmol, 82% yield) as a yellow solid.

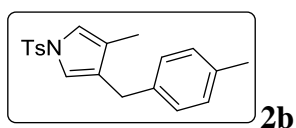
¹H NMR (400 MHz, CDCl₃): 7.80 (d, *J* = 8.3 Hz, 2H), 7.58 (d, *J* = 6.8 Hz, 2H), 7.38 – 7.23 (m, 8H), 7.03 (d, *J* = 6.6 Hz, 2H), 5.60 (s, 1H), 4.32 (s, 2H), 4.20 (s, 2H), 2.33 (s, 3H).

VIII. Data of products 2, 4, 6, 7, 8



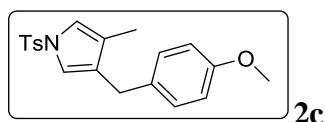
3-benzyl-4-methyl-1-tosyl-1H-pyrrole, M.P.= 97-99 °C, 67%, yellow solid, 21.5mg.
CAS: 862170-74-9

¹H NMR (400 MHz, CDCl₃): 7.69 (d, *J* = 8.3 Hz, 2H), 7.25 (t, *J* = 7.3 Hz, 4H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.09 (d, *J* = 7.0 Hz, 2H), 6.86 (s, 1H), 6.79 (s, 1H), 3.65 (s, 2H), 2.39 (s, 3H), 1.84 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): 144.48, 139.56, 136.28, 129.77, 128.49, 128.45, 128.32, 126.64, 126.04, 124.47, 118.75, 118.38, 31.56, 21.53, 10.25. IR (cm⁻¹): 3128, 3061, 3026, 2921, 1916, 1655, 1595, 1517, 1493, 1452, 1366, 1305, 1283, 1169, 1093, 1065, 964, 812, 791, 728, 701, 672.



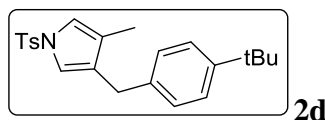
3-methyl-4-(4-methylbenzyl)-1-tosyl-1H-pyrrole, oil, 44%, 15 mg.

^1H NMR (400 MHz, CDCl_3): 7.69 (d, $J = 8.3$ Hz, 2H), 7.27 (d, $J = 8.1$ Hz, 2H), 7.06 (d, $J = 7.8$ Hz, 2H), 6.99 (d, $J = 7.9$ Hz, 2H), 6.85 (s, 1H), 6.78 (s, 1H), 3.61 (s, 2H), 2.40 (s, 3H), 2.31 (s, 3H), 1.84 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): 144.46, 136.47, 136.37, 135.54, 129.79, 129.04, 128.76, 128.41, 126.68, 124.52, 118.71, 118.36, 31.17, 21.58, 20.97, 10.30. IR (cm^{-1}): 3128, 2920, 1595, 1513, 1493, 1451, 1366, 1305, 1287, 1170, 1093, 1065, 1018, 964, 912, 811, 787, 757, 703, 673. HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{21}\text{NO}_2\text{SNa}^+$ ($\text{M}+\text{Na}$) $^+$ 362.11852, found 362.11853.



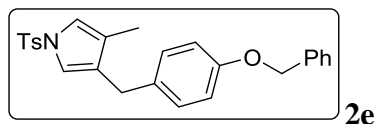
3-(4-methoxybenzyl)-4-methyl-1-tosyl-1H-pyrrole, M.P. = 75-77 $^{\circ}\text{C}$, 65%, 23mg.
CAS: 923297-68-1.

^1H NMR (400 MHz, CDCl_3): 7.69 (d, $J = 8.3$ Hz, 2H), 7.27 (d, $J = 8.1$ Hz, 2H), 7.01 (d, $J = 8.6$ Hz, 2H), 6.85 (s, 1H), 6.80 (d, $J = 8.6$ Hz, 2H), 6.76 (s, 1H), 3.78 (s, 3H), 3.59 (s, 2H), 2.40 (s, 3H), 1.84 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): 157.89, 144.44, 136.33, 131.57, 129.76, 129.43, 128.95, 126.65, 118.61, 118.36, 113.74, 55.19, 30.70, 21.55, 10.25. IR (cm^{-1}): 2978, 2928, 2835, 1611, 1596, 1511, 1463, 1370, 1280, 1246, 1171, 1124, 1093, 1065, 1035, 960, 848, 813, 791, 704, 673.



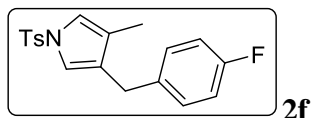
3-(4-(tert-butyl)benzyl)-4-methyl-1-tosyl-1H-pyrrole, M.P.= 128-130 $^{\circ}\text{C}$, 66%, 25 mg.

^1H NMR (400 MHz, CDCl_3): 7.69 (d, $J = 8.3$ Hz, 2H), 7.27 (d, $J = 8.2$ Hz, 4H), 7.03 (d, $J = 8.2$ Hz, 2H), 6.86 (s, 1H), 6.81 (s, 1H), 3.62 (s, 2H), 2.40 (s, 3H), 1.85 (s, 3H), 1.30 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): 148.87, 144.46, 136.48, 136.37, 129.79, 128.63, 128.14, 126.68, 125.24, 124.59, 118.75, 118.33, 34.33, 31.37, 31.01, 21.58, 10.32. IR (cm^{-1}): 3128, 2961, 2866, 1596, 1514, 1494, 1457, 1366, 1306, 1290, 1170, 1093, 1066, 1017, 965, 812, 792, 729, 703, 672. HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{27}\text{NO}_2\text{SNa}^+$ ($\text{M}+\text{Na}$) $^+$ 404.16547, found 404.16556.

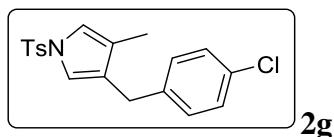


3-(4-(benzyloxy)benzyl)-4-methyl-1-tosyl-1H-pyrrole, oil, 52%, 22 mg.

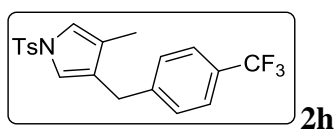
^1H NMR (400 MHz, CDCl_3): 7.69 (d, $J = 8.3$ Hz, 2H), 7.45 – 7.36 (m, 4H), 7.33 (d, $J = 7.2$ Hz, 1H), 7.26 (d, $J = 7.9$ Hz, 2H), 7.01 (d, $J = 8.5$ Hz, 2H), 6.90 – 6.84 (m, 3H), 6.76 (s, 1H), 5.04 (s, 2H), 3.59 (s, 2H), 2.40 (s, 3H), 1.84 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): 157.18, 144.46, 137.10, 136.35, 131.92, 129.78, 129.48, 128.90, 128.54, 127.89, 127.46, 126.67, 124.44, 118.66, 118.38, 114.73, 83.47, 70.04, 30.74, 21.57, 10.28. IR (cm^{-1}): 3031, 2977, 2923, 1610, 1596, 1509, 1453, 1369, 1281, 1239, 1170, 1123, 1093, 1065, 960, 848, 812, 791, 741, 703, 672. HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{25}\text{NO}_3\text{SNa}^+$ ($\text{M}+\text{Na}$) $^+$ 454.14474, found 454.14490.



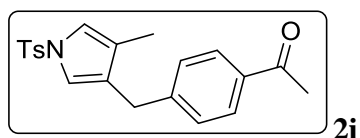
3-(4-fluorobenzyl)-4-methyl-1-tosyl-1H-pyrrole, M.P.= 132-134 °C, 69%, 24 mg.
¹H NMR (400 MHz, CDCl₃): 7.69 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 7.07 – 7.02 (m, 2H), 6.94 (t, *J* = 8.7 Hz, 2H), 6.87 (s, 1H), 6.77 (s, 1H), 3.63 (s, 2H), 2.40 (s, 3H), 1.83 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): 162.57 (d, *J* = 243.0 Hz), 160.14, 144.58, 136.28, 135.23 (d, *J* = 4.0 Hz), 135.19, 129.91, 129.82, 128.33, 126.70, 124.29, 118.69 (d, *J* = 17.0 Hz), 118.52, 115.22 (d, *J* = 21.0 Hz), 115.01, 30.81, 21.58, 10.25. ¹⁹F NMR (376 MHz, CDCl₃): -117.25 (s). IR (cm⁻¹): 3123, 3049, 2921, 2846, 1598, 1507, 1440, 1356, 1306, 1282, 1216, 1169, 1092, 1065, 1015, 965, 840, 808, 785, 762, 703, 673. HRMS (ESI) *m/z* calcd for C₁₉H₁₈FNO₂SNa⁺ (M+Na)⁺ 366.09345, found 366.09369.



3-(4-chlorobenzyl)-4-methyl-1-tosyl-1H-pyrrole, oil, 64%, 23 mg.
¹H NMR (400 MHz, CDCl₃): 7.70 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 10.4 Hz, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 7.02 (d, *J* = 8.2 Hz, 2H), 6.87 (s, 1H), 6.78 (s, 1H), 3.62 (s, 2H), 2.41 (s, 3H), 1.83 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): 144.60, 138.11, 136.31, 131.88, 129.86, 129.84, 128.49, 127.89, 126.72, 124.25, 118.77, 118.57, 31.00, 21.60. IR (cm⁻¹): 3129, 2922, 2852, 1596, 1490, 1452, 1367, 1300, 1284, 1169, 1092, 1065, 1015, 966, 909, 811, 787, 733, 670. HRMS (ESI) *m/z* calcd for C₁₉H₁₈ClNO₂SNa⁺ (M+Na)⁺ 382.06390, found 382.06403.

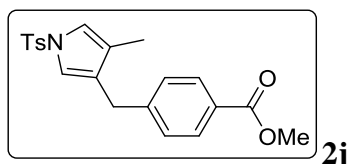


3-methyl-1-tosyl-4-(4-(trifluoromethyl)benzyl)-1H-pyrrole, M.P.= 71-73 °C, 71%, 28 mg.
¹H NMR (400 MHz, CDCl₃): 7.70 (d, *J* = 8.3 Hz, 2H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.88 (s, 1H), 6.81 (s, 1H), 3.72 (s, 2H), 2.41 (s, 3H), 1.83 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): 144.69, 143.80, 136.24, 129.86, 129.00 (q, *J* = 32.0 Hz), 128.80, 128.67, 128.35, 128.30 (q, *J* = 270.0 Hz), 128.03, 127.29, 126.72, 125.60, 125.37 (q, *J* = 4.0 Hz), 125.33, 125.29, 125.25, 124.19, 122.90, 120.19, 118.85, 118.64, 31.43, 21.57, 10.24. ¹⁹F NMR (376 MHz, CDCl₃): -62.33 (s). IR (cm⁻¹): 3133, 2923, 1617, 1596, 1517, 1367, 1325, 1170, 1122, 1093, 1066, 1018, 966, 812, 794, 703, 671. HRMS (ESI) *m/z* calcd for C₂₀H₁₈F₃NO₂SNa⁺ (M+Na)⁺ 416.09026, found 416.09033.



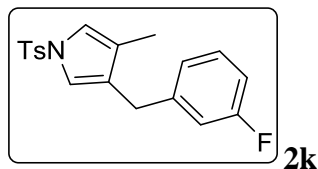
1-(4-((4-methyl-1-tosyl-1H-pyrrol-3-yl)methyl)phenyl)ethan-1-one, M.P.= 88-90 °C, 41%, 15mg.

¹H NMR (400 MHz, CDCl₃): 7.86 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 6.88 (s, 1H), 6.80 (s, 1H), 3.72 (s, 2H), 2.59 (s, 3H), 2.41 (s, 3H), 1.83 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): 197.83, 145.38, 144.66, 136.21, 135.31, 129.86, 128.72, 128.55, 127.35, 126.70, 124.22, 118.83, 118.57, 31.63, 26.56, 21.60, 10.26. IR (cm⁻¹): 3127, 2922, 1680, 1605, 1518, 1494, 1412, 1364, 1267, 1169, 1093, 1065, 1016, 959, 812, 792, 730, 703, 674. HRMS (ESI) *m/z* calcd for C₂₁H₂₁NO₃SNa⁺ (M+Na)⁺ 390.11344, found 390.11346.



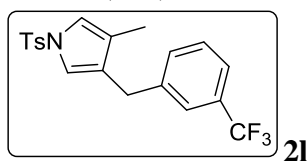
methyl 4-((4-methyl-1-tosyl-1H-pyrrol-3-yl)methyl)benzoate, oil, 58%, 22 mg.

¹H NMR (400 MHz, CDCl₃): 7.93 (d, *J* = 8.3 Hz, 2H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 8.2 Hz, 2H), 6.88 (s, 1H), 6.80 (s, 1H), 3.90 (s, 3H), 3.71 (s, 2H), 2.41 (s, 3H), 1.82 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): 167.00, 145.10, 144.63, 136.18, 129.83, 129.70, 128.52, 128.11, 127.43, 126.67, 124.25, 118.83, 118.56, 51.99, 31.62, 21.57, 10.23. IR (cm⁻¹): 3128, 2951, 2922, 1719, 1610, 1434, 1366, 1280, 1170, 1093, 1066, 1019, 965, 812, 790, 744, 703, 670. HRMS (ESI) *m/z* calcd for C₂₁H₂₁NO₄SNa⁺ (M+Na)⁺ 406.10835, found 406.10852.



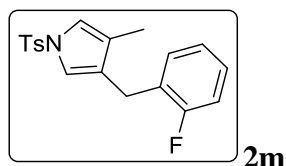
3-(3-fluorobenzyl)-4-methyl-1-tosyl-1H-pyrrole, oil, 72%, 25 mg.

¹H NMR (400 MHz, CDCl₃): 7.70 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.24 – 7.18 (m, 1H), 6.91 – 6.85 (m, 3H), 6.82 (s, 1H), 6.74 (d, *J* = 10.0 Hz, 1H), 3.66 (s, 2H), 2.40 (s, 3H), 1.83 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): 164.15 (d, *J* = 244.0 Hz), 161.71, 144.64, 142.33 (d, *J* = 7.0 Hz), 142.26, 136.24, 129.84, 129.78, 129.70, 127.63, 126.67, 124.35, 124.16 (d, *J* = 2.0 Hz), 124.14, 118.92, 118.62, 115.40 (d, *J* = 21.0 Hz), 115.19, 113.11 (d, *J* = 21.0 Hz), 112.90, 31.28 (d, *J* = 2.0 Hz), 31.26, 21.56, 10.22. ¹⁹F NMR (376 MHz, CDCl₃): -113.57 (s). IR (cm⁻¹): 3134, 2922, 1615, 1588, 1518, 1486, 1447, 1366, 1290, 1247, 1170, 1093, 1066, 946, 812, 780, 751, 672. HRMS (ESI) *m/z* calcd for C₁₉H₁₈FNO₂SNa⁺ (M+Na)⁺ 366.09345, found 366.09360.



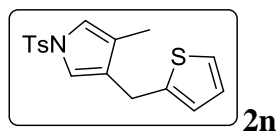
3-methyl-1-tosyl-4-(3-(trifluoromethyl)benzyl)-1H-pyrrole, M.P.= 99-101 °C, 69%, 27 mg.

^1H NMR (400 MHz, CDCl_3): 7.69 (d, $J = 8.3$ Hz, 2H), 7.45 (d, $J = 7.7$ Hz, 1H), 7.37 (t, $J = 7.6$ Hz, 1H), 7.31 – 7.25 (m, 4H), 6.88 (s, 1H), 6.80 (s, 1H), 3.72 (s, 2H), 2.40 (s, 3H), 1.83 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): 144.70, 140.64, 136.16, 131.93, 130.83 (d, $J = 32.0$ Hz), 130.51, 129.86, 128.81, 127.48, 126.63, 125.18 (q, $J = 4.0$ Hz), 125.14, 125.10, 125.07, 124.25, 123.11 (q, $J = 4.0$ Hz), 123.07, 123.03, 122.99, 118.96, 118.72, 31.34, 21.56, 10.24. ^{19}F NMR (376 MHz, CDCl_3): -62.58 (s). IR (cm^{-1}): 2923, 1596, 1518, 1493, 1448, 1367, 1332, 1294, 1168, 1123, 1093, 1066, 811, 790, 702, 670. HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{18}\text{F}_3\text{NO}_2\text{SNa}^+$ ($\text{M}+\text{Na}$) $^+$ 416.09026, found 416.09033.



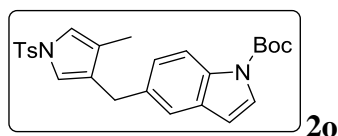
3-(2-fluorobenzyl)-4-methyl-1-tosyl-1H-pyrrole, M.P.= 117-119 °C, 68%, 23 mg.

^1H NMR (400 MHz, CDCl_3): 7.69 (d, $J = 8.3$ Hz, 2H), 7.26 (d, $J = 7.8$ Hz, 2H), 7.17 (dd, $J = 10.1, 4.1$ Hz, 1H), 7.01 (q, $J = 8.4, 6.6$ Hz, 3H), 6.86 (s, 1H), 6.81 (s, 1H), 3.67 (s, 2H), 2.40 (s, 3H), 1.88 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): 162.05 (d, $J = 244.0$ Hz), 159.61, 144.54, 136.30, 130.49 (d, $J = 4.0$ Hz), 130.45, 129.81, 127.94 (d, $J = 8.0$ Hz), 127.86, 127.00, 126.67, 124.36, 124.00 (d, $J = 3.0$ Hz), 123.97, 118.94, 118.35, 115.28 (d, $J = 22.0$ Hz), 115.06, 24.35 (d, $J = 4.0$ Hz), 24.31, 21.57, 10.15. ^{19}F NMR (376 MHz, CDCl_3): -118.25 (s). IR (cm^{-1}): 3129, 2922, 1595, 1585, 1491, 1455, 1367, 1287, 1229, 1170, 1093, 1066, 966, 811, 756, 704, 672. HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{18}\text{FNO}_2\text{SNa}^+$ ($\text{M}+\text{Na}$) $^+$ 366.09345, found 366.09360.



3-methyl-4-(thiophen-2-ylmethyl)-1-tosyl-1H-pyrrole, oil, 46%, 15 mg.

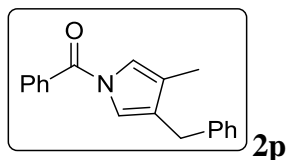
^1H NMR (400 MHz, CDCl_3): 7.70 (d, $J = 8.4$ Hz, 2H), 7.27 (d, $J = 8.0$ Hz, 2H), 7.12 (d, $J = 4.0$ Hz, 1H), 6.95 – 6.82 (m, 3H), 6.72 (d, $J = 4.4$ Hz, 1H), 3.85 (s, 2H), 2.40 (s, 3H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): 144.56, 142.87, 136.28, 129.83, 127.90, 126.71, 126.67, 124.86, 124.16, 123.68, 118.76, 118.41, 25.91, 21.58, 10.13. IR (cm^{-1}): 3127, 2921, 1595, 1517, 1493, 1439, 1366, 1307, 1283, 1170, 1093, 1065, 850, 812, 794, 702, 672. HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{17}\text{NO}_2\text{S}_2\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 354.05929, found 354.05933.



tert-butyl 5-((4-methyl-1-tosyl-1H-pyrrol-3-yl)methyl)-1H-indole-1-carboxylate, oil, 51%, 24 mg.

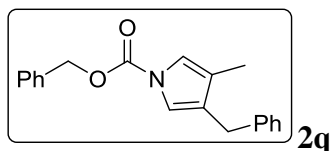
^1H NMR (400 MHz, CDCl_3): 8.01 (d, $J = 8.1$ Hz, 1H), 7.69 (d, $J = 8.3$ Hz, 2H), 7.56 (d, $J = 3.5$ Hz, 1H), 7.26 (d, $J = 8.0$ Hz, 3H), 7.07 (d, $J = 8.5$ Hz, 1H), 6.86 (s, 1H),

6.79 (s, 1H), 6.47 (d, $J = 3.6$ Hz, 1H), 3.74 (s, 2H), 2.40 (s, 3H), 1.84 (s, 3H), 1.66 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): 149.75, 144.45, 136.34, 133.88, 130.73, 129.78, 129.09, 126.67, 126.04, 125.03, 124.53, 120.52, 118.76, 118.40, 114.91, 107.09, 83.55, 31.48, 28.16, 21.57, 10.32. IR (cm^{-1}): 3125, 2976, 2923, 1731, 1595, 1468, 1370, 1349, 1292, 1255, 1216, 1169, 1133, 1065, 1023, 910, 765, 730, 671. HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{28}\text{N}_2\text{O}_4\text{SNa}^+$ ($\text{M}+\text{Na}$) $^+$ 487.16620, found 487.16653.



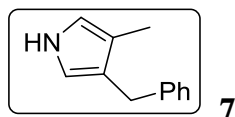
(3-benzyl-4-methyl-1H-pyrrol-1-yl)(phenyl)methanone, oil, 58%, 16 mg.

^1H NMR (400 MHz, CDCl_3): 7.70 (d, $J = 7.0$ Hz, 2H), 7.57 (t, $J = 7.4$ Hz, 1H), 7.48 (t, $J = 7.5$ Hz, 2H), 7.31 – 7.27 (m, 2H), 7.21 (d, $J = 7.5$ Hz, 3H), 6.99 (s, 2H), 3.75 (s, 2H), 1.92 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): 133.54, 131.84, 129.25, 128.57, 128.39, 128.34, 128.10, 126.06, 124.01, 119.07, 119.01, 31.76, 10.43. IR (cm^{-1}): 3060, 3026, 2920, 1687, 1601, 1527, 1493, 1446, 1391, 1353, 1332, 1246, 1179, 1133, 1074, 1028, 998, 880, 792, 718, 697, 664. HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{17}\text{NNaO}^+$ ($\text{M}+\text{Na}$) $^+$ 298.12024, found 298.12030.



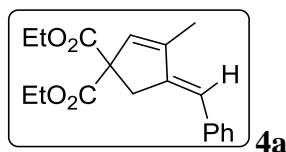
benzyl 3-benzyl-4-methyl-1H-pyrrole-1-carboxylate, oil, 61%, 18.6 mg.

^1H NMR (400 MHz, CDCl_3): 7.38 (dt, $J = 14.2, 7.0$ Hz, 5H), 7.29 – 7.24 (m, 2H), 7.20 – 7.16 (m, 3H), 7.02 (s, 1H), 6.95 (s, 1H), 5.31 (s, 2H), 3.71 (s, 2H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): 150.16, 140.08, 135.14, 128.63, 128.58, 128.55, 128.35, 127.19, 125.97, 123.08, 117.94, 117.66, 68.47, 31.66, 10.31. IR (cm^{-1}): 3061, 3027, 2921, 1741, 1530, 1494, 1453, 1409, 1355, 1333, 1239, 1109, 1074, 984, 789, 765, 730, 696. HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{19}\text{NNaO}_2^+$ ($\text{M}+\text{Na}$) $^+$ 328.13080, found 328.13091.



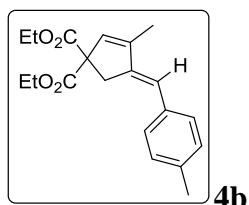
3-benzyl-4-methyl-1H-pyrrole, oil, 90%, 31 mg.

^1H NMR (400 MHz, CDCl_3): 7.78 (s, 1H), 7.29 – 7.14 (m, 5H), 6.53 (s, 1H), 6.41 (s, 1H), 3.79 (s, 2H), 1.98 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): 141.83, 128.59, 128.18, 125.54, 122.13, 117.79, 116.22, 115.88, 31.69, 10.17. IR (cm^{-1}): 3437, 3081, 3059, 3024, 2920, 1602, 1492, 1451, 1284, 1250, 1180, 1062, 1028, 980, 783, 722, 631.



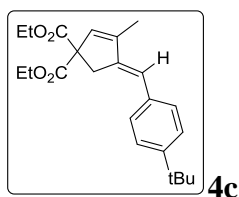
diethyl 3-benzyl-4-methylcyclopenta-2,4-diene-1,1-dicarboxylate, oil, 78%, 24.5 mg.

^1H NMR (400 MHz, CDCl_3): 7.41 (d, $J = 7.6$ Hz, 2H), 7.35 (t, $J = 7.7$ Hz, 2H), 7.21 (t, $J = 7.2$ Hz, 1H), 6.30 (s, 1H), 5.98 (s, 1H), 4.20 (q, $J = 7.1$ Hz, 4H), 3.49 (s, 2H), 1.95 (s, 3H), 1.26 (t, $J = 7.1$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3): 170.73, 145.51, 144.37, 137.48, 130.15, 128.41, 128.37, 126.53, 120.17, 64.45, 61.72, 37.56, 14.00, 13.02. IR (cm^{-1}): 2979, 1731, 1595, 1491, 1445, 1386, 1365, 1249, 1215, 1183, 1140, 1094, 1062, 866, 751, 694, 616. HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{22}\text{O}_4\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 337.14103, found 337.14105.



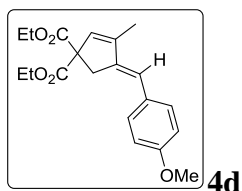
diethyl 3-methyl-4-(4-methylbenzyl)cyclopenta-2,4-diene-1,1-dicarboxylate, oil, 70%, 23 mg.

^1H NMR (400 MHz, CDCl_3): 7.31 (d, $J = 8.1$ Hz, 2H), 7.16 (d, $J = 7.9$ Hz, 2H), 6.27 (s, 1H), 5.95 (s, 1H), 4.20 (q, $J = 6.9$ Hz, 4H), 3.48 (s, 2H), 2.35 (s, 3H), 1.94 (s, 3H), 1.26 (t, $J = 7.1$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3): 170.83, 145.62, 143.40, 136.35, 134.66, 129.63, 129.15, 128.32, 120.07, 64.45, 61.71, 37.56, 21.16, 14.01, 13.05. IR (cm^{-1}): 2979, 2920, 1732, 1511, 1445, 1386, 1365, 1249, 1213, 1182, 1140, 1094, 1064, 1011, 872, 797, 711. HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{24}\text{O}_4\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 351.15668, found 351.15662.



diethyl 3-(4-(tert-butyl)benzyl)-4-methylcyclopenta-2,4-diene-1,1-dicarboxylate, oil, 65%, 24 mg.

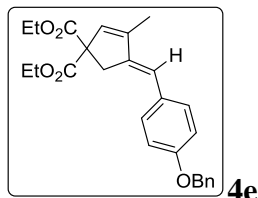
^1H NMR (400 MHz, CDCl_3): 7.40 – 7.34 (m, 4H), 6.28 (s, 1H), 5.95 (s, 1H), 4.23 – 4.17 (m, 4H), 3.49 (s, 2H), 1.94 (s, 3H), 1.33 (s, 9H), 1.27 (t, $J = 7.1$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3): 170.85, 149.57, 145.68, 143.63, 134.73, 129.68, 128.17, 125.38, 119.93, 64.47, 61.72, 37.61, 34.53, 31.26, 14.05, 13.09. IR (cm^{-1}): 2962, 2868, 1732, 1509, 1462, 1445, 1387, 1364, 1249, 1207, 1181, 1140, 1095, 1064, 874, 825, 799. HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{30}\text{O}_4\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 393.20363, found 393.20370.



diethyl 3-(4-methoxybenzyl)-4-methylcyclopenta-2,4-diene-1,1-dicarboxylate, M.P.= 60-62 $^{\circ}\text{C}$, 63%, white solid, 22 mg.

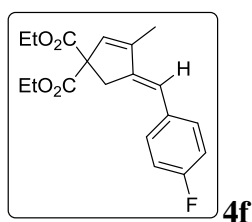
^1H NMR (400 MHz, CDCl_3): 7.36 (d, $J = 8.8$ Hz, 2H), 6.90 (d, $J = 8.8$ Hz, 2H), 6.25 (s, 1H), 5.92 (s, 1H), 4.20 (q, $J = 6.8$ Hz, 4H), 3.82 (s, 3H), 3.46 (s, 2H), 1.93 (s, 3H),

1.27 (t, $J = 7.1$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3): 170.88, 158.22, 145.64, 142.19, 130.31, 129.65, 129.08, 119.63, 113.88, 64.44, 61.70, 55.23, 37.52, 14.02, 13.06. IR (cm^{-1}): 2979, 2836, 1731, 1604, 1510, 1463, 1443, 1387, 1365, 1251, 1178, 1140, 1064, 1033, 871, 827, 801, 768. HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{24}\text{O}_5\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 367.15159, found 367.15125.



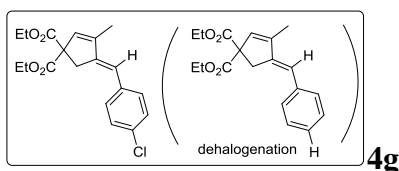
diethyl 3-(4-(benzyloxy)benzyl)-4-methylcyclopenta-2,4-diene-1,1-dicarboxylate, M.P.= 101-103 °C, 52%, white solid, 22 mg.

^1H NMR (400 MHz, CDCl_3): 7.45 – 7.32 (m, 7H), 6.97 (d, $J = 8.8$ Hz, 2H), 6.24 (s, 1H), 5.92 (s, 1H), 5.07 (s, 2H), 4.20 (q, $J = 7.0$ Hz, 4H), 3.46 (s, 2H), 1.93 (s, 3H), 1.26 (t, $J = 7.1$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3): 170.86, 157.43, 145.62, 142.31, 136.87, 130.57, 129.65, 129.15, 128.55, 127.94, 127.44, 119.61, 114.83, 69.96, 64.45, 61.70, 37.53, 14.02, 13.04. IR (cm^{-1}): 3032, 2979, 2936, 1730, 1602, 1508, 1453, 1384, 1365, 1248, 1177, 1139, 1064, 1012, 870, 826, 737, 697, 626. HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{28}\text{O}_5\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 443.18290, found 443.18268.



diethyl 3-(4-fluorobenzyl)-4-methylcyclopenta-2,4-diene-1,1-dicarboxylate, oil, 50%, 16.6 mg.

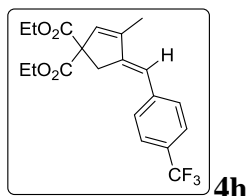
^1H NMR (400 MHz, CDCl_3): 7.41 – 7.34 (m, 2H), 7.04 (t, $J = 8.7$ Hz, 2H), 6.26 (s, 1H), 5.98 (s, 1H), 4.21 (q, $J = 7.0$ Hz, 4H), 3.44 (s, 2H), 1.94 (s, 3H), 1.27 (t, $J = 7.1$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3): 170.71, 162.58 (d, $J = 245.0$ Hz), 160.13, 145.39, 143.97, 143.95, 133.67 (d, $J = 3.0$ Hz), 133.64, 130.12, 129.93 (d, $J = 7.0$ Hz), 129.86, 119.02, 115.47 (d, $J = 22.0$ Hz), 115.25, 64.41, 61.80, 37.43, 14.02, 13.02. ^{19}F NMR (376 MHz, CDCl_3): -115.08 (s). IR (cm^{-1}): 2980, 2937, 1731, 1599, 1507, 1445, 1387, 1366, 1249, 1182, 1159, 1140, 1095, 1064, 1011, 871, 828, 804, 779, 711. HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{21}\text{FO}_4\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 355.13161, found 355.13166.



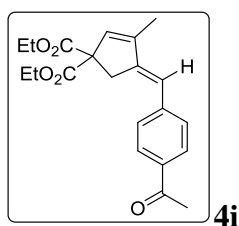
diethyl 3-(4-chlorobenzyl)-4-methylcyclopenta-2,4-diene-1,1-dicarboxylate, oil, 54%, 19 mg, main product:by-product=5.2:1.

^1H NMR (400 MHz, CDCl_3): 7.44 – 7.28 (m, 4H), 6.25 (s, 1H), 6.00 (s, 1H), 4.21 (q, $J = 7.1$ Hz, 4H), 3.44 (s, 2H), 1.94 (d, $J = 5.2$ Hz, 3H), 1.27 (t, $J = 7.1$ Hz, 6H). ^{13}C

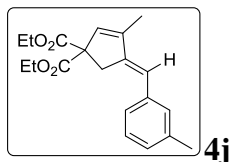
NMR (100 MHz, CDCl₃): 170.61, 145.35, 145.02, 135.96, 132.10, 130.68, 130.14, 129.54, 128.58, 128.43, 128.38, 126.54, 120.18, 118.99, 64.45, 61.82, 61.75, 37.51, 14.02, 13.00. IR (cm⁻¹): 2979, 1731, 1630, 1490, 1444, 1386, 1365, 1250, 1215, 1183, 1141, 1093, 1064, 1010, 870, 754, 694. HRMS (ESI) m/z calcd for C₁₉H₂₁ClO₄Na⁺ (M+Na)⁺ 371.10206, found 371.10217.



diethyl 3-methyl-4-(4-(trifluoromethyl)benzyl)cyclopenta-2,4-diene-1,1-dicarboxylate, oil, 61%, 23 mg. ¹H NMR (400 MHz, CDCl₃): 7.60 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 6.32 (s, 1H), 6.06 (s, 1H), 4.22 (q, *J* = 7.1 Hz, 4H), 3.48 (s, 2H), 1.96 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): 170.49, 147.01, 145.26, 140.98, 131.74, 128.40, 128.25 (q, *J* = 270.0 Hz), 125.54, 125.40 (q, *J* = 4.0 Hz), 125.37, 125.33, 125.29, 122.84, 120.15, 118.90, 64.49, 61.91, 37.61, 14.02, 13.00. ¹⁹F NMR (376 MHz, CDCl₃): -62.40 (s). IR (cm⁻¹): 2981, 1732, 1610, 1445, 1366, 1325, 1251, 1164, 1121, 1067, 1014, 875, 829, 801. HRMS (ESI) m/z calcd for C₂₀H₂₁F₃O₄Na⁺ (M+Na)⁺ 405.12841, found 405.12857.

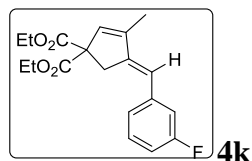


diethyl 3-(4-acetylbenzyl)-4-methylcyclopenta-2,4-diene-1,1-dicarboxylate, M.P.= 118-120 °C, 66%, white solid, 23.5 mg. ¹H NMR (400 MHz, CDCl₃): 7.95 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 8.3 Hz, 2H), 6.34 (s, 1H), 6.08 (s, 1H), 4.22 (q, *J* = 7.1 Hz, 4H), 3.50 (s, 2H), 2.60 (s, 3H), 1.96 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): 197.45, 170.41, 147.35, 145.34, 142.23, 134.78, 131.90, 128.55, 128.30, 119.30, 64.49, 61.85, 37.73, 26.49, 13.97, 12.95. IR (cm⁻¹): 2980, 2937, 1731, 1680, 1598, 1558, 1444, 1411, 1360, 1252, 1218, 1184, 1141, 1094, 1064, 1011, 956, 876, 800, 713. HRMS (ESI) m/z calcd for C₂₁H₂₄O₅Na⁺ (M+Na)⁺ 379.15159, found 379.15149.



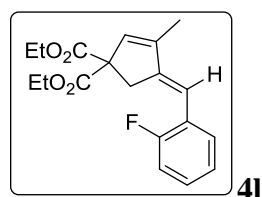
diethyl 3-methyl-4-(3-methylbenzyl)cyclopenta-2,4-diene-1,1-dicarboxylate, M.P.= 69-71 °C, 67%, white solid, 22 mg. ¹H NMR (400 MHz, CDCl₃): 7.23 (t, *J* = 6.4 Hz, 3H), 7.03 (d, *J* = 6.4 Hz, 1H), 6.27 (s, 1H), 5.96 (s, 1H), 4.21 (q, *J* = 7.1 Hz, 4H), 3.48 (s, 2H), 2.37 (s, 3H), 1.94 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): 170.81, 145.59, 144.13, 137.95, 137.43, 129.97, 129.16, 128.32, 127.39, 125.46, 120.29, 64.46, 61.73, 37.55,

21.49, 14.02, 13.05. IR (cm⁻¹): 2979, 1732, 1600, 1445, 1385, 1365, 1249, 1208, 1182, 1139, 1094, 1064, 1011, 905, 861, 778, 694. HRMS (ESI) m/z calcd for C₂₀H₂₄O₄Na⁺ (M+Na)⁺ 351.15668, found 351.15659.



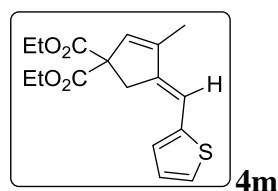
diethyl 3-(3-fluorobenzyl)-4-methylcyclopenta-2,4-diene-1,1-dicarboxylate, M.P.= 54-56 °C, 61%, white solid, 20 mg.

¹H NMR (400 MHz, CDCl₃): 7.29 (dd, *J* = 13.8, 5.8 Hz, 1H), 7.14 (dd, *J* = 23.7, 9.2 Hz, 2H), 6.91 (t, *J* = 8.1 Hz, 1H), 6.26 (s, 1H), 6.02 (s, 1H), 4.21 (q, *J* = 7.0 Hz, 4H), 3.46 (s, 2H), 1.94 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): 170.56, 164.09 (d, *J* = 243.0 Hz), 161.66, 145.76 (d, *J* = 48.0 Hz), 145.28, 139.74 (d, *J* = 7.0 Hz), 139.67, 131.09, 129.83 (d, *J* = 9.0 Hz), 129.74, 124.25 (d, *J* = 3.0 Hz), 124.22, 119.15 (d, *J* = 2.0 Hz), 119.13, 114.85 (d, *J* = 22.0 Hz), 114.63, 113.46 (d, *J* = 21.0 Hz), 113.25, 64.47, 61.82, 37.53, 14.01, 12.98. ¹⁹F NMR (376 MHz, CDCl₃): -113.36 (s). IR (cm⁻¹): 2980, 2938, 1731, 1606, 1579, 1484, 1444, 1387, 1366, 1248, 1209, 1183, 1142, 1095, 1064, 1009, 952, 872, 779, 686. HRMS (ESI) m/z calcd for C₁₉H₂₁FO₄Na⁺ (M+Na)⁺ 355.13161, found 355.13177.



diethyl 3-(2-fluorobenzyl)-4-methylcyclopenta-2,4-diene-1,1-dicarboxylate, oil, 68%, 22.5 mg.

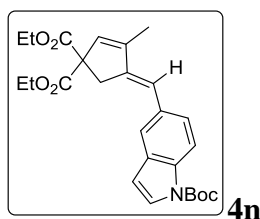
¹H NMR (400 MHz, CDCl₃): 7.52 (t, *J* = 8.6 Hz, 1H), 7.16 (dt, *J* = 20.5, 7.0 Hz, 2H), 7.08 – 7.02 (m, 1H), 6.48 (s, 1H), 6.02 (s, 1H), 4.21 (q, *J* = 7.1 Hz, 4H), 3.43 (s, 2H), 1.96 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): 170.62, 161.47 (d, *J* = 247.0 Hz), 159.00, 146.16, 146.14, 145.48, 130.92, 128.56 (d, *J* = 3.0 Hz), 128.53, 128.11 (d, *J* = 8.0 Hz), 128.03, 125.44 (d, *J* = 12.0 Hz), 125.32, 123.86 (d, *J* = 4.0 Hz), 123.82, 115.46 (d, *J* = 22.0 Hz), 115.24, 111.59 (d, *J* = 5.0 Hz), 111.54, 64.35, 61.78, 37.38, 14.00, 12.98. ¹⁹F NMR (376 MHz, CDCl₃): -116.43 (s). IR (cm⁻¹): 2980, 1732, 1484, 1446, 1388, 1366, 1250, 1212, 1181, 1141, 1095, 1065, 873, 793, 754. HRMS (ESI) m/z calcd for C₁₉H₂₁FO₄Na⁺ (M+Na)⁺ 355.13161, found 355.13202.



diethyl 3-methyl-4-(thiophen-2-ylmethyl)cyclopenta-2,4-diene-1,1-dicarboxylate, M.P.= 50-52 °C 55%, yellow solid, 17.6 mg.

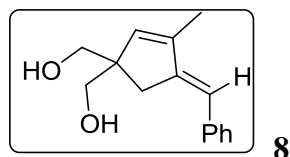
¹H NMR (400 MHz, CDCl₃): 7.28 (d, *J* = 5.9 Hz, 1H), 7.05 (d, *J* = 4.6 Hz, 2H), 6.53 (s, 1H), 5.98 (s, 1H), 4.25 – 4.19 (m, 4H), 3.41 (s, 2H), 1.93 (s, 3H), 1.27 (t, *J* = 7.1

Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3): 170.64, 144.83, 142.81, 141.73, 130.66, 127.25, 126.60, 125.05, 113.26, 64.48, 61.77, 37.67, 14.02, 12.86. IR (cm^{-1}): 3105, 2979, 2936, 1731, 1444, 1385, 1366, 1248, 1200, 1181, 1139, 1094, 1051, 862, 698. HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{20}\text{O}_4\text{SNa}^+$ ($\text{M}+\text{Na}$) $^+$ 343.09745, found 343.09738.



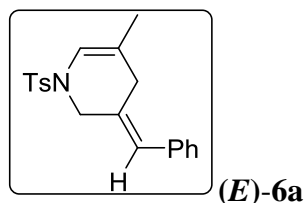
Diethyl-3-methyl-4-((1-methyl-1H-indol-5-yl)methyl)cyclopenta-2,4-diene-1,1-dicarboxylate, oil, 46%, 20.8 mg.

^1H NMR (400 MHz, CDCl_3): 8.09 (d, $J = 7.8$ Hz, 1H), 7.61 (d, $J = 16.0$ Hz, 2H), 7.36 (d, $J = 8.7$ Hz, 1H), 6.58 (d, $J = 3.7$ Hz, 1H), 6.41 (s, 1H), 5.96 (s, 1H), 4.22 (q, $J = 7.0$ Hz, 4H), 3.55 (s, 2H), 1.97 (s, 3H), 1.68 (s, 9H), 1.27 (t, $J = 7.1$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3): 170.92, 149.67, 145.68, 143.01, 133.78, 132.24, 130.84, 129.38, 126.35, 125.39, 120.55, 120.42, 115.01, 107.47, 83.71, 64.49, 61.74, 37.63, 28.16, 14.03, 13.10. IR (cm^{-1}): 2978, 2934, 1732, 1466, 1369, 1251, 1163, 1131, 1083, 1023, 857, 765, 727. HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{31}\text{NO}_6\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 476.20436, found 476.20480.



(3-benzyl-4-methylcyclopenta-2,4-diene-1,1-diyl)dimethanol, M.P.= 100-102 $^\circ\text{C}$, 78%, white solid, 27 mg.

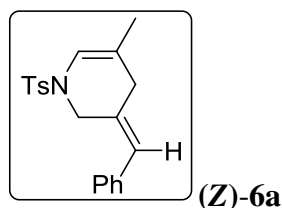
^1H NMR (400 MHz, CDCl_3): 7.40 (d, $J = 6.9$ Hz, 2H), 7.33 (t, $J = 7.7$ Hz, 2H), 7.18 (t, $J = 7.3$ Hz, 1H), 6.26 (s, 1H), 5.80 (s, 1H), 3.70 – 3.61 (m, 4H), 2.77 (s, 2H), 2.52 (s, 2H), 1.91 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): 146.71, 144.65, 138.05, 134.96, 128.39, 128.22, 126.19, 119.17, 68.67, 54.20, 36.86, 13.23. IR (cm^{-1}): 3356, 3022, 2917, 2871, 1626, 1594, 1489, 1444, 1383, 1196, 1077, 1026, 909, 863, 750, 693, 617.



(E)-3-benzylidene-5-methyl-1-tosyl-1,2,3,4-tetrahydropyridine, M.P.= 115-117 $^\circ\text{C}$, 51.3%, white solid, 35 mg.

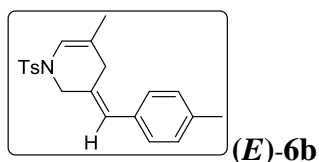
^1H NMR (400 MHz, CDCl_3): 7.69 (d, $J = 8.3$ Hz, 2H), 7.34 – 7.28 (m, 4H), 7.23 (t, $J = 7.9$ Hz, 1H), 7.03 (d, $J = 7.2$ Hz, 2H), 6.49 (s, 1H), 6.22 (s, 1H), 4.00 (s, 2H), 2.80 (s, 2H), 2.41 (s, 3H), 1.68 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): 143.48, 136.57, 135.20, 129.73, 129.54, 128.67, 128.12, 127.34, 127.15, 126.90, 120.50, 118.82, 51.07, 31.51, 21.49, 20.37. IR (cm^{-1}): 3054, 3025, 2961, 2919, 2852, 1675, 1597,

1492, 1446, 1348, 1304, 1209, 1164, 1090, 1055, 1030, 973, 915, 865, 813, 748, 700, 670.



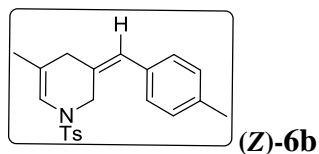
(Z)-3-benzylidene-5-methyl-1-tosyl-1,2,3,4-tetrahydropyridine, M.P.= 116-118 °C, 19.7%, white solid, 13 mg.

¹H NMR (400 MHz, CDCl₃): 7.71 (d, *J* = 8.3 Hz, 2H), 7.30 (tt, *J* = 13.5, 7.2 Hz, 5H), 7.09 (d, *J* = 7.2 Hz, 2H), 6.25 (d, *J* = 4.8 Hz, 2H), 3.93 (s, 2H), 3.79 (s, 2H), 2.43 (s, 3H), 1.75 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): 143.49, 136.21, 135.10, 134.02, 129.48, 129.26, 128.95, 128.08, 127.66, 126.78, 124.55, 119.97, 49.64, 49.42, 20.78. IR (cm⁻¹): 3023, 2958, 2923, 2852, 1734, 1647, 1596, 1493, 1448, 1346, 1162, 1092, 1030, 961, 894, 814, 751, 700, 672, 600.



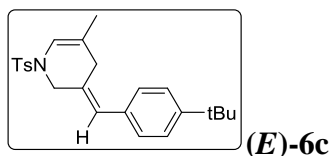
(E)-5-methyl-3-(4-methylbenzylidene)-1-tosyl-1,2,3,4-tetrahydropyridine, oil, 42.7%, 30 mg.

¹H NMR (400 MHz, CDCl₃): 7.69 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 6.49 (s, 1H), 6.18 (s, 1H), 4.00 (s, 2H), 2.81 (s, 2H), 2.41 (s, 3H), 2.35 (s, 3H), 1.69 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): 143.40, 136.64, 135.15, 133.62, 129.48, 128.90, 128.76, 128.54, 127.27, 127.00, 120.40, 118.88, 51.04, 31.49, 21.44, 21.08, 20.33. IR (cm⁻¹): 3026, 2966, 2920, 2858, 2735, 1679, 1597, 1575, 1511, 1493, 1448, 1347, 1266, 1210, 1162, 1091, 1054, 974, 914, 870, 814, 736, 704, 671, 626. HRMS (ESI) *m/z* calcd for C₂₁H₂₃NO₂SNa⁺ (M+Na)⁺ 376.13417, found 376.13425.



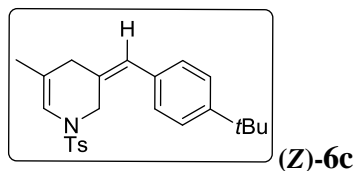
(Z)-5-methyl-3-(4-methylbenzylidene)-1-tosyl-1,2,3,4-tetrahydropyridine, M.P.= 115-117 °C, 14.3%, white solid, 10 mg.

¹H NMR (400 MHz, CDCl₃): 7.71 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 7.9 Hz, 2H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.26 (s, 1H), 6.21 (s, 1H), 3.92 (s, 2H), 3.78 (s, 2H), 2.43 (s, 3H), 2.36 (s, 3H), 1.74 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): 143.46, 136.60, 134.65, 134.16, 133.37, 129.47, 128.90, 128.82, 128.70, 127.69, 124.57, 120.16, 49.70, 49.44, 21.47, 21.15, 20.77. IR (cm⁻¹): 3022, 2920, 2733, 1913, 1646, 1597, 1509, 1493, 1450, 1377, 1345, 1304, 1162, 1092, 1037, 1017, 960, 898, 854, 814, 737, 712, 671, 652, 629. HRMS (ESI) *m/z* calcd for C₂₁H₂₃NO₂SNa⁺ (M+Na)⁺ 376.13417, found 376.13425.



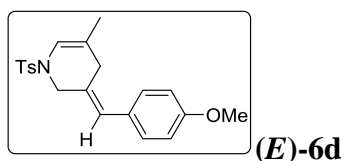
(E)-3-(4-(tert-butyl)benzylidene)-5-methyl-1-tosyl-1,2,3,4-tetrahydropyridine, oil, 51.0%, 39.8 mg.

^1H NMR (400 MHz, CDCl_3): 7.70 (d, $J = 8.3$ Hz, 2H), 7.35 (d, $J = 8.4$ Hz, 2H), 7.30 (d, $J = 8.1$ Hz, 2H), 7.00 (d, $J = 8.3$ Hz, 2H), 6.48 (s, 1H), 6.20 (s, 1H), 4.00 (s, 2H), 2.83 (s, 2H), 2.42 (s, 3H), 1.69 (s, 3H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): 149.90, 143.42, 135.21, 133.71, 129.53, 129.08, 128.43, 127.30, 126.94, 125.03, 120.41, 118.78, 51.11, 34.50, 31.56, 21.48, 20.36. IR (cm^{-1}): 3051, 2962, 2867, 1734, 1674, 1599, 1508, 1494, 1460, 1407, 1347, 1304, 1267, 1231, 1164, 1121, 1091, 1053, 1033, 1010, 974, 914, 873, 835, 814, 768, 736, 705, 670, 622. HRMS (ESI) m/z calcd for $\text{C}_{24}\text{H}_{29}\text{NO}_2\text{SNa}^+$ ($\text{M}+\text{Na}$) $^+$ 418.18112, found 418.18134.



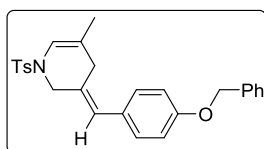
(Z)-3-(4-(tert-butyl)benzylidene)-5-methyl-1-tosyl-1,2,3,4-tetrahydropyridine, M.P.= 141-143 °C, 16%, white solid, 12.5 mg.

^1H NMR (400 MHz, CDCl_3): 7.71 (d, $J = 8.3$ Hz, 2H), 7.35 (d, $J = 8.4$ Hz, 2H), 7.29 (d, $J = 8.0$ Hz, 2H), 7.05 (d, $J = 8.3$ Hz, 2H), 6.30 (s, 1H), 6.22 (s, 1H), 3.92 (s, 2H), 3.78 (s, 2H), 2.43 (s, 3H), 1.75 (s, 3H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): 149.82, 143.45, 134.62, 134.13, 133.41, 129.49, 128.78, 128.72, 127.70, 125.04, 124.49, 120.25, 49.71, 49.44, 34.52, 31.26, 21.47, 20.76. IR (cm^{-1}): 3026, 2961, 2867, 1647, 1597, 1507, 1493, 1450, 1394, 1377, 1347, 1304, 1267, 1226, 1163, 1092, 1037, 1016, 961, 899, 851, 814, 784, 755, 738, 707, 671, 648, 627. HRMS (ESI) m/z calcd for $\text{C}_{24}\text{H}_{29}\text{NO}_2\text{SNa}^+$ ($\text{M}+\text{Na}$) $^+$ 418.18112, found 418.18134.



(E)-3-(4-methoxybenzylidene)-5-methyl-1-tosyl-1,2,3,4-tetrahydropyridine, oil, 36.3%, 26.9 mg.

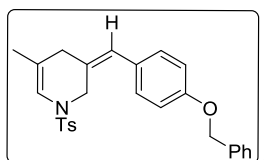
^1H NMR (400 MHz, CDCl_3): 7.69 (d, $J = 8.3$ Hz, 2H), 7.29 (d, $J = 8.0$ Hz, 2H), 6.99 (d, $J = 8.7$ Hz, 2H), 6.85 (d, $J = 6.8$ Hz, 2H), 6.48 (s, 1H), 6.16 (s, 1H), 3.97 (s, 2H), 3.82 (s, 3H), 2.79 (s, 2H), 2.41 (s, 3H), 1.68 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): 158.44, 143.42, 135.23, 129.92, 129.52, 129.15, 128.13, 127.34, 126.68, 120.50, 118.79, 113.55, 55.24, 51.10, 31.54, 21.51, 20.41. IR (cm^{-1}): 3062, 2960, 2929, 2837, 1699, 1661, 1597, 1572, 1510, 1455, 1422, 1344, 1305, 1250, 1162, 1121, 1091, 1032, 1009, 973, 914, 836, 816, 761, 735, 705, 670, 622. HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{23}\text{NO}_3\text{SNa}^+$ ($\text{M}+\text{Na}$) $^+$ 392.12909, found 392.12903.



(E)-6e

(E)-3-(4-(benzyloxy)benzylidene)-5-methyl-1-tosyl-1,2,3,4-tetrahydropyridine, oil, 48%, 43 mg.

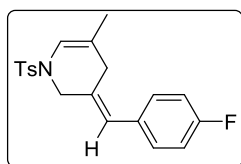
^1H NMR (400 MHz, CDCl_3): 7.69 (d, $J = 8.3$ Hz, 2H), 7.46 – 7.35 (m, 5H), 7.29 (d, $J = 8.1$ Hz, 2H), 6.99 (d, $J = 8.7$ Hz, 2H), 6.93 (d, $J = 8.8$ Hz, 2H), 6.48 (s, 1H), 6.16 (s, 1H), 5.08 (s, 2H), 3.98 (s, 2H), 2.80 (s, 2H), 2.40 (s, 3H), 1.69 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): 157.64, 143.41, 136.80, 135.21, 129.93, 129.51, 129.40, 128.59, 128.20, 128.01, 127.42, 127.32, 126.64, 120.50, 118.78, 114.47, 69.98, 51.10, 31.53, 21.49, 20.40. IR (cm^{-1}): 3062, 3032, 2920, 1675, 1603, 1572, 1508, 1453, 1380, 1346, 1293, 1245, 1164, 1119, 1091, 1053, 1033, 973, 914, 872, 833, 814, 736, 697, 670, 629, 608. HRMS (ESI) m/z calcd for $\text{C}_{27}\text{H}_{27}\text{NO}_3\text{SNa}^+$ ($\text{M}+\text{Na}$) $^+$ 468.16039, found 468.16049.



(Z)-6e

(Z)-3-(4-(benzyloxy)benzylidene)-5-methyl-1-tosyl-1,2,3,4-tetrahydropyridine, M.P.= 83-85 °C, 16%, white solid, 14 mg.

^1H NMR (400 MHz, CDCl_3): 7.71 (d, $J = 8.2$ Hz, 2H), 7.44 (dt, $J = 14.6, 7.2$ Hz, 5H), 7.28 (d, $J = 7.4$ Hz, 2H), 7.04 (d, $J = 8.7$ Hz, 2H), 6.94 (d, $J = 8.8$ Hz, 2H), 6.25 (s, 1H), 6.18 (s, 1H), 5.09 (s, 2H), 3.91 (s, 2H), 3.78 (s, 2H), 2.41 (s, 3H), 1.75 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): 157.70, 143.43, 136.85, 134.48, 134.17, 130.21, 129.45, 129.10, 128.58, 128.03, 127.98, 127.68, 127.42, 124.19, 120.12, 114.49, 69.98, 49.75, 49.47, 21.46, 20.77. IR (cm^{-1}): 3031, 2923, 1917, 1646, 1603, 1571, 1507, 1452, 1378, 1344, 1293, 1245, 1161, 1092, 1017, 959, 899, 847, 814, 775, 737, 697, 673, 656, 628, 614. HRMS (ESI) m/z calcd for $\text{C}_{27}\text{H}_{27}\text{NO}_3\text{SNa}^+$ ($\text{M}+\text{Na}$) $^+$ 468.16039, found 468.16049.

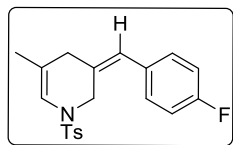


(E)-6f

(E)-3-(4-fluorobenzylidene)-5-methyl-1-tosyl-1,2,3,4-tetrahydropyridine, oil, 56.7%, 40 mg.

^1H NMR (400 MHz, CDCl_3): 7.69 (d, $J = 8.3$ Hz, 2H), 7.29 (d, $J = 8.0$ Hz, 2H), 7.00 (d, $J = 7.1$ Hz, 4H), 6.48 (s, 1H), 6.18 (s, 1H), 3.97 (s, 2H), 2.76 (s, 2H), 2.41 (s, 3H), 1.68 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): 162.78 (d, $J = 245.0$ Hz), 160.33, 143.49, 135.12, 132.55 (d, $J = 3.0$ Hz), 132.52, 130.28 (d, $J = 8.0$ Hz), 130.20, 129.71, 129.53, 127.33, 126.06, 120.56, 118.58, 115.16 (d, $J = 21.0$ Hz), 114.95, 50.96, 31.40, 21.47, 20.34. ^{19}F NMR (376 MHz, CDCl_3): -114.66 (s). IR (cm^{-1}): 3067, 2922, 1673, 1598,

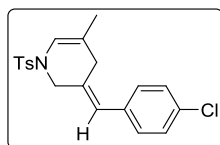
1507, 1448, 1345, 1305, 1229, 1160, 1121, 1091, 1053, 1033, 1010, 974, 840, 815, 760, 735, 705, 670, 604. HRMS (ESI) m/z calcd for $C_{20}H_{20}FNO_2SNa^+$ ($M+Na$)⁺ 380.10910, found 380.10913.



(Z)-6f

(Z)-3-(4-fluorobenzylidene)-5-methyl-1-tosyl-1,2,3,4-tetrahydropyridine, M.P.= 98-100 °C, 16.3%, white solid, 11.6 mg.

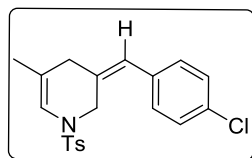
¹H NMR (400 MHz, CDCl₃): 7.70 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 8.1 Hz, 2H), 7.08 – 6.97 (m, 4H), 6.19 (s, 2H), 3.91 (s, 2H), 3.78 (s, 2H), 2.42 (s, 3H), 1.76 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): 162.87 (d, J = 246.0 Hz), 160.41, 143.52, 135.46, 134.10, 132.25 (d, J = 4.0 Hz), 130.56 (d, J = 7.0 Hz), 130.49, 129.50, 129.33, 127.69, 123.40, 119.70, 115.15 (d, J = 21.0 Hz), 114.94, 49.59 (d, J = 15.0 Hz), 49.44, 21.47, 20.80. ¹⁹F NMR (376 MHz, CDCl₃): -114.94 (s). IR (cm⁻¹): 3041, 2922, 1913, 1681, 1648, 1598, 1506, 1450, 1345, 1227, 1162, 1092, 1037, 1016, 961, 898, 848, 815, 765, 712, 671, 624. HRMS (ESI) m/z calcd for $C_{20}H_{20}FNO_2SNa^+$ ($M+Na$)⁺ 380.10910, found 380.10913.



(E)-6g

(E)-3-(4-chlorobenzylidene)-5-methyl-1-tosyl-1,2,3,4-tetrahydropyridine, M.P.= 120-122 °C, 50.5%, white solid, 38 mg.

¹H NMR (400 MHz, CDCl₃): 7.68 (d, J = 8.2 Hz, 2H), 7.31 – 7.25 (m, 4H), 6.96 (d, J = 8.4 Hz, 2H), 6.49 (s, 1H), 6.16 (s, 1H), 3.98 (s, 2H), 2.75 (s, 2H), 2.41 (s, 3H), 1.68 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): 143.49, 135.11, 134.91, 132.65, 130.51, 129.90, 129.52, 128.28, 127.31, 125.95, 120.58, 118.52, 83.45, 50.93, 31.44, 24.97, 21.47, 20.32. IR (cm⁻¹): 3064, 2976, 2919, 2855, 1912, 1676, 1596, 1490, 1448, 1348, 1304, 1280, 1210, 1165, 1123, 1090, 1055, 1013, 974, 959, 914, 887, 868, 835, 813, 774, 737, 721, 705, 668, 637, 616. HRMS (ESI) m/z calcd for $C_{20}H_{20}ClNO_2SNa^+$ ($M+Na$)⁺ 396.07955, found 396.07962.

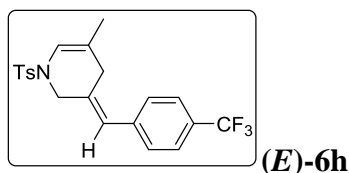


(Z)-6g

(Z)-3-(4-chlorobenzylidene)-5-methyl-1-tosyl-1,2,3,4-tetrahydropyridine, M.P.= 130-132 °C, 14.5%, white solid, 11 mg.

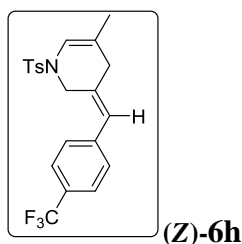
¹H NMR (400 MHz, CDCl₃): 7.70 (d, J = 8.3 Hz, 2H), 7.29 (d, J = 8.4 Hz, 4H), 7.02 (d, J = 8.4 Hz, 2H), 6.17 (s, 2H), 3.91 (s, 2H), 3.78 (s, 2H), 2.42 (s, 3H), 1.76 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): 143.55, 135.88, 134.67, 134.10, 132.57, 130.22, 129.98, 129.50, 128.29, 127.68, 123.24, 49.57, 49.44, 21.48, 20.82. IR (cm⁻¹): 3050, 2965, 2923, 1913, 1734, 1646, 1597, 1489, 1450, 1399, 1377, 1345, 1305, 1265, 1226, 1162,

1091, 1037, 1012, 961, 898, 850, 813, 784, 754, 736, 719, 669, 641, 621. HRMS (ESI) m/z calcd for $C_{20}H_{20}ClNO_2SNa^+$ ($M+Na$) $^+$ 396.07955, found 396.07962.



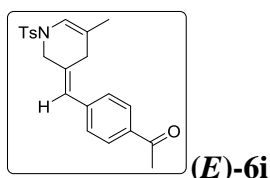
(E)-5-methyl-1-tosyl-3-(4-(trifluoromethyl)benzylidene)-1,2,3,4-tetrahydropyridine, oil, 57%, 46 mg.

1H NMR (400 MHz, $CDCl_3$): 7.69 (d, $J = 8.3$ Hz, 2H), 7.56 (d, $J = 8.2$ Hz, 2H), 7.30 (d, $J = 8.1$ Hz, 2H), 7.13 (d, $J = 8.1$ Hz, 2H), 6.50 (s, 1H), 6.24 (s, 1H), 4.01 (s, 2H), 2.78 (s, 2H), 2.41 (s, 3H), 1.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 143.57, 140.09, 135.07, 132.08, 129.56, 129.30 (q, $J = 32.0$ Hz), 128.98, 128.84, 128.66, 128.34, 128.08 (q, $J = 270.0$ Hz), 127.32, 125.82, 125.38, 125.08 (q, $J = 4.0$ Hz), 125.05, 125.01, 124.97, 122.68, 120.63, 119.97, 118.44, 50.90, 31.46, 21.44, 20.25. ^{19}F NMR (376 MHz, $CDCl_3$): -62.52 (s). IR (cm^{-1}): 3065, 2967, 2923, 2856, 1922, 1734, 1679, 1615, 1597, 1575, 1494, 1448, 1411, 1324, 1267, 1164, 1123, 1067, 1016, 974, 958, 914, 871, 839, 814, 736, 705, 636, 611. HRMS (ESI) m/z calcd for $C_{21}H_{20}F_3NO_2SNa^+$ ($M+Na$) $^+$ 430.10591, found 430.10617.



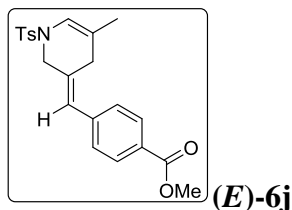
(Z)-5-methyl-1-tosyl-3-(4-(trifluoromethyl)benzylidene)-1,2,3,4-tetrahydropyridine, M.P.= 133-135 °C, 18%, white solid, 15 mg.

1H NMR (400 MHz, $CDCl_3$): 7.71 (d, $J = 8.2$ Hz, 2H), 7.57 (d, $J = 8.2$ Hz, 2H), 7.29 (d, $J = 8.3$ Hz, 2H), 7.20 (d, $J = 8.1$ Hz, 2H), 6.24 (s, 1H), 6.20 (s, 1H), 3.94 (s, 2H), 3.80 (s, 2H), 2.43 (s, 3H), 1.77 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 143.65, 139.87, 136.81, 134.06, 131.32, 129.56, 129.15, 128.54, 128.19 (q, $J = 270.0$ Hz), 127.70, 125.49, 125.11 (q, $J = 4.0$ Hz), 125.07, 125.03, 124.99, 122.98, 122.78, 120.08, 119.47, 49.50, 49.43, 21.49, 20.86. ^{19}F NMR (376 MHz, $CDCl_3$): -62.47 (s). IR (cm^{-1}): 2924, 2852, 1923, 1735, 1647, 1612, 1597, 1493, 1450, 1412, 1378, 1324, 1265, 1226, 1162, 1121, 1092, 1067, 1038, 1015, 952, 899, 872, 853, 814, 787, 766, 735, 706, 676, 662, 635, 619. HRMS (ESI) m/z calcd for $C_{21}H_{20}F_3NO_2SNa^+$ ($M+Na$) $^+$ 430.10591, found 430.10617.



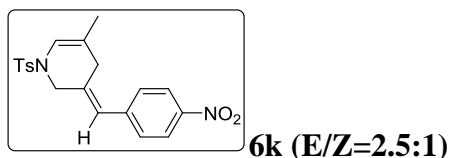
(E)-1-(4-((5-methyl-1-tosyl-1,4-dihydropyridin-3(2H)-ylidene)methyl)phenyl)ethan-1-one (E/Z=2:1), 45%, 34 mg.

^1H NMR (400 MHz, CDCl_3): 7.91 (dd, $J = 8.3, 4.5$ Hz, 2H), 7.70 (t, $J = 7.5$ Hz, 2H), 7.29 (d, $J = 5.1$ Hz, 2H), 7.15 (dd, $J = 25.7, 8.3$ Hz, 2H), 6.24 (s, 2H), 4.01 (s, 1H), 3.94 (s, 1H), 3.79 (s, 1H), 2.80 (q, $J = 1.7$ Hz, 1H), 2.61 (d, $J = 3.7$ Hz, 3H), 2.42 (d, $J = 5.6$ Hz, 3H), 1.68 (d, $J = 4.0$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): 197.54, 143.64, 141.23, 136.82, 135.29, 134.05, 131.41, 129.54, 129.07, 128.78, 128.23, 127.68, 127.33, 126.25, 123.41, 120.64, 119.68, 50.99, 49.58, 49.43, 31.65, 26.54, 21.51, 20.88, 20.32. IR (cm^{-1}): 3052, 2921, 1679, 1599, 1558, 1493, 1449, 1410, 1345, 1304, 1267, 1162, 11119, 1091, 1015, 959, 872, 853, 814, 786, 736, 705, 671, 626. HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{23}\text{NO}_3\text{SNa}^+$ ($\text{M}+\text{Na}$) $^+$ 404.12909, found 404.12921.



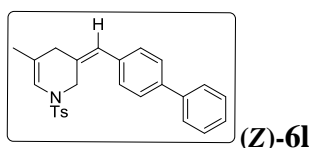
methyl (E)-4-((5-methyl-1-tosyl-1,4-dihydropyridin-3(2H)-ylidene)methyl)benzoate, M.P.= 110-112 $^{\circ}\text{C}$, 29.5%, yellow solid, 23 mg.

^1H NMR (400 MHz, CDCl_3): 7.97 (d, $J = 8.3$ Hz, 2H), 7.69 (d, $J = 8.3$ Hz, 2H), 7.29 (d, $J = 7.0$ Hz, 2H), 7.08 (d, $J = 8.2$ Hz, 2H), 6.49 (s, 1H), 6.22 (s, 1H), 4.01 (s, 2H), 3.93 (s, 3H), 2.79 (s, 2H), 2.41 (s, 3H), 1.69 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): 166.72, 143.56, 141.17, 135.18, 131.98, 129.56, 129.41, 128.58, 127.34, 126.31, 120.68, 118.54, 52.09, 51.02, 31.62, 21.49, 20.30. IR (cm^{-1}): 2950, 2920, 2853, 1932, 1719, 1605, 1565, 1493, 1435, 1413, 1348, 1279, 1165, 1105, 1055, 1017, 973, 913, 814, 761, 735, 707, 664, 614. HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{23}\text{NO}_4\text{SNa}^+$ ($\text{M}+\text{Na}$) $^+$ 420.12400, found 420.12405.



(E)-5-methyl-3-(4-nitrobenzylidene)-1-tosyl-1,2,3,4-tetrahydropyridine, 65%, yellow solid, 50 mg.

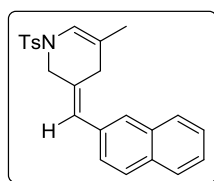
^1H NMR (400 MHz, CDCl_3): 8.16 (d, $J = 8.8$ Hz, 2H), 7.69 (d, $J = 8.2$ Hz, 2H), 7.30 (d, $J = 8.1$ Hz, 2H), 7.18 (d, $J = 8.7$ Hz, 2H), 6.50 (s, 1H), 6.27 (s, 1H), 4.01 (s, 2H), 2.79 (s, 2H), 2.41 (s, 3H), 1.69 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): 146.34, 143.65, 143.14, 134.97, 133.87, 129.58, 129.52, 129.31, 127.64, 127.31, 125.24, 123.44, 120.72, 118.06, 50.87, 31.60, 21.47, 20.24. IR (cm^{-1}): 3068, 2921, 2853, 1678, 1594, 1516, 1493, 1449, 1401, 1343, 1305, 1267, 1212, 1163, 1108, 1091, 1055, 1033, 1011, 974, 959, 912, 877, 854, 814, 780, 747, 736, 703, 665, 635, 614. HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_4\text{SNa}^+$ ($\text{M}+\text{Na}$) $^+$ 407.10360, found 407.10373.



(Z)-3-([1,1'-biphenyl]-4-ylmethylene)-5-methyl-1-tosyl-1,2,3,4-tetrahydropyridine,

M.P.= 149-151 °C, 31.3%, white solid, 26 mg.

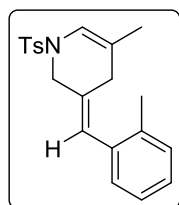
¹H NMR (400 MHz, CDCl₃): 7.73 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 7.2 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.30 (d, *J* = 9.4 Hz, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 6.33 (s, 1H), 6.27 (s, 1H), 3.96 (s, 2H), 3.81 (s, 2H), 2.43 (s, 3H), 1.78 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): 143.52, 140.60, 139.57, 135.31, 135.30, 134.17, 129.51, 129.43, 128.78, 127.71, 127.32, 126.91, 126.79, 124.18, 120.11, 49.72, 49.48, 21.49, 20.83. IR (cm⁻¹): 3027, 2962, 2922, 1646, 1596, 1486, 1448, 1376, 1344, 1304, 1263, 1226, 1161, 1092, 960, 853, 814, 763, 735, 698, 672, 654, 603. HRMS (ESI) *m/z* calcd for C₂₆H₂₅NO₂SNa⁺ (M+Na)⁺ 438.14982, found 438.14996.



(E)-6m

(E)-5-methyl-3-(naphthalen-2-ylmethylene)-1-tosyl-1,2,3,4-tetrahydropyridine, oil, 36.7%, 32 mg.

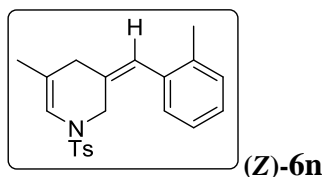
¹H NMR (400 MHz, CDCl₃): 7.86 (d, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 3H), 7.57 (d, *J* = 8.3 Hz, 1H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.44 (q, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.09 (d, *J* = 7.0 Hz, 1H), 6.75 (s, 1H), 6.53 (s, 1H), 4.20 (d, *J* = 1.1 Hz, 2H), 2.65 (s, 2H), 2.44 (s, 3H), 1.60 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): 143.46, 135.47, 133.57, 133.40, 131.82, 131.46, 129.70, 128.34, 127.63, 127.27, 126.28, 125.86, 125.84, 125.11, 124.89, 124.68, 120.02, 118.11, 50.77, 31.54, 21.59, 20.29. IR (cm⁻¹): 3058, 2964, 2916, 2854, 1733, 1676, 1596, 1507, 1493, 1448, 1347, 1265, 1215, 1163, 1091, 1058, 972, 913, 803, 782, 735, 704, 671, 659, 601. HRMS (ESI) *m/z* calcd for C₂₄H₂₃NO₂SNa⁺ (M+Na)⁺ 412.13417, found 412.13425.



(E)-6n

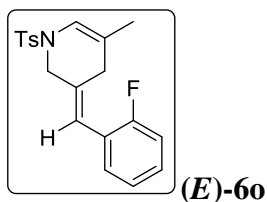
(E)-5-methyl-3-(2-methylbenzylidene)-1-tosyl-1,2,3,4-tetrahydropyridine, oil, 43.2%, 30.5 mg.

¹H NMR (400 MHz, CDCl₃): 7.73 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.18 – 7.11 (m, 3H), 6.91 (d, *J* = 6.9 Hz, 1H), 6.51 (s, 1H), 6.32 (s, 1H), 4.07 (s, 2H), 2.66 (s, 2H), 2.43 (s, 3H), 2.07 (s, 3H), 1.65 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): 143.40, 136.37, 135.54, 135.35, 130.08, 129.79, 129.63, 128.69, 127.19, 127.16, 125.90, 125.34, 119.93, 117.73, 50.70, 31.20, 21.44, 20.31, 19.56. IR (cm⁻¹): 3061, 2968, 2921, 2856, 1919, 1734, 1678, 1597, 1493, 1452, 1347, 1215, 1164, 1091, 1055, 1009, 973, 914, 814, 746, 704, 670, 601. HRMS (ESI) *m/z* calcd for C₂₁H₂₃NO₂SNa⁺ (M+Na)⁺ 376.13417, found 376.13431.



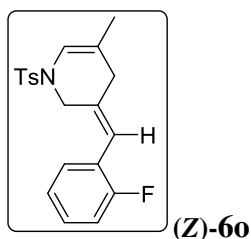
(Z)-5-methyl-3-(2-methylbenzylidene)-1-tosyl-1,2,3,4-tetrahydropyridine, M.P.= 132-134 °C, 10.8%, white solid, 7.6 mg.

¹H NMR (400 MHz, CDCl₃): 7.73 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.20 – 7.10 (m, 3H), 6.89 (d, *J* = 7.0 Hz, 1H), 6.25 (s, 1H), 6.07 (s, 1H), 3.97 (s, 2H), 3.77 (s, 2H), 2.45 (s, 3H), 2.23 (s, 3H), 1.72 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): 143.51, 136.49, 135.12, 134.60, 134.11, 129.85, 129.83, 129.56, 129.49, 127.67, 127.13, 125.21, 123.47, 120.14, 49.34, 49.32, 21.49, 20.77, 19.91. IR (cm⁻¹): 3018, 2921, 1648, 1597, 1451, 1377, 1345, 1305, 1162, 1092, 1036, 960, 899, 852, 814, 747, 666, 606. HRMS (ESI) *m/z* calcd for C₂₁H₂₃NO₂SNa⁺ (M+Na)⁺ 376.13417, found 376.13431.



(E)-3-(2-fluorobenzylidene)-5-methyl-1-tosyl-1,2,3,4-tetrahydropyridine, oil, 30%, 21 mg.

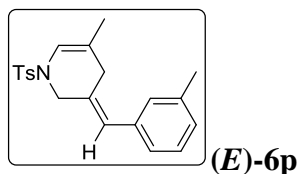
¹H NMR (400 MHz, CDCl₃): 7.69 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.26 – 7.20 (m, 1H), 7.10 – 6.99 (m, 3H), 6.49 (s, 1H), 6.24 (s, 1H), 4.05 (s, 2H), 2.69 (s, 2H), 2.41 (s, 3H), 1.67 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): 161.08 (d, *J* = 247.0 Hz), 158.61, 143.50, 135.03, 132.18, 130.24 (d, *J* = 4.0 Hz), 130.20, 129.58, 128.91 (d, *J* = 8.0 Hz), 128.83, 127.21, 124.16 (d, *J* = 15.0 Hz), 124.01, 123.57 (d, *J* = 3.0 Hz), 123.54, 120.32, 119.85 (d, *J* = 3.0 Hz), 119.82, 118.41, 115.54 (d, *J* = 22.0 Hz), 115.32, 50.85, 31.59 (d, *J* = 2.0 Hz), 31.57, 21.45, 20.30. ¹⁹F NMR (376 MHz, CDCl₃): -114.12 (s). IR (cm⁻¹): 3063, 2971, 2923, 1922, 1680, 1610, 1597, 1485, 1453, 1345, 1306, 1231, 1163, 1121, 1092, 1033, 1009, 952, 814, 758, 736, 704, 670, 635. HRMS (ESI) *m/z* calcd for C₂₀H₂₀FNO₂SNa⁺ (M+Na)⁺ 380.10910, found 380.10919.



(Z)-3-(2-fluorobenzylidene)-5-methyl-1-tosyl-1,2,3,4-tetrahydropyridine, M.P.= 116-118 °C, 20%, white solid, 14 mg.

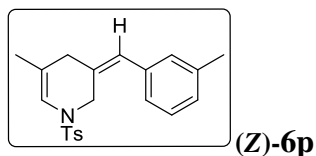
¹H NMR (400 MHz, CDCl₃): 7.71 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 7.26 – 7.21 (m, 1H), 7.06 (dq, *J* = 15.4, 7.5 Hz, 3H), 6.24 (s, 1H), 6.14 (s, 1H), 3.96 (s, 2H), 3.78 (s, 2H), 2.42 (s, 3H), 1.75 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): 161.37 (d, *J* = 247.0 Hz), 158.90, 143.56, 135.87, 134.02, 131.09, 131.06, 129.54, 128.71 (d, *J* = 8.0

Hz), 128.63, 127.69, 124.00 (d, $J = 15.0$ Hz), 123.85, 123.48 (d, $J = 3.0$ Hz), 123.45, 119.84, 117.11 (d, $J = 3.0$ Hz), 117.08, 115.47 (d, $J = 22.0$ Hz), 115.25, 49.46 (d, $J = 12.0$ Hz), 49.34, 21.48, 20.84. ^{19}F NMR (376 MHz, CDCl_3): -114.88 (s). IR (cm^{-1}): 3061, 2923, 1919, 1647, 1597, 1574, 1484, 1451, 1378, 1346, 1305, 1233, 1162, 1092, 1034, 960, 898, 854, 814, 758, 671, 603. HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{20}\text{FNO}_2\text{SNa}^+$ ($\text{M}+\text{Na}$) $^+$ 380.10910, found 380.10919.



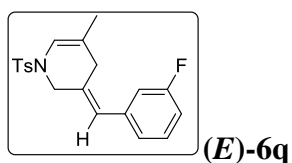
(E)-5-methyl-3-(3-methylbenzylidene)-1-tosyl-1,2,3,4-tetrahydropyridine, oil, 36%, 25 mg.

^1H NMR (400 MHz, CDCl_3): 7.70 (d, $J = 8.3$ Hz, 2H), 7.33 – 7.28 (m, 2H), 7.21 (t, $J = 7.6$ Hz, 1H), 7.05 (d, $J = 7.6$ Hz, 1H), 6.90 – 6.77 (m, 2H), 6.49 (s, 1H), 6.17 (s, 1H), 4.00 (s, 2H), 2.80 (s, 2H), 2.42 (s, 3H), 2.35 (s, 3H), 1.69 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): 143.39, 137.67, 136.53, 135.28, 129.52, 129.50, 129.38, 127.99, 127.65, 127.34, 127.22, 125.68, 120.47, 118.91, 51.08, 31.52, 21.47, 21.40, 20.35. IR (cm^{-1}): 3049, 2965, 2921, 2858, 1673, 1598, 1493, 1448, 1346, 1304, 1211, 1162, 1091, 1053, 1033, 1009, 975, 915, 814, 738, 703, 671. HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{23}\text{NO}_2\text{SNa}^+$ ($\text{M}+\text{Na}$) $^+$ 376.13417, found 376.13425.



(Z)-5-methyl-3-(3-methylbenzylidene)-1-tosyl-1,2,3,4-tetrahydropyridine, oil, 18%, 13 mg.

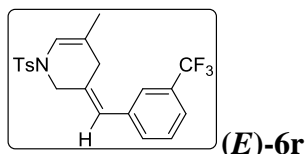
^1H NMR (400 MHz, CDCl_3): 7.71 (d, $J = 8.2$ Hz, 2H), 7.29 (d, $J = 8.1$ Hz, 2H), 7.22 (t, $J = 7.5$ Hz, 1H), 7.06 (d, $J = 7.6$ Hz, 1H), 6.89 (d, $J = 9.2$ Hz, 2H), 6.23 (d, $J = 12.7$ Hz, 2H), 3.93 (s, 2H), 3.79 (s, 2H), 2.43 (s, 3H), 2.36 (s, 3H), 1.75 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): 143.43, 137.66, 136.20, 134.87, 134.22, 129.63, 129.47, 129.15, 127.98, 127.68, 127.58, 126.07, 124.69, 120.11, 49.67, 49.44, 21.47, 21.39, 20.78. IR (cm^{-1}): 3029, 2920, 2733, 1647, 1598, 1580, 1492, 1450, 1345, 1305, 1161, 1092, 1037, 1017, 962, 896, 812, 736, 702, 672, 655, 606. HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{23}\text{NO}_2\text{SNa}^+$ ($\text{M}+\text{Na}$) $^+$ 376.13417, found 376.13425.



(E)-3-(3-fluorobenzylidene)-5-methyl-1-tosyl-1,2,3,4-tetrahydropyridine, oil, 37.3%, 26.5 mg.

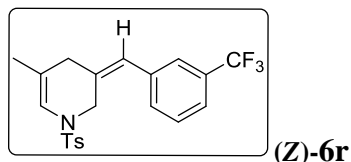
^1H NMR (400 MHz, CDCl_3): 7.69 (d, $J = 8.3$ Hz, 2H), 7.27 (dd, $J = 19.2, 8.0$ Hz, 3H), 6.92 (t, $J = 8.4$ Hz, 1H), 6.80 (d, $J = 7.7$ Hz, 1H), 6.68 (d, $J = 10.0$ Hz, 1H), 6.50 (s, 1H), 6.15 (s, 1H), 3.99 (s, 2H), 2.77 (s, 2H), 2.41 (s, 3H), 1.69 (s, 3H). ^{13}C NMR (100

MHz, CDCl₃): 163.69 (d, *J* = 245.0 Hz), 161.24, 143.58, 138.72 (d, *J* = 8.0 Hz), 138.64, 135.14, 130.99, 129.63, 129.55, 127.33, 126.00 (d, *J* = 2.0 Hz), 125.98, 124.39 (d, *J* = 2.0 Hz), 124.37, 120.63, 118.83, 115.43 (d, *J* = 21.0 Hz), 115.22, 113.88 (d, *J* = 21.0 Hz), 113.67, 50.93, 31.47, 21.42, 20.31. ¹⁹F NMR (376 MHz, CDCl₃): -113.28 (s). IR (cm⁻¹): 3066, 2966, 2919, 2855, 1919, 1677, 1611, 1581, 1485, 1442, 1347, 1305, 1252, 1163, 1091, 1055, 973, 914, 813, 789, 694, 671. HRMS (ESI) *m/z* calcd for C₂₀H₂₀FNO₂SNa⁺ (M+Na)⁺ 380.10910, found 380.10919.



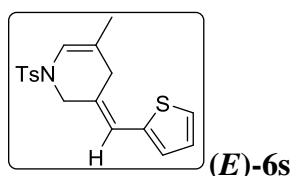
(E)-5-methyl-1-tosyl-3-(3-(trifluoromethyl)benzylidene)-1,2,3,4-tetrahydropyridine, oil, 34.6%, 28 mg.

¹H NMR (400 MHz, CDCl₃): 7.69 (d, *J* = 8.3 Hz, 2H), 7.50 – 7.40 (m, 2H), 7.32 – 7.28 (m, 2H), 7.21 (d, *J* = 12.6 Hz, 2H), 6.50 (s, 1H), 6.19 (s, 1H), 4.02 (s, 2H), 2.75 (s, 2H), 2.40 (s, 3H), 1.70 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): 143.66, 137.21, 135.17, 131.73, 131.64, 131.04 (q, *J* = 32.0 Hz), 130.72, 130.40, 130.08, 129.54, 128.62, 128.02 (q, *J* = 270.0 Hz), 127.38, 125.72, 125.32 (q, *J* = 4.0 Hz), 125.28, 125.24, 125.21, 123.65 (q, *J* = 4.0 Hz), 123.61, 123.57, 123.53, 122.61, 120.74, 119.90, 118.84, 50.90, 31.38, 21.35, 20.30. ¹⁹F NMR (376 MHz, CDCl₃): -62.70 (s). IR (cm⁻¹): 3066, 2965, 2920, 2856, 1675, 1597, 1493, 1437, 1330, 1305, 1222, 1164, 1125, 1092, 1073, 975, 912, 813, 704, 664, 600. HRMS (ESI) *m/z* calcd for C₂₁H₂₀F₃NO₂SNa⁺ (M+Na)⁺ 430.10591, found 430.10599.



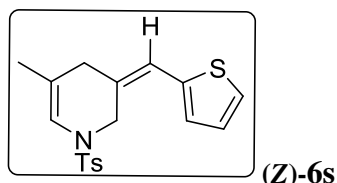
(Z)-5-methyl-1-tosyl-3-(3-(trifluoromethyl)benzylidene)-1,2,3,4-tetrahydropyridine, oil, 12.4%, 10 mg.

¹H NMR (400 MHz, CDCl₃): 7.71 (d, *J* = 8.3 Hz, 2H), 7.51 – 7.41 (m, 2H), 7.30 – 7.24 (m, 4H), 6.23 (s, 1H), 6.14 (s, 1H), 3.97 (s, 2H), 3.83 (s, 2H), 2.41 (s, 3H), 1.76 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): 143.70, 136.96, 136.71, 134.35, 132.14, 131.01 (q, *J* = 32.0 Hz), 130.89, 130.69, 130.37, 130.05, 129.50, 128.60, 128.09 (q, *J* = 271.0 Hz), 127.67, 125.57 (q, *J* = 4.0 Hz), 125.53, 125.49, 125.46, 125.39, 123.49 (q, *J* = 4.0 Hz), 123.46, 123.42, 123.38, 122.84, 122.68, 119.97, 119.34, 49.51, 49.48, 21.39, 20.83. ¹⁹F NMR (376 MHz, CDCl₃): -62.70 (s). IR (cm⁻¹): 3062, 2924, 2851, 1647, 1597, 1493, 1438, 1330, 1216, 1161, 1124, 1092, 1073, 1017, 962, 907, 813, 766, 704, 664, 605. HRMS (ESI) *m/z* calcd for C₂₁H₂₀F₃NO₂SNa⁺ (M+Na)⁺ 430.10591, found 430.10599.

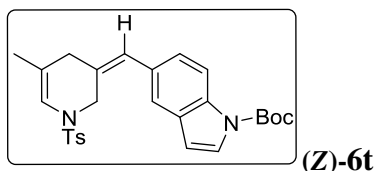


(E)-5-methyl-3-(thiophen-2-ylmethylene)-1-tosyl-1,2,3,4-tetrahydropyridine, M.P.= 118-120 °C, 29.4%, yellow solid, 20 mg.

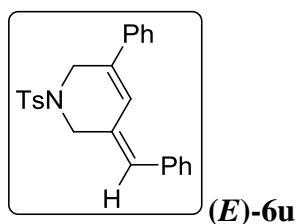
¹H NMR (400 MHz, CDCl₃): 7.66 (d, *J* = 8.3 Hz, 2H), 7.26 (t, *J* = 8.3 Hz, 3H), 7.02 – 6.98 (m, 1H), 6.88 (d, *J* = 3.4 Hz, 1H), 6.50 (s, 1H), 6.33 (s, 1H), 3.97 (s, 2H), 2.86 (s, 2H), 2.35 (s, 3H), 1.76 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): 143.61, 139.36, 134.89, 129.52, 128.27, 127.44, 127.26, 126.88, 125.46, 120.77, 119.88, 118.97, 50.90, 31.83, 21.45, 20.40. IR (cm⁻¹): 3066, 2963, 2919, 2852, 1676, 1596, 1493, 1446, 1347, 1305, 1218, 1163, 1091, 1056, 970, 913, 813, 705, 672. HRMS (ESI) *m/z* calcd for C₁₈H₁₉NO₂S₂Na⁺ (*M*+Na)⁺ 368.07494, found 368.07504.



(Z)-5-methyl-3-(thiophen-2-ylmethylene)-1-tosyl-1,2,3,4-tetrahydropyridine, M.P.= 173-175 °C, 21.8%, yellow solid, 15 mg. ¹H NMR (400 MHz, CDCl₃): 7.68 (d, *J* = 8.2 Hz, 2H), 7.27 (t, *J* = 7.2 Hz, 3H), 7.04 – 6.98 (m, 1H), 6.90 (d, *J* = 3.5 Hz, 1H), 6.55 (s, 1H), 6.29 (s, 1H), 3.90 (s, 2H), 3.77 (s, 2H), 2.39 (s, 3H), 1.82 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): 143.59, 139.10, 135.90, 133.90, 129.46, 127.82, 127.65, 126.90, 125.59, 120.20, 117.43, 49.74, 49.37, 21.46, 21.03. IR (cm⁻¹): 3113, 3080, 3045, 2925, 2819, 1635, 1594, 1492, 1449, 1348, 1307, 1290, 1217, 1163, 1090, 1065, 1033, 954, 903, 873, 817, 808, 791, 709, 684, 657, 602. HRMS (ESI) *m/z* calcd for C₁₈H₁₉NO₂S₂Na⁺ (*M*+Na)⁺ 368.07494, found 368.07504.

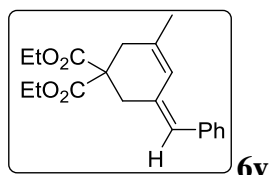


tert-butyl-(Z)-5-((5-methyl-1-tosyl-1,4-dihydropyridin-3(2H)-ylidene)methyl)-1H-indole-1-carboxylate, oil, 24.3%, 23 mg. ¹H NMR (400 MHz, CDCl₃): 7.72 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 3.6 Hz, 1H), 7.30 – 7.23 (m, 3H), 7.04 (d, *J* = 10.0 Hz, 1H), 6.55 (s, 1H), 6.34 (s, 1H), 6.28 (s, 1H), 3.96 (s, 2H), 3.81 (s, 2H), 2.42 (s, 3H), 1.75 (d, *J* = 1.4 Hz, 3H), 1.70 (s, 9H). ¹³C NMR (101 MHz, CDCl₃): 149.62, 143.43, 134.63, 134.29, 130.80, 130.45, 129.47, 128.49, 127.70, 126.36, 125.51, 125.04, 121.26, 120.24, 114.69, 107.24, 83.77, 65.81, 49.77, 49.52, 28.15, 21.48, 20.78, 15.23. IR (cm⁻¹): 2977, 2929, 1732, 1647, 1597, 1571, 1535, 1467, 1369, 1343, 1258, 1224, 1162, 1135, 1084, 1023, 965, 946, 906, 814, 787, 766, 732, 677, 662. HRMS (ESI) *m/z* calcd for C₂₇H₃₀N₂O₄SNa⁺ (*M*+Na)⁺ 501.18185, found 501.18219.



(E)-3-benzylidene-5-phenyl-1-tosyl-1,2,3,6-tetrahydropyridine, oil, 35%, 28 mg. CAS: 2387526-01-2

^1H NMR (400 MHz, CDCl_3): 7.70 (d, $J = 8.2$ Hz, 2H), 7.35 – 7.28 (m, 7H), 7.21 (d, $J = 8.0$ Hz, 3H), 7.07 (d, $J = 7.3$ Hz, 2H), 6.80 (s, 1H), 6.40 (s, 1H), 4.34 (s, 2H), 4.07 (s, 2H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): 143.56, 137.72, 136.00, 134.49, 129.52, 129.14, 128.68, 128.36, 128.23, 127.71, 127.37, 127.15, 125.34, 120.80, 49.61, 47.38, 21.44. IR (cm^{-1}): 3055, 2956, 2923, 1734, 1596, 1493, 1445, 1345, 1241, 1163, 1092, 1075, 1031, 953, 909, 814, 758, 699, 675, 654.

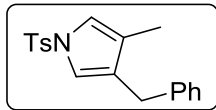


diethyl-5-benzylidene-3-methylcyclohex-3-ene-1,1-dicarboxylate (E/Z=2:1), oil, 87%, 57 mg. CAS: 145204-29-1

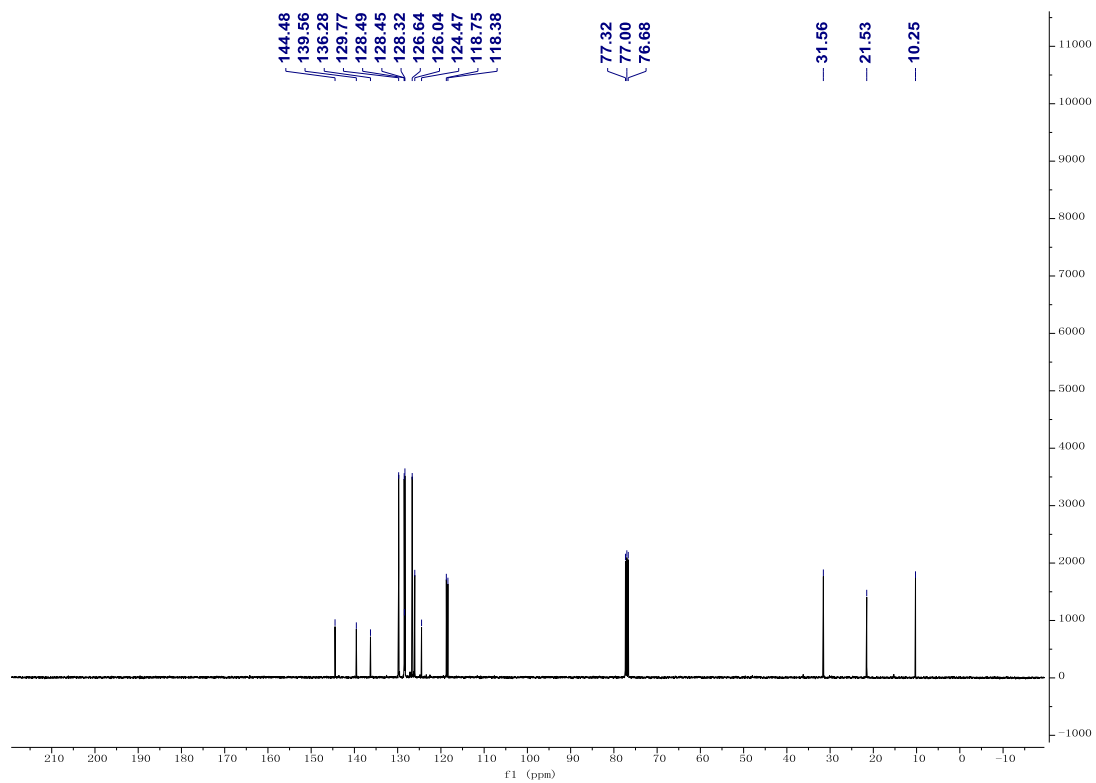
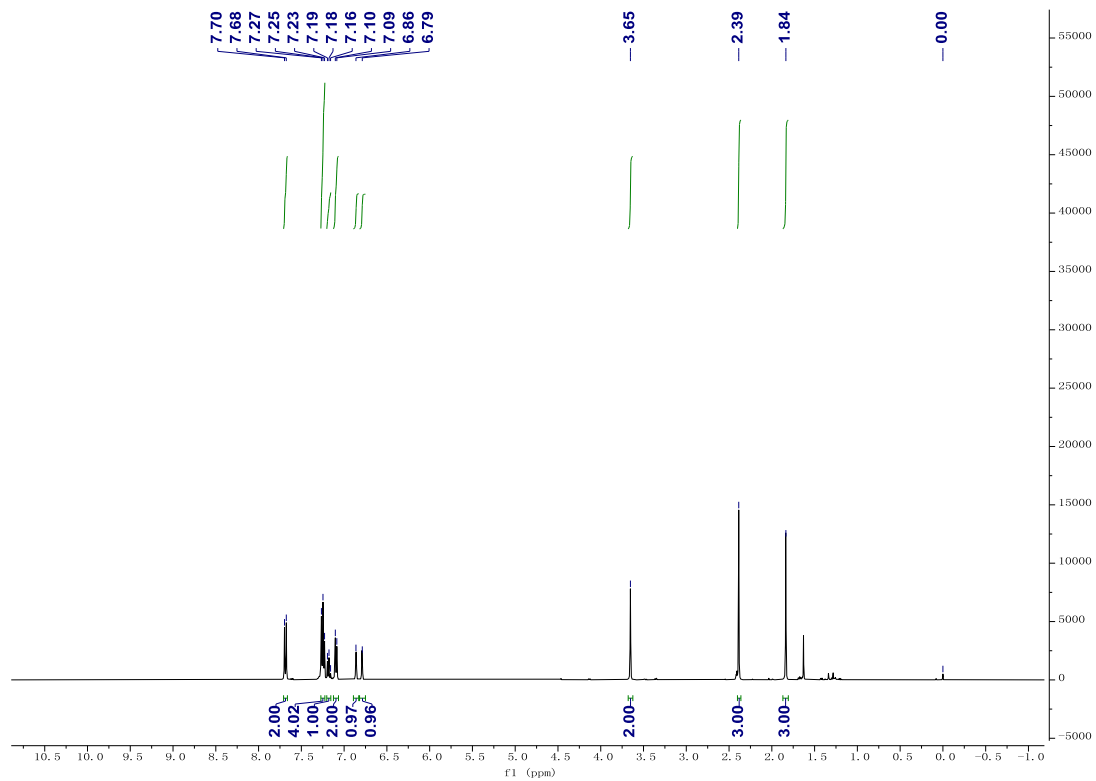
^1H NMR (400 MHz, CDCl_3): 7.34 (q, $J = 7.4$ Hz, 2H), 7.25 (t, $J = 6.4$ Hz, 3H), 6.45 (s, 1H), 5.70 (s, 1H), 4.23 (dd, $J = 11.8, 7.1$ Hz, 4H), 2.99 (s, 1H), 2.94 (s, 2H), 2.68 (s, 1H), 1.87 (s, 1H), 1.78 (s, 2H), 1.28 (dt, $J = 14.0, 7.1$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3): 170.80, 170.65, 137.68, 133.57, 128.99, 128.73, 128.03, 127.97, 126.37, 126.26, 126.21, 124.93, 120.51, 118.88, 61.40, 61.34, 57.10, 38.90, 37.32, 36.40, 33.79, 23.68, 23.39, 13.99. IR (cm^{-1}): 3053, 3022, 2978, 2934, 2907, 1733, 1645, 1598, 1574, 1492, 1445, 1388, 1365, 1244, 1181, 1094, 1051, 1020, 912, 858, 748, 699, 637.

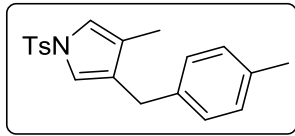
IX. ^1H NMR, ^{13}C NMR and ^{19}F NMR spectra of compound 2, 4, 6, 7,

8, 5u-d1

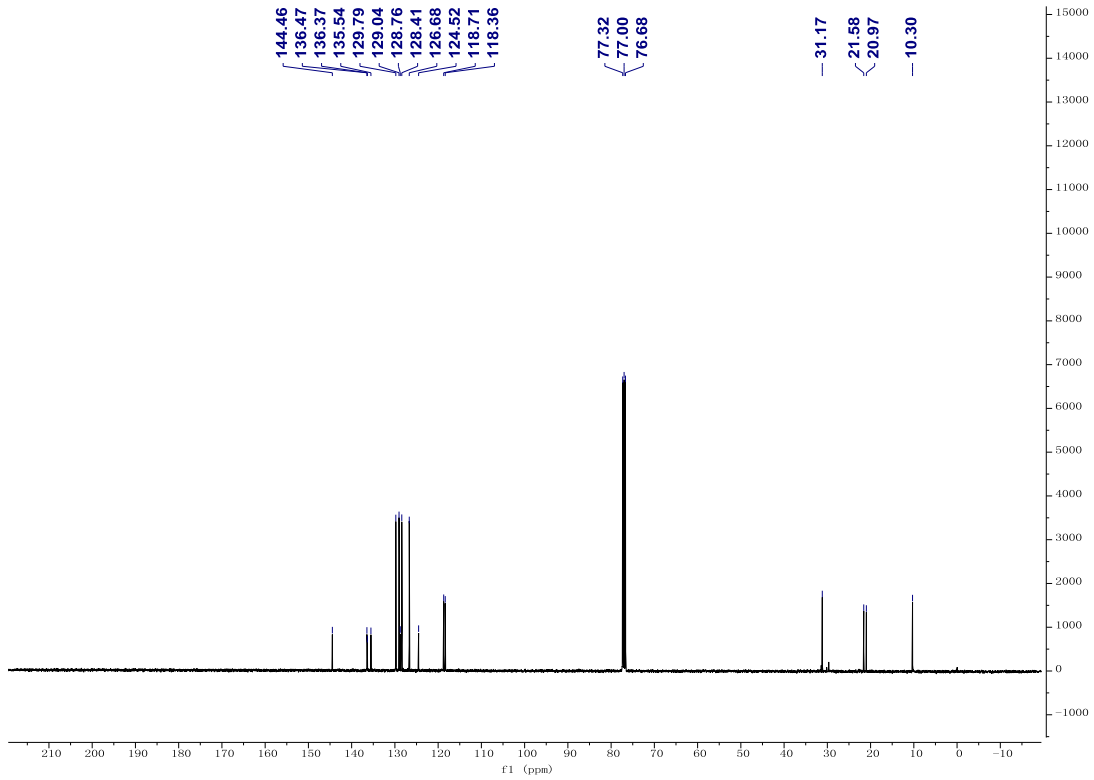
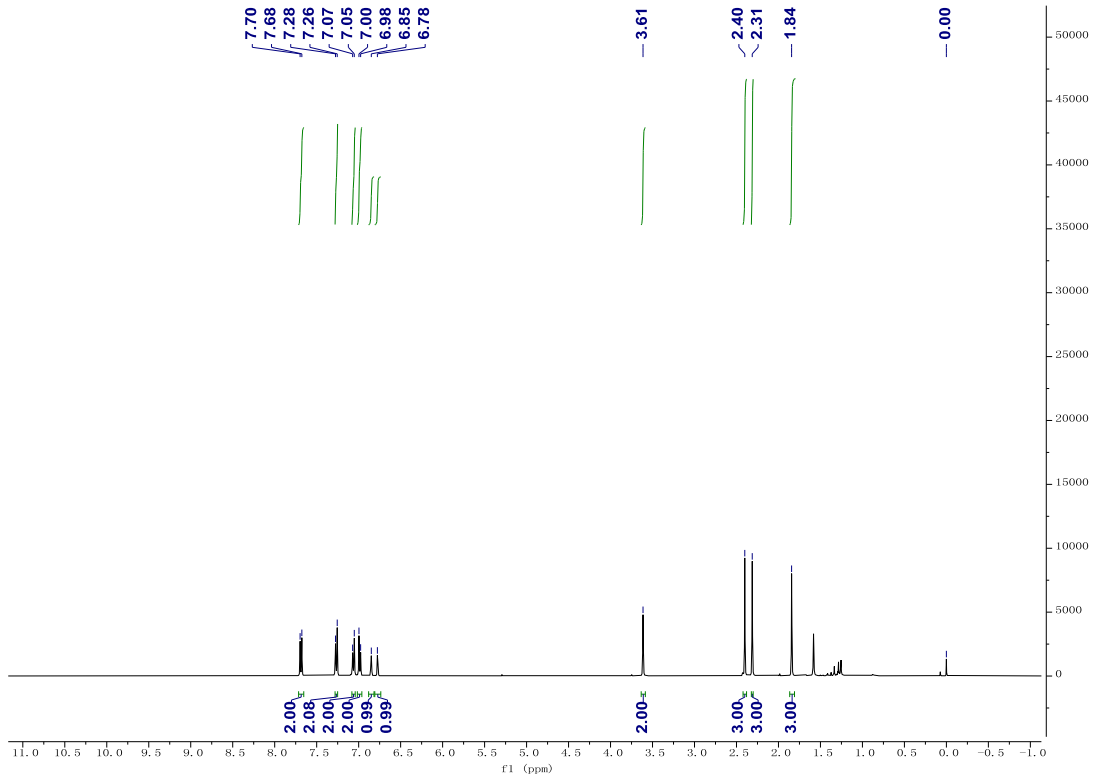


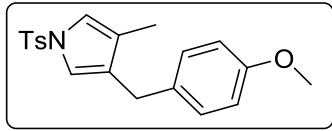
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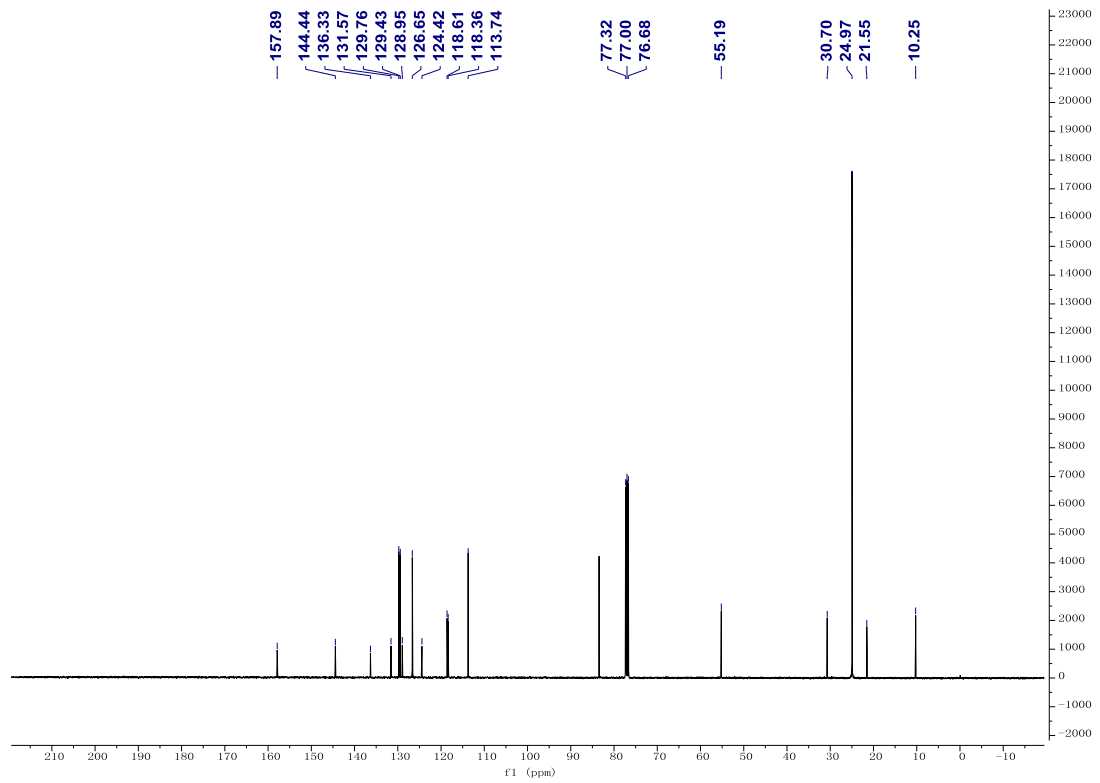
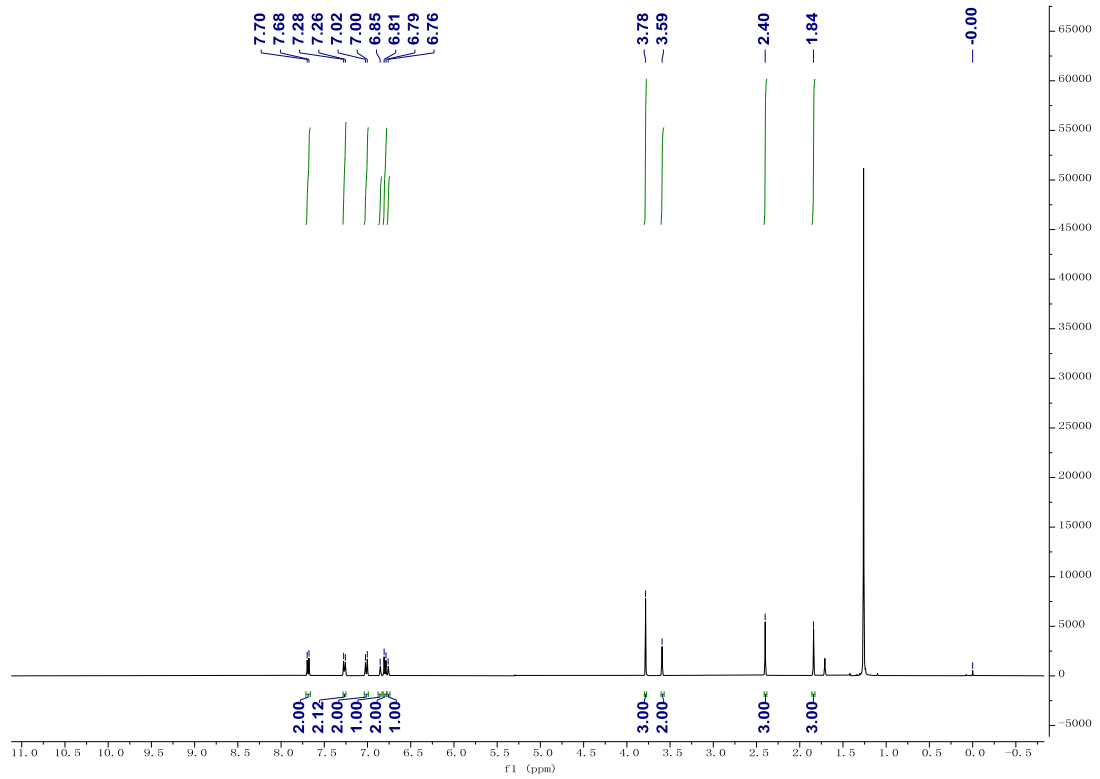


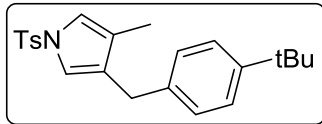
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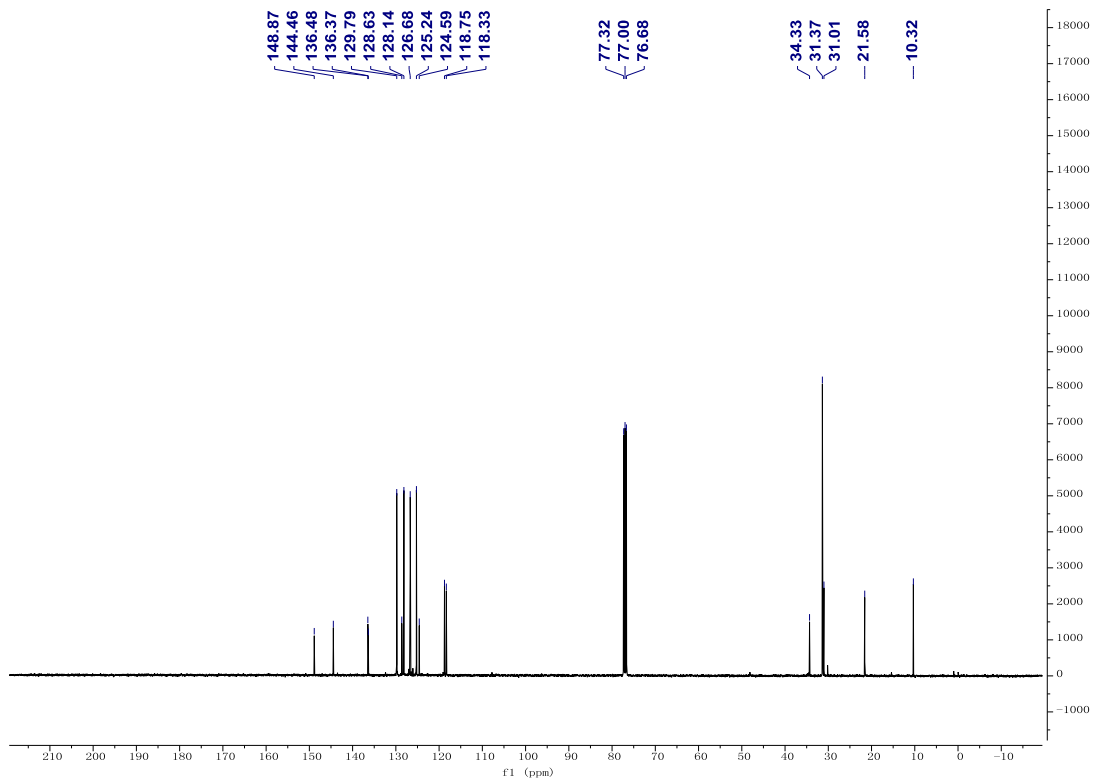
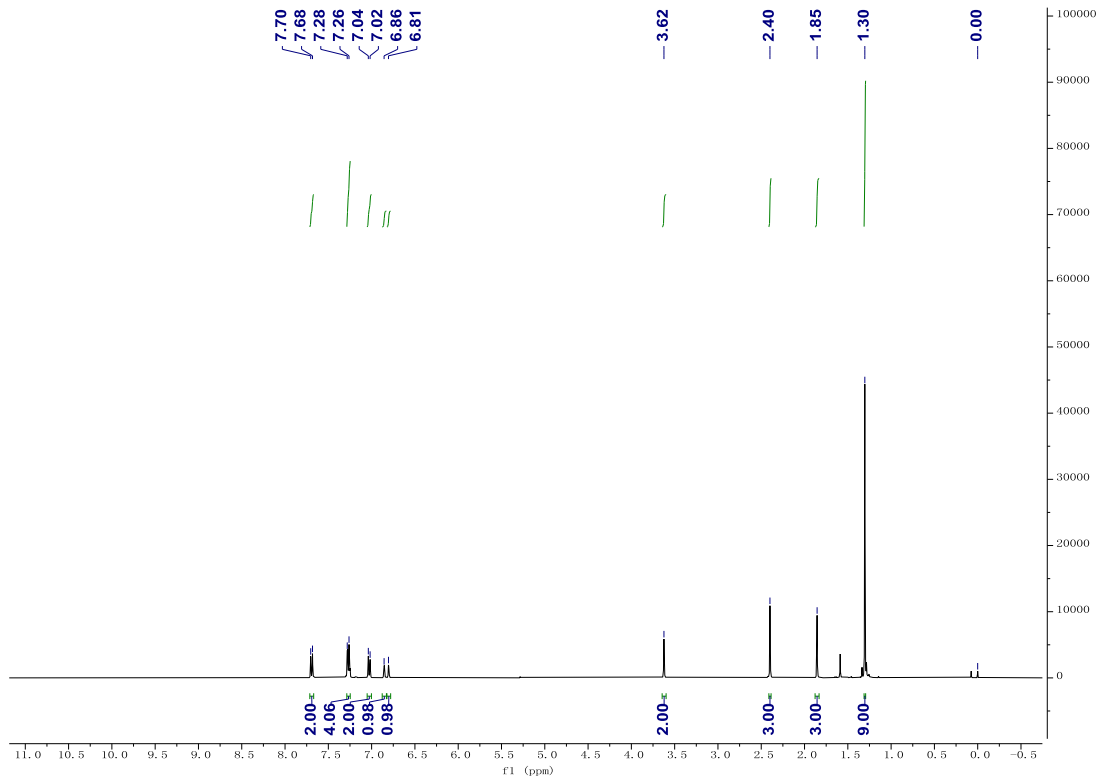


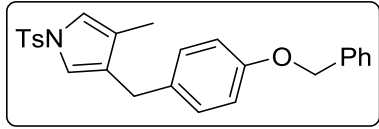
2c



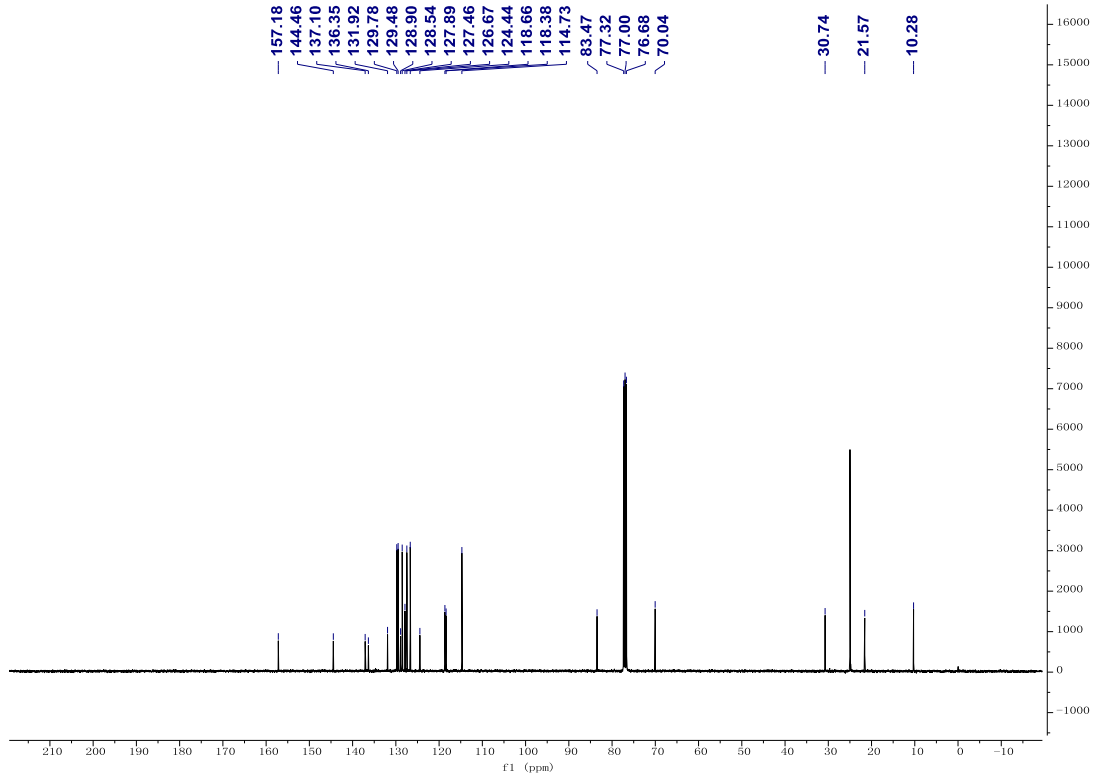
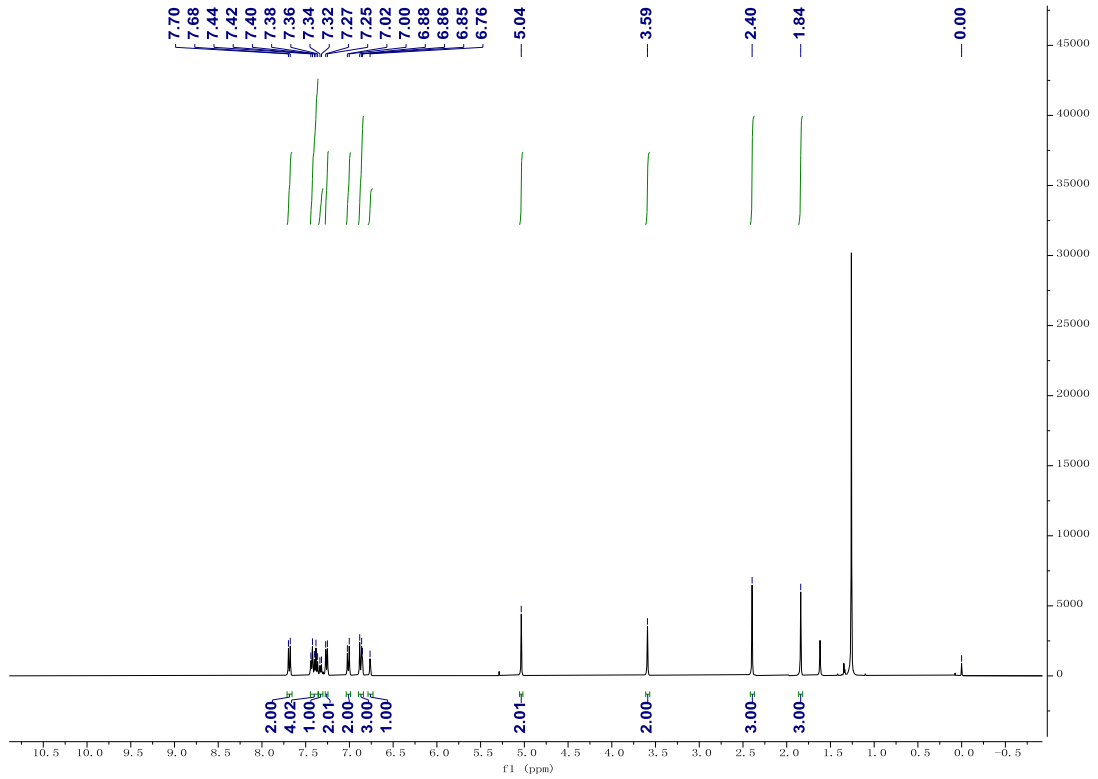


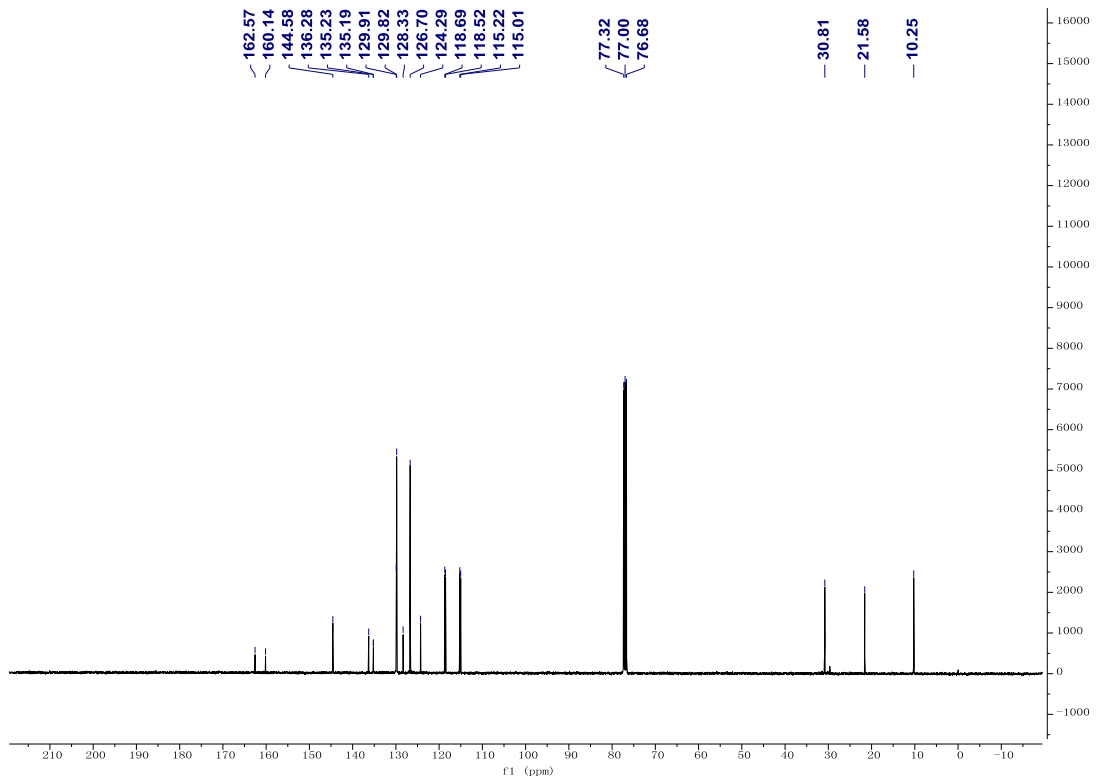
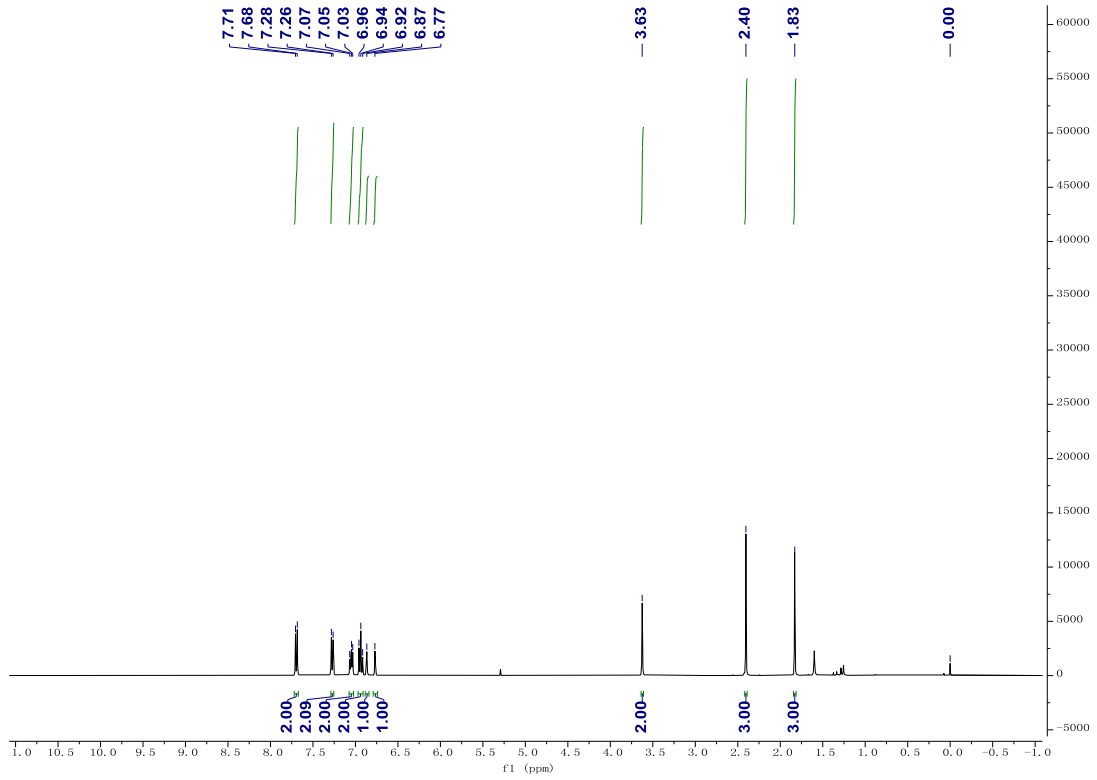
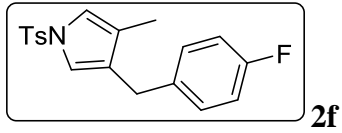
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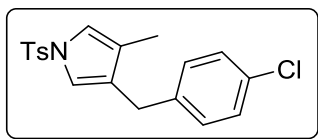
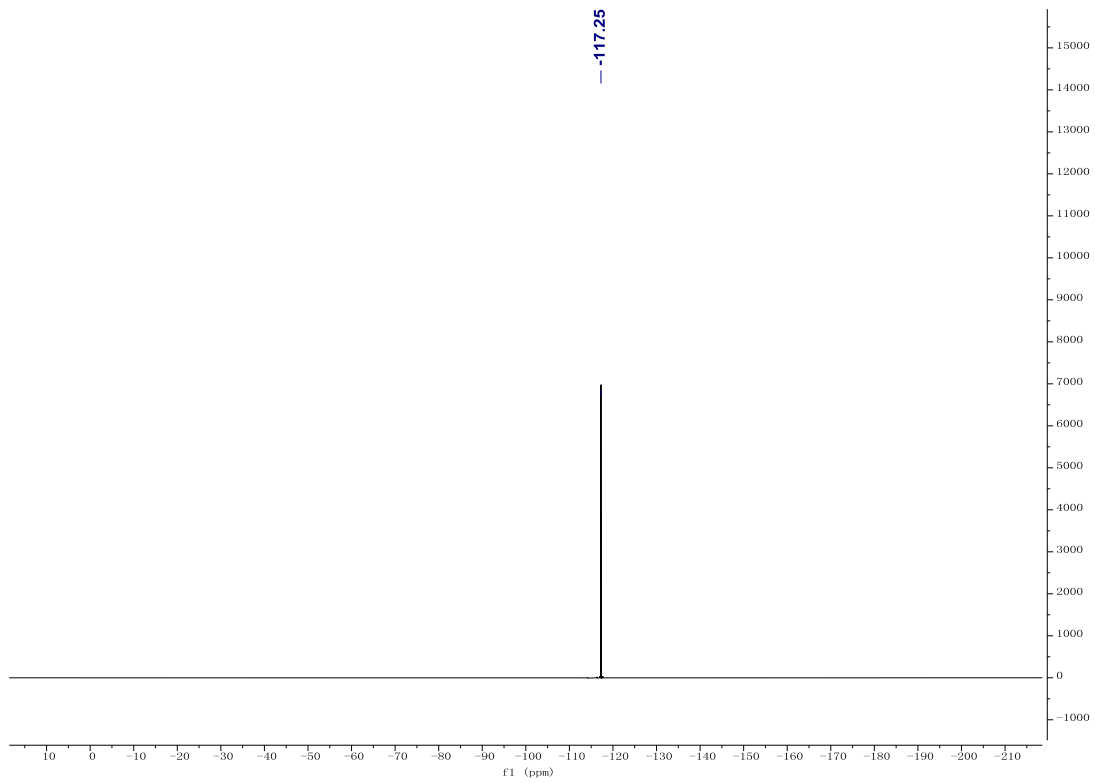




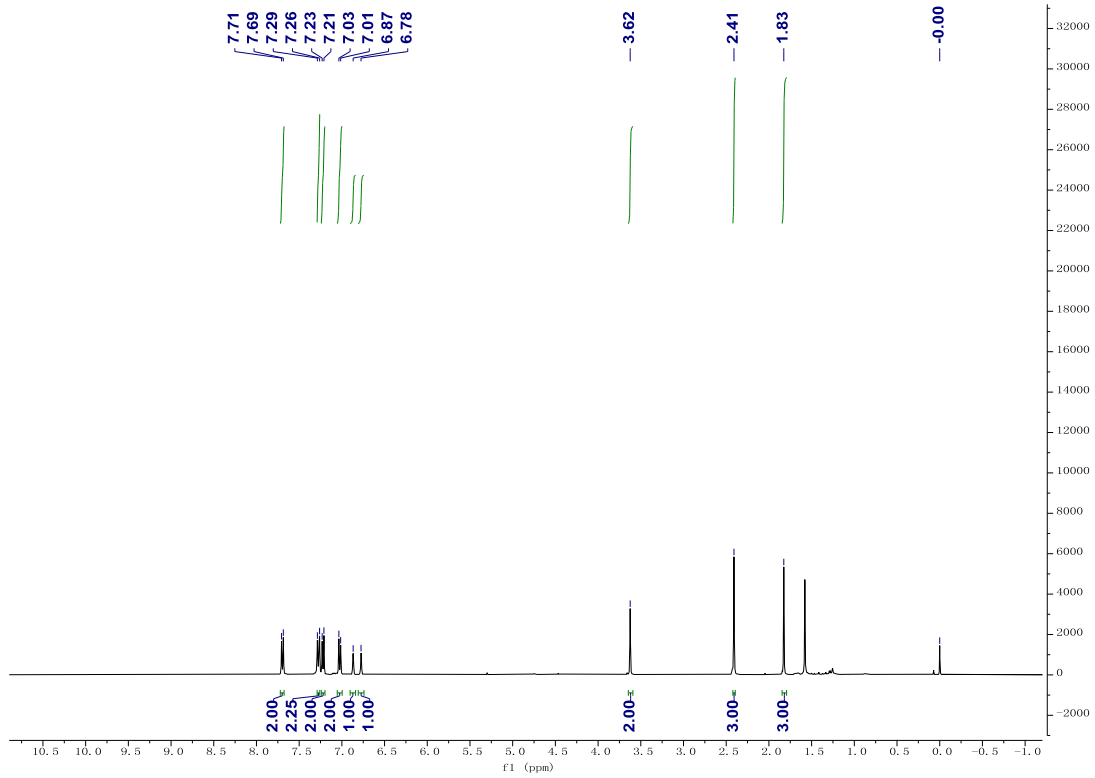
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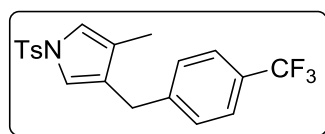
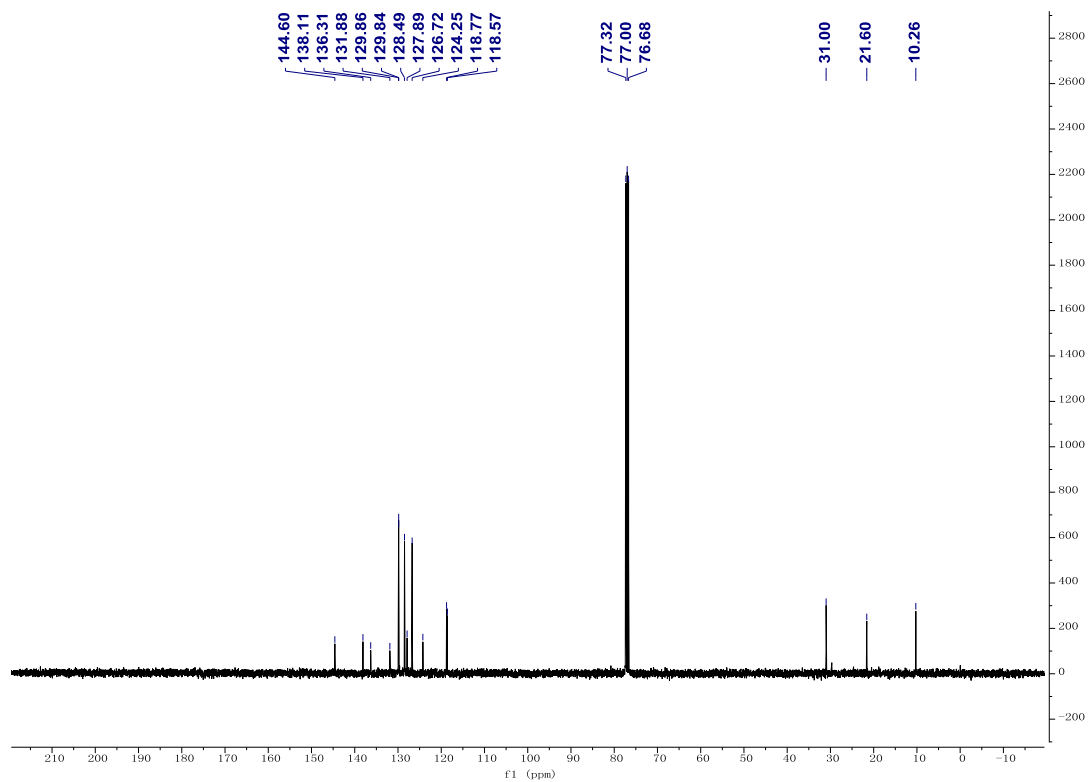




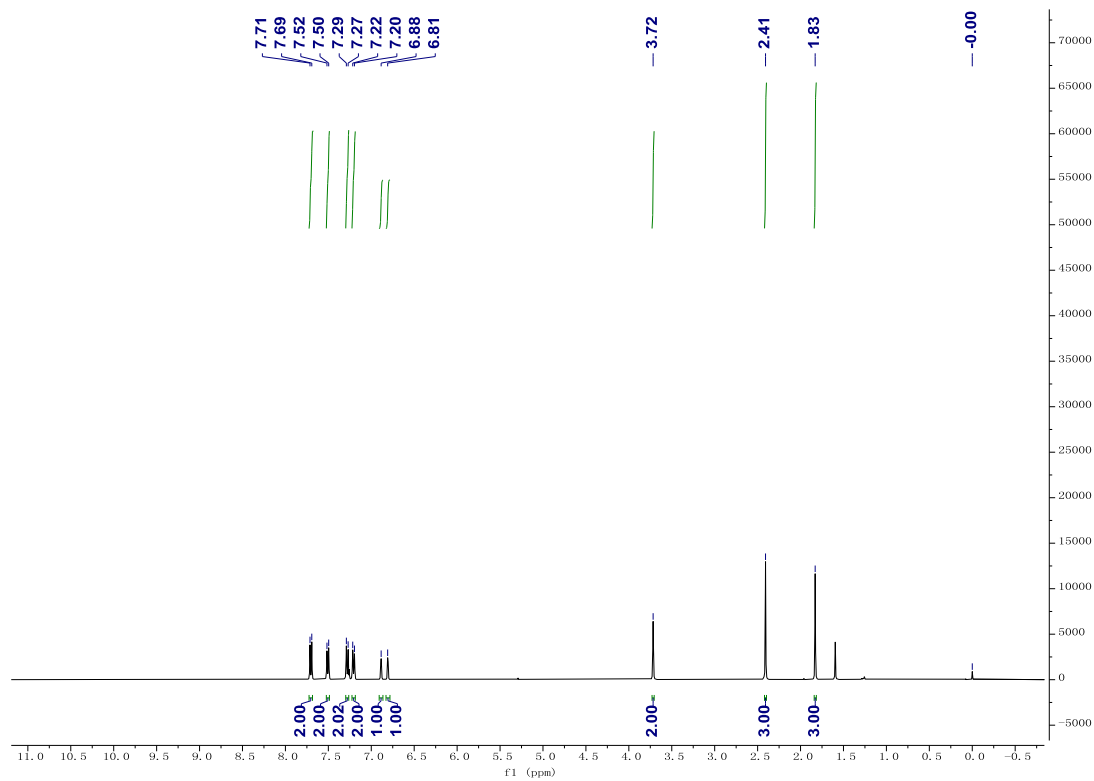


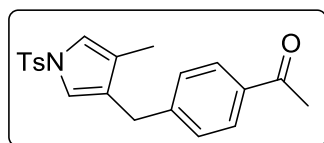
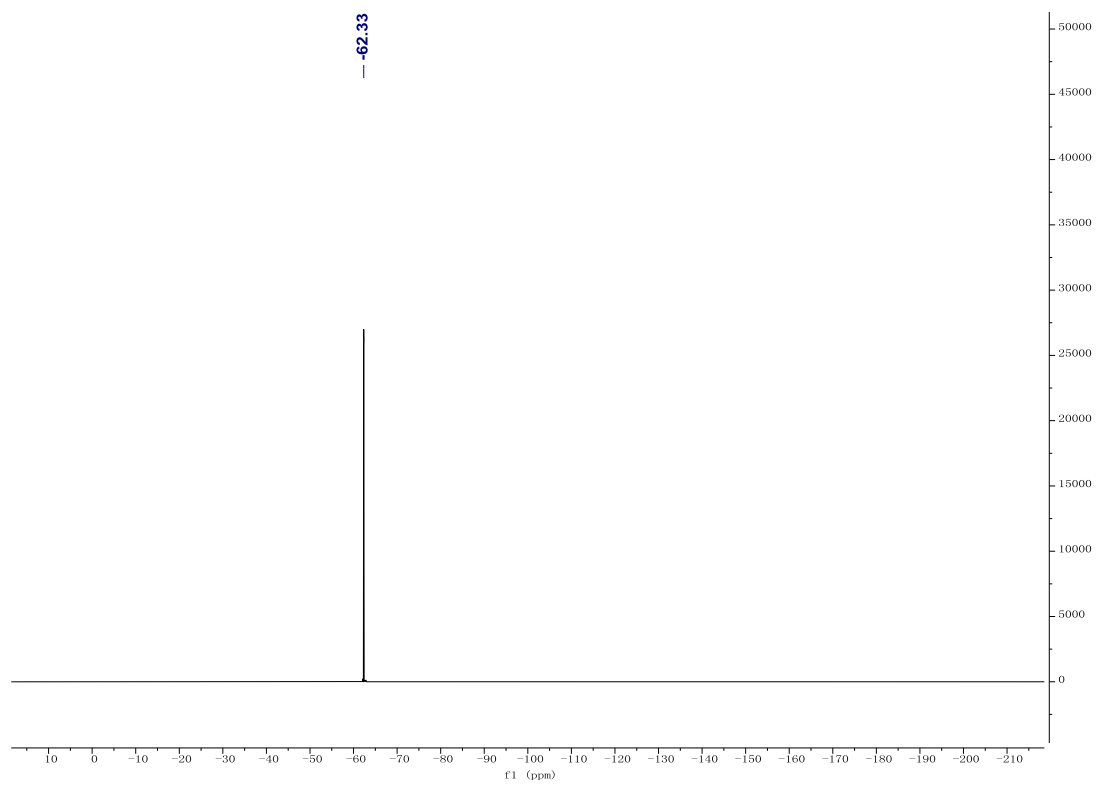
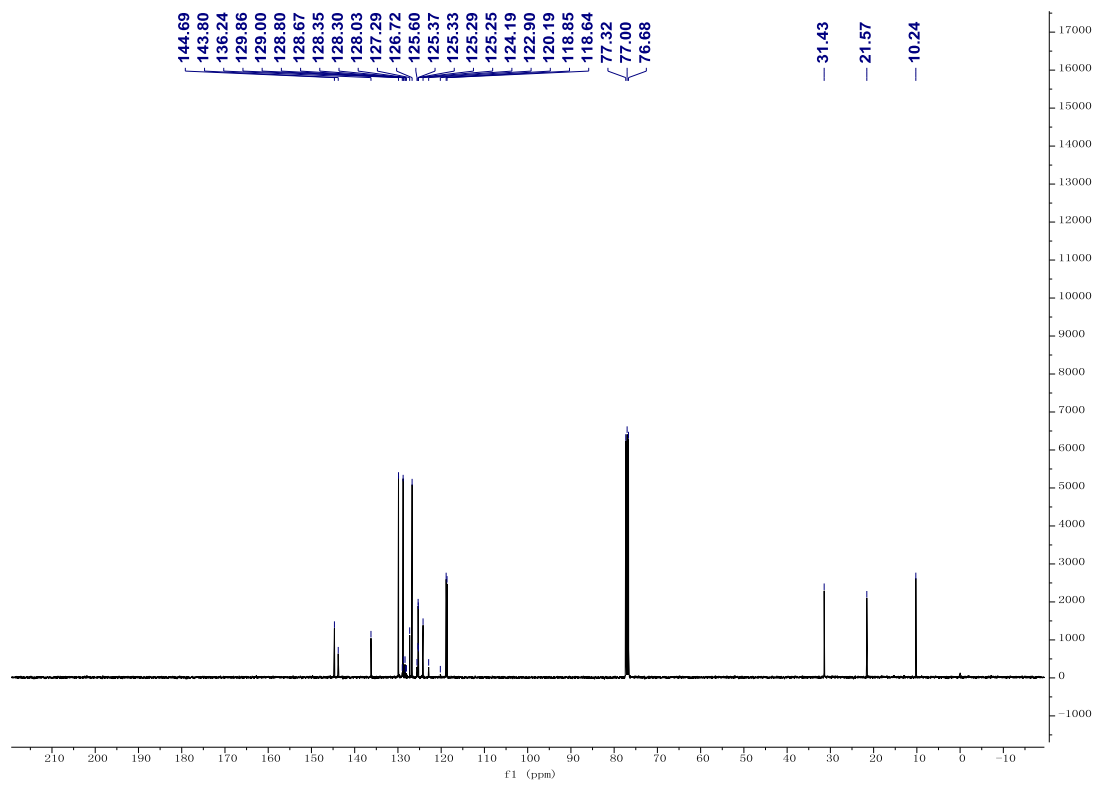
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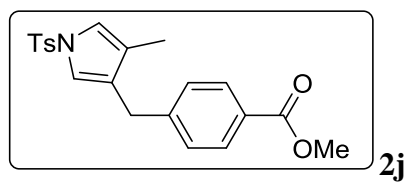
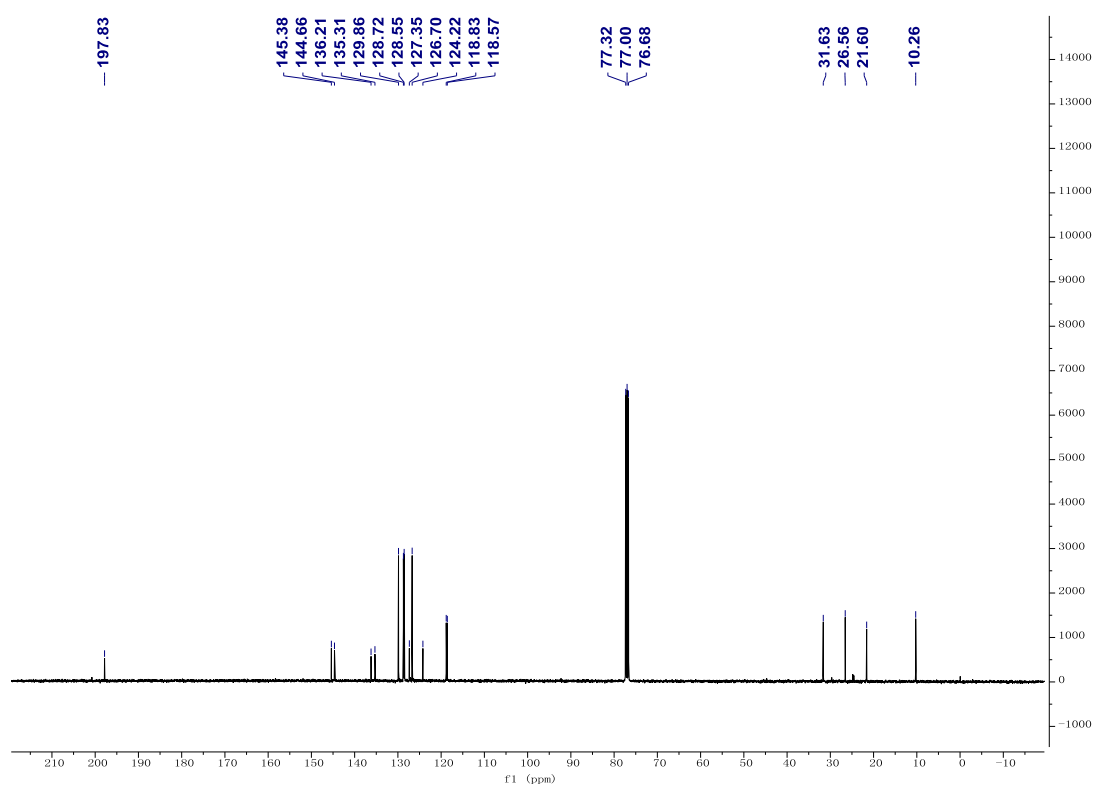
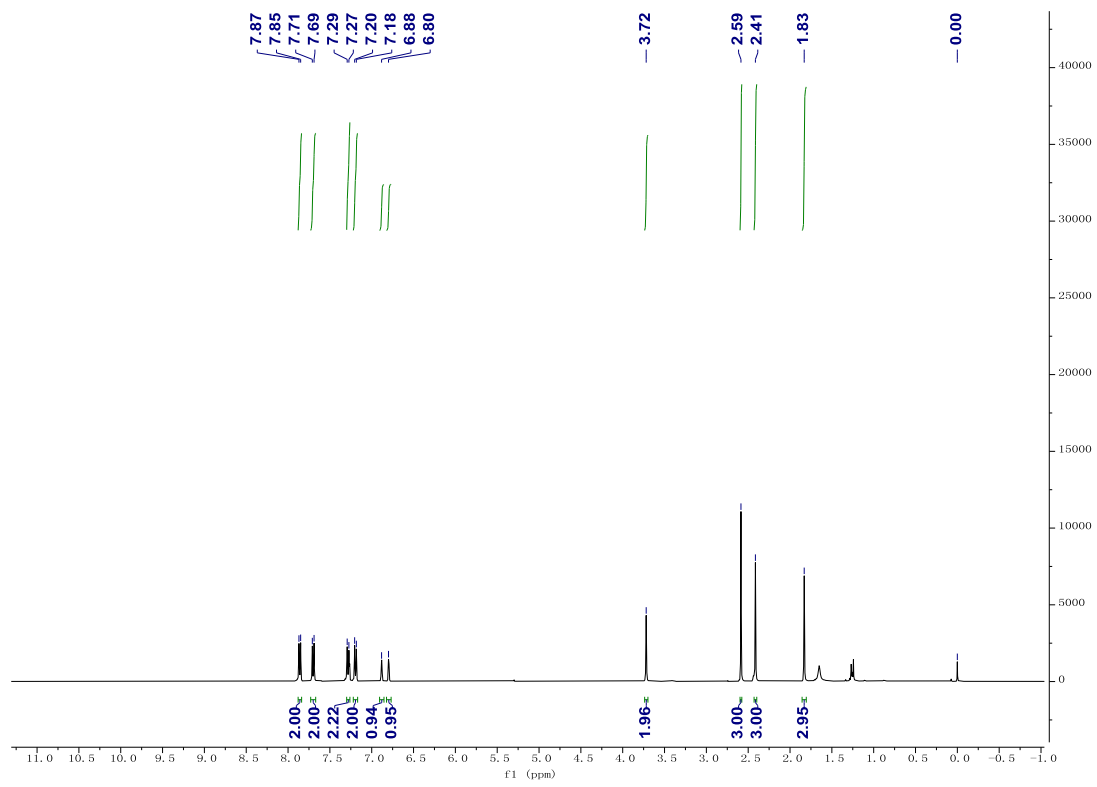


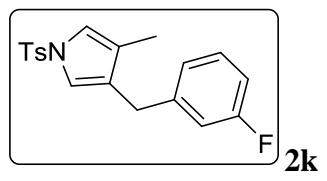
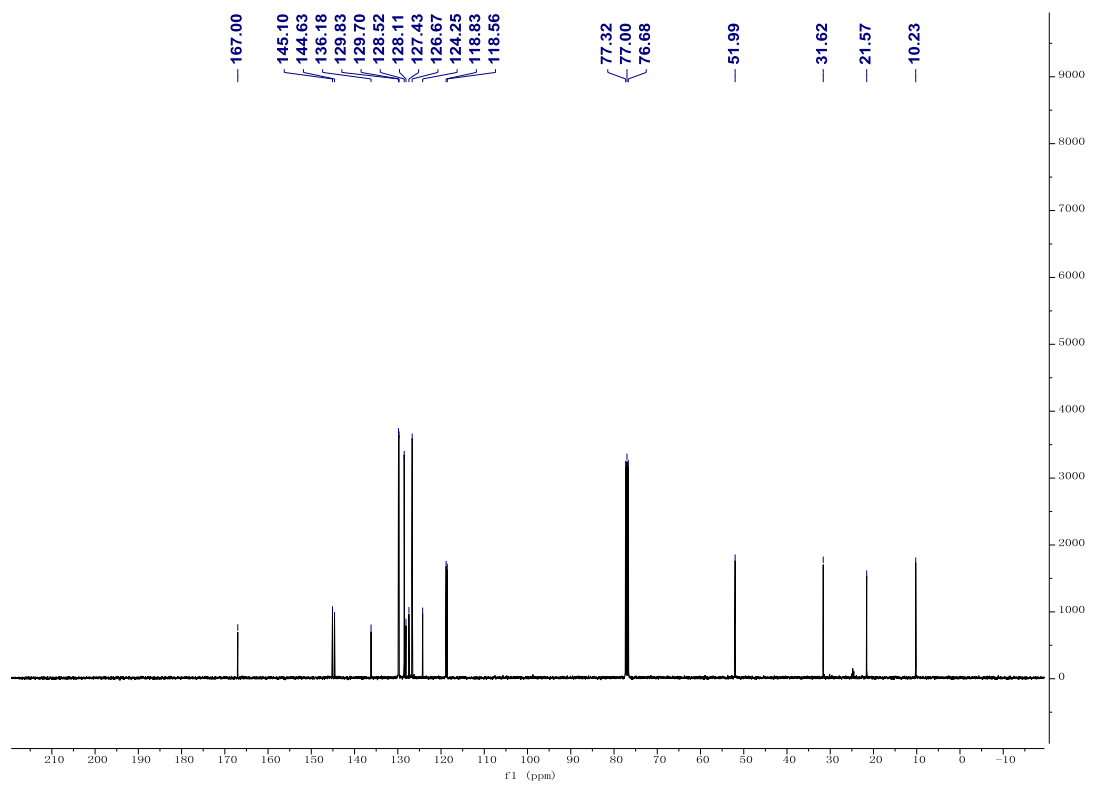
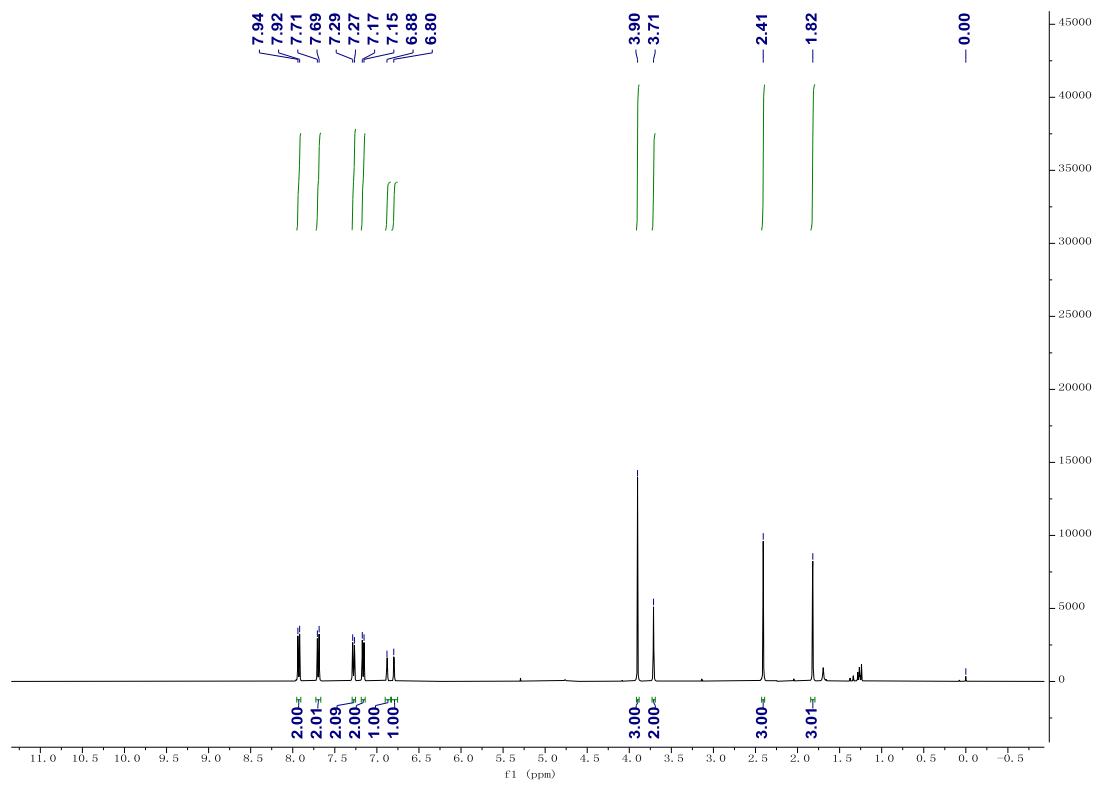
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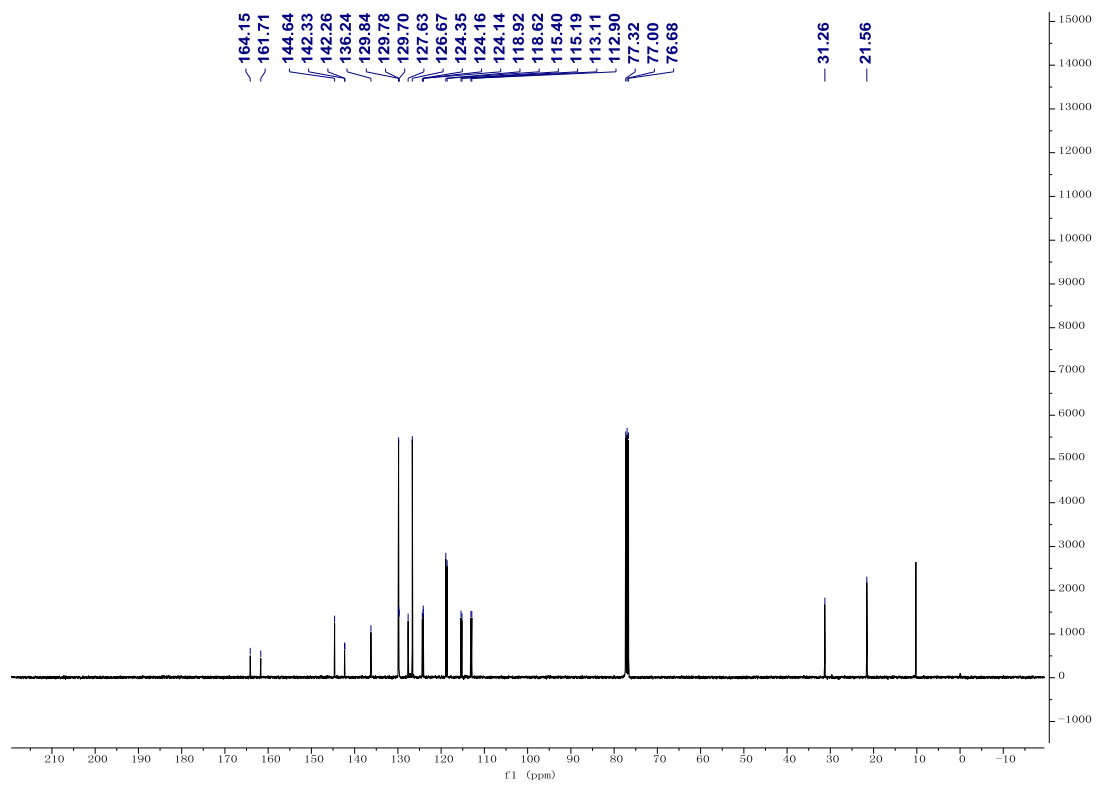
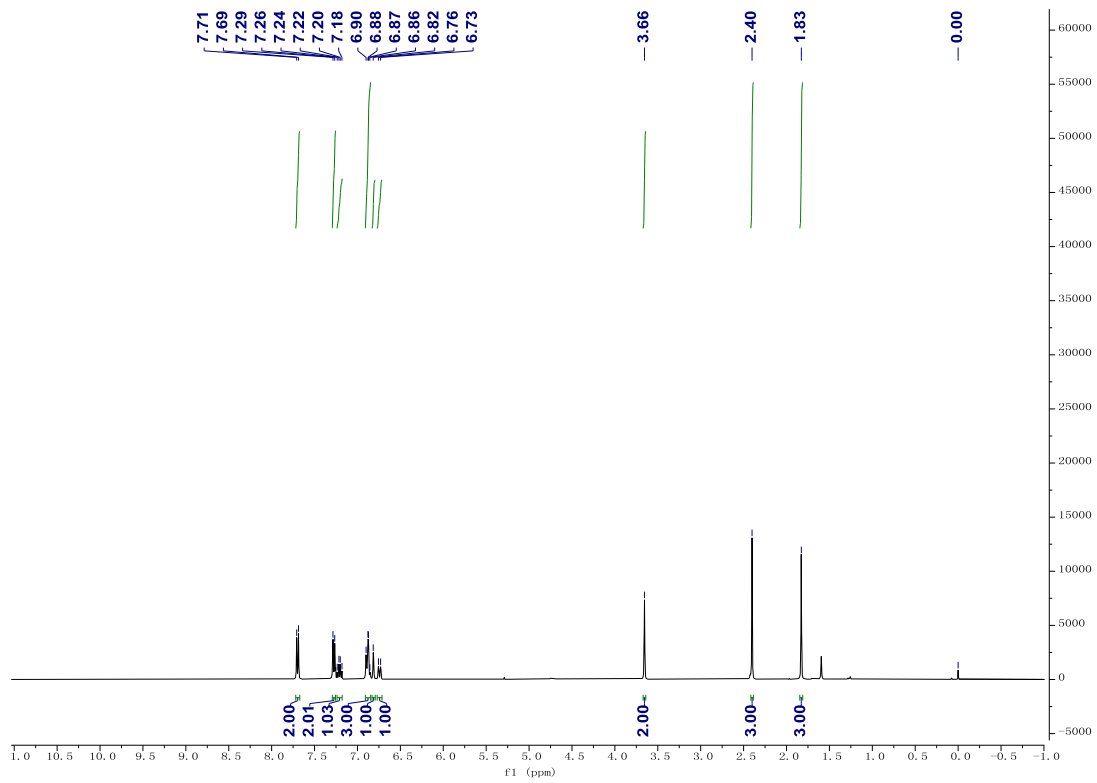


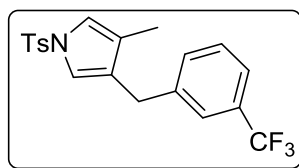
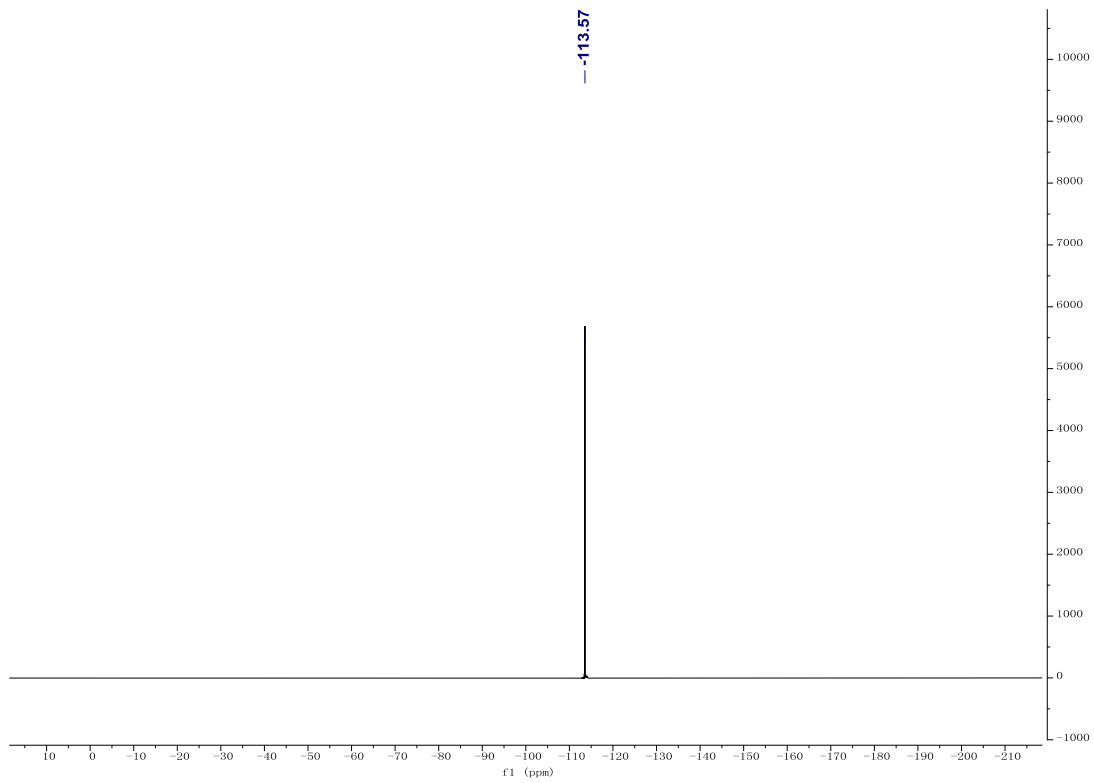


2i

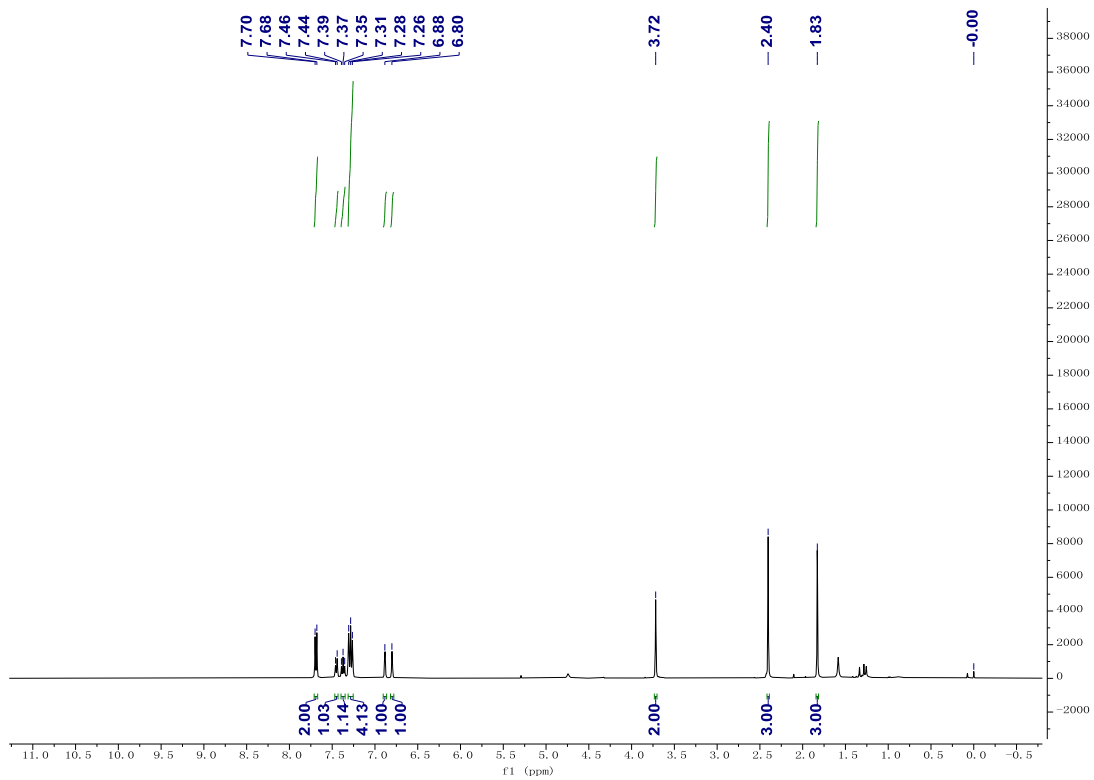


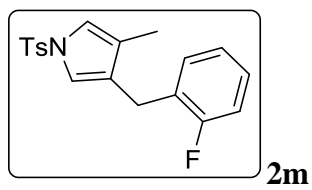
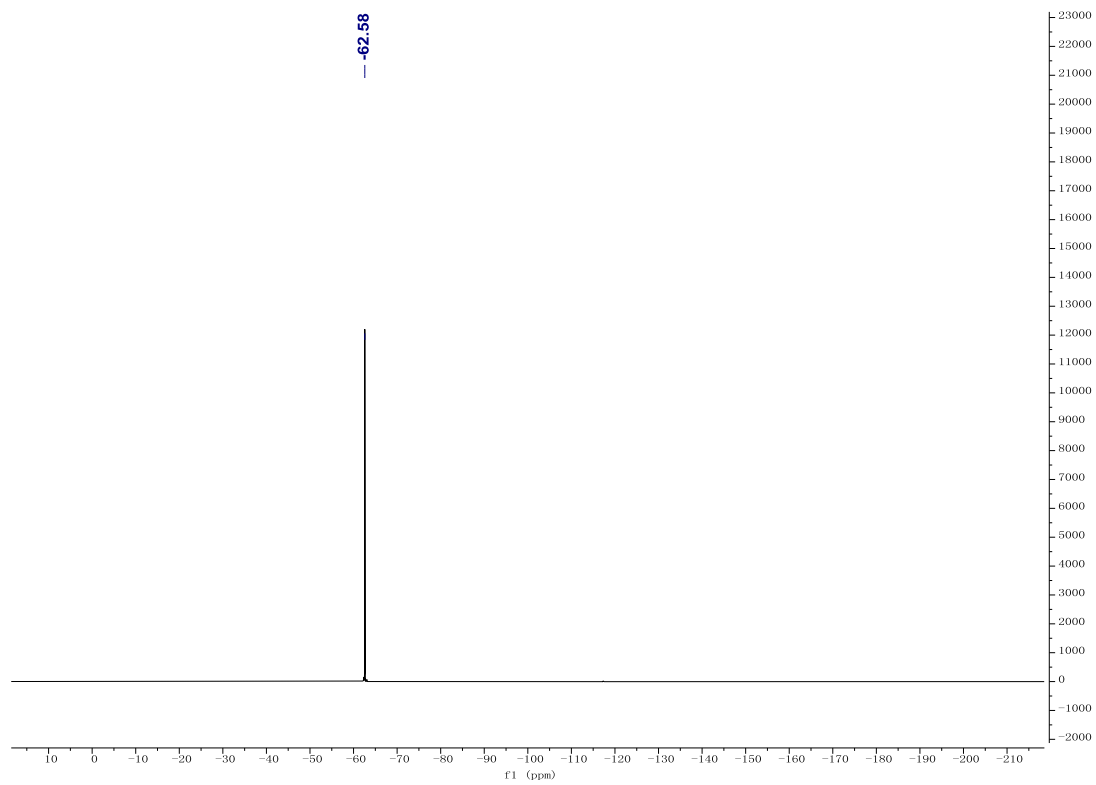
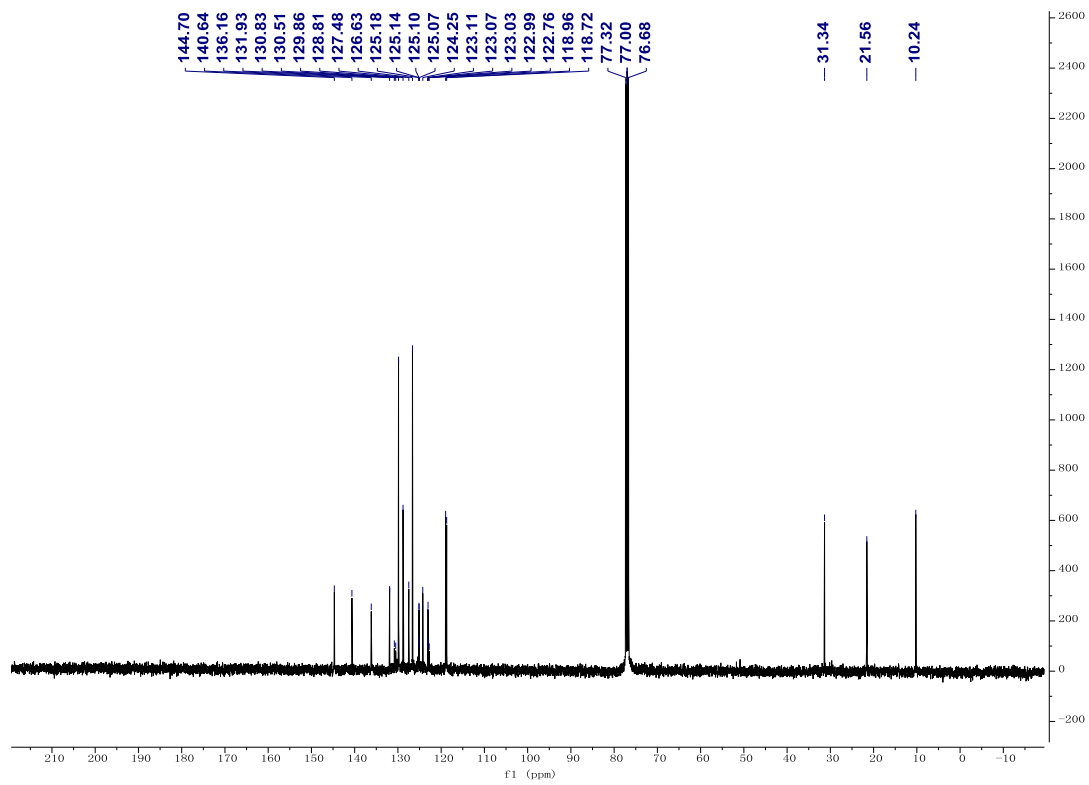


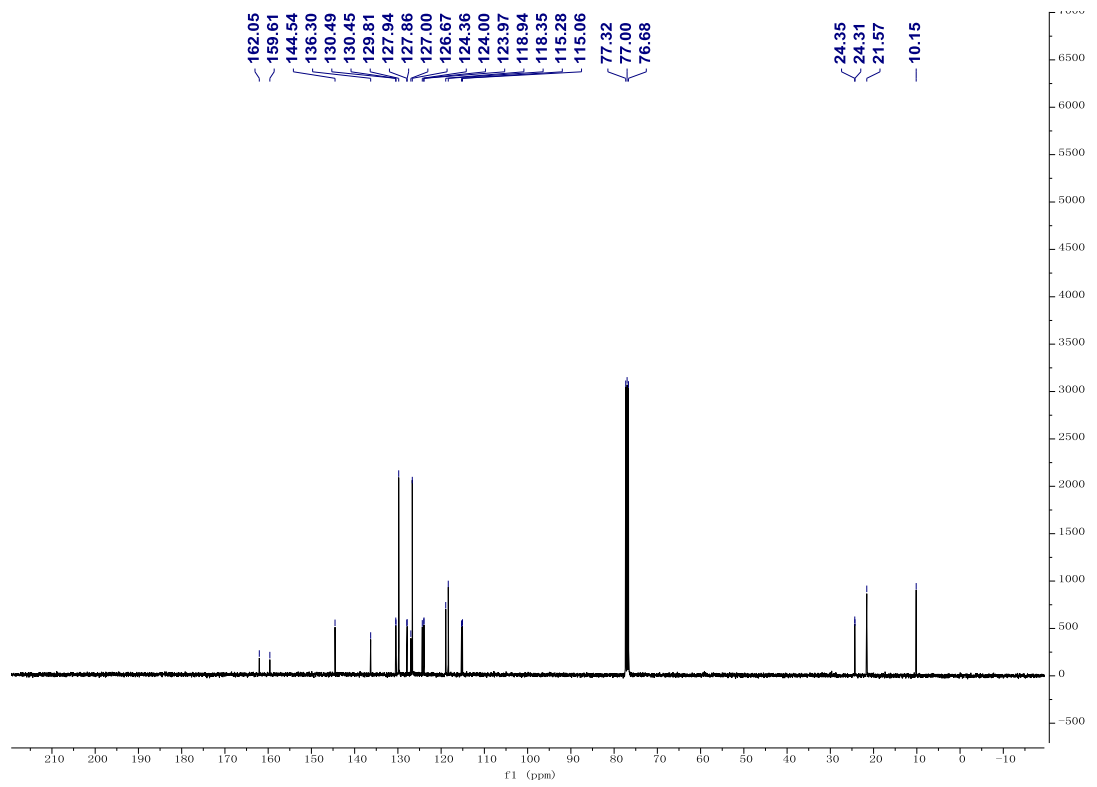
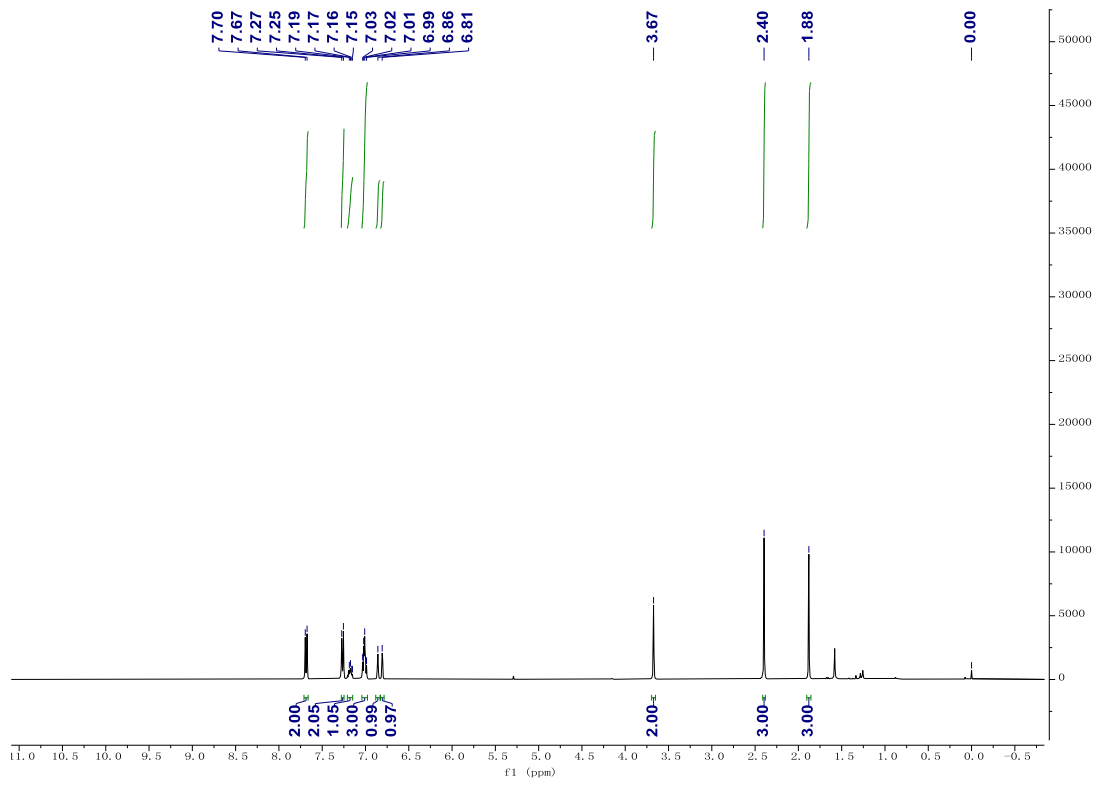


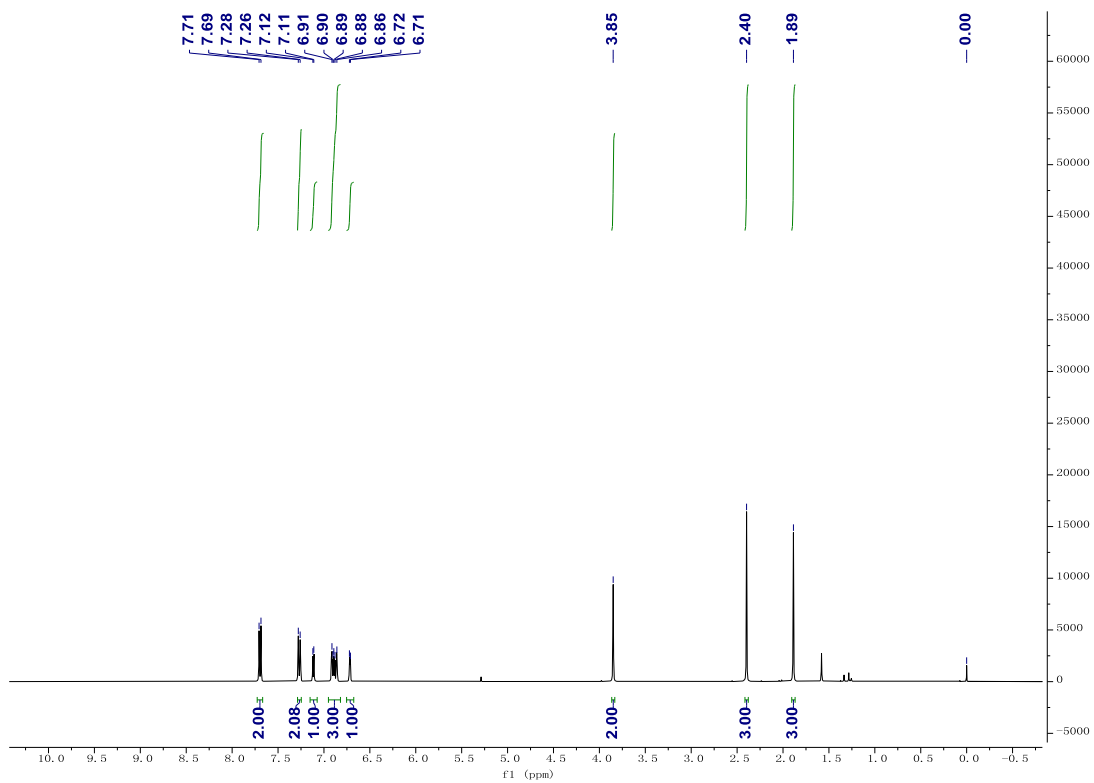
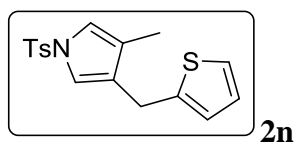
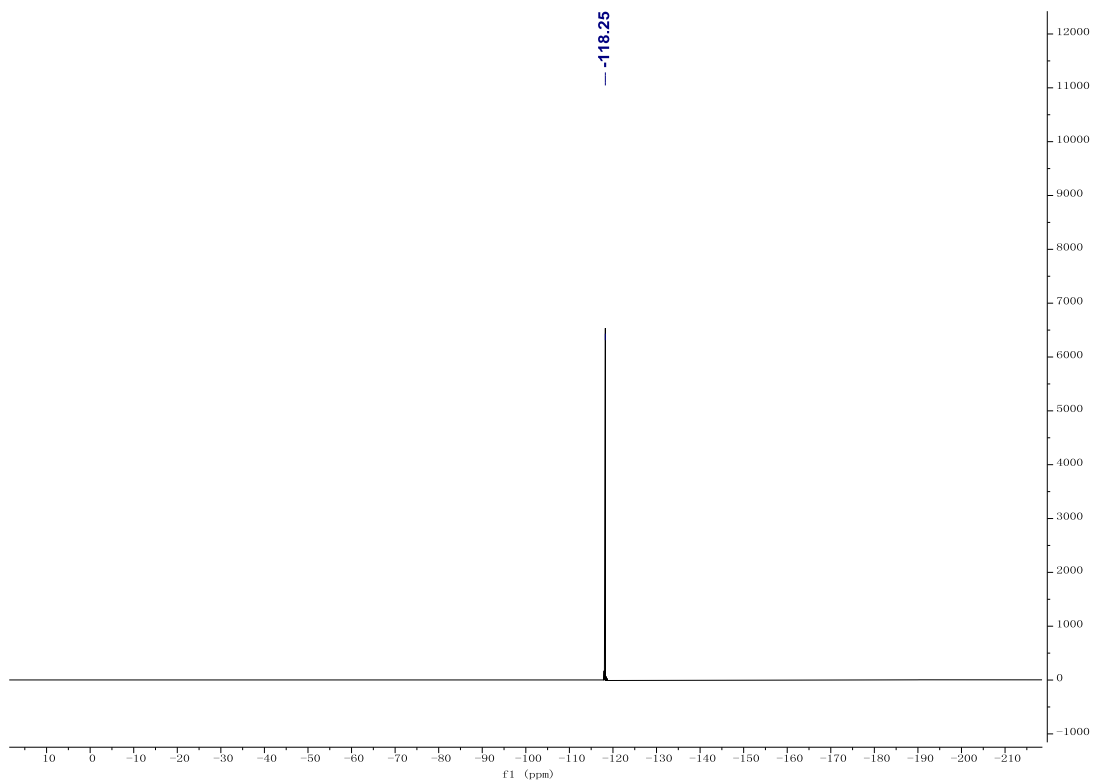


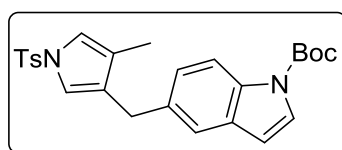
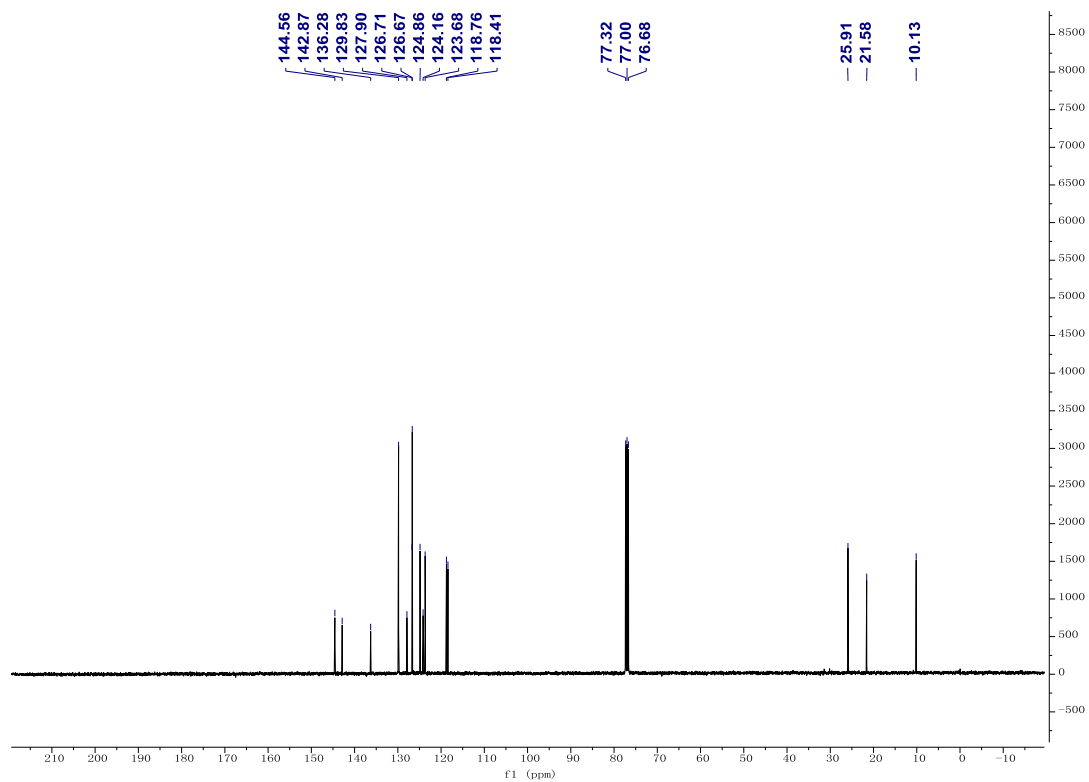
2l



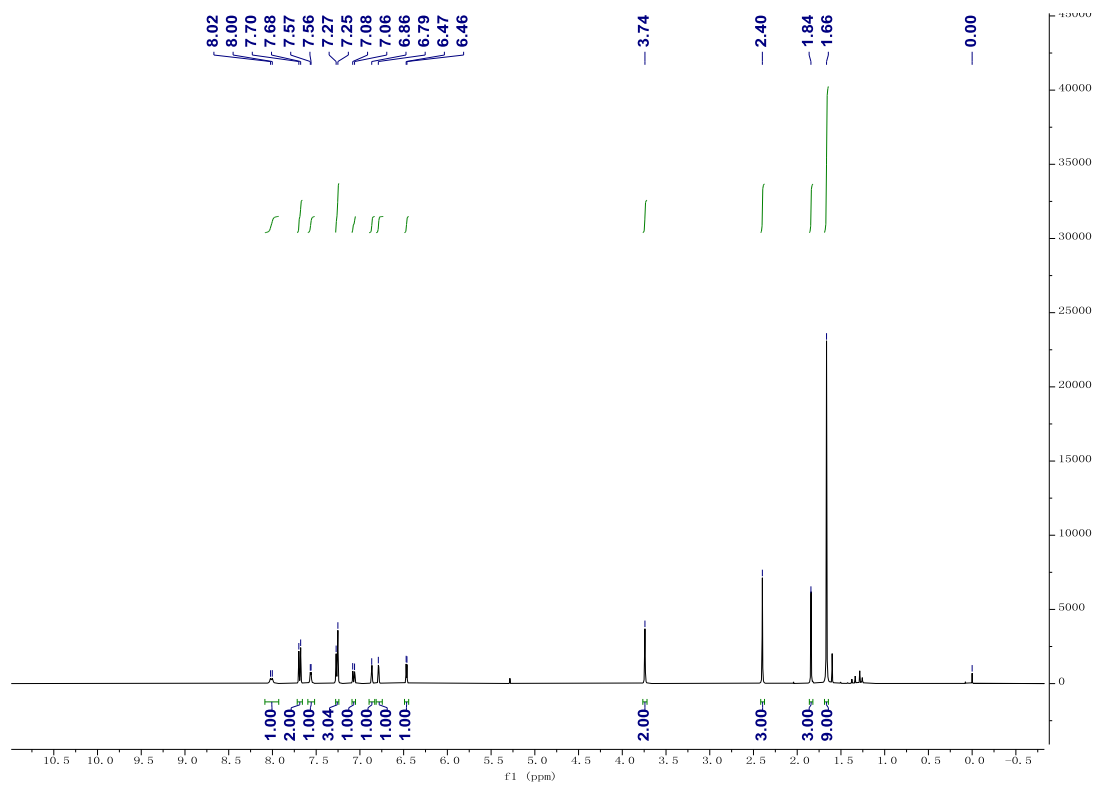


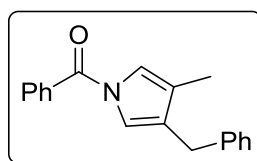
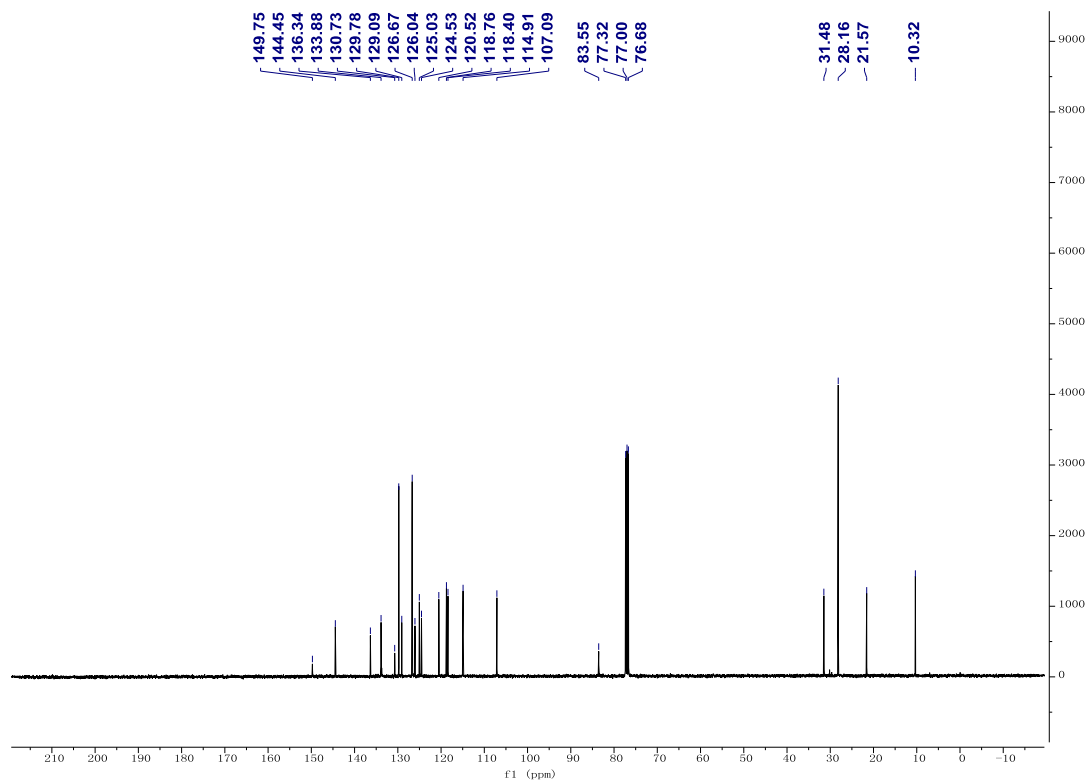




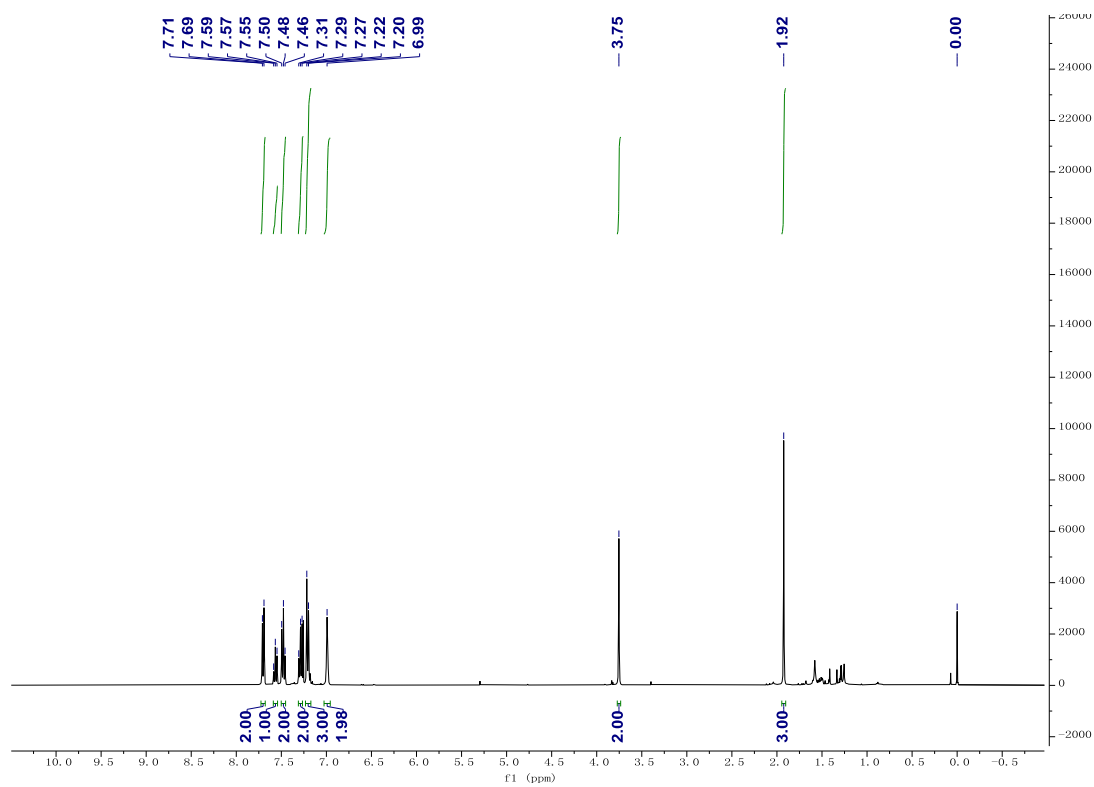


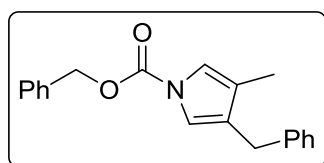
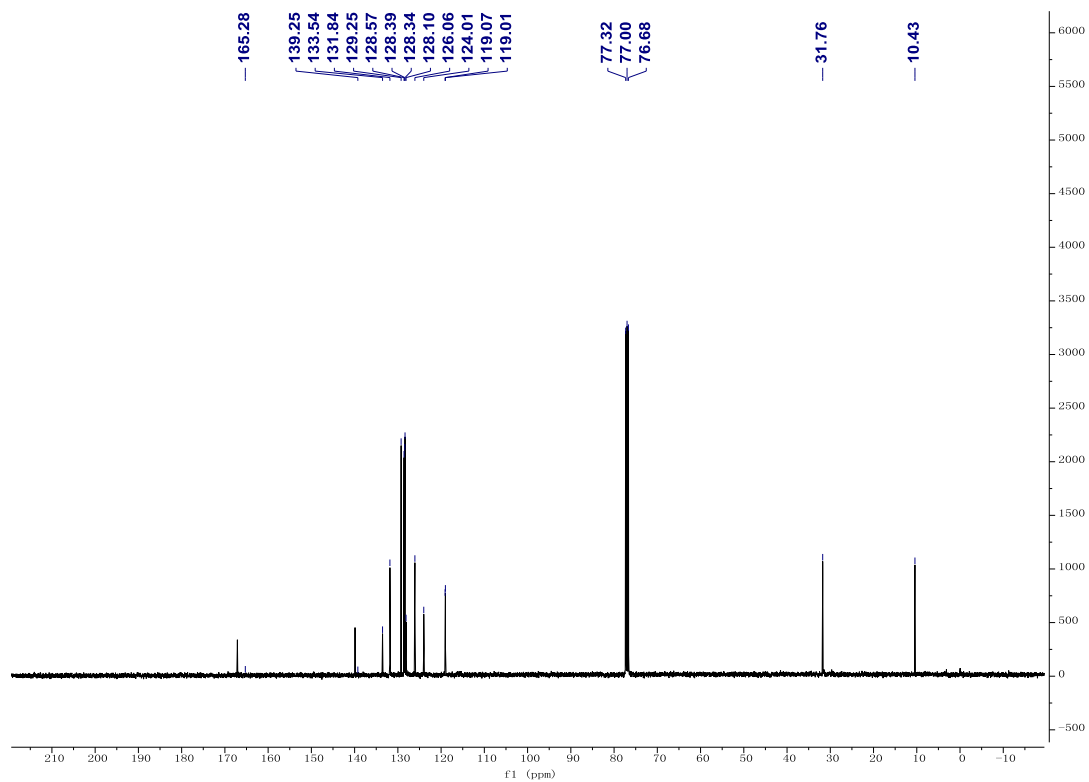
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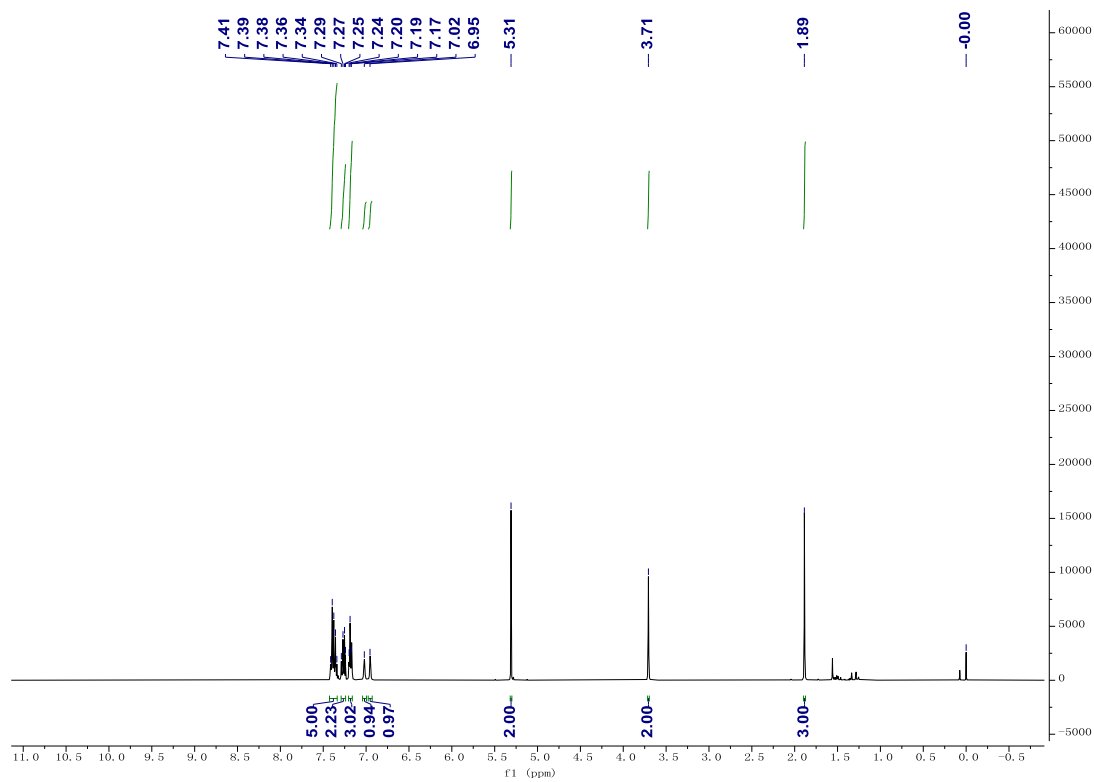


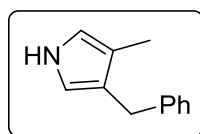
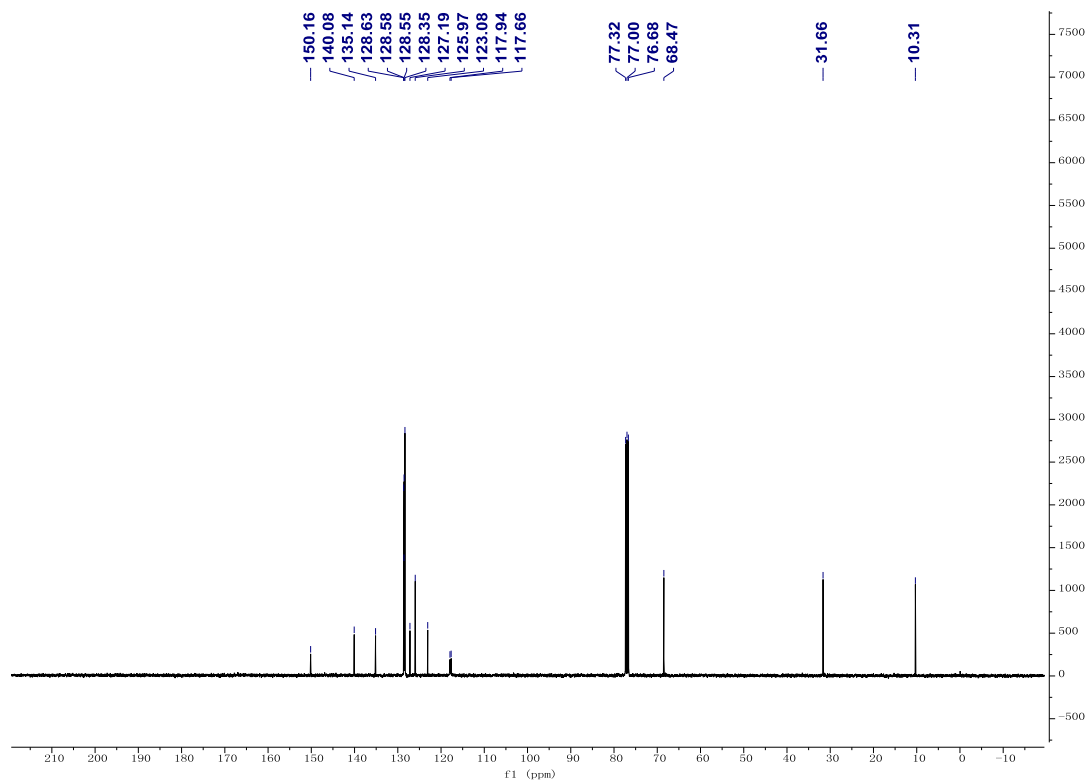
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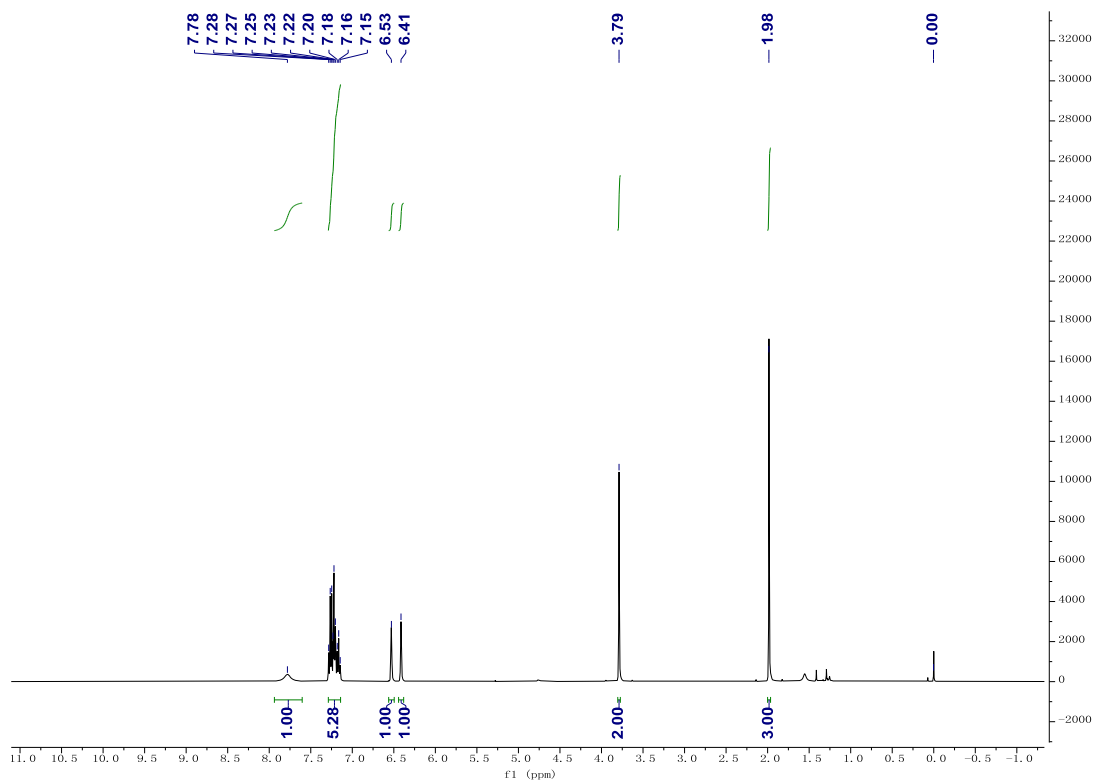


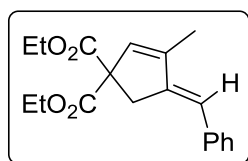
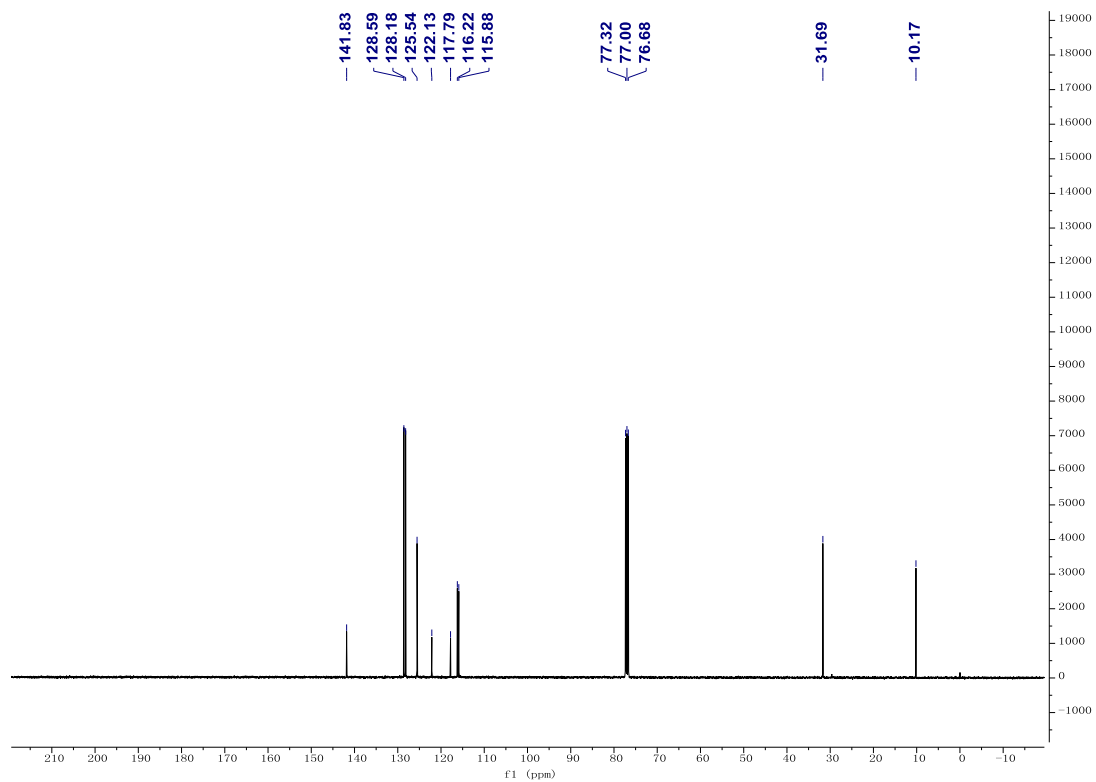
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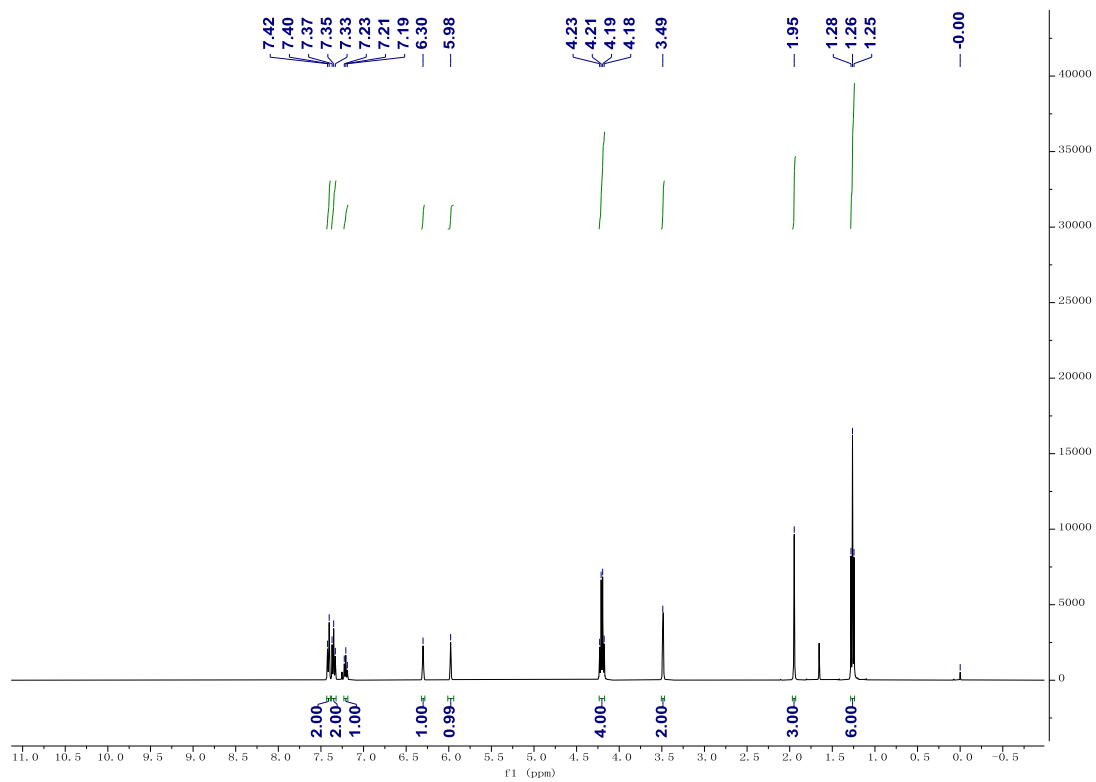


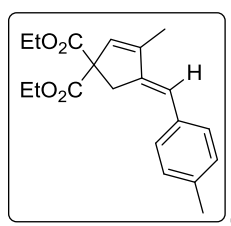
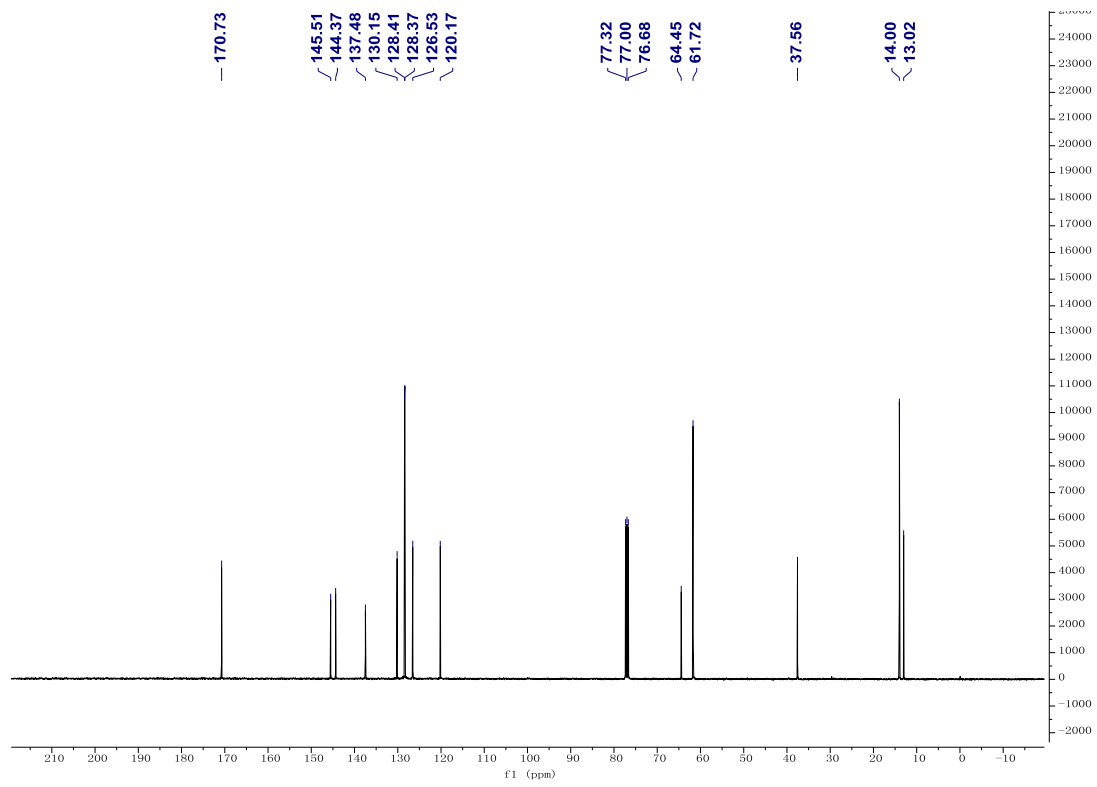
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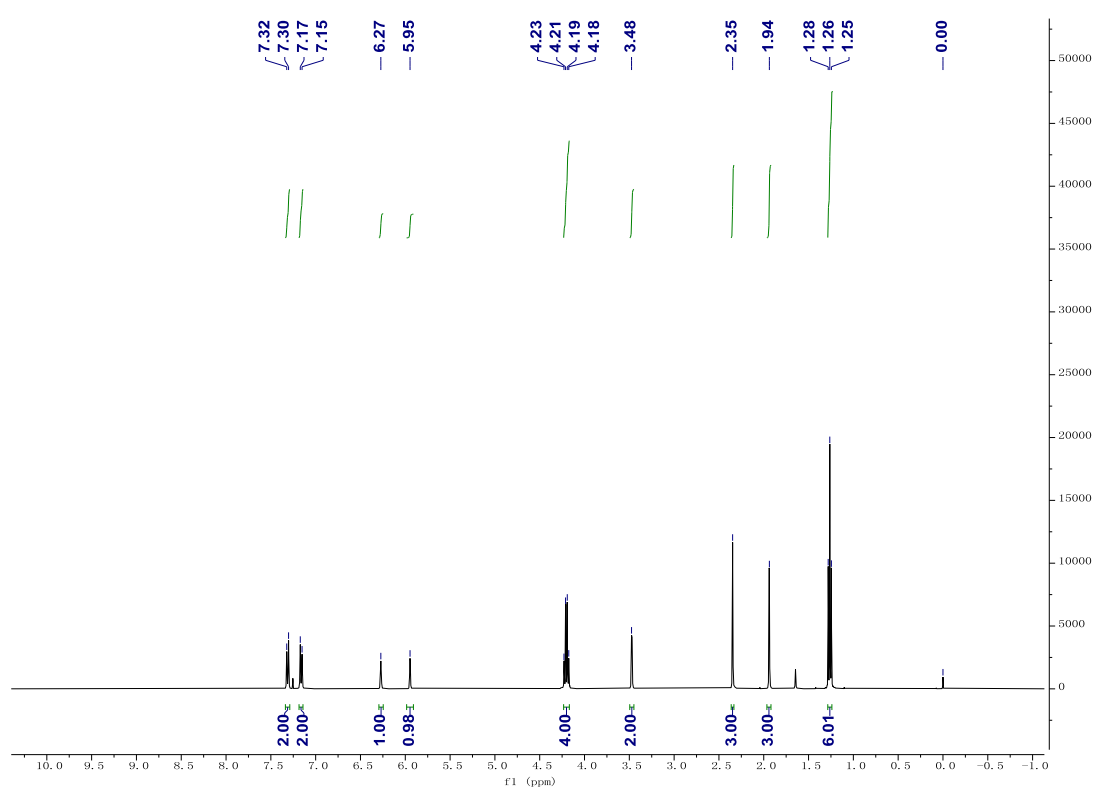


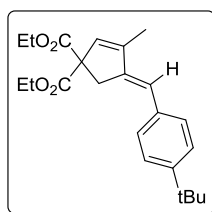
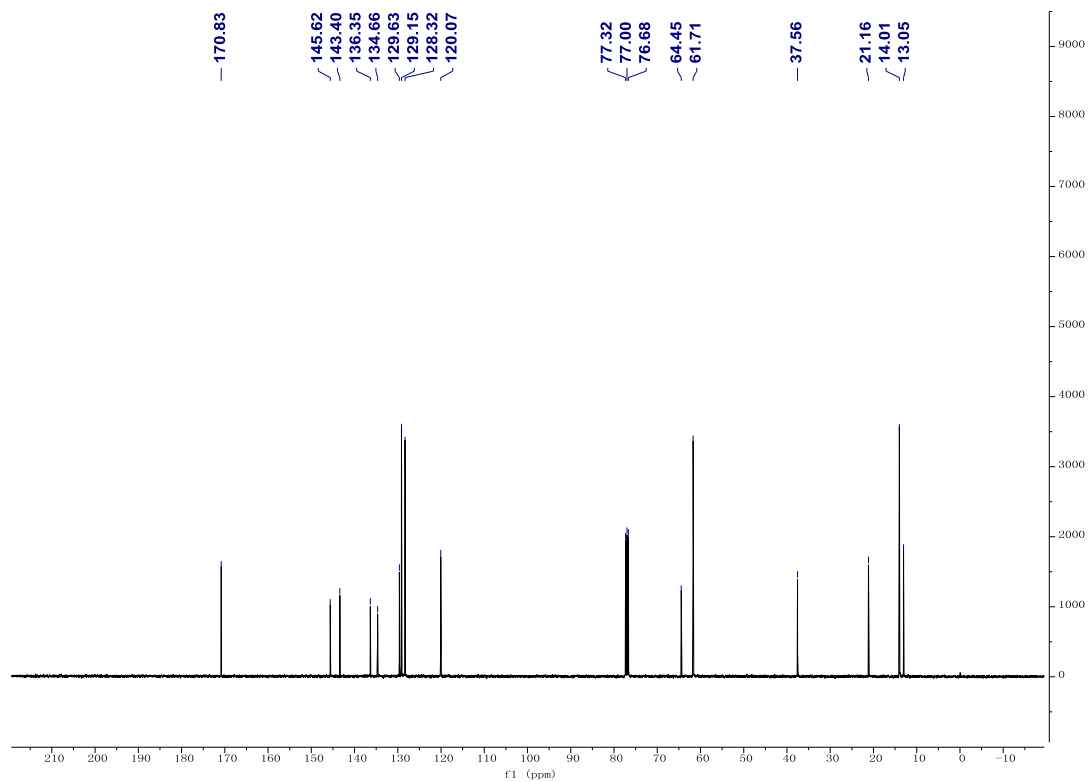
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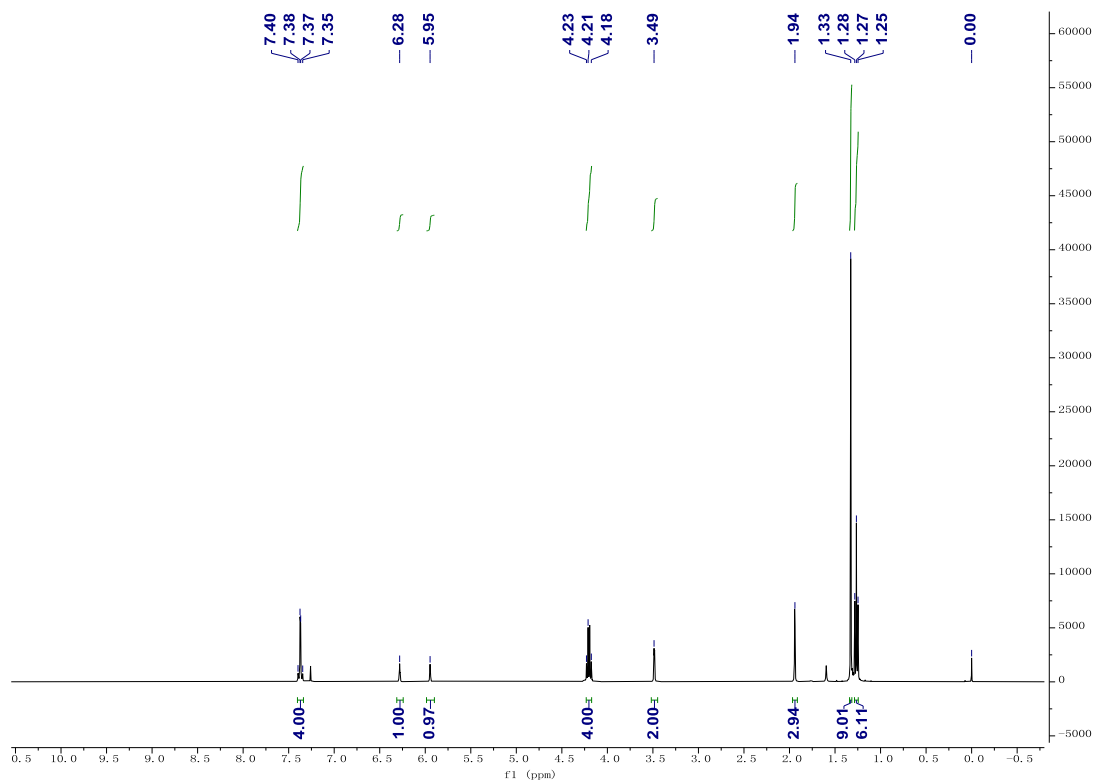


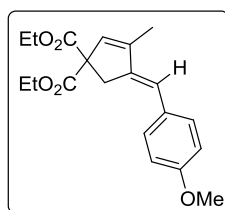
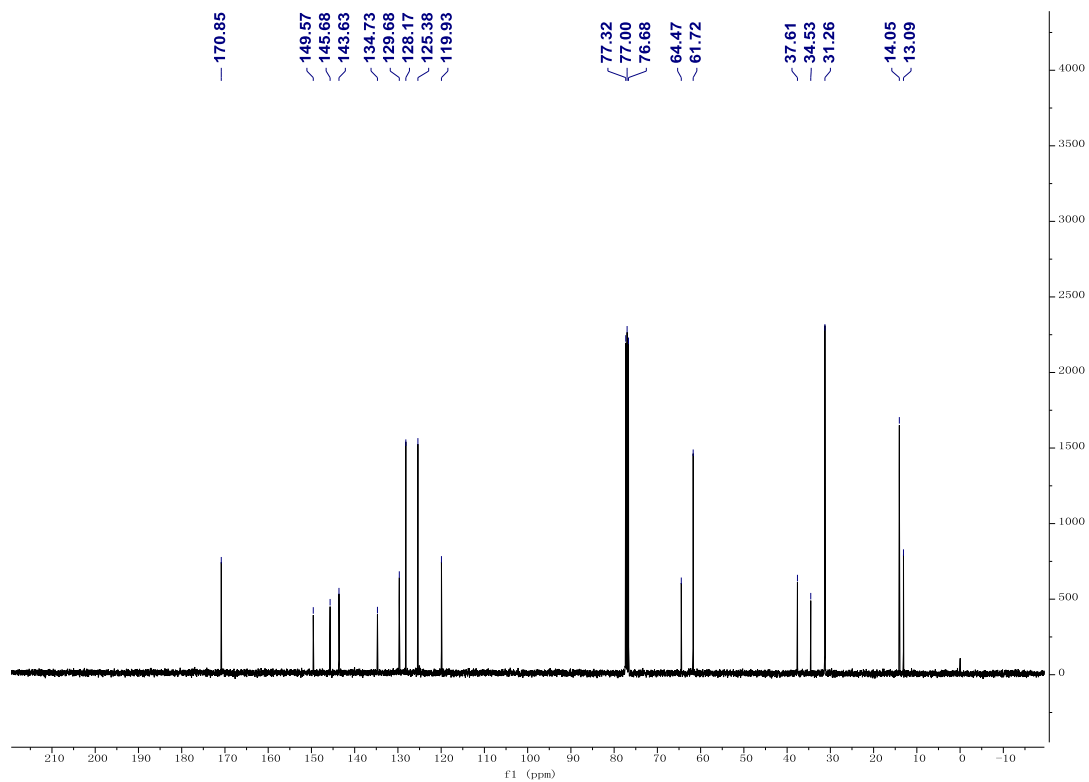
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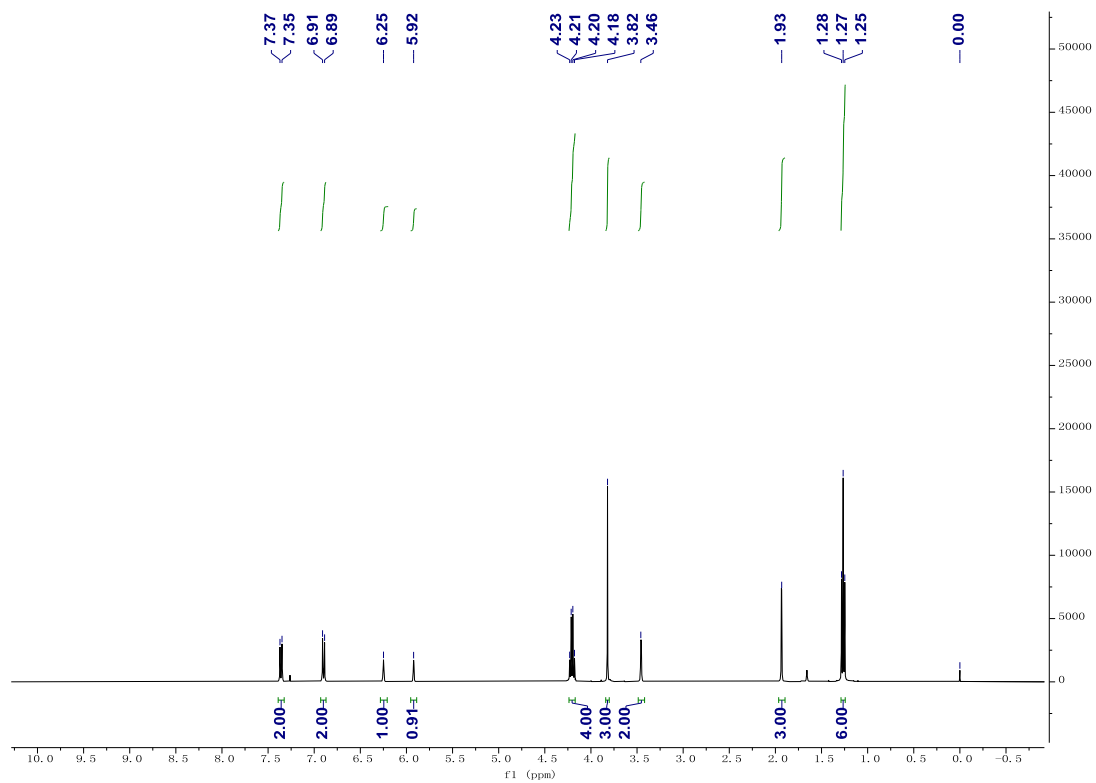


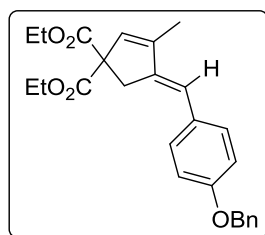
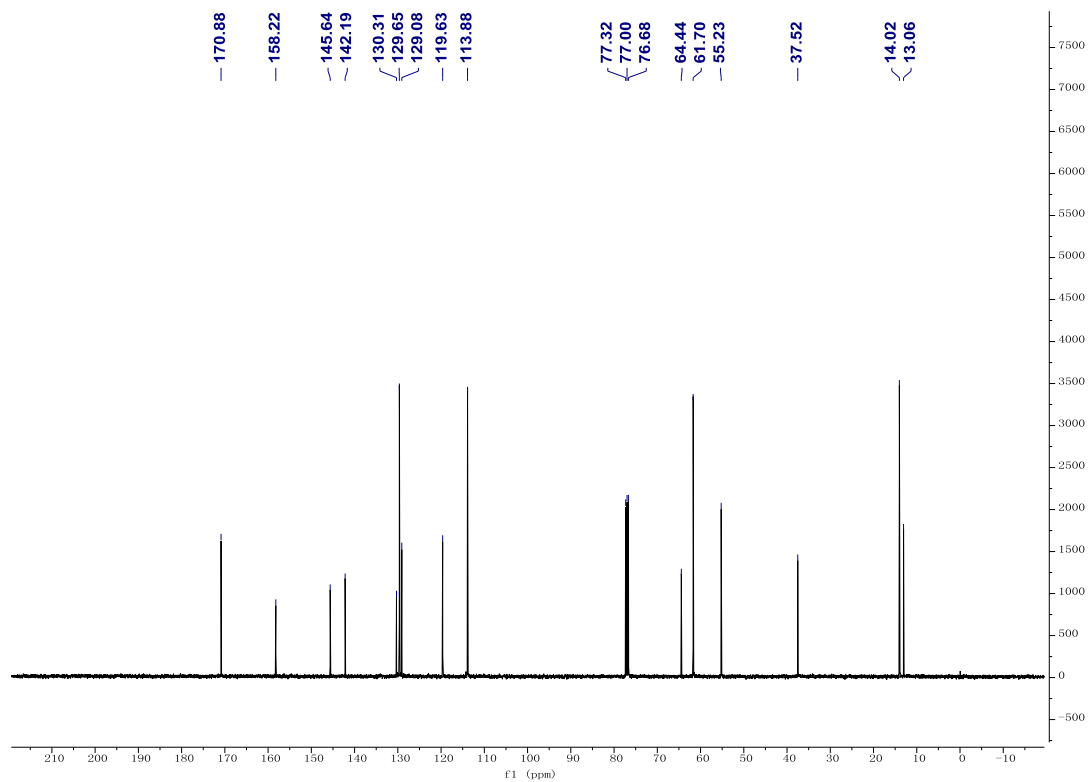
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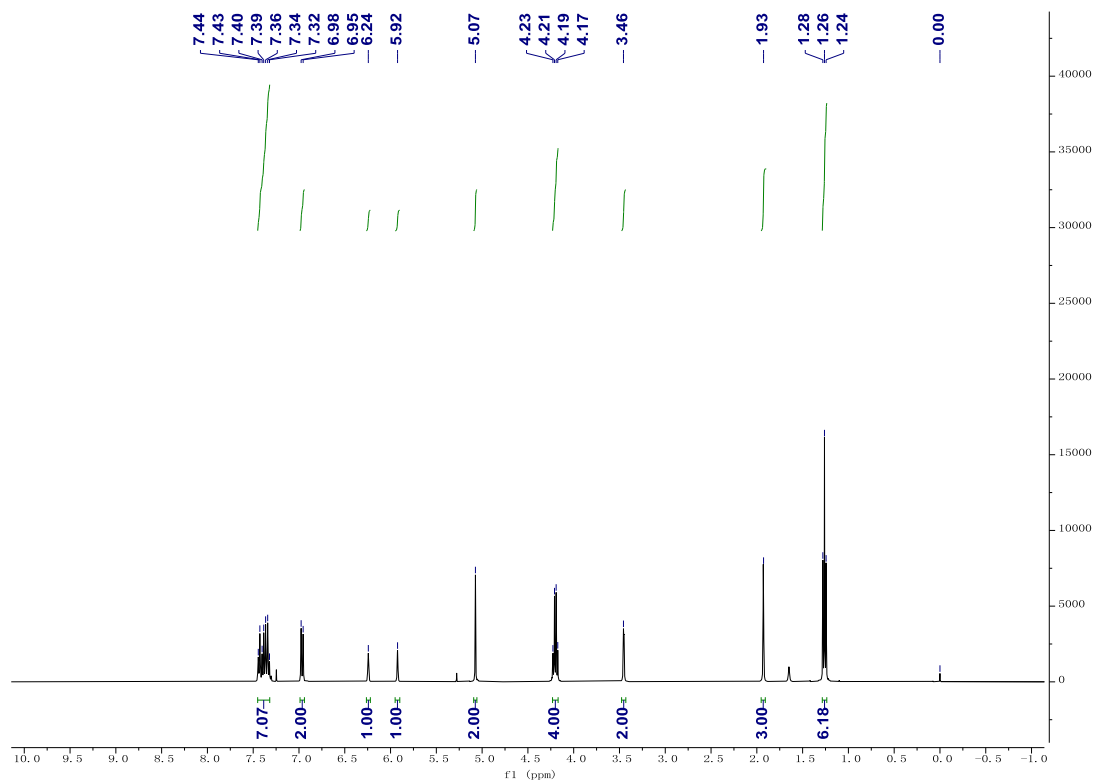


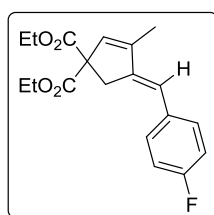
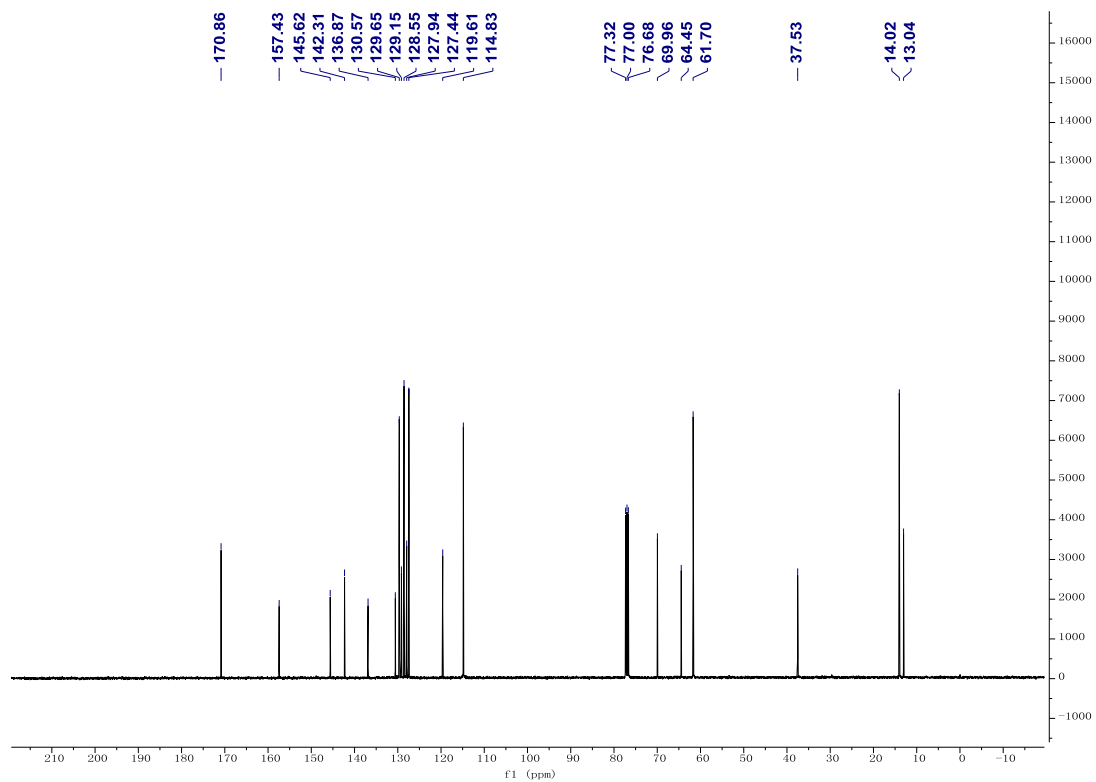
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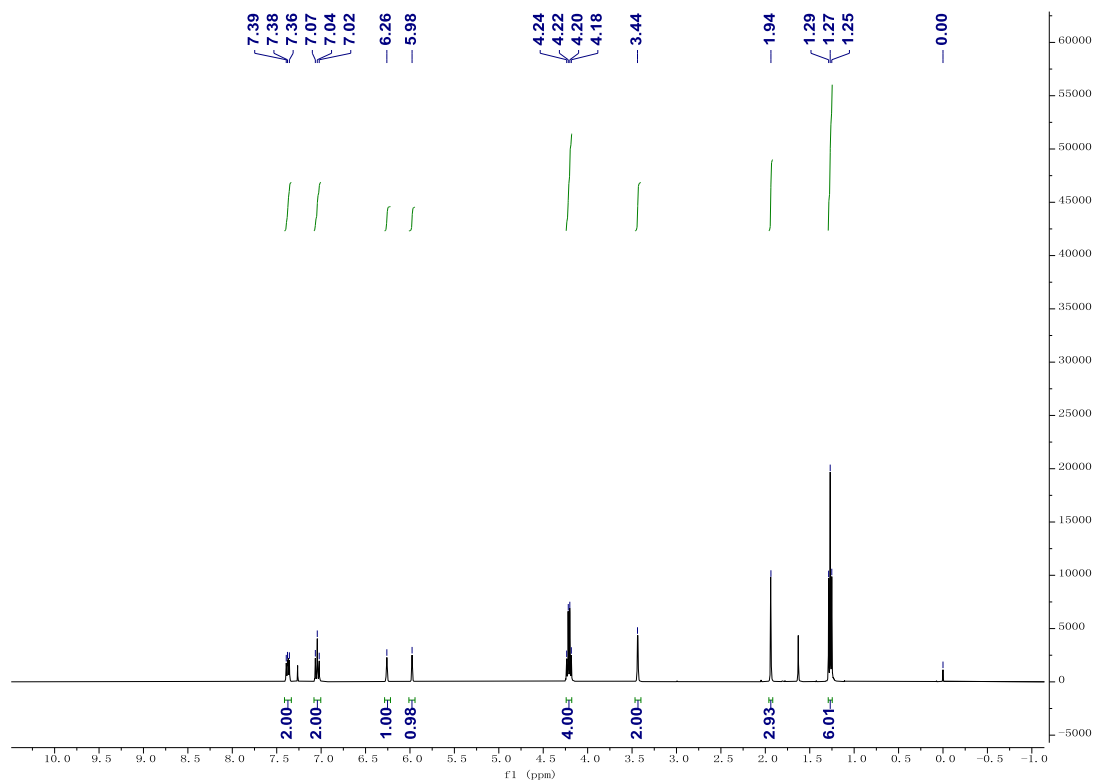


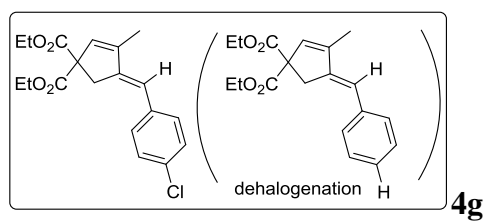
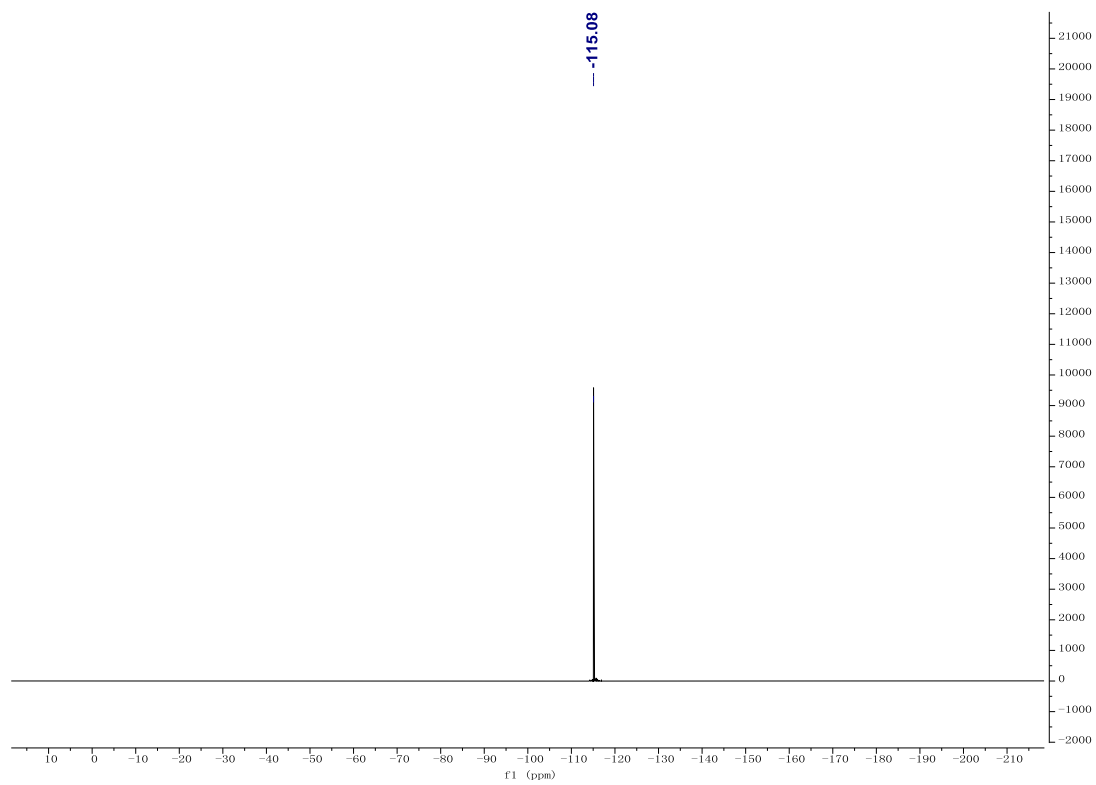
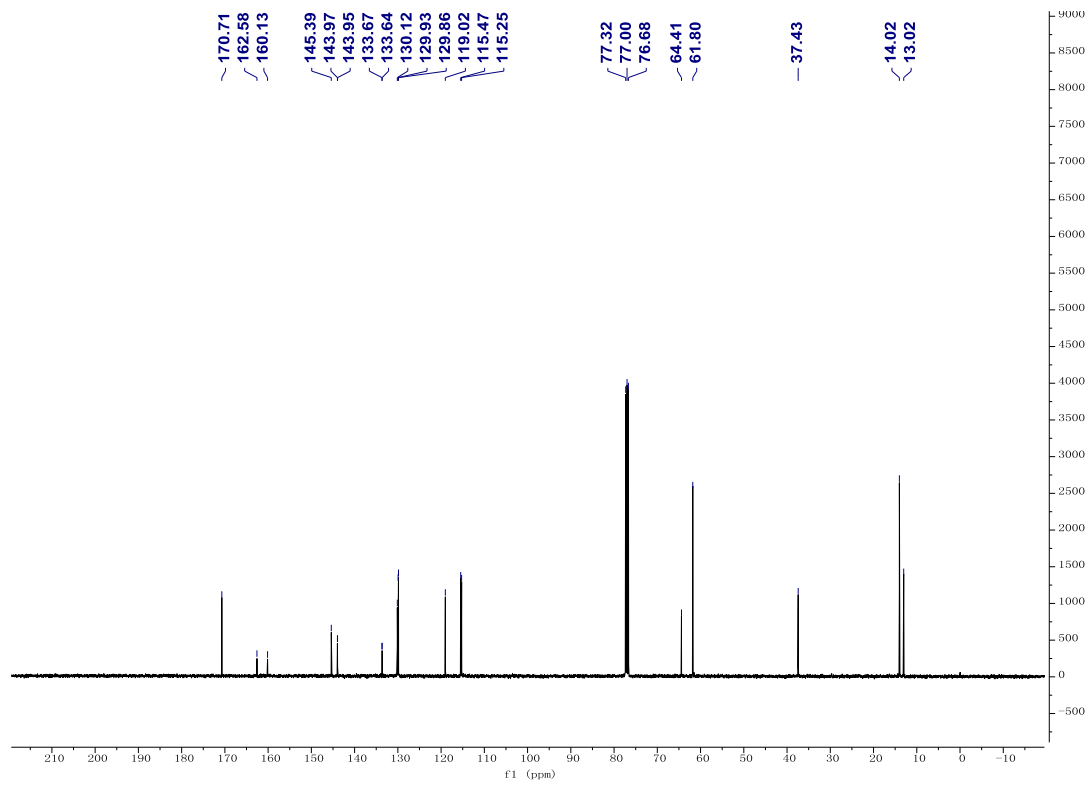
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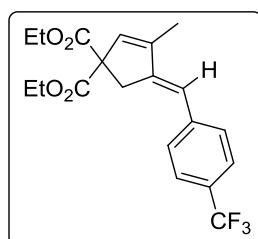
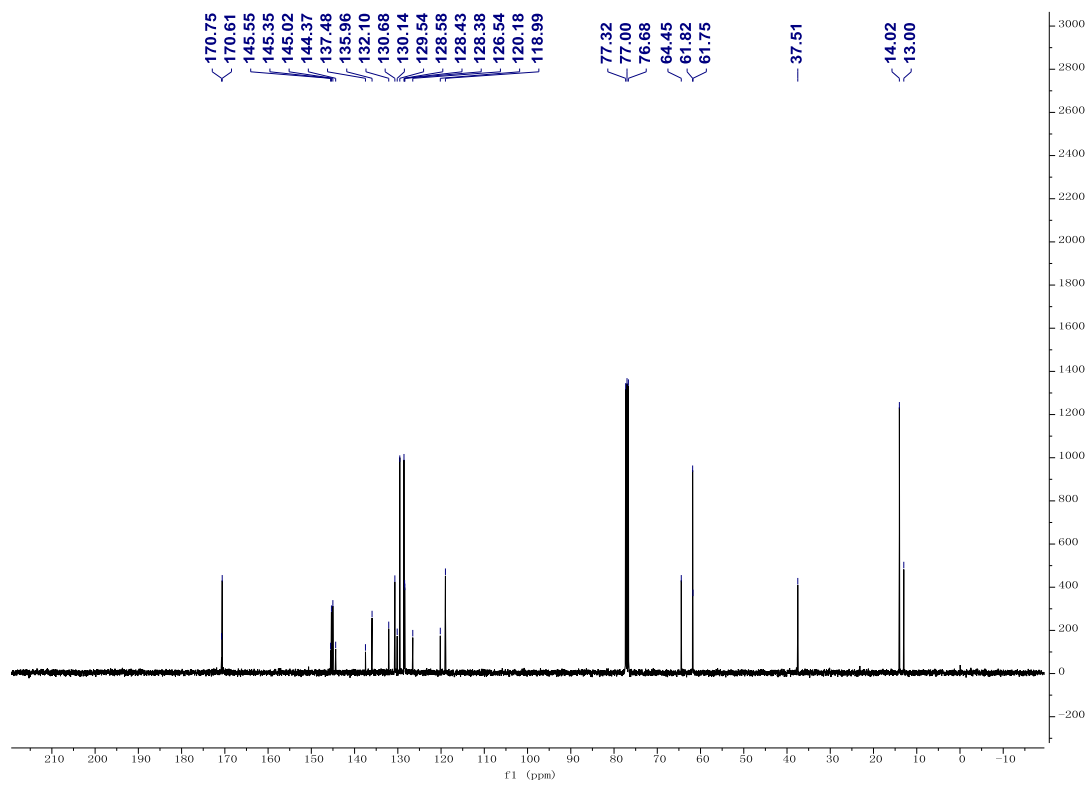
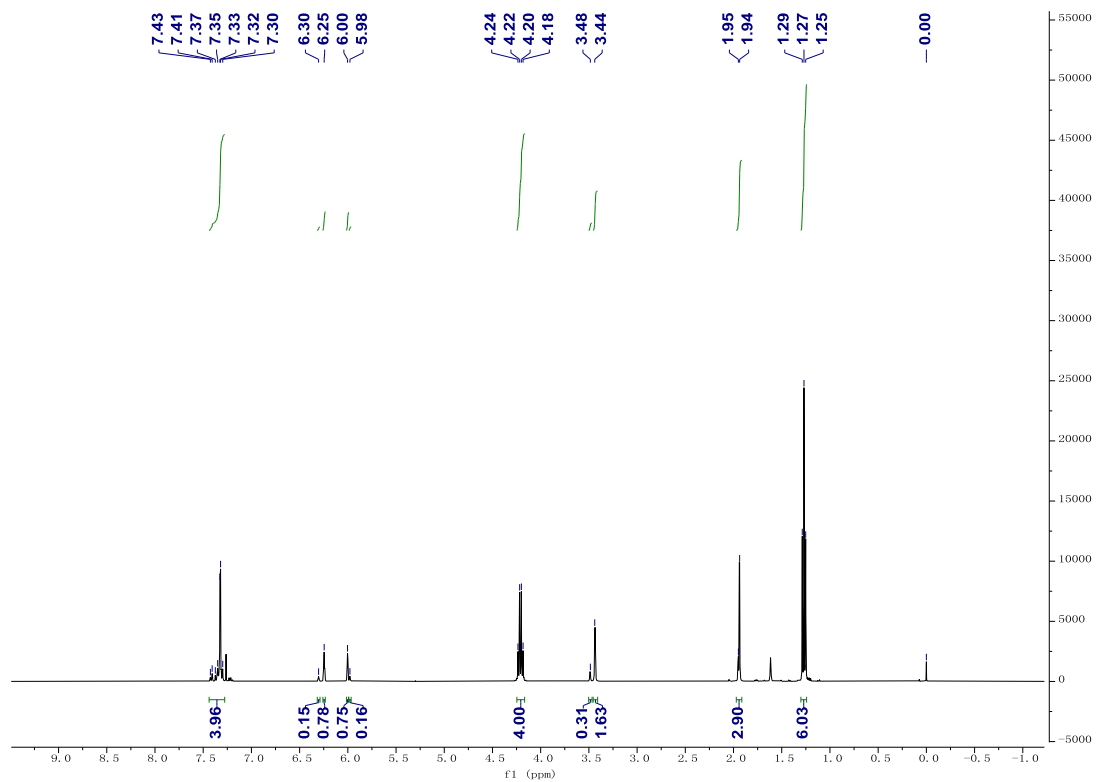




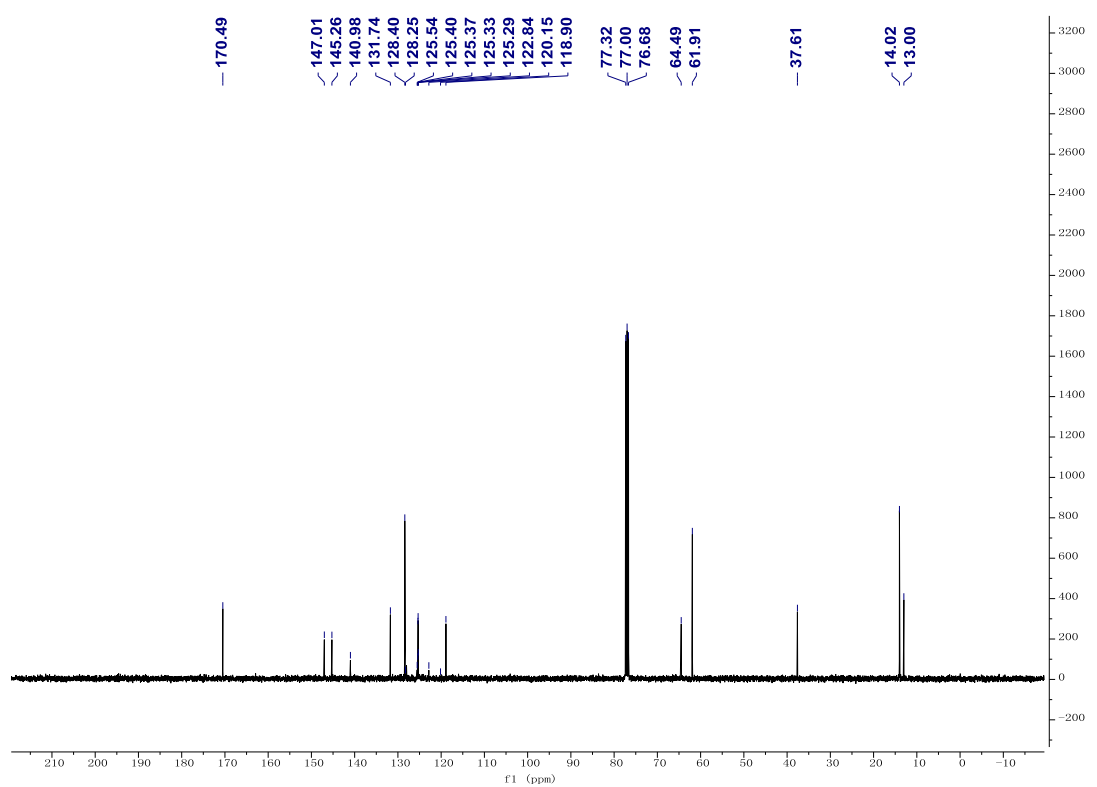
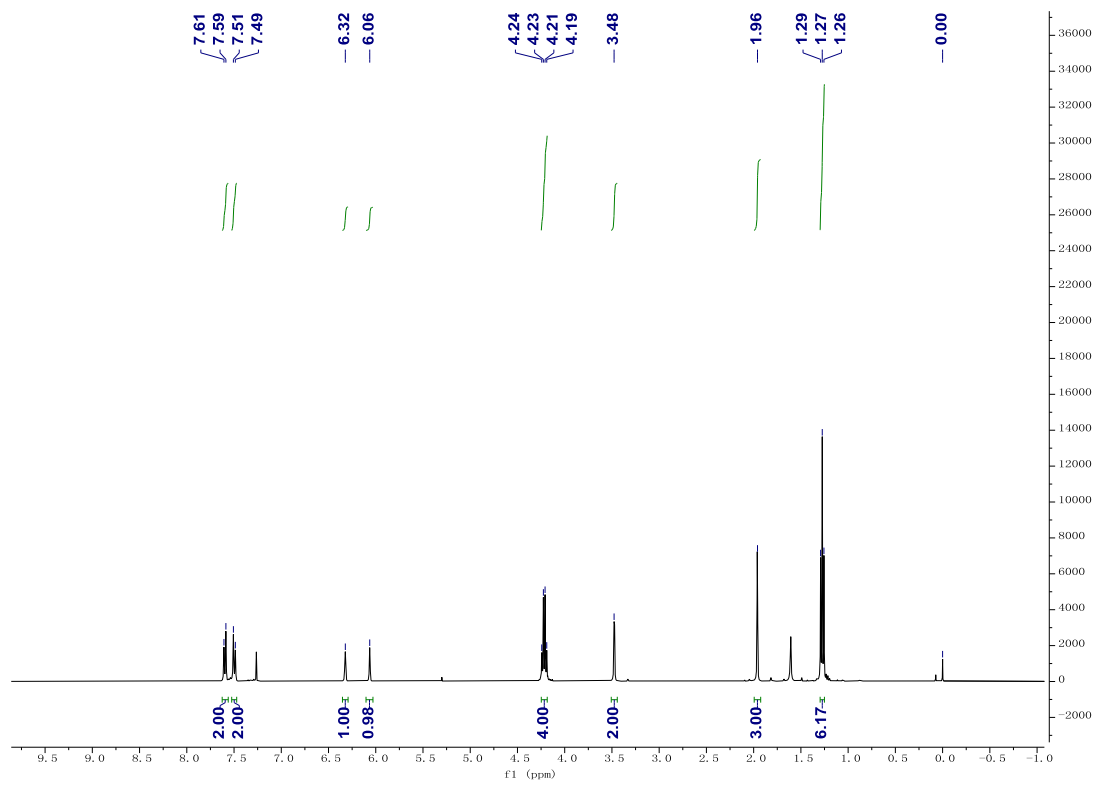
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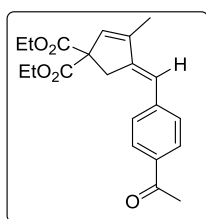
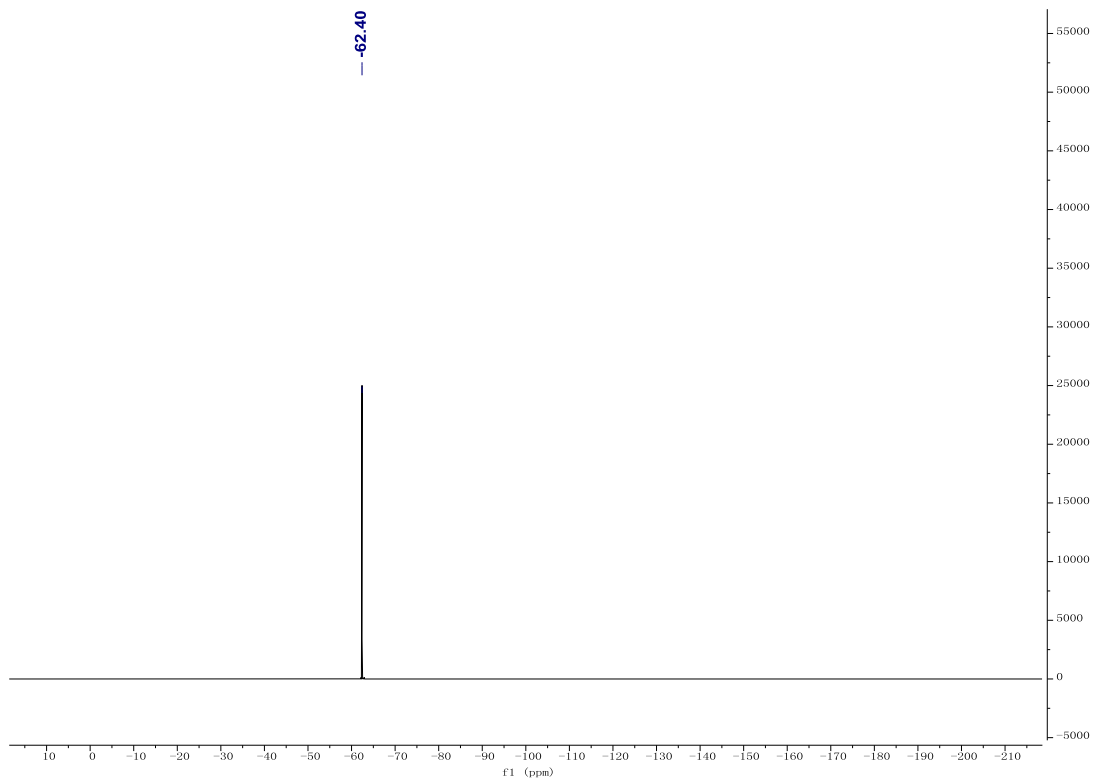




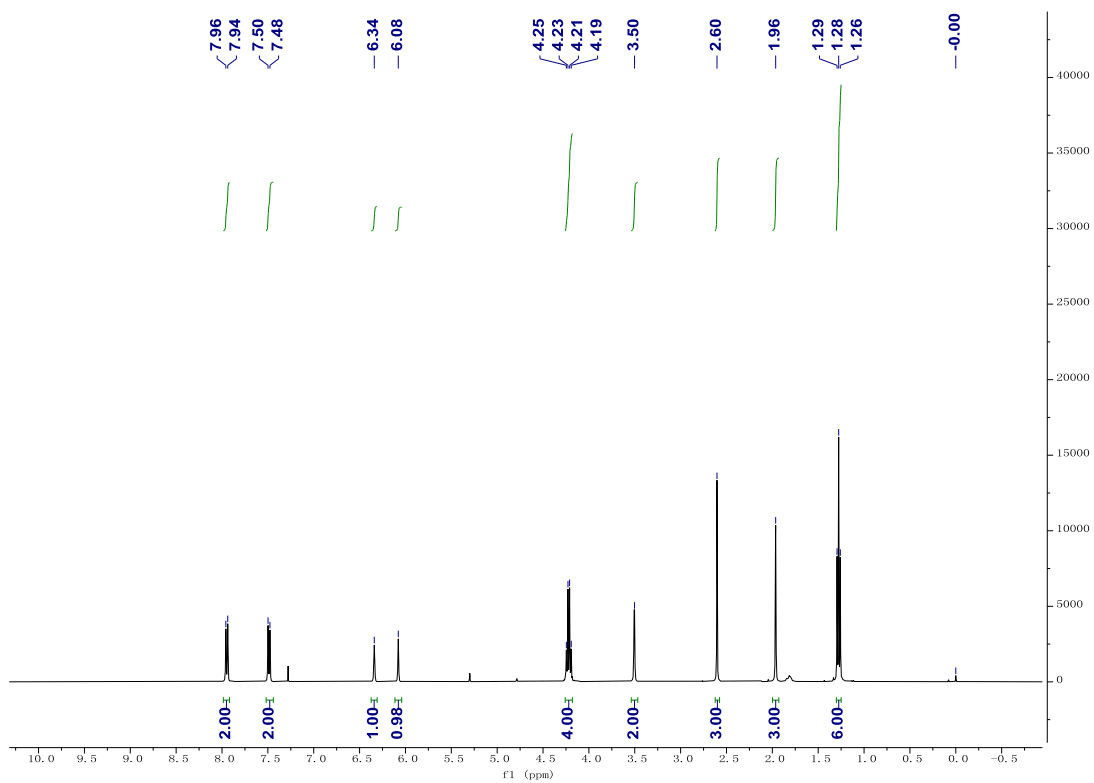


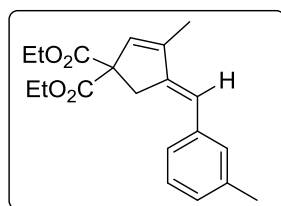
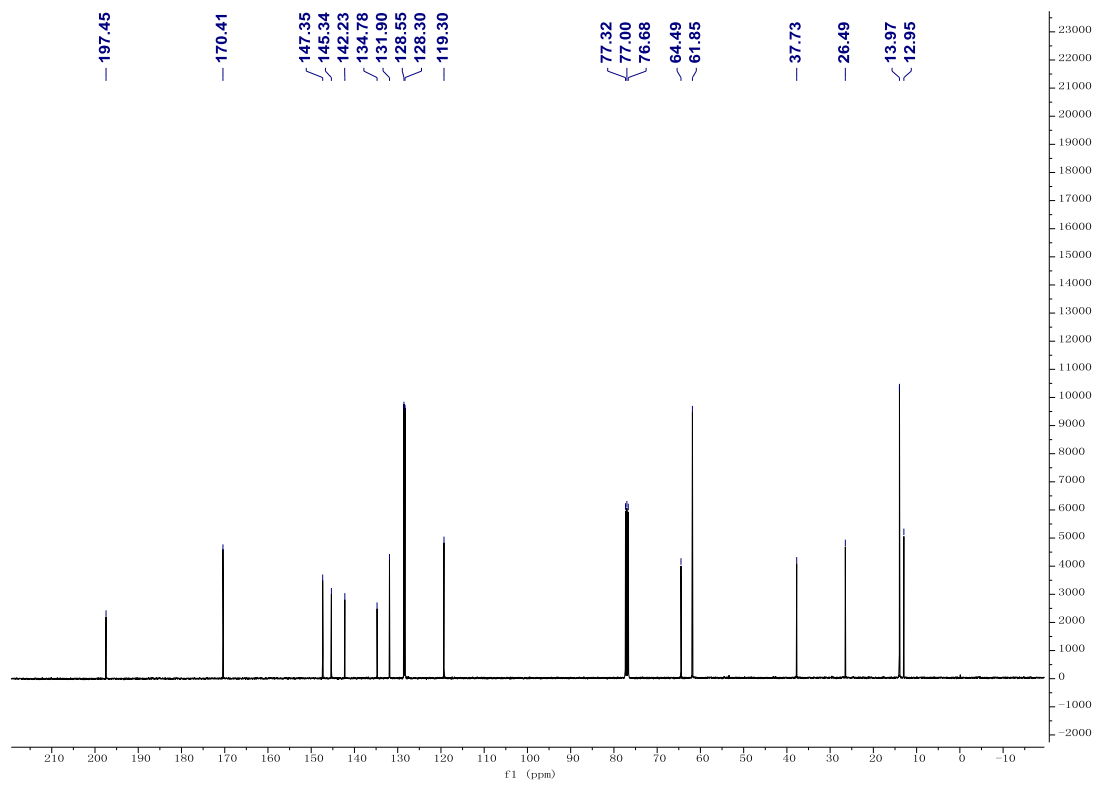
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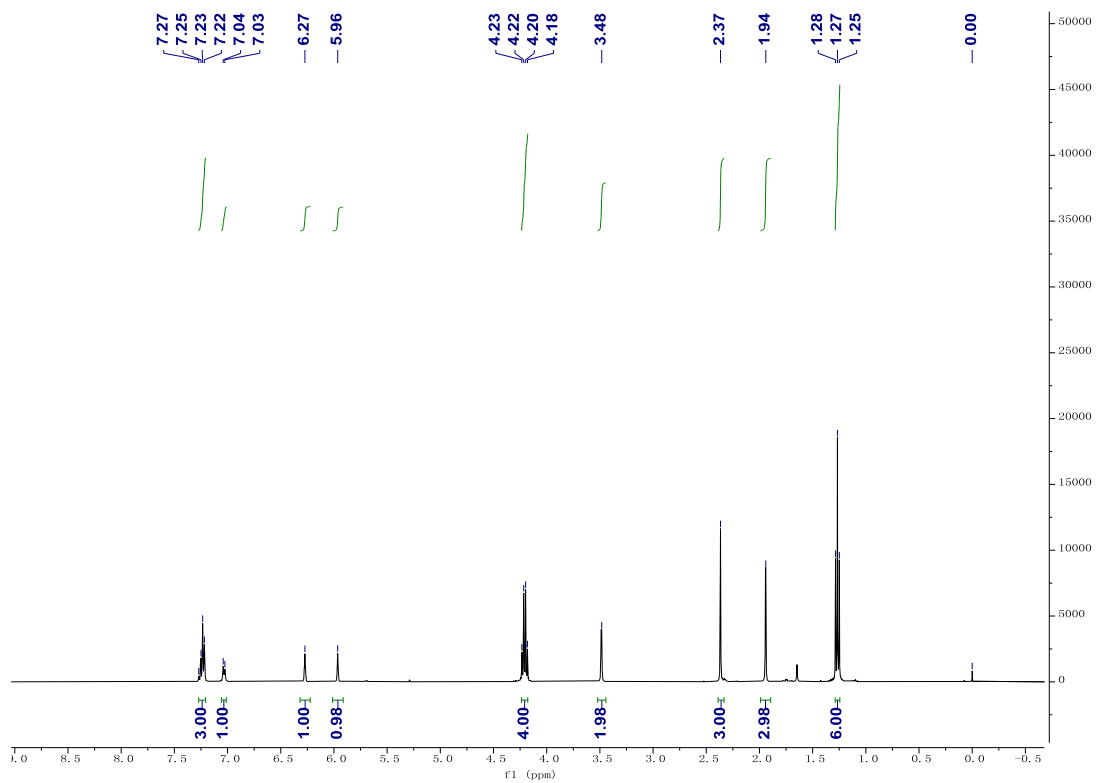


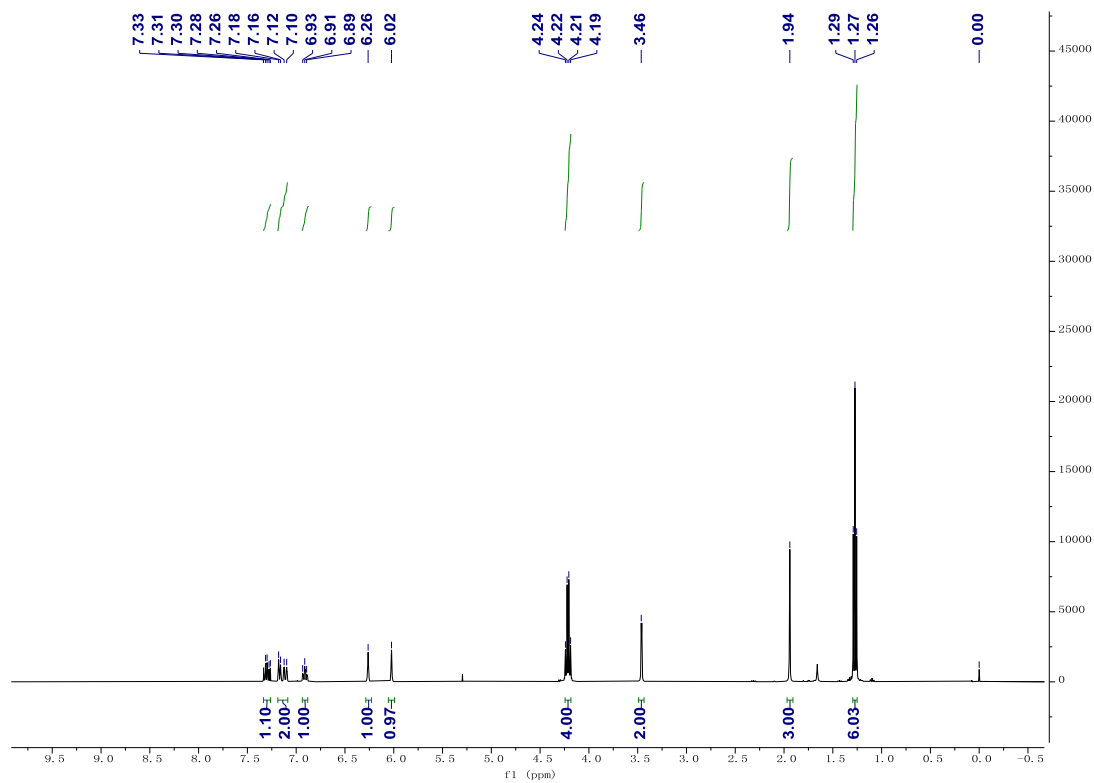
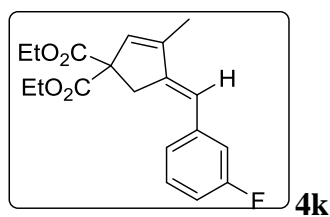
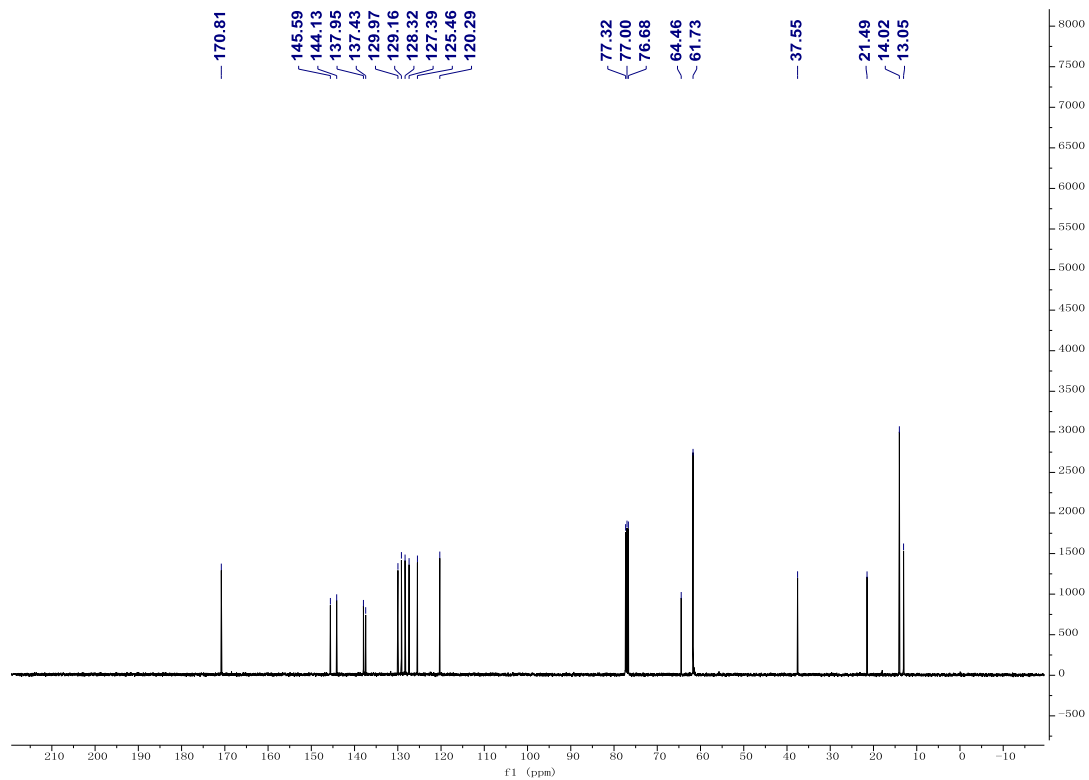
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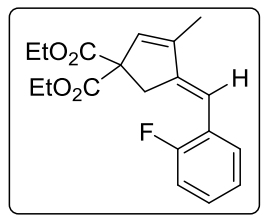
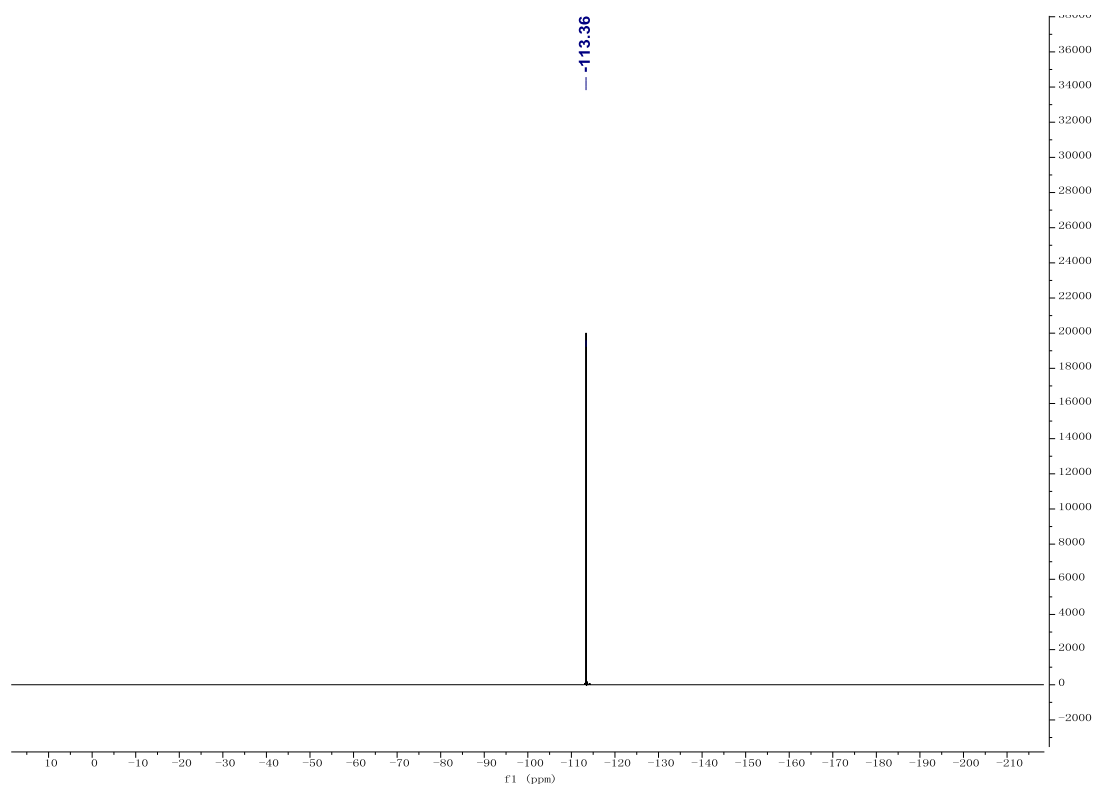
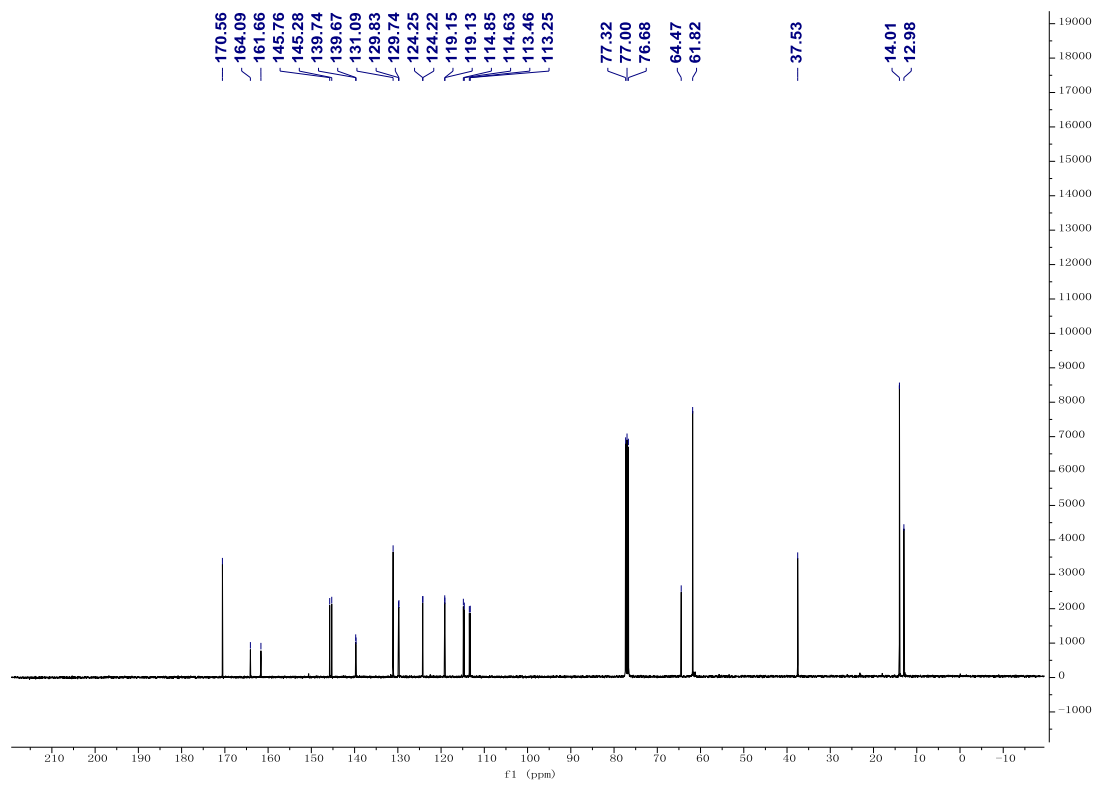




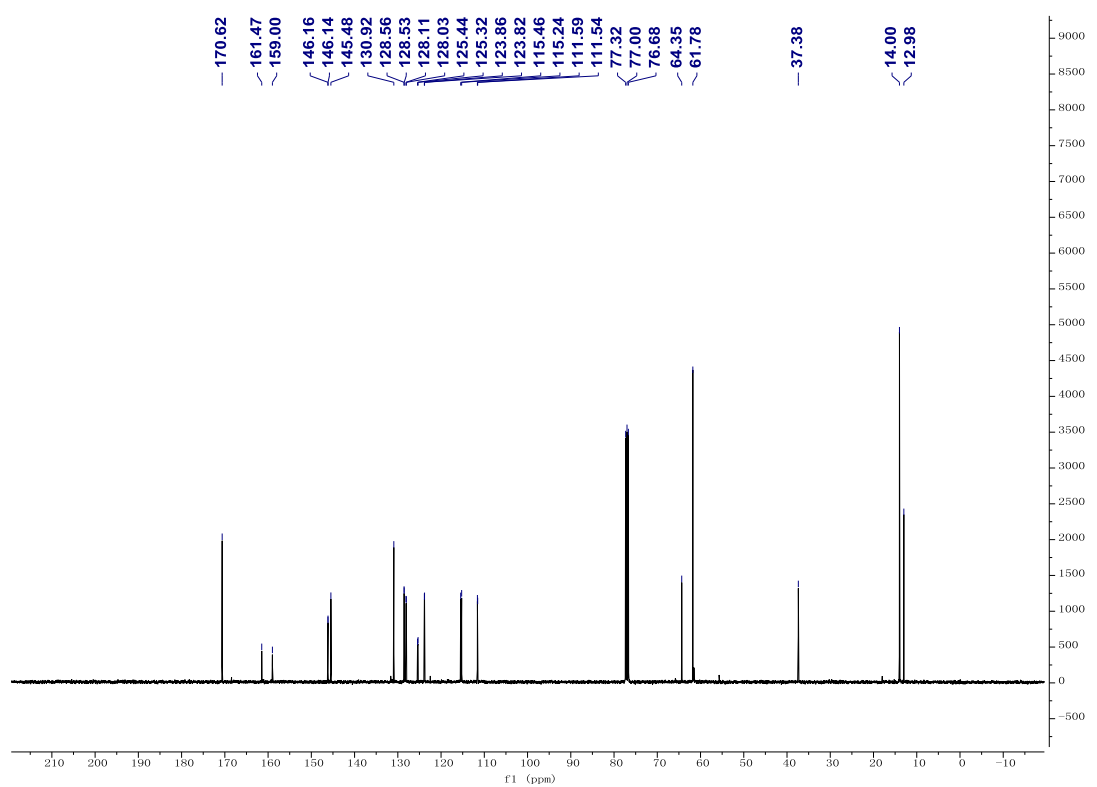
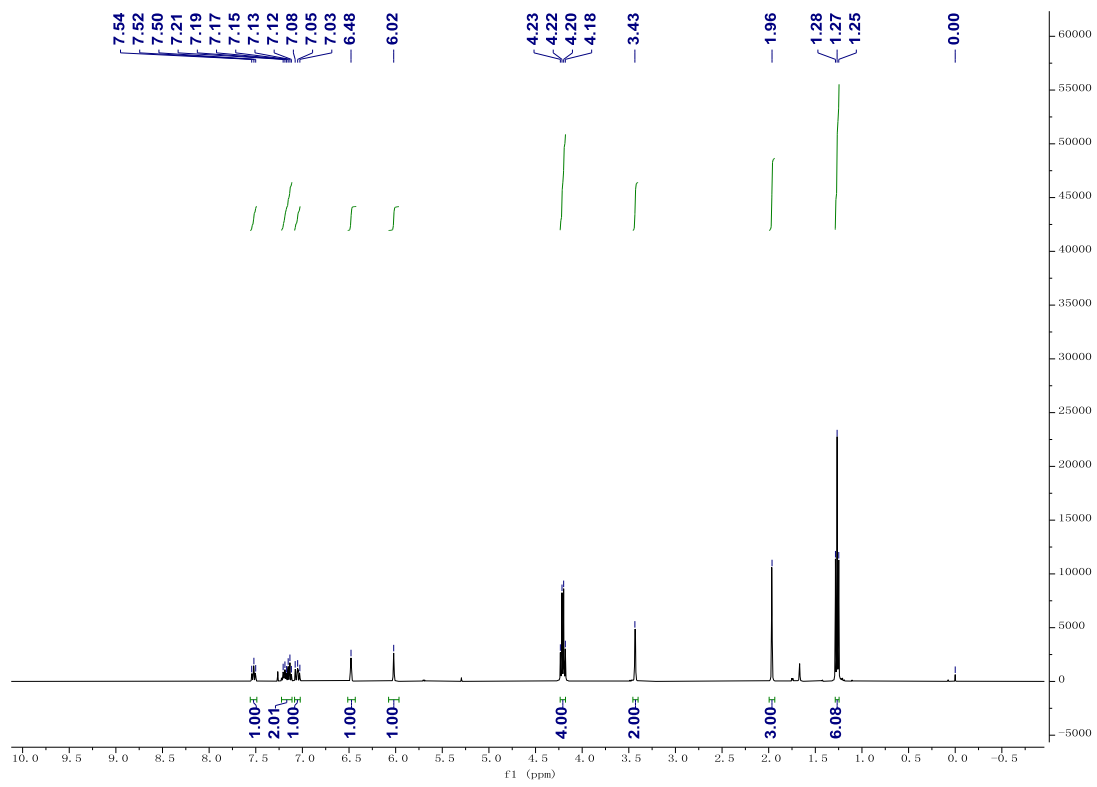
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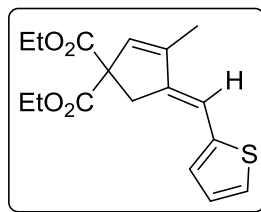
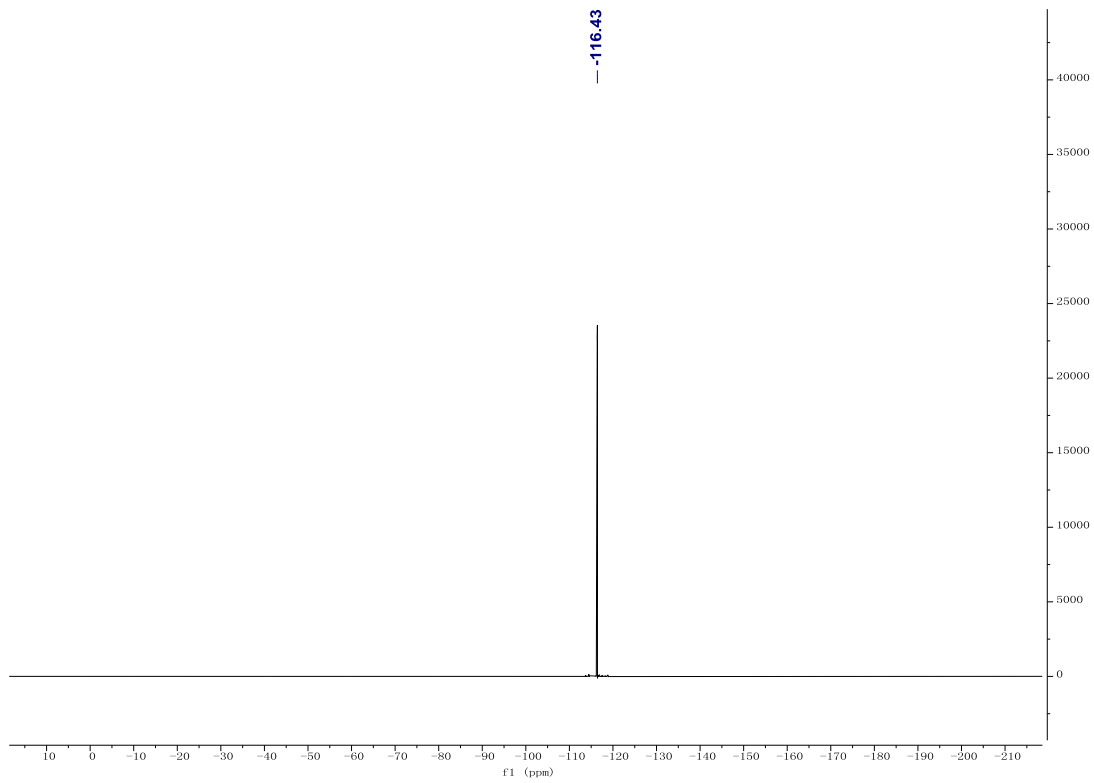




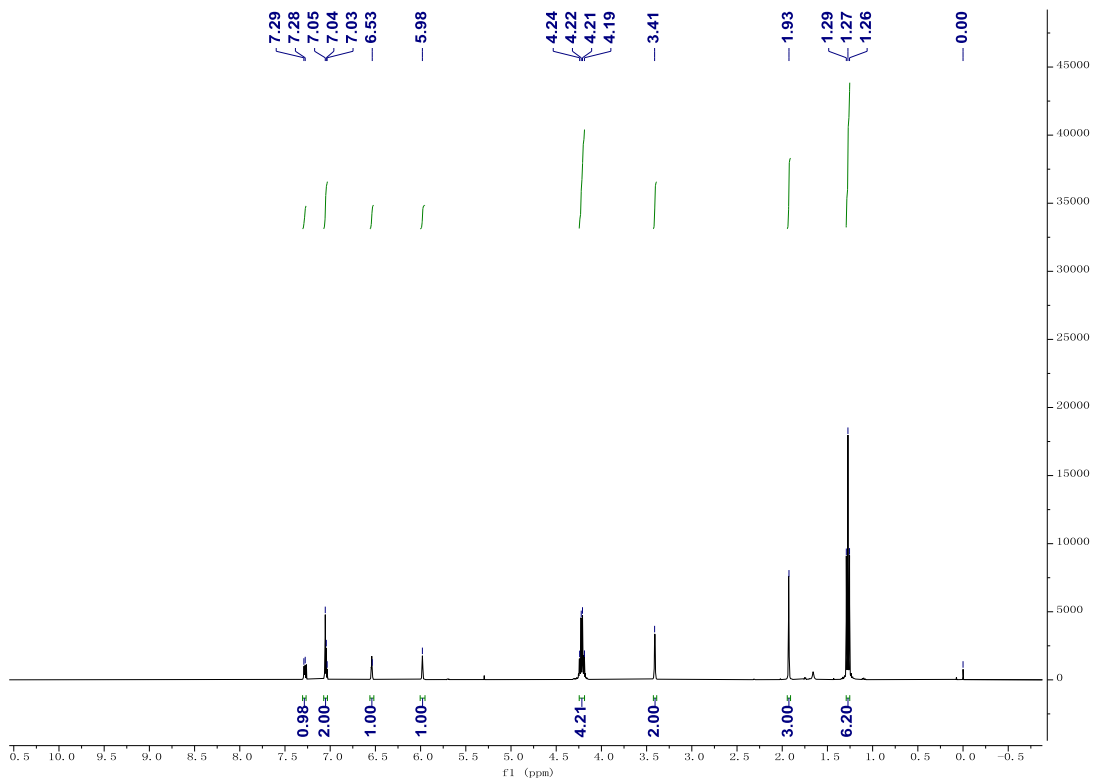


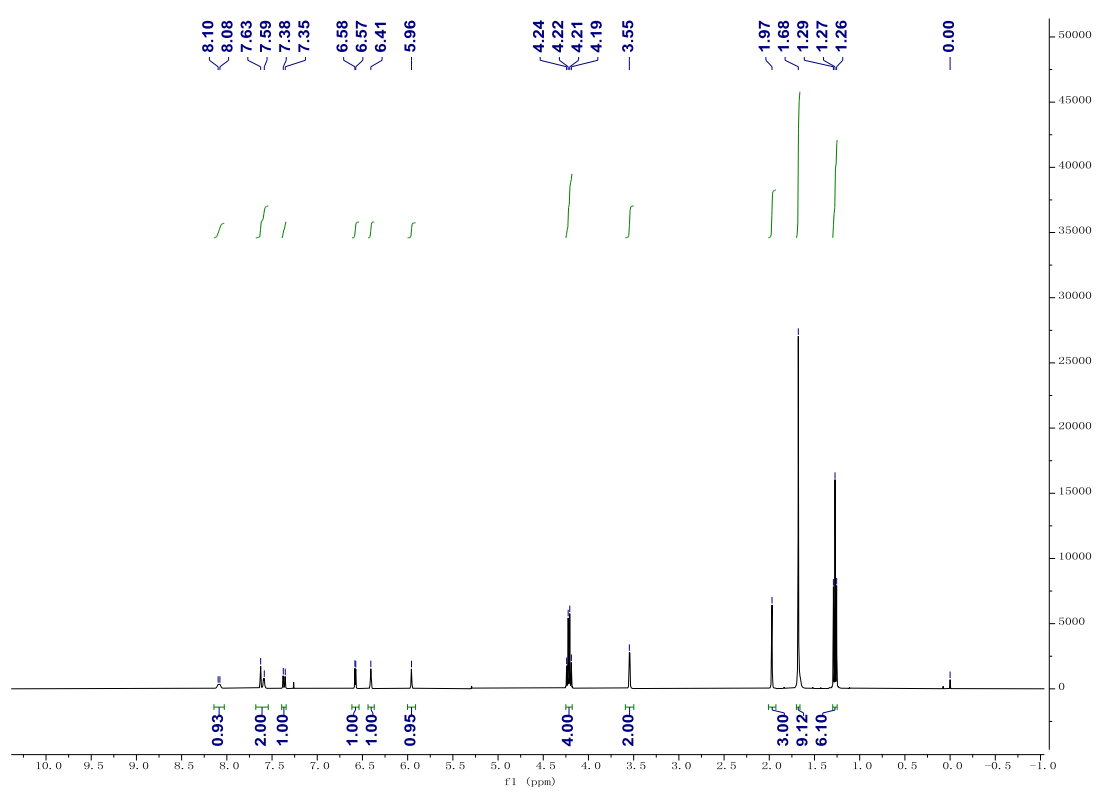
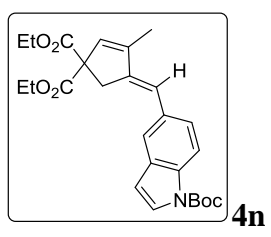
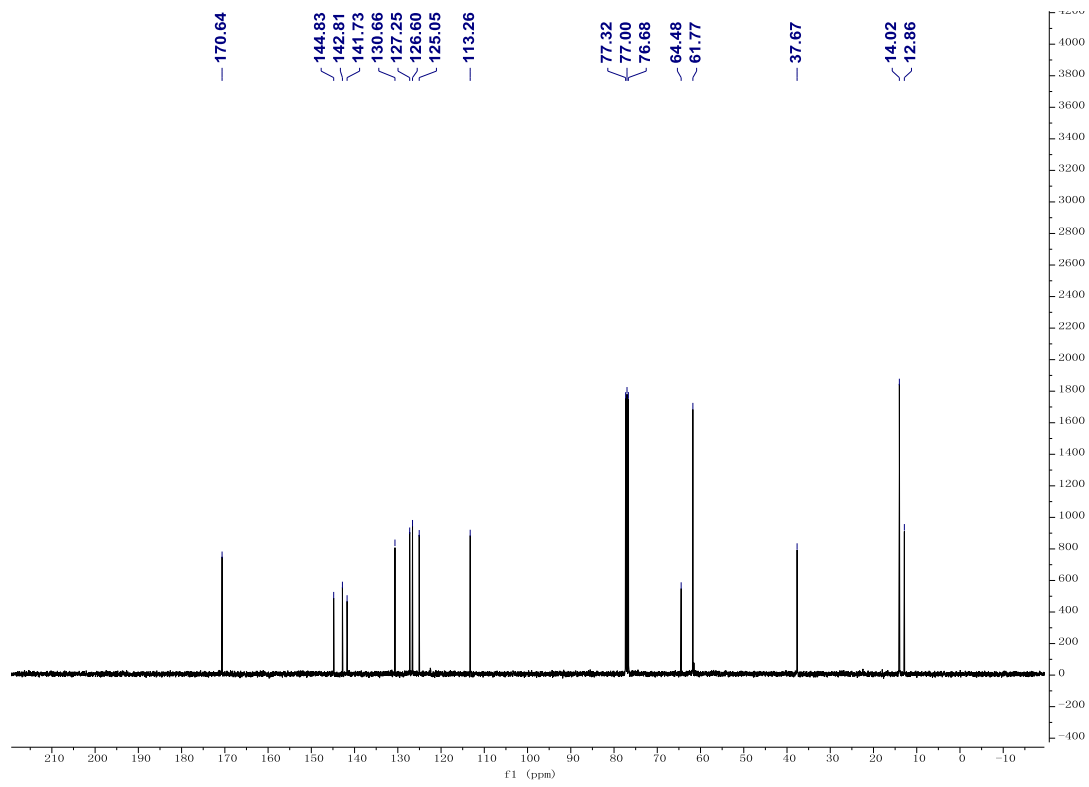
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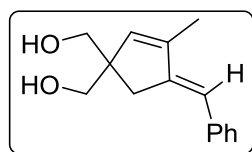
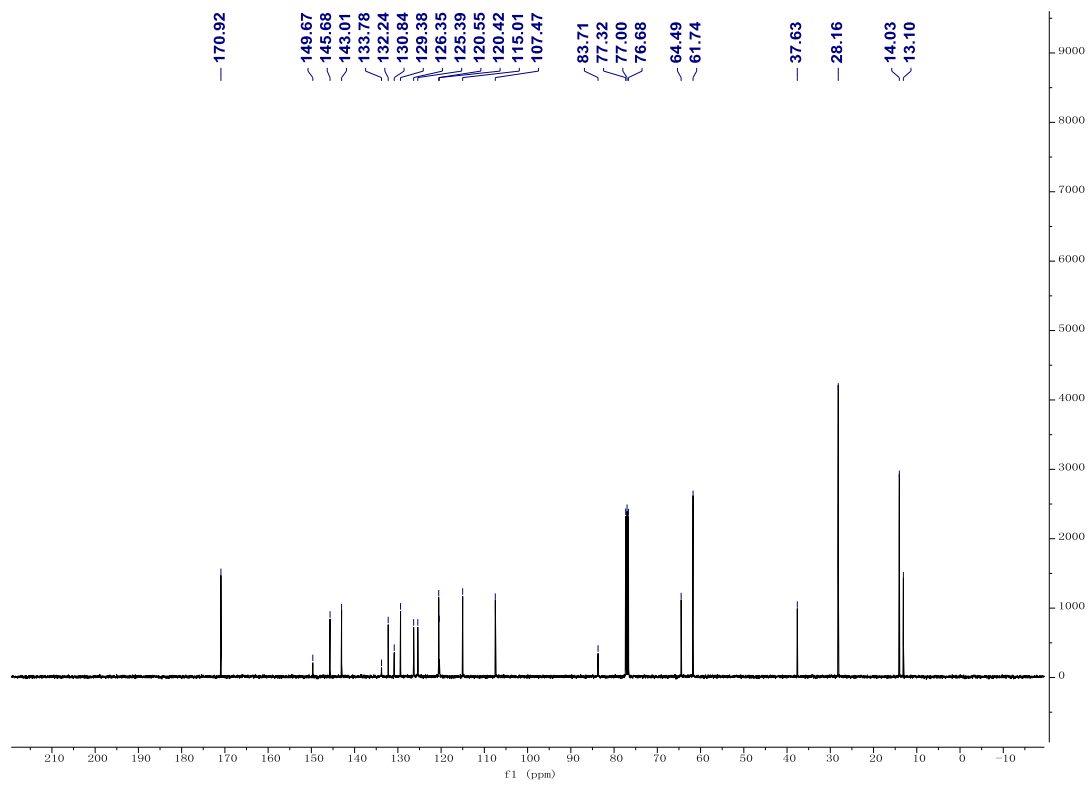




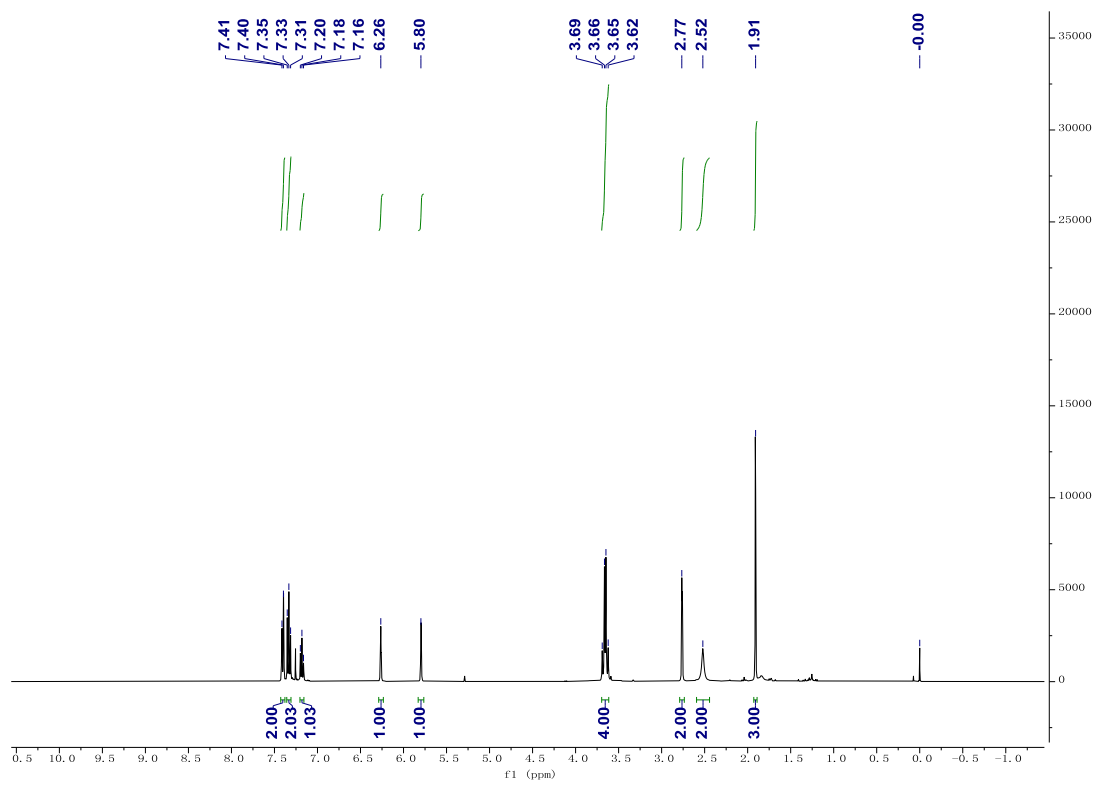
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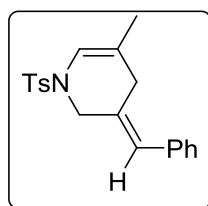
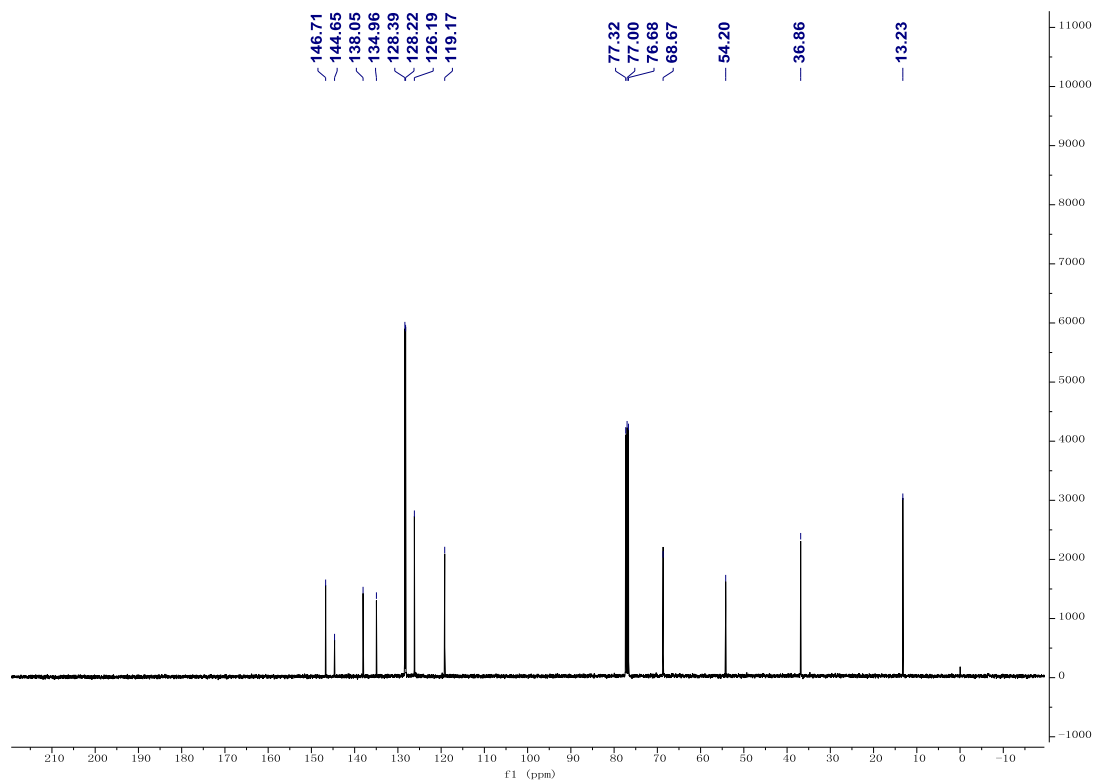




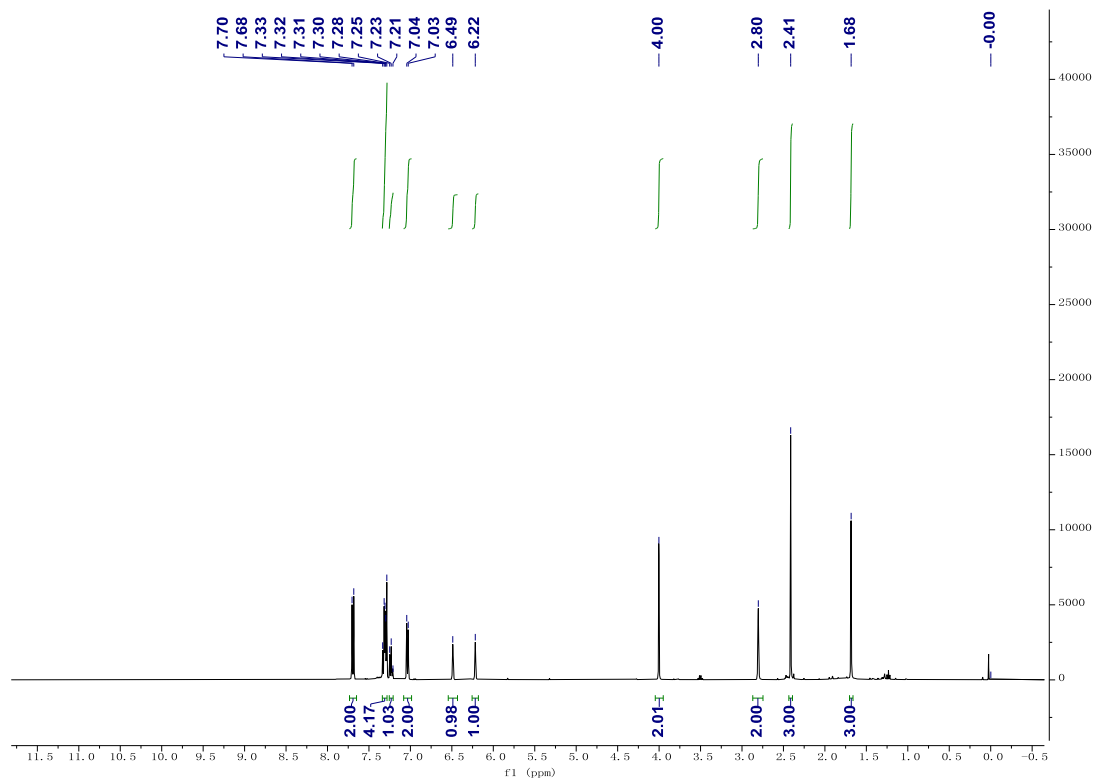


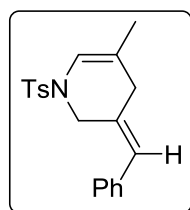
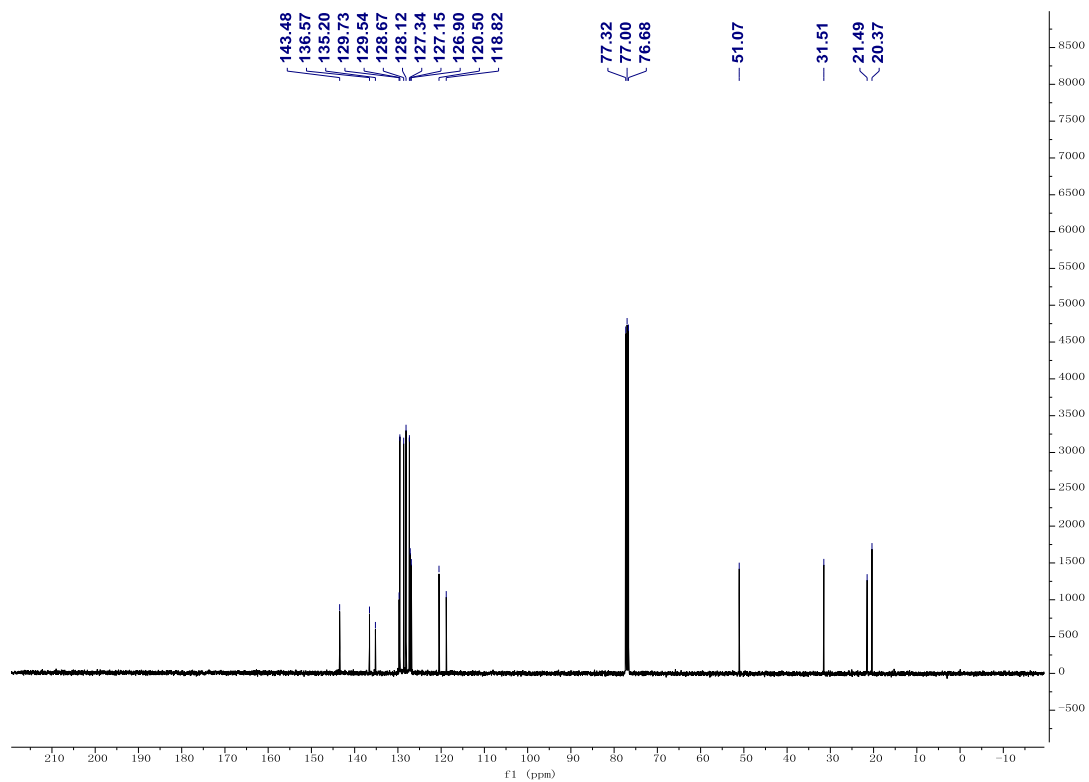
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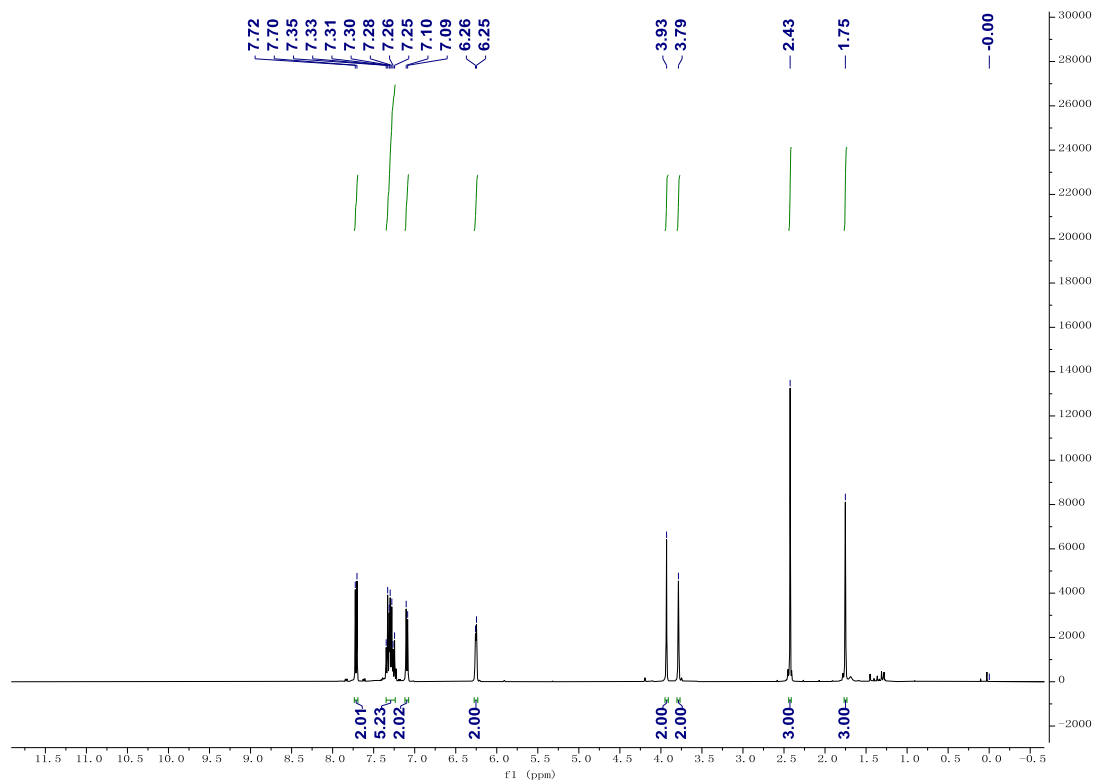


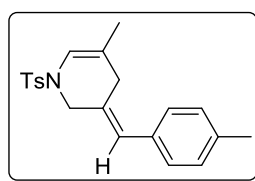
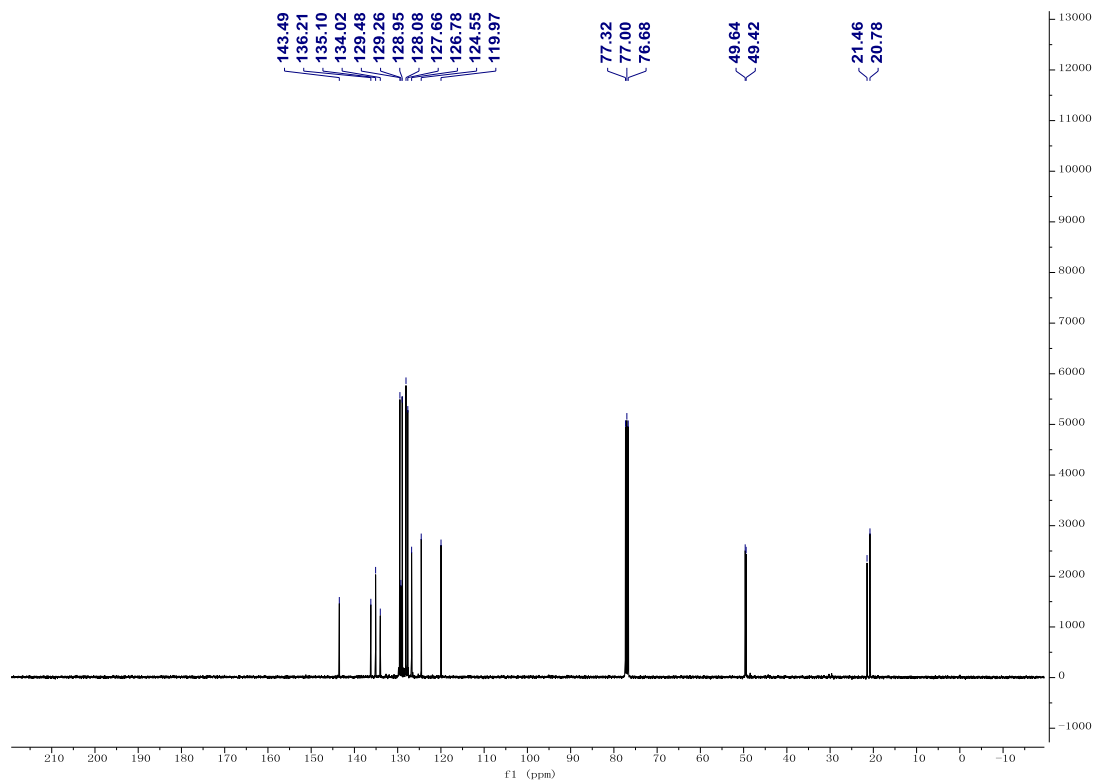
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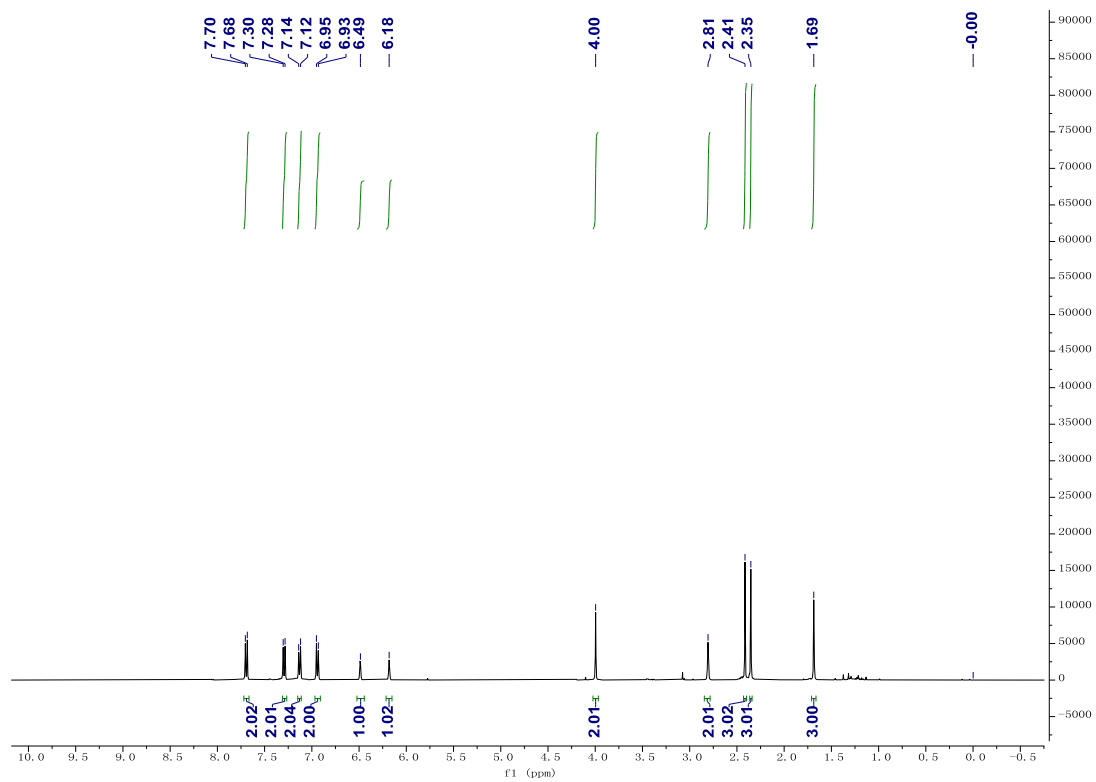


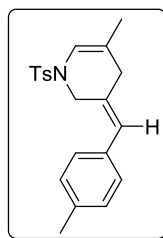
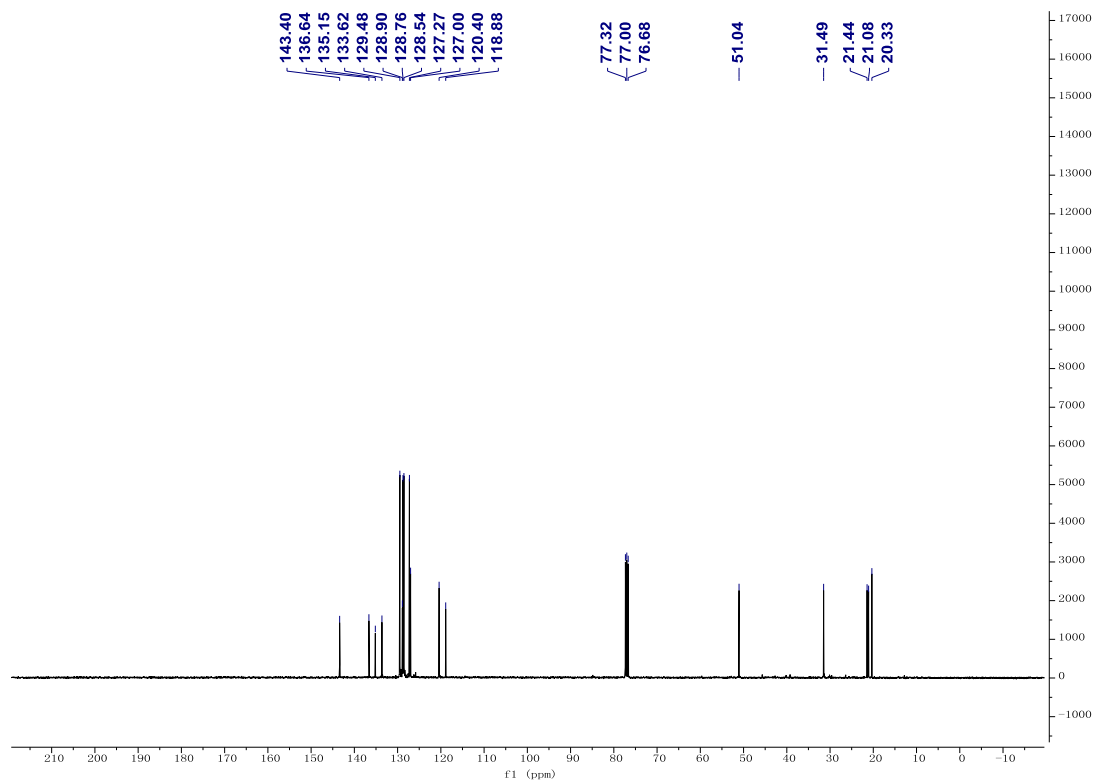
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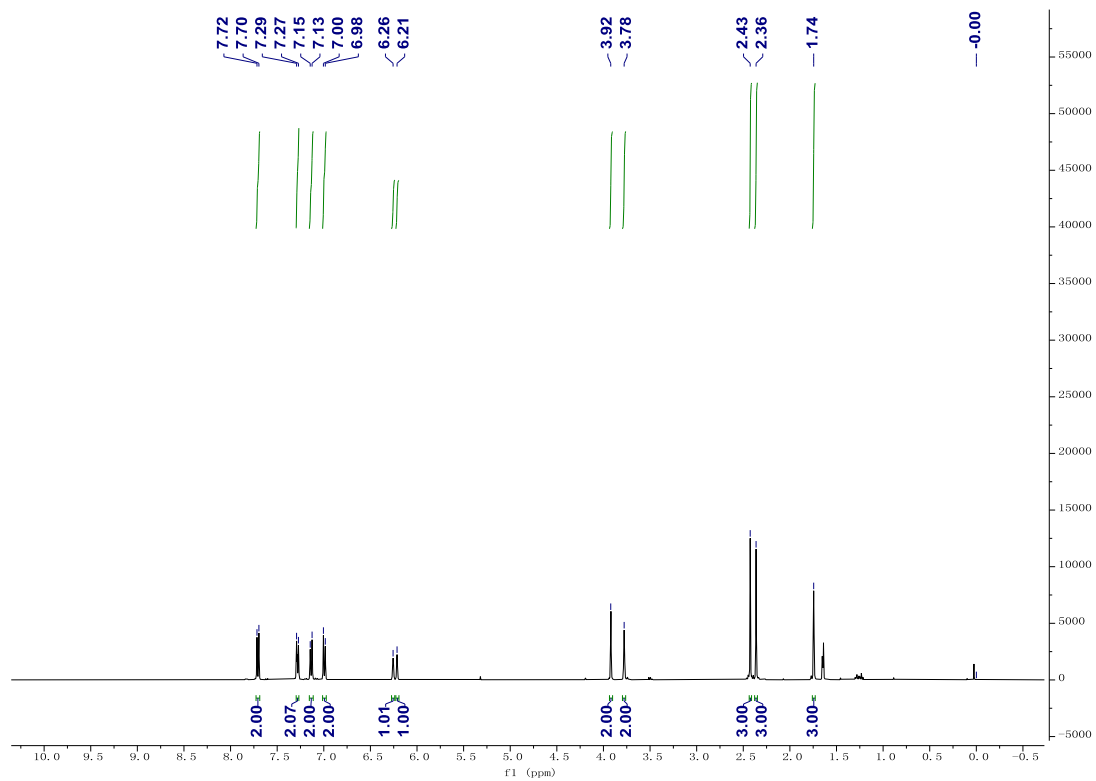


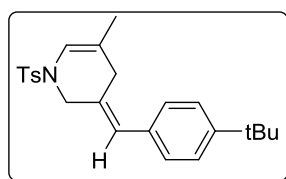
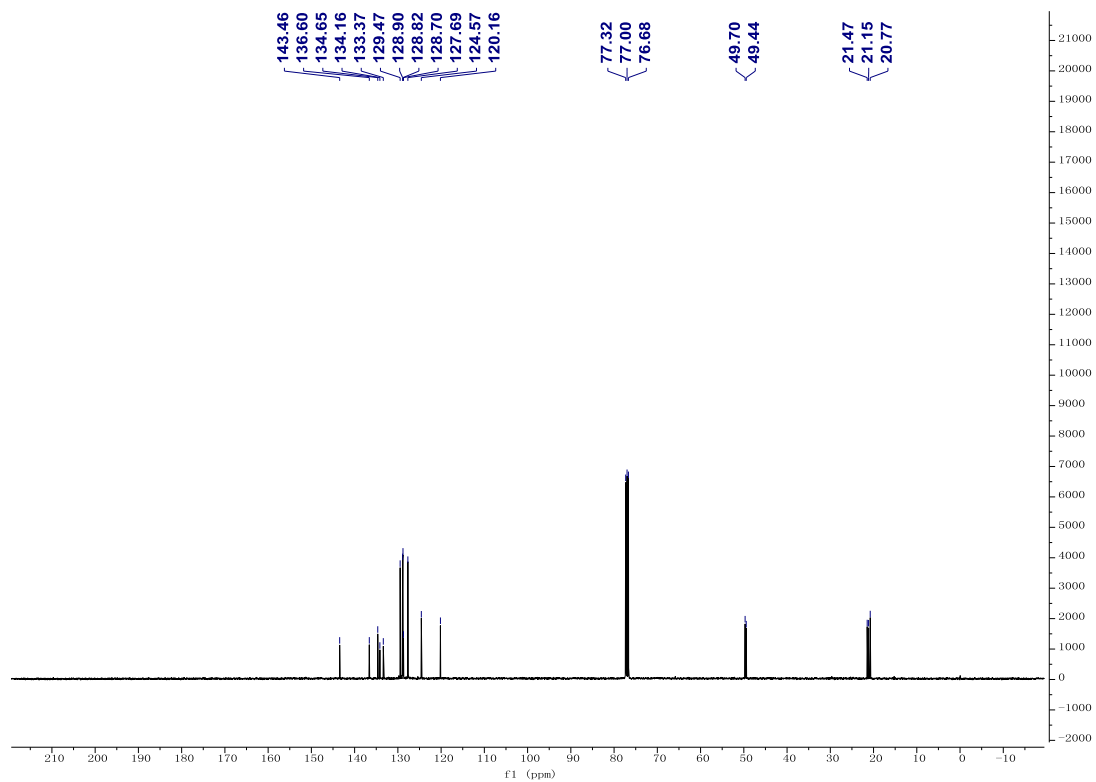
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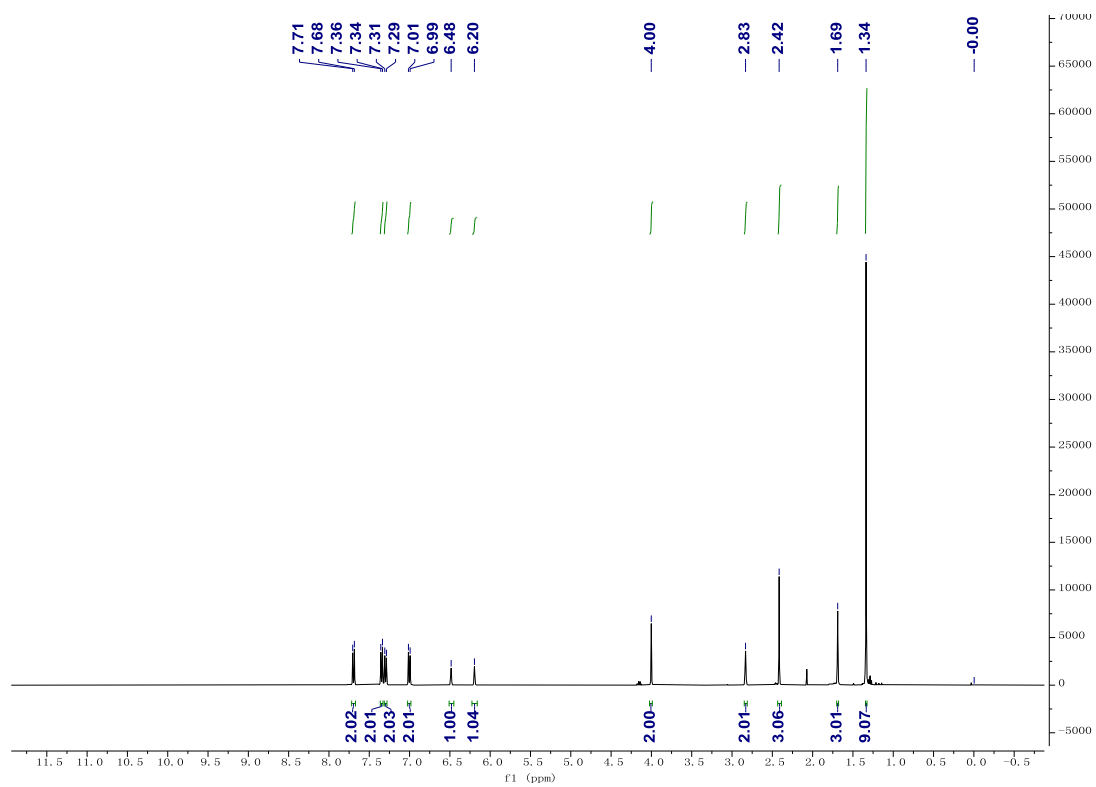


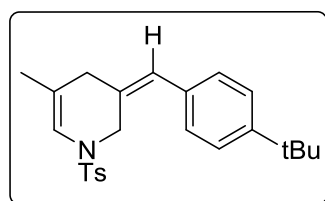
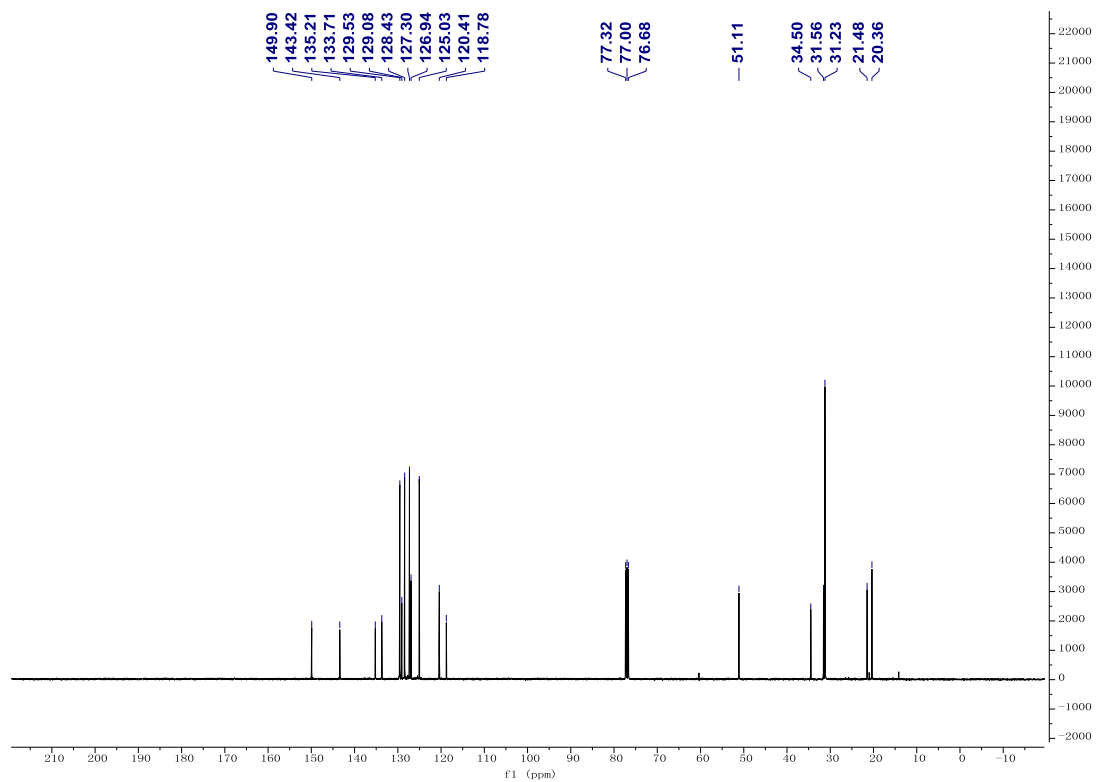
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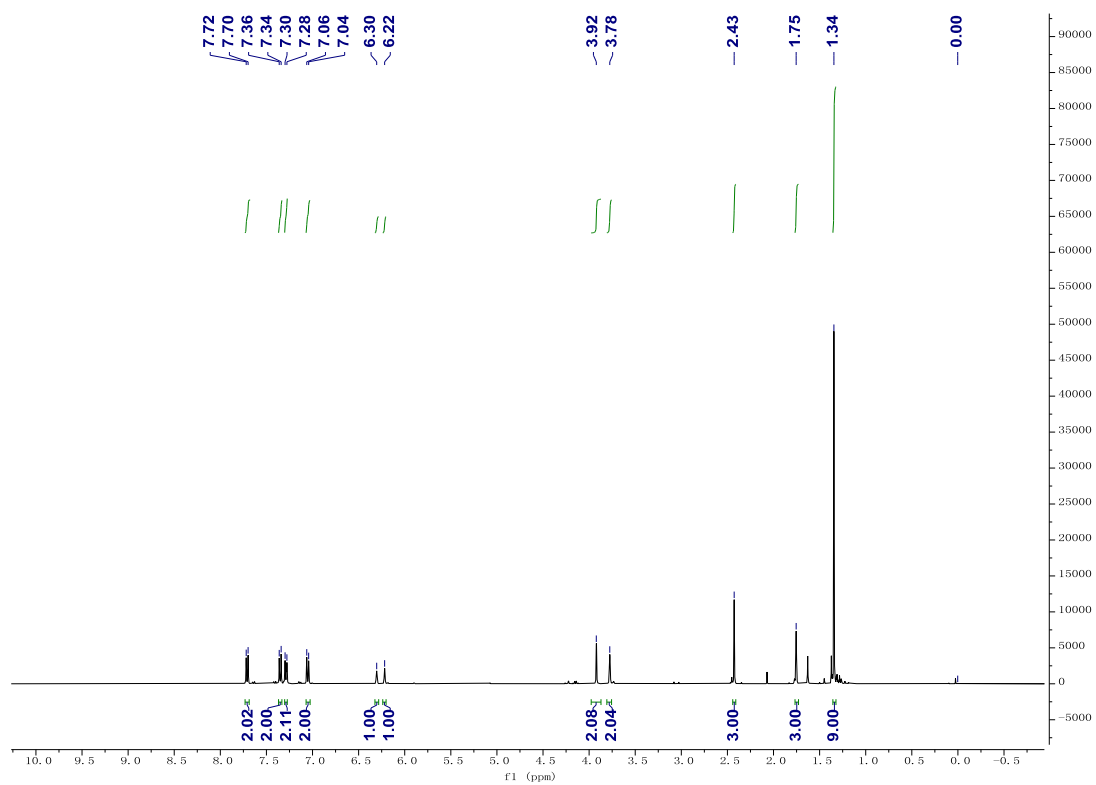


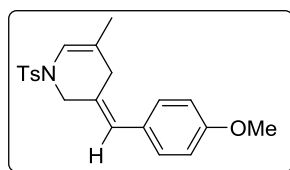
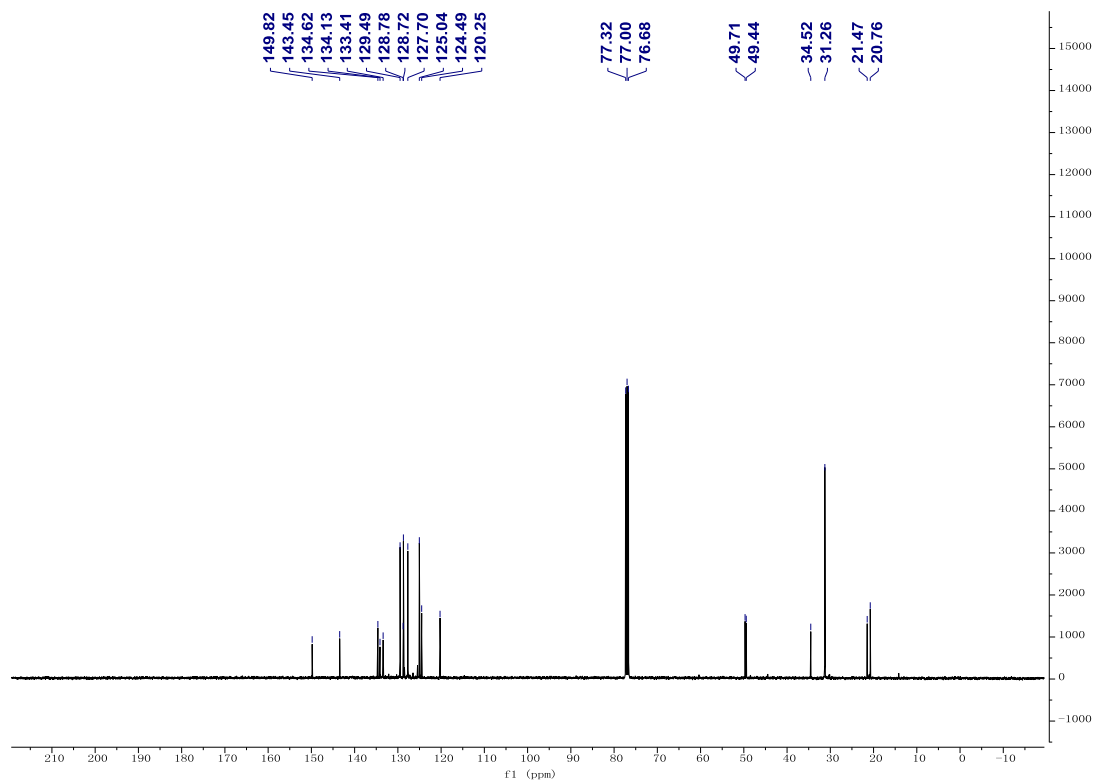
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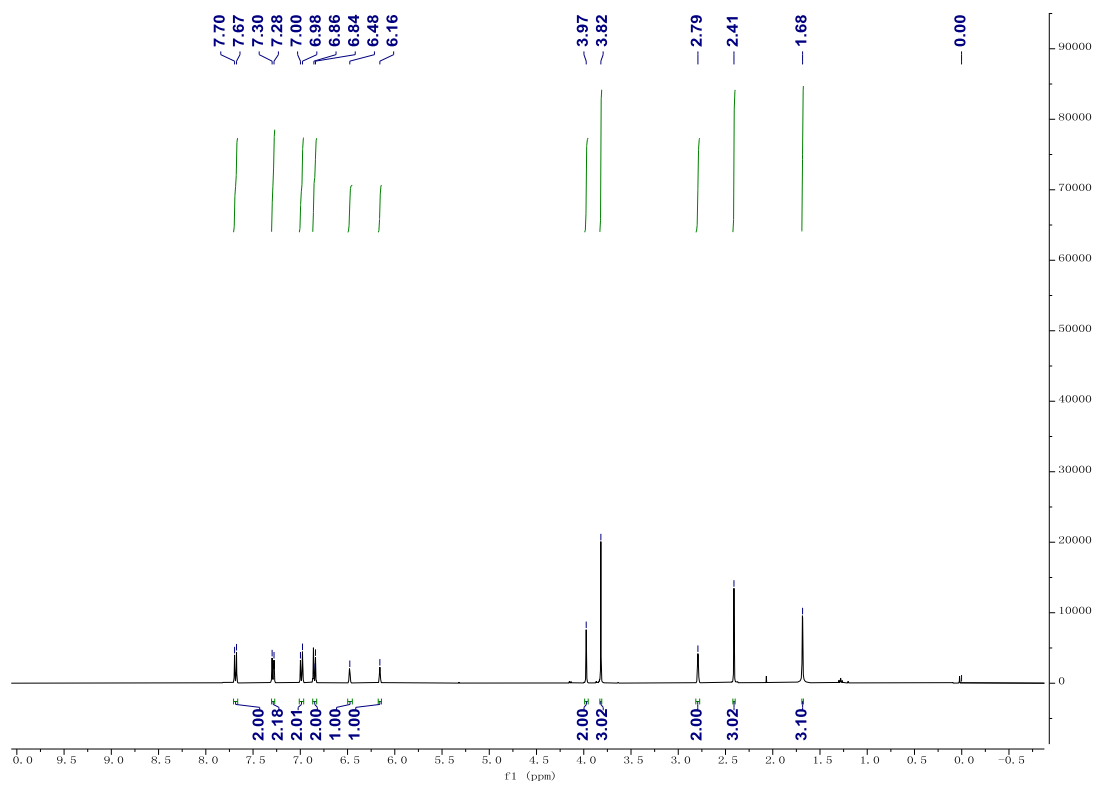


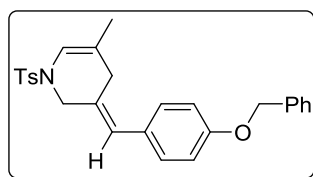
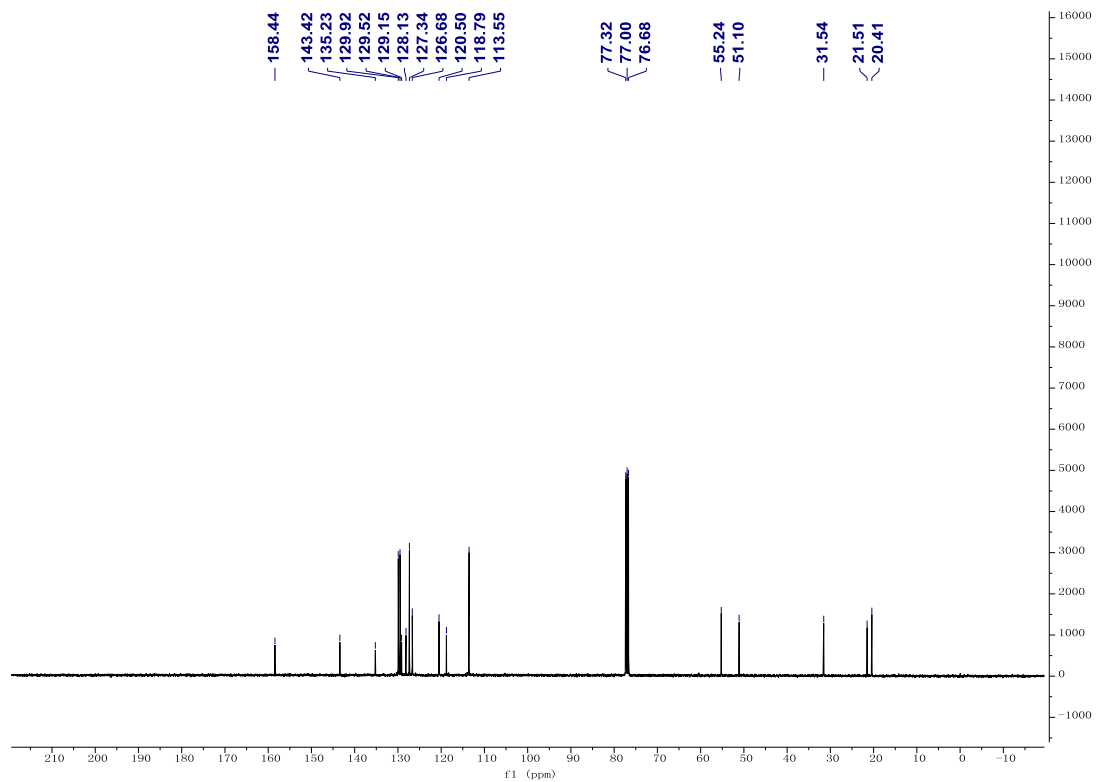
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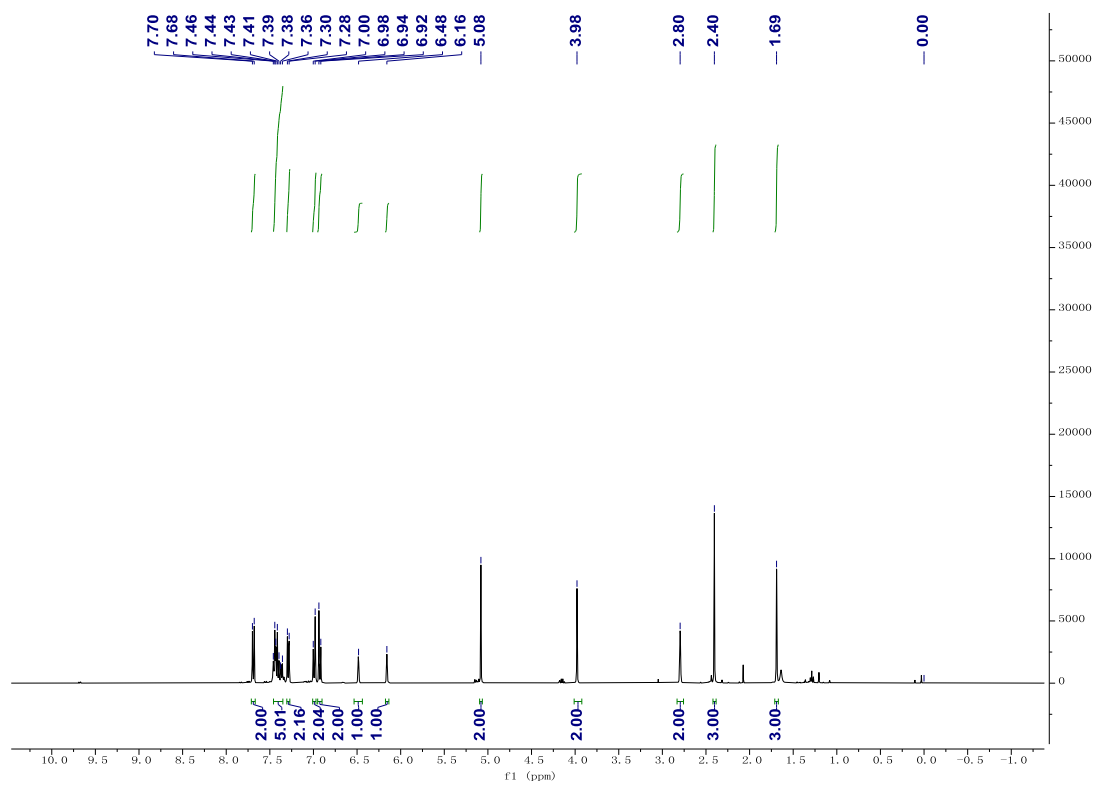


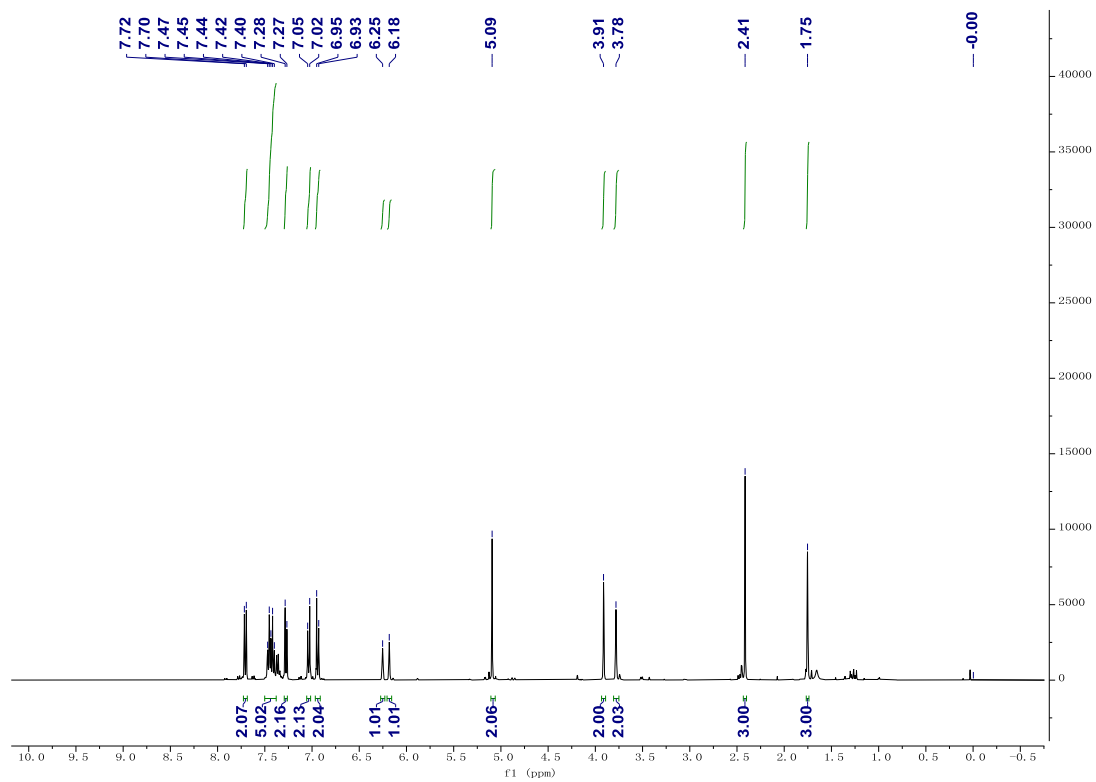
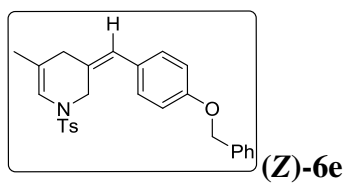
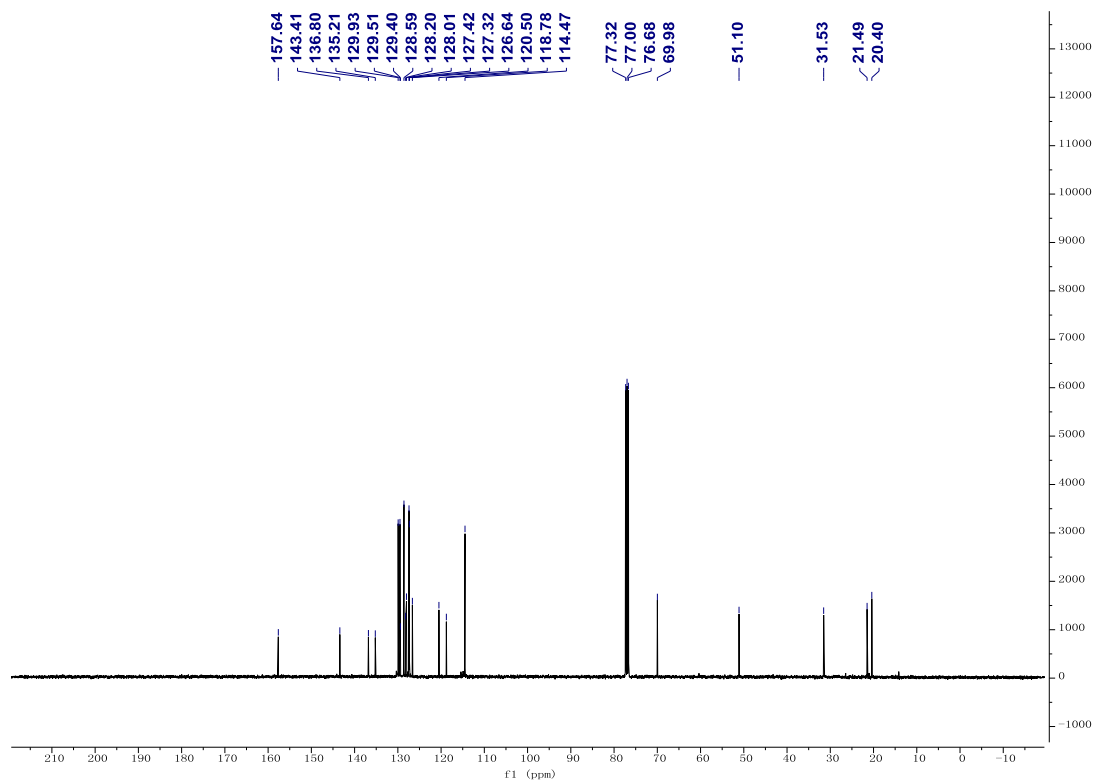
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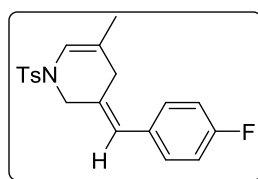
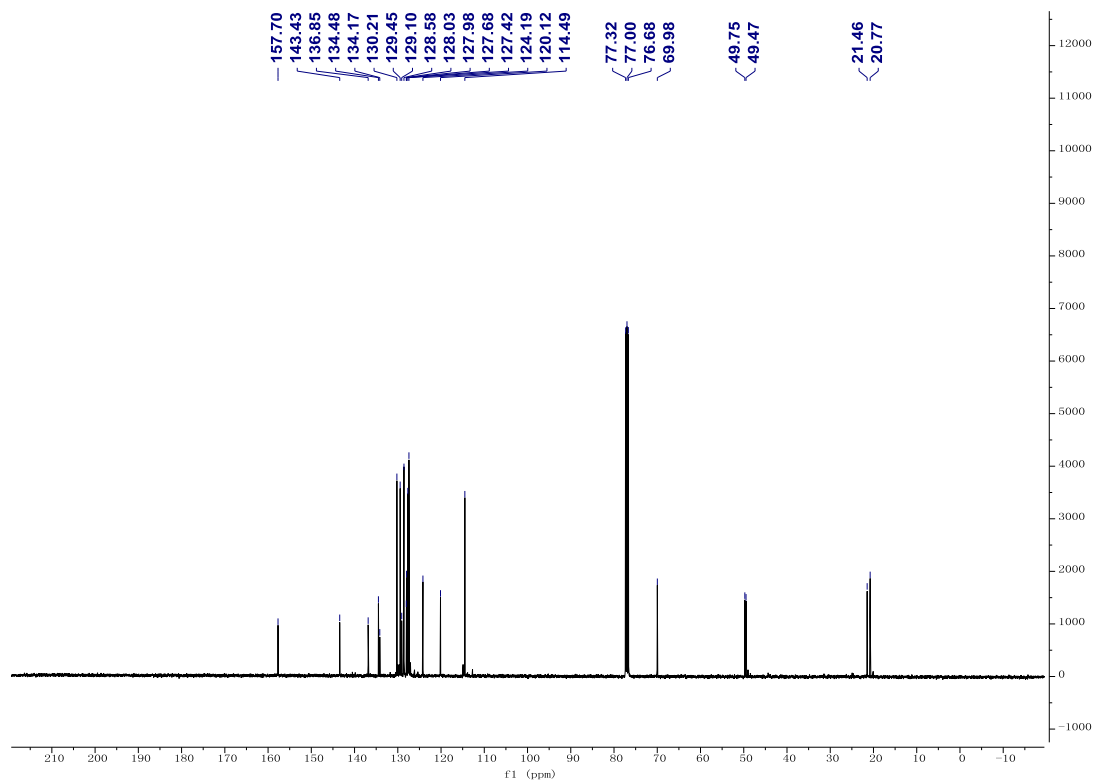




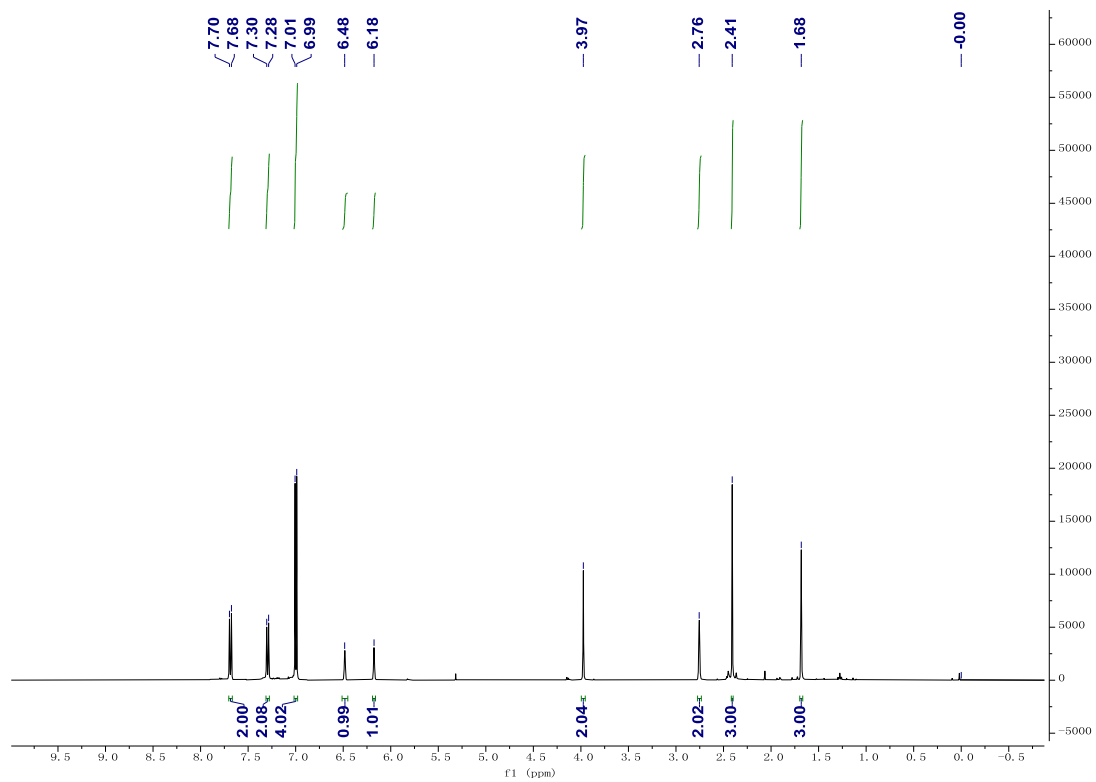
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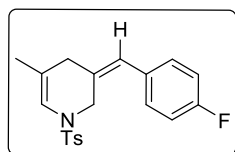
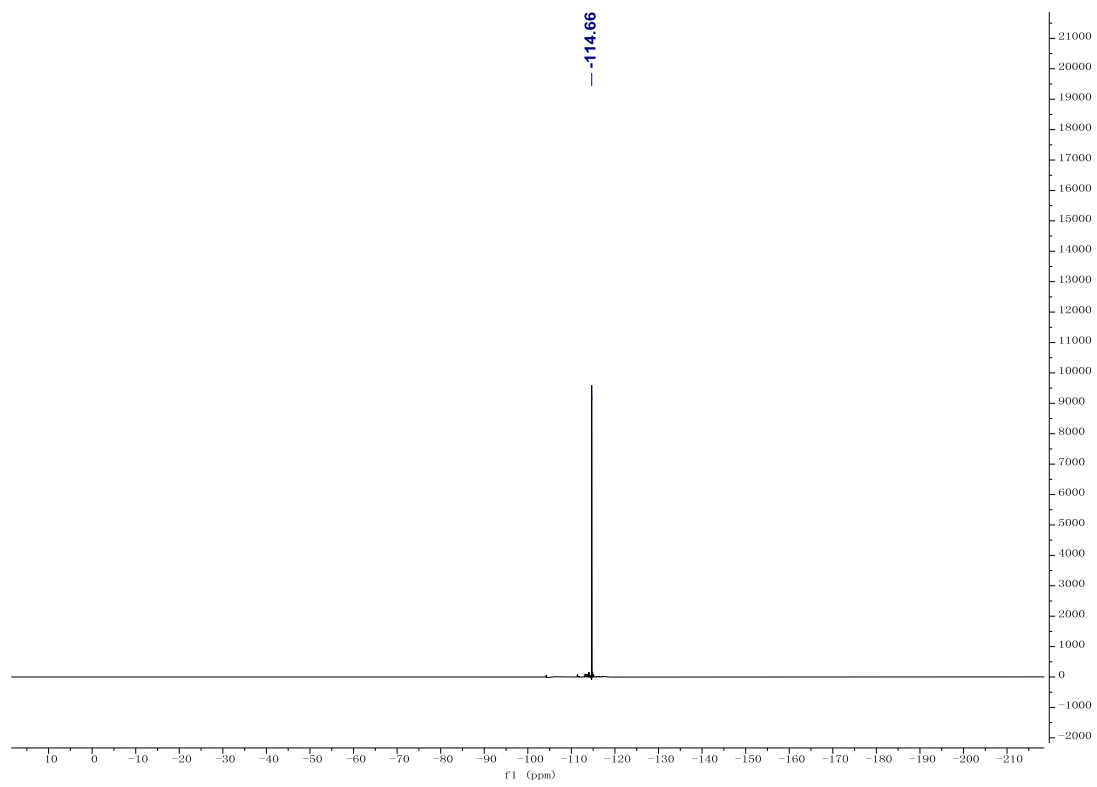
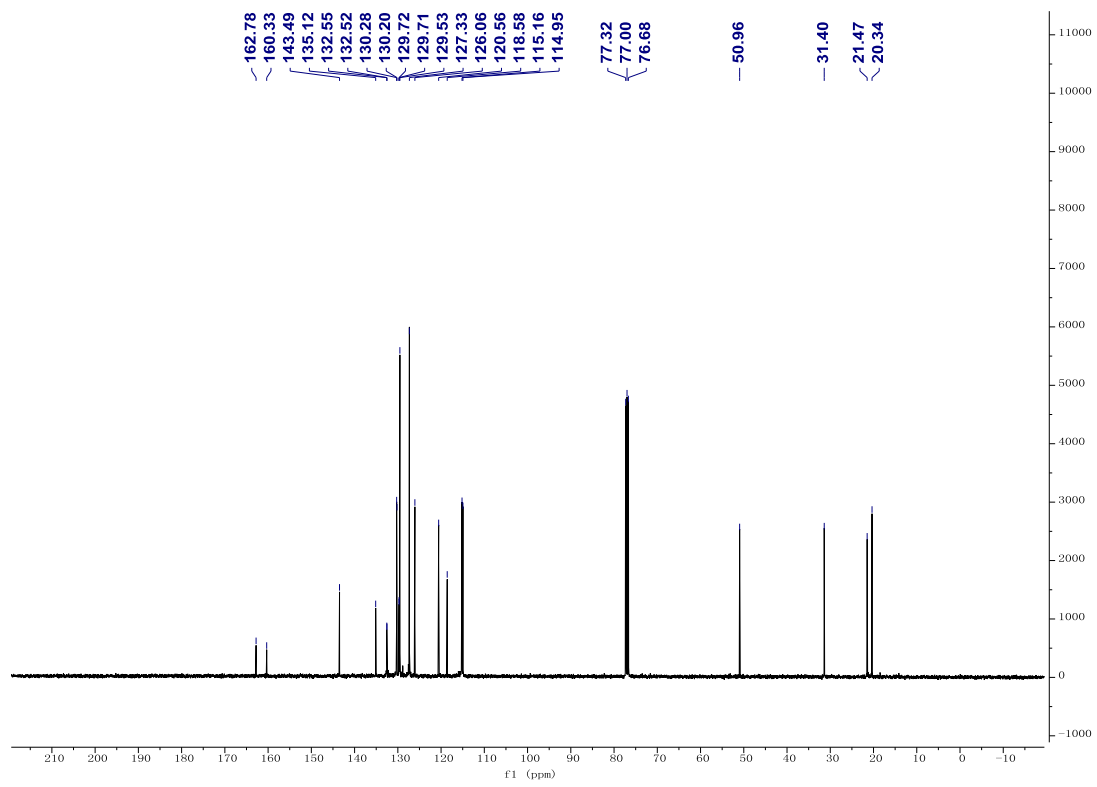




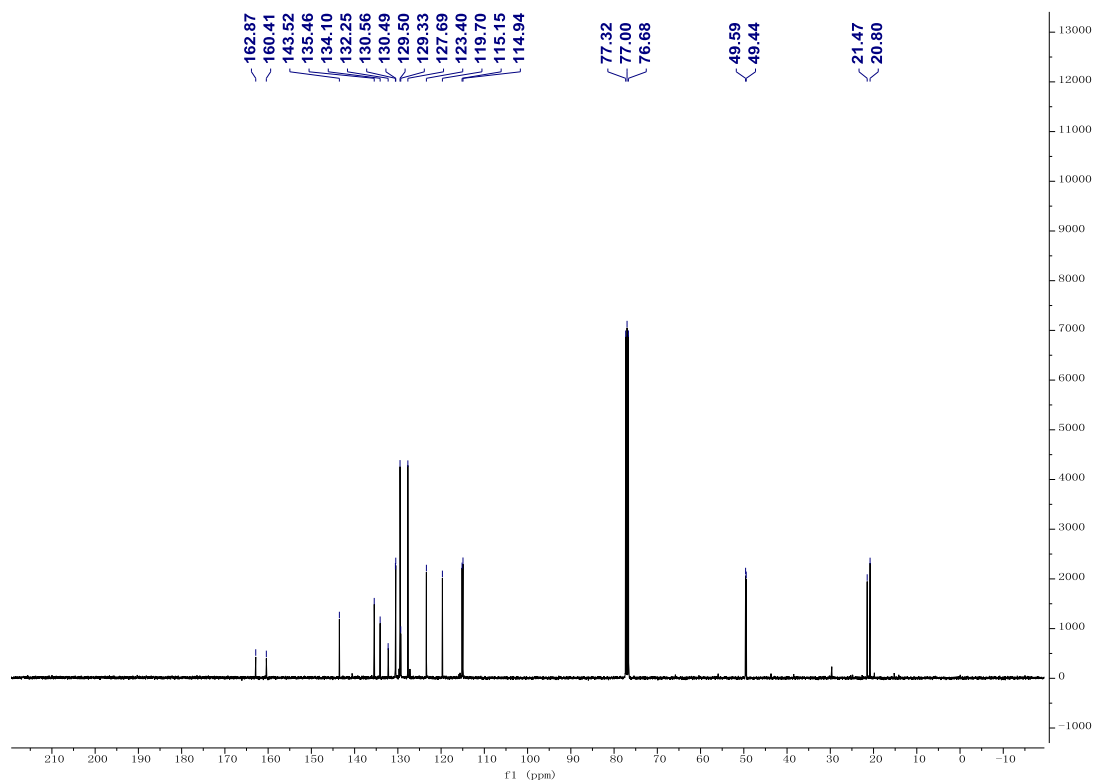
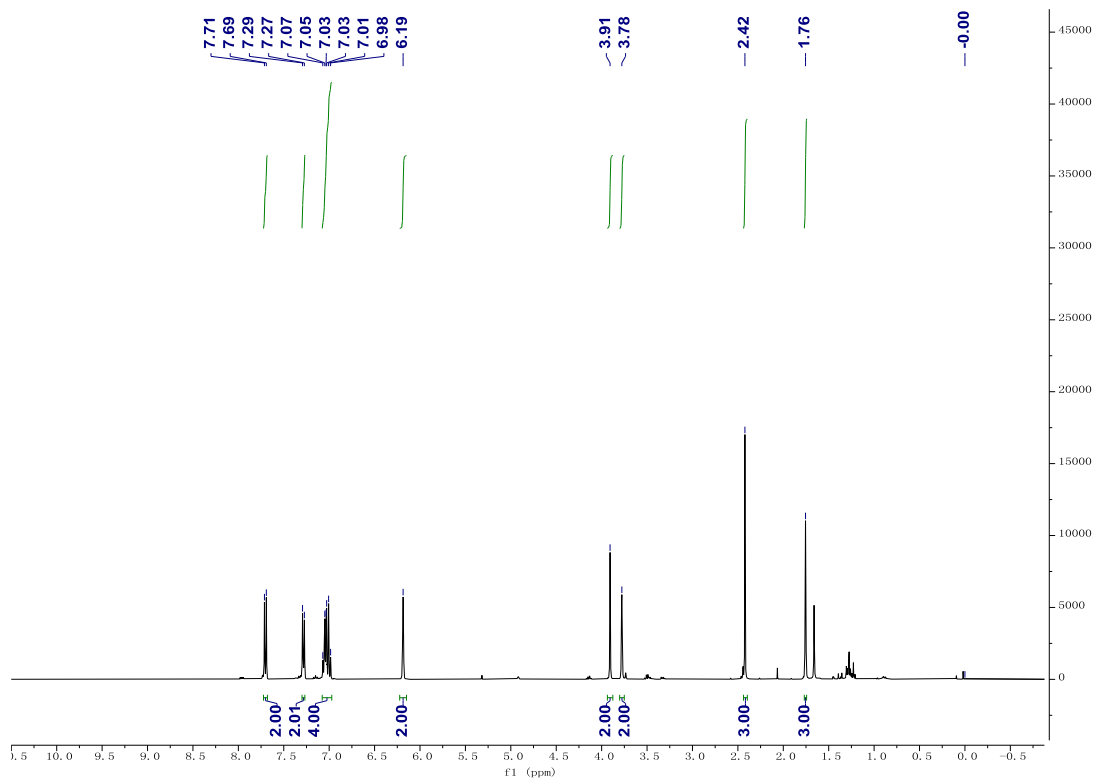


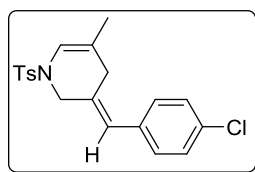
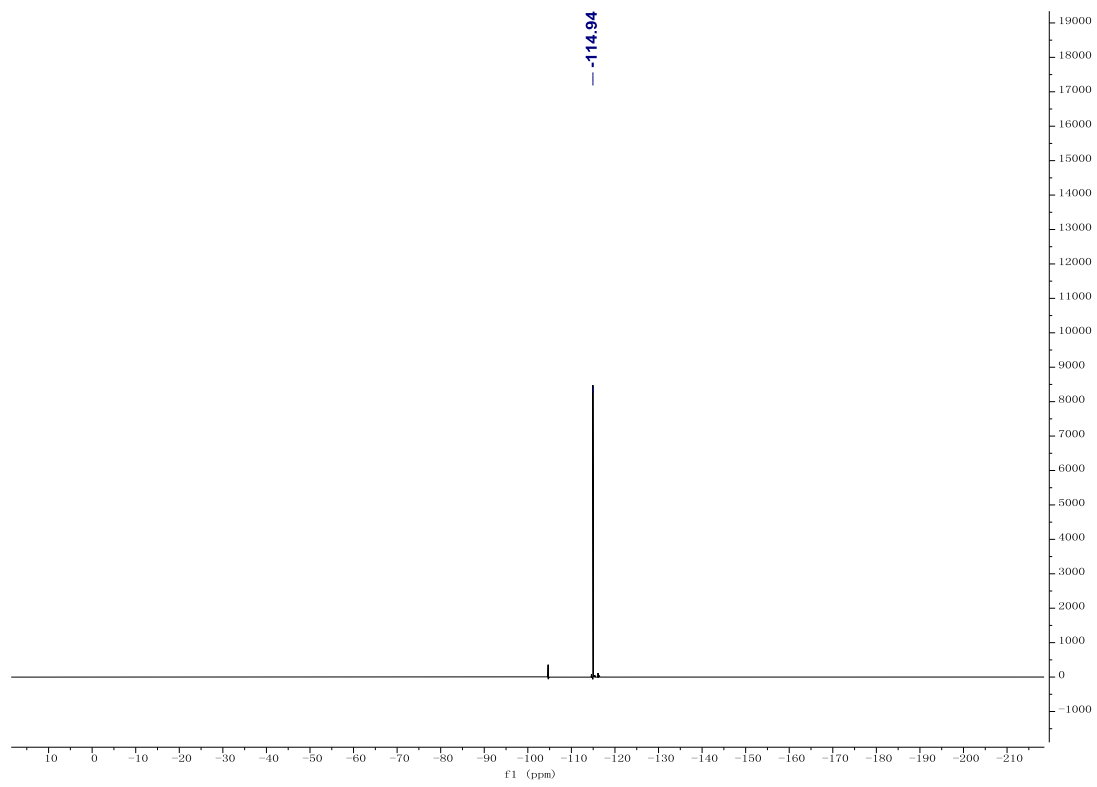
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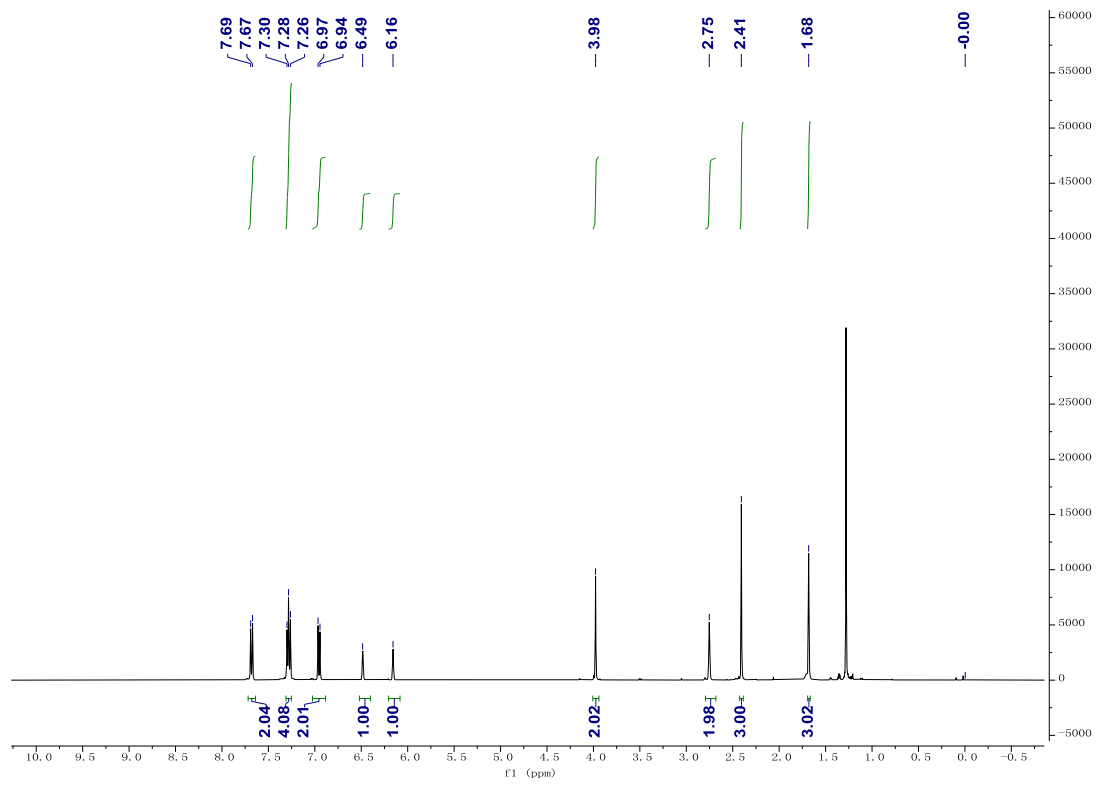


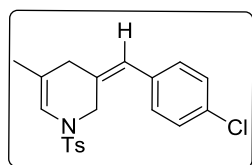
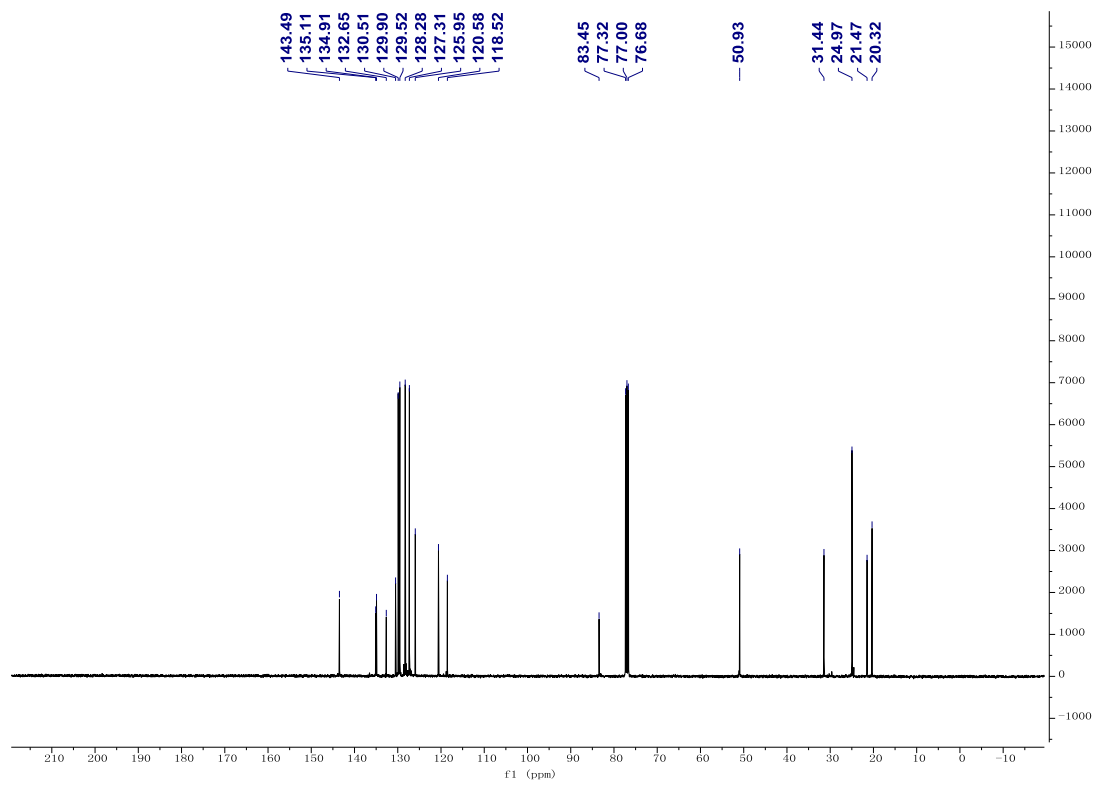
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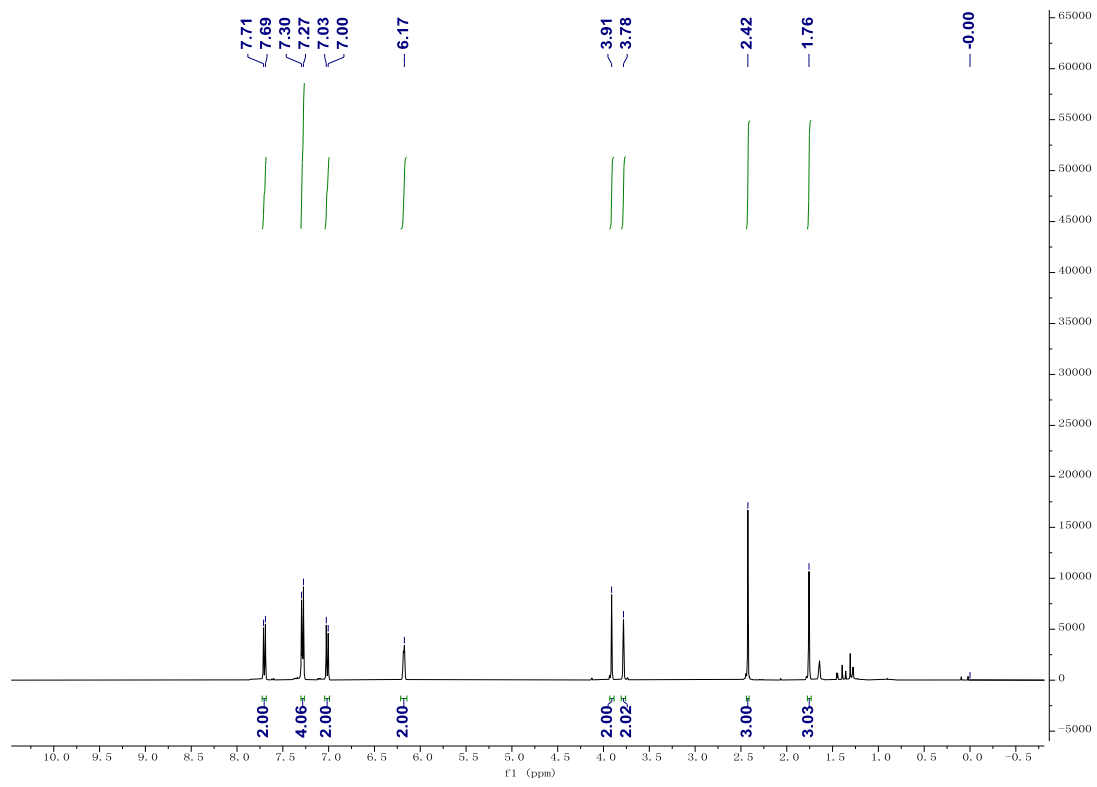


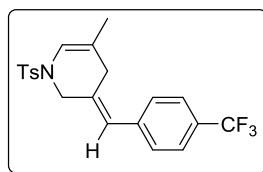
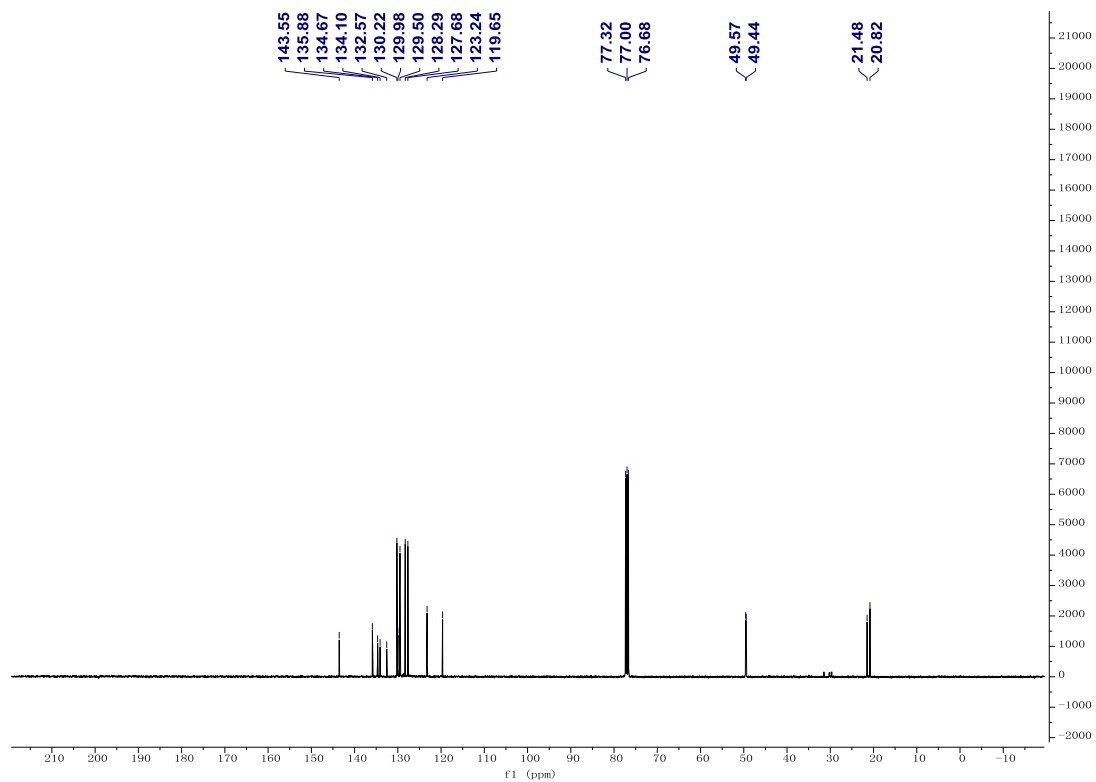
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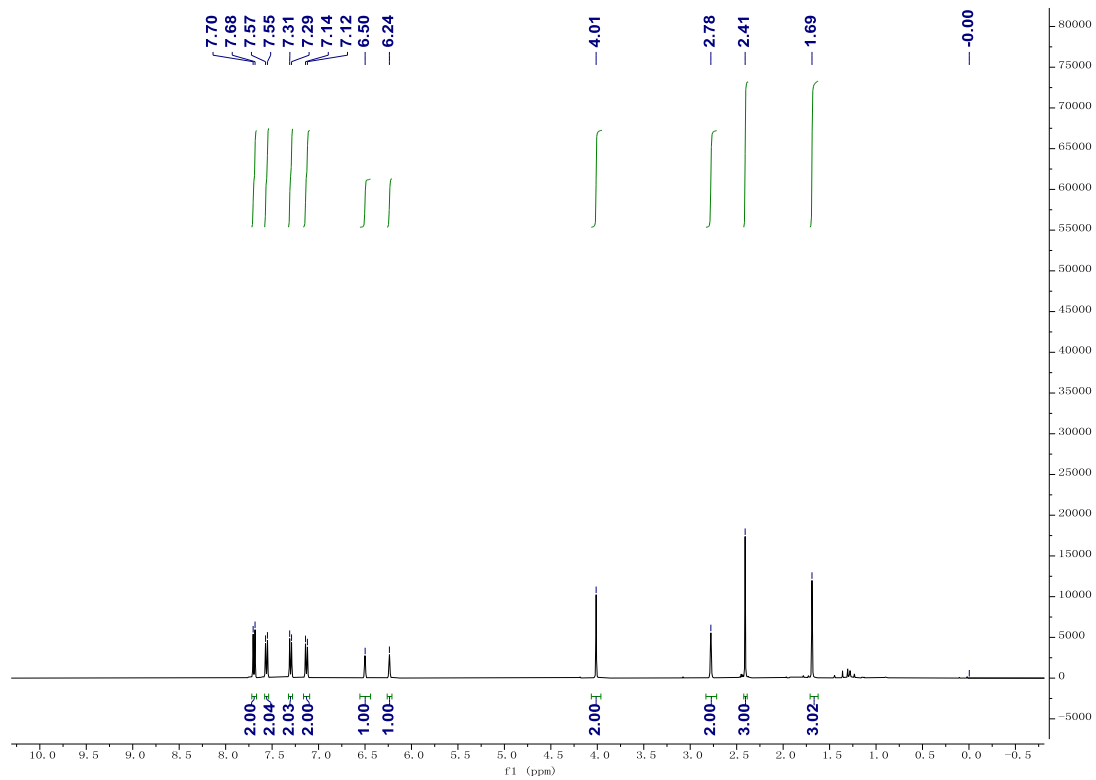


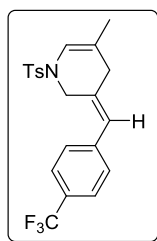
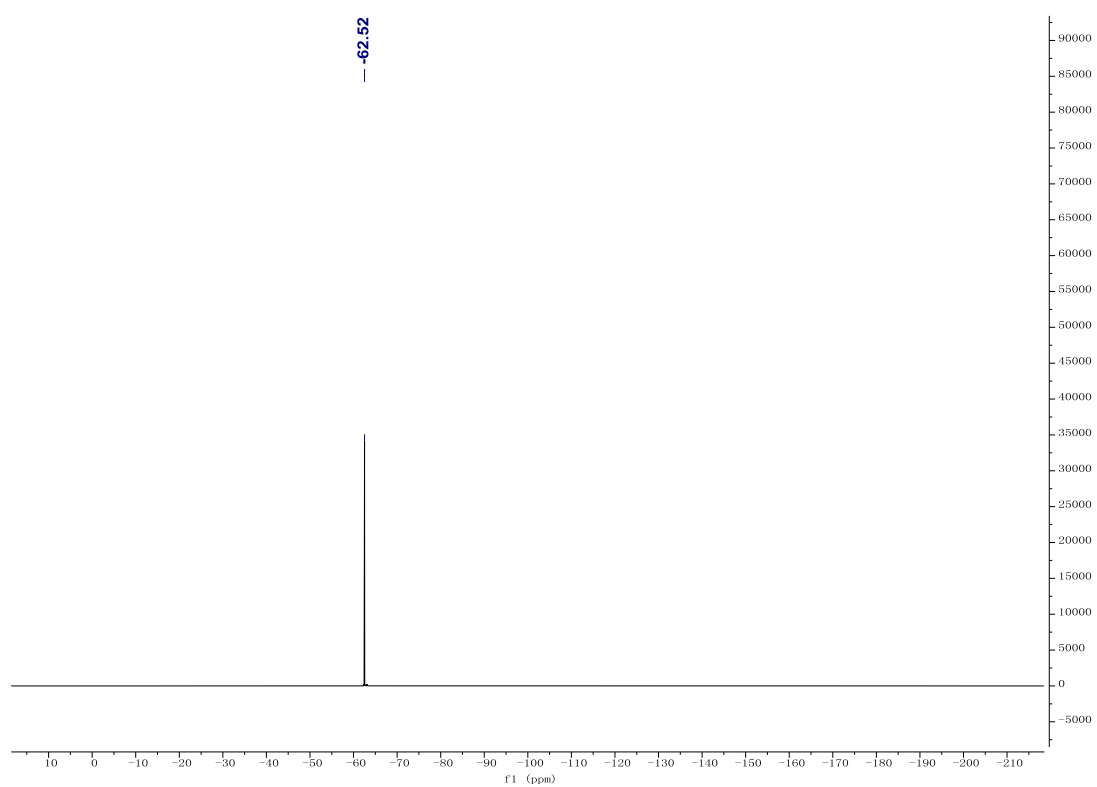
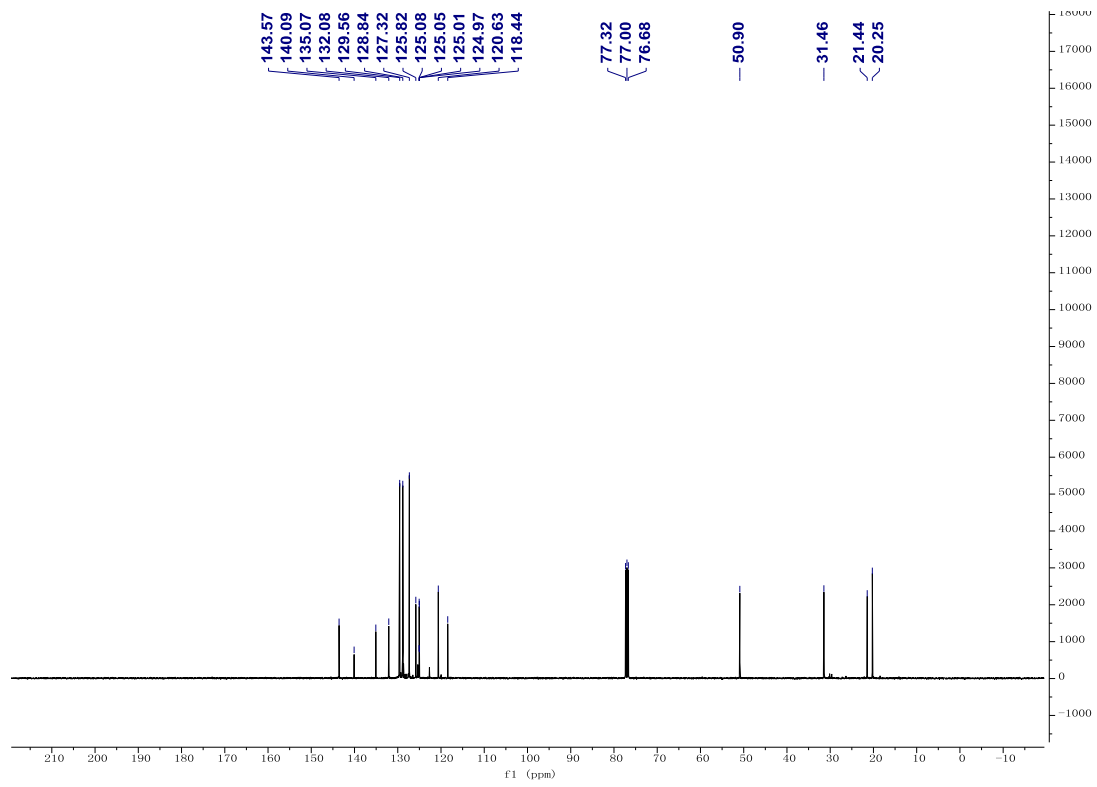
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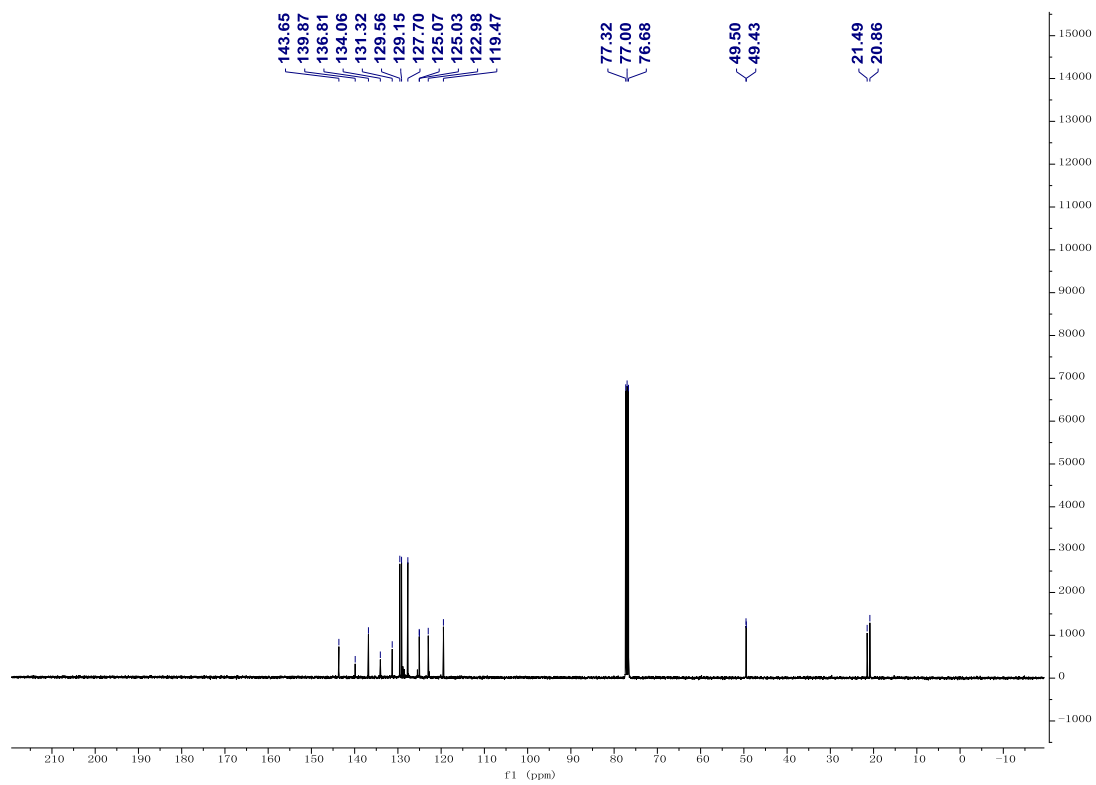
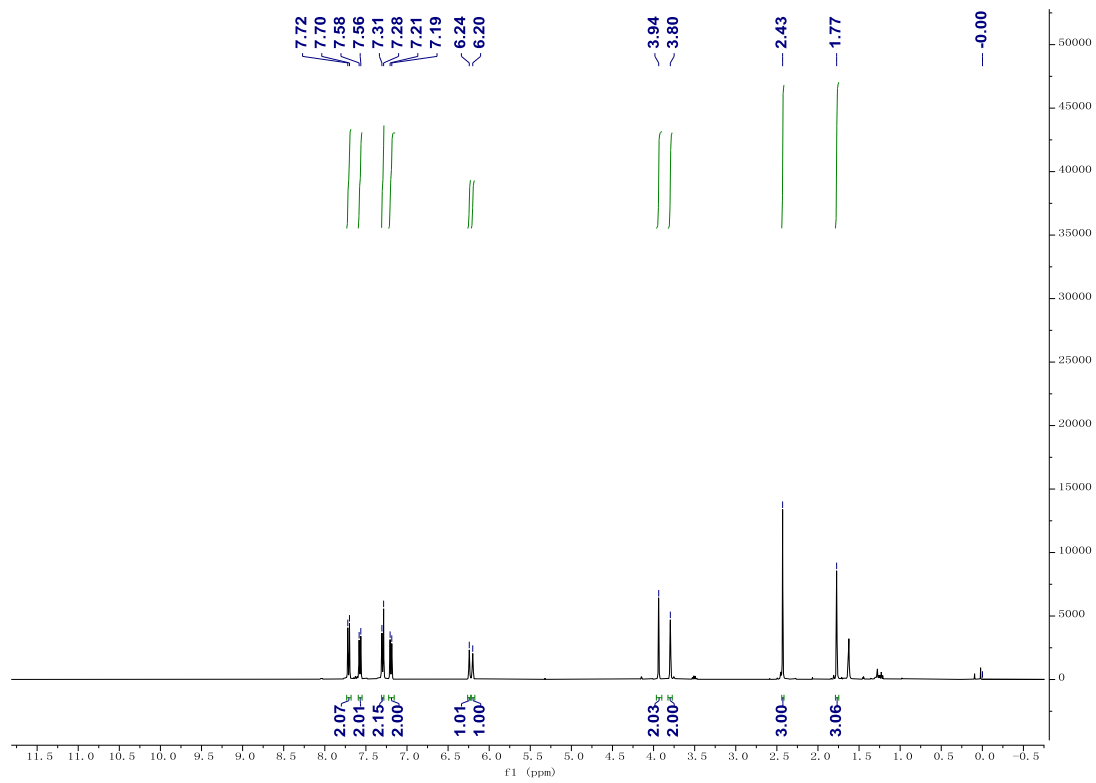


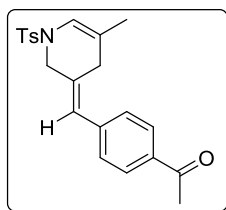
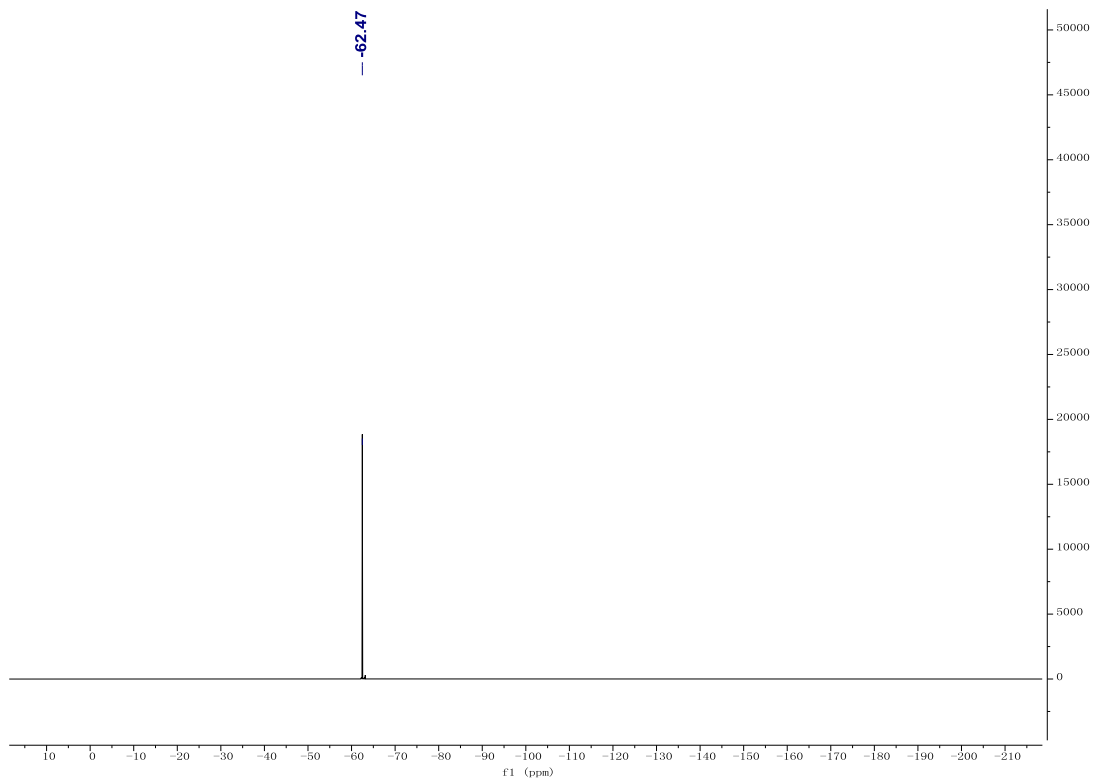
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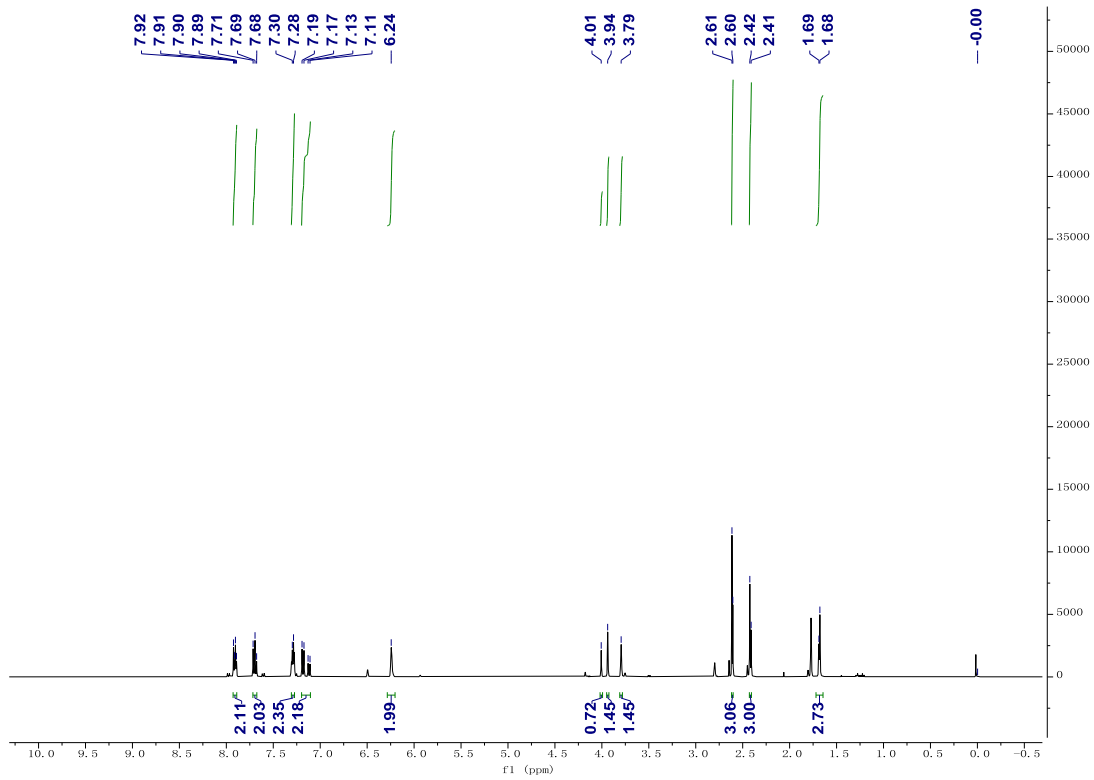


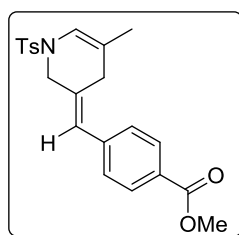
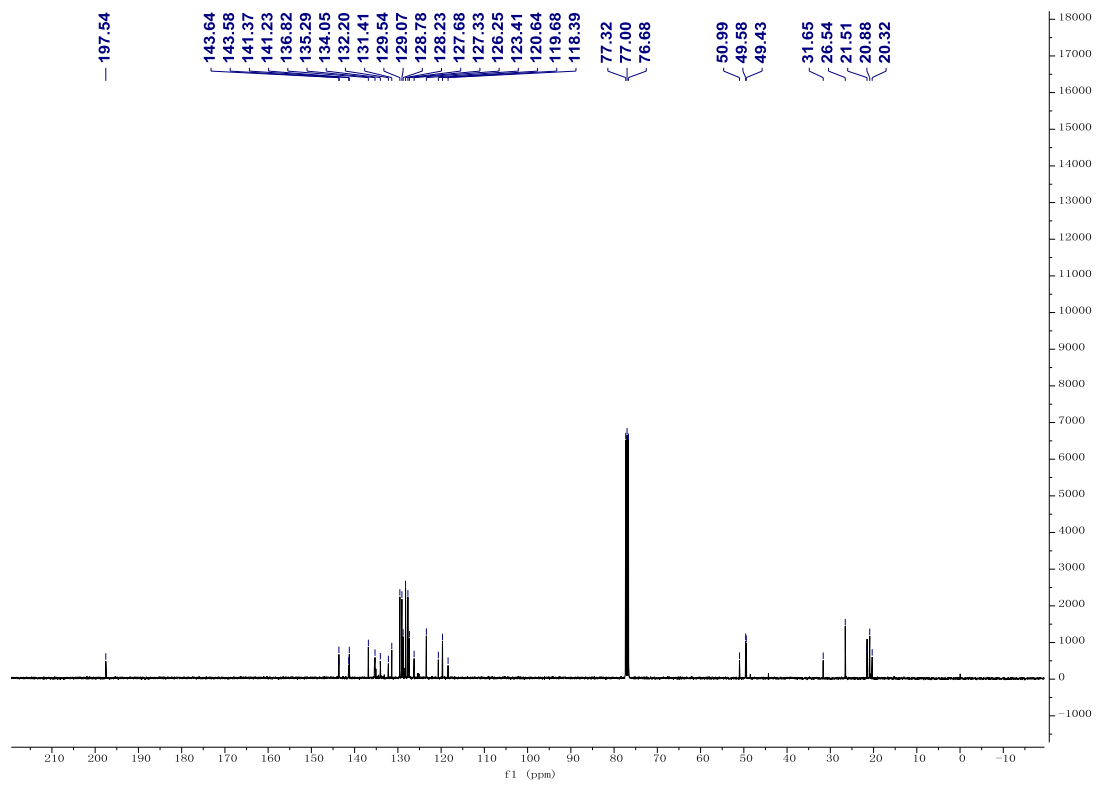
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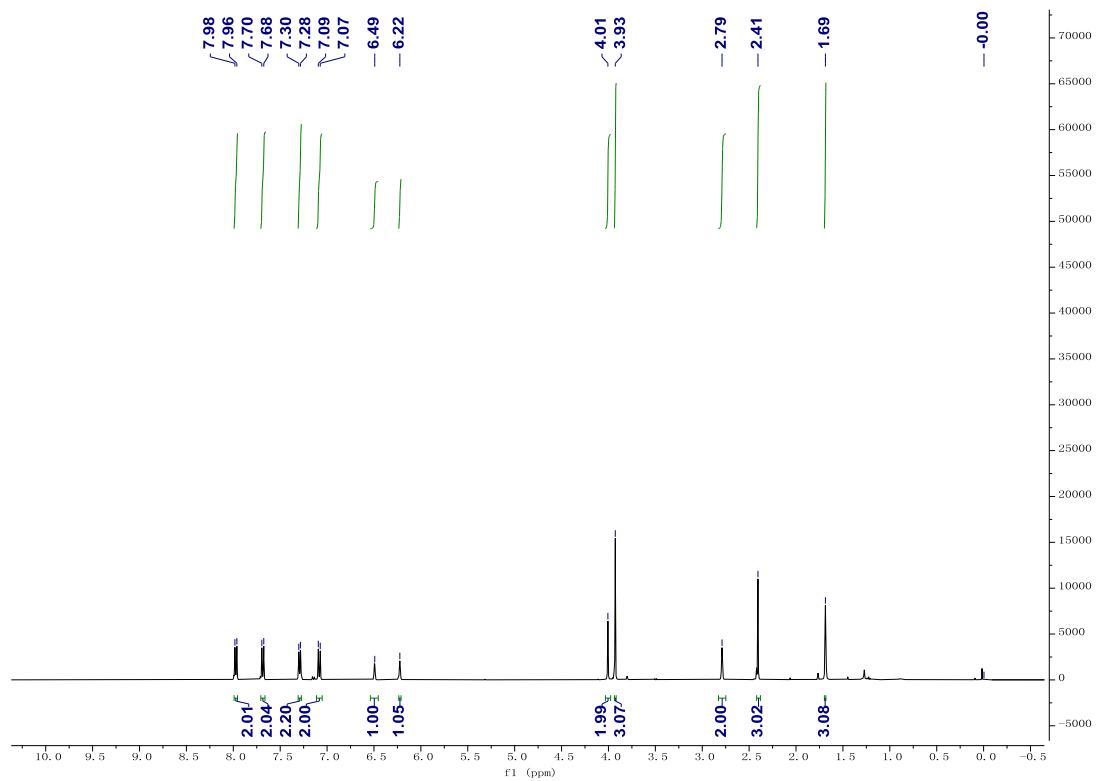


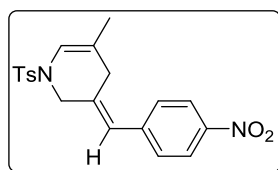
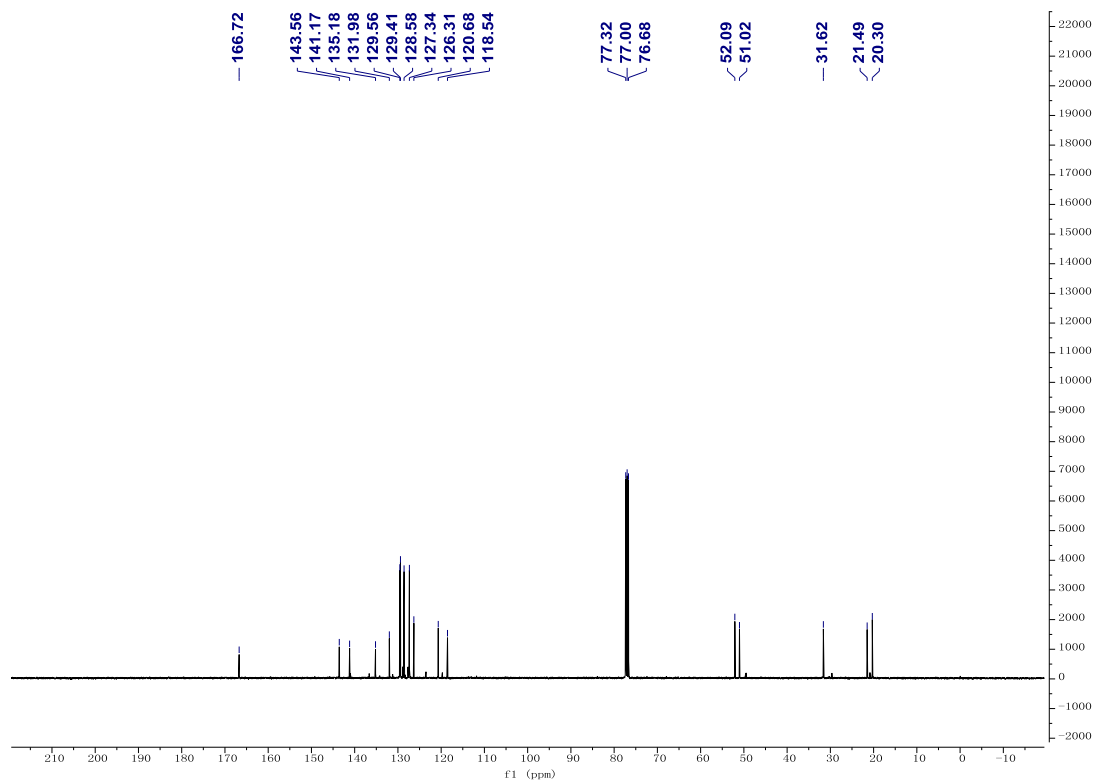
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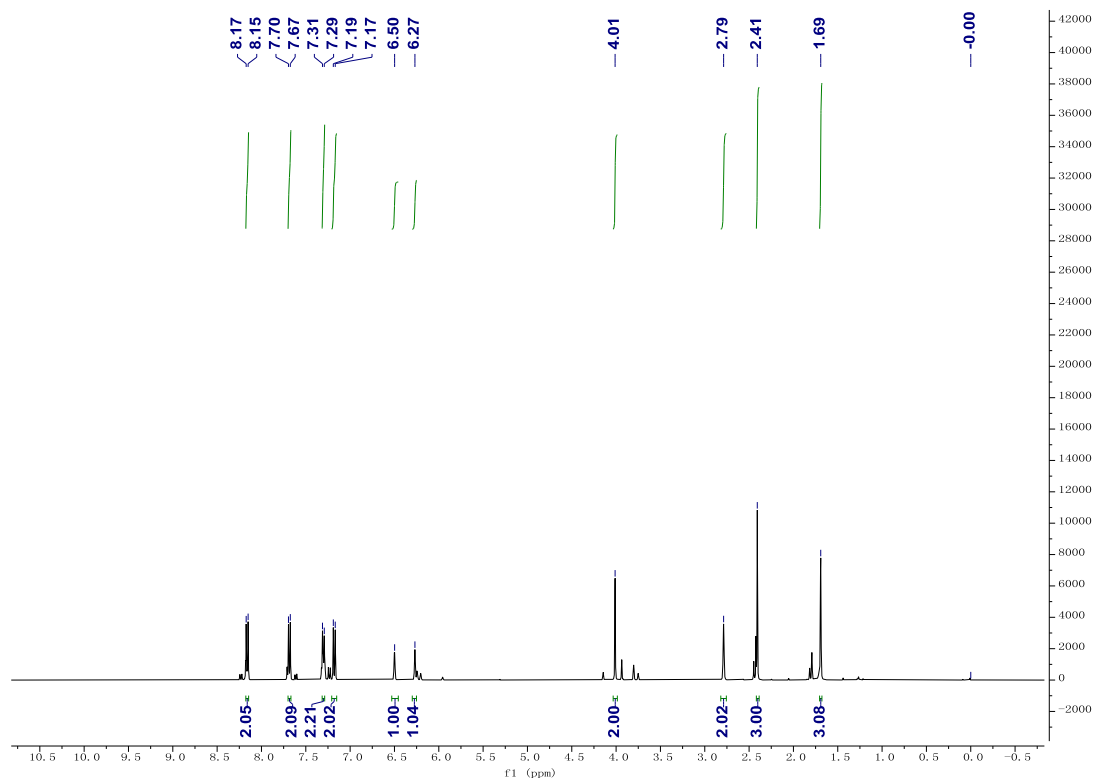


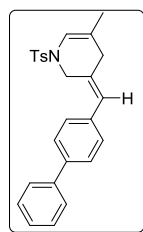
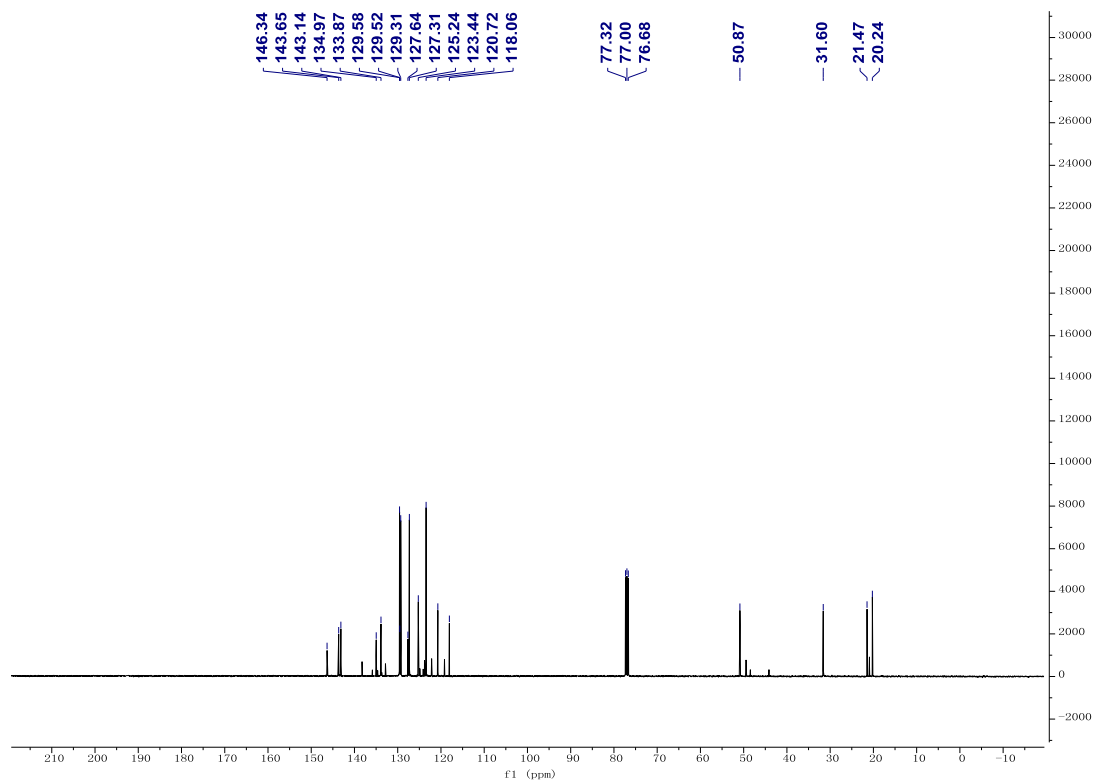
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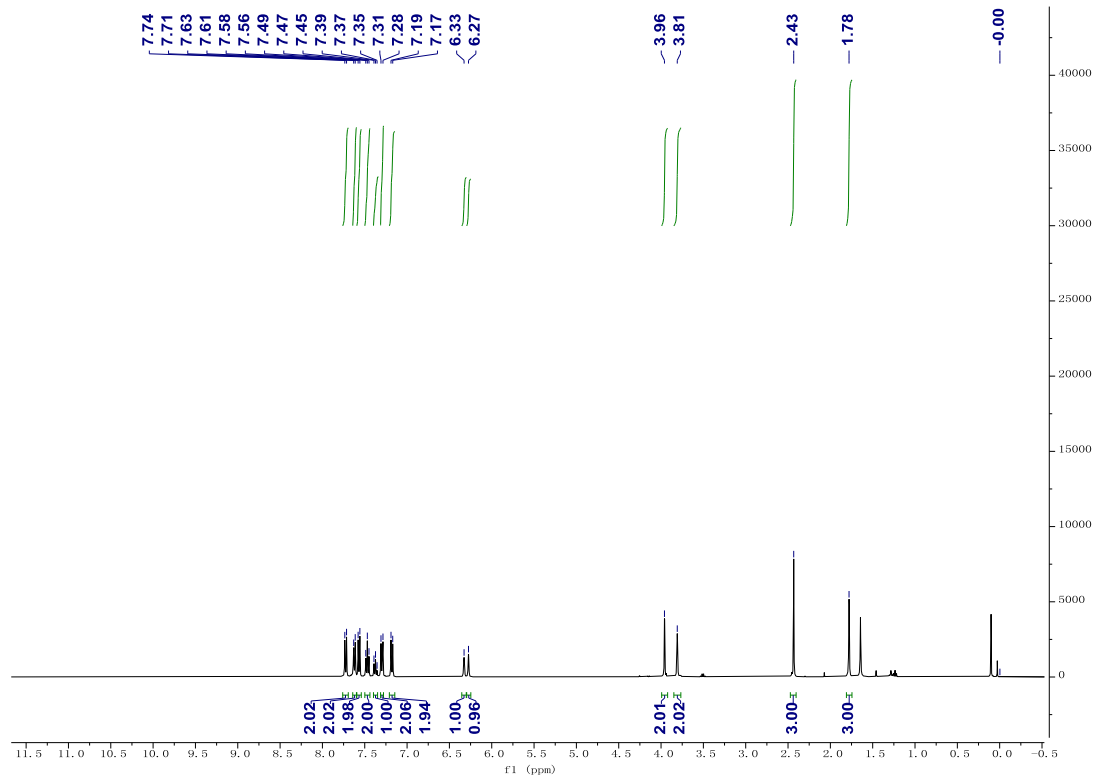


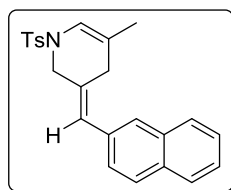
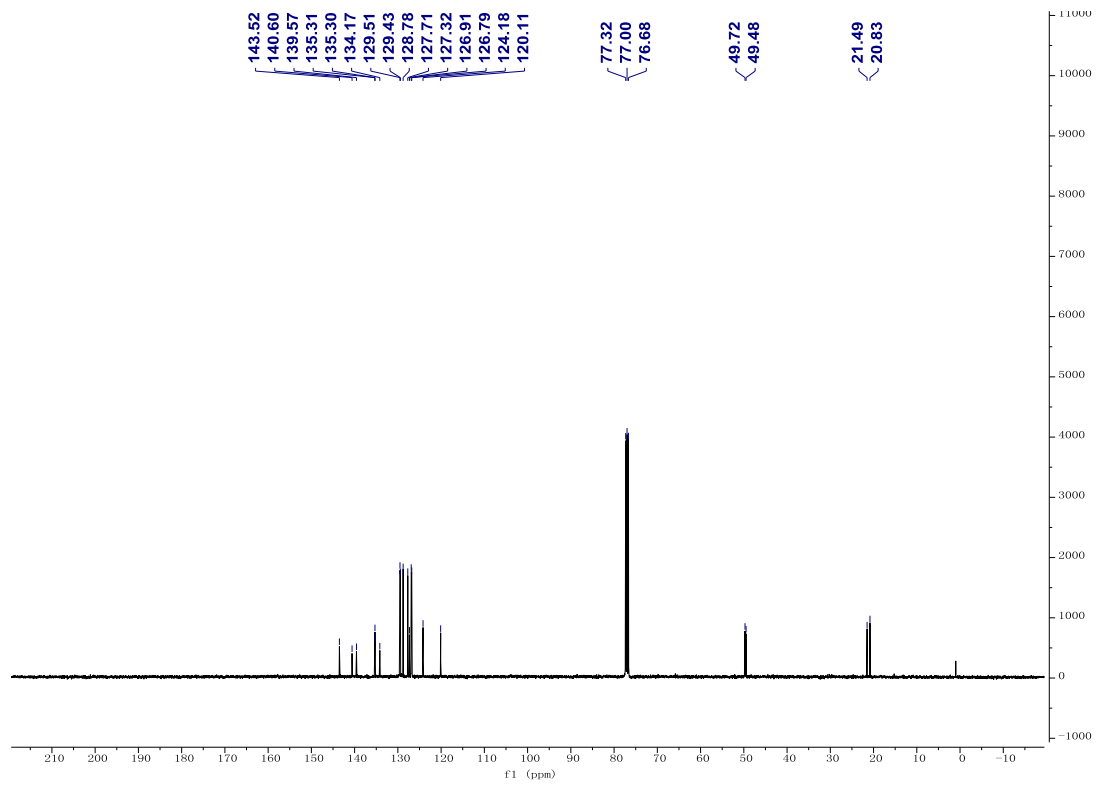
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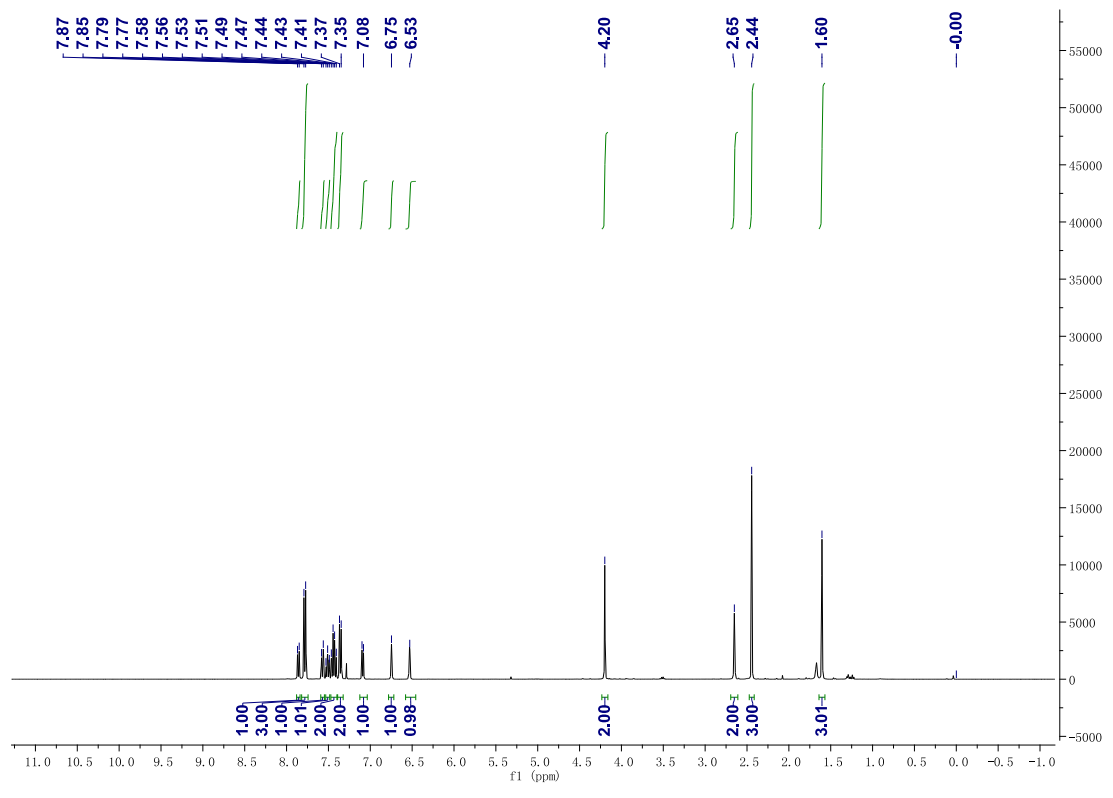


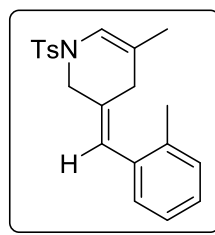
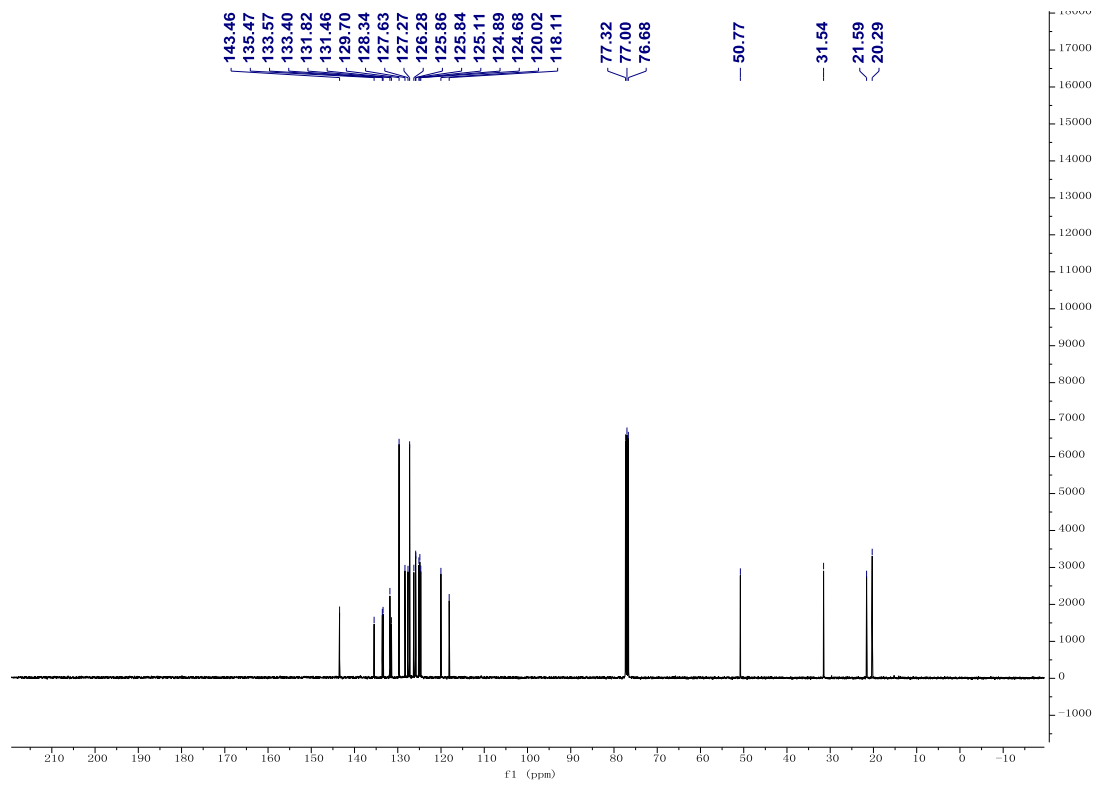
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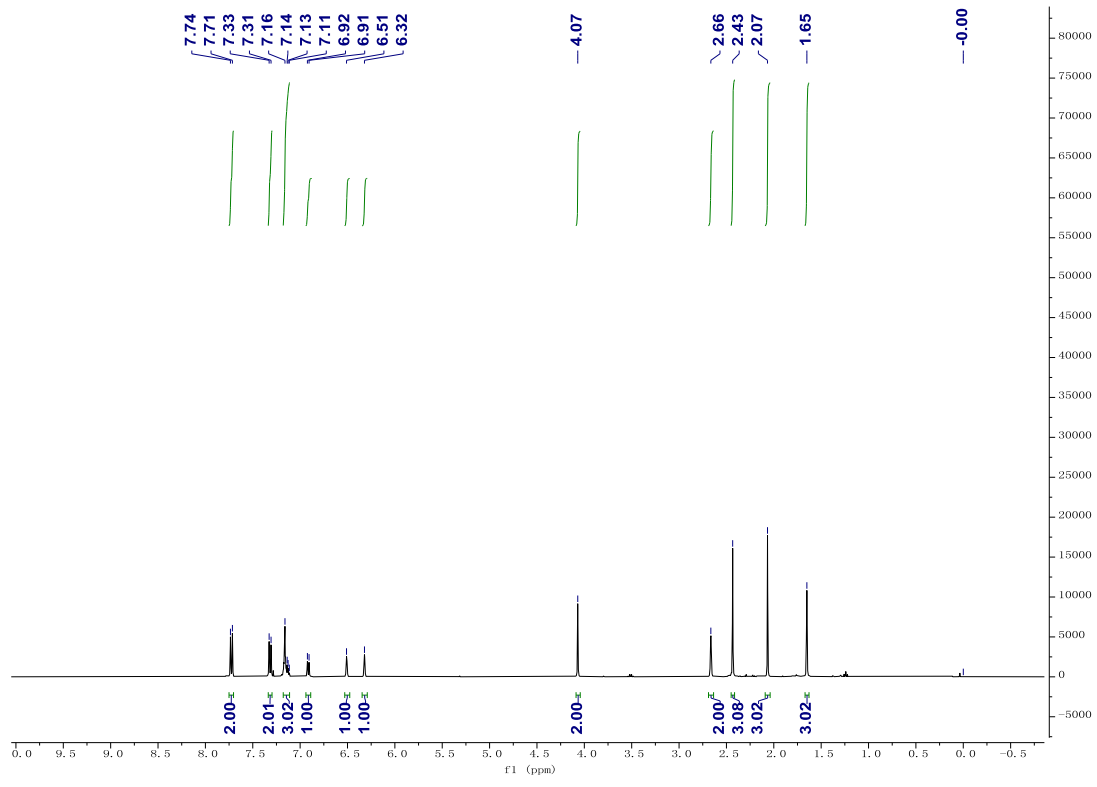


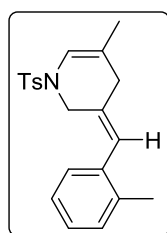
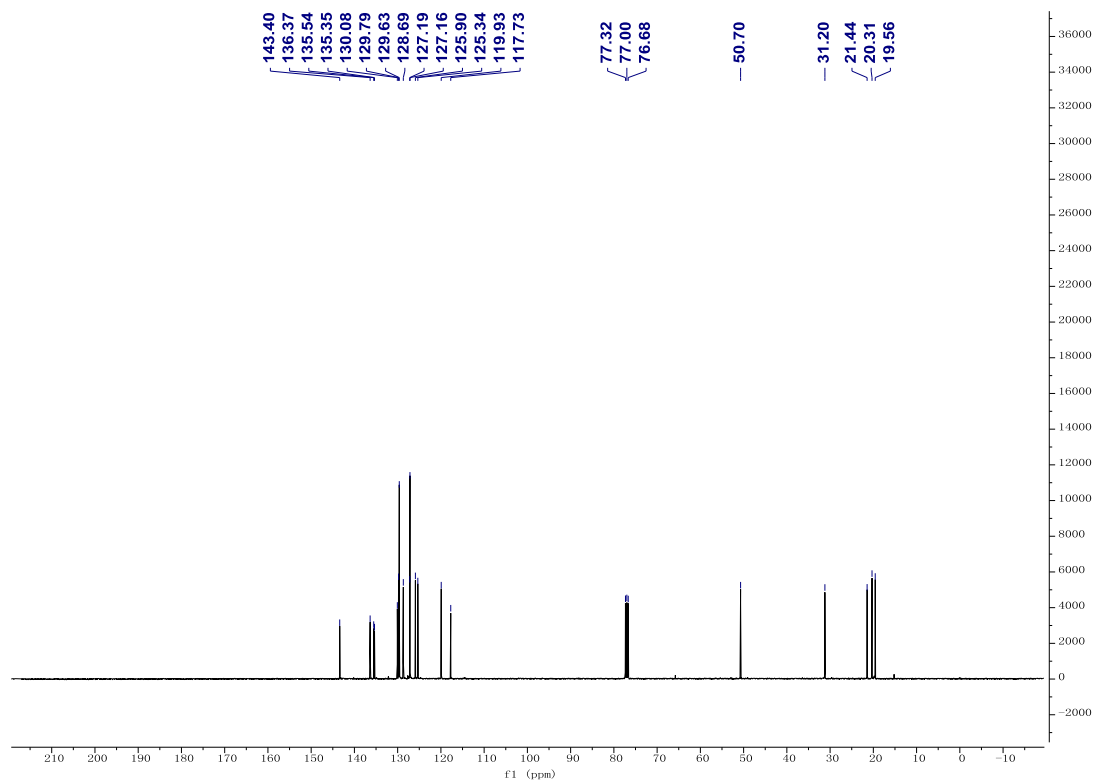
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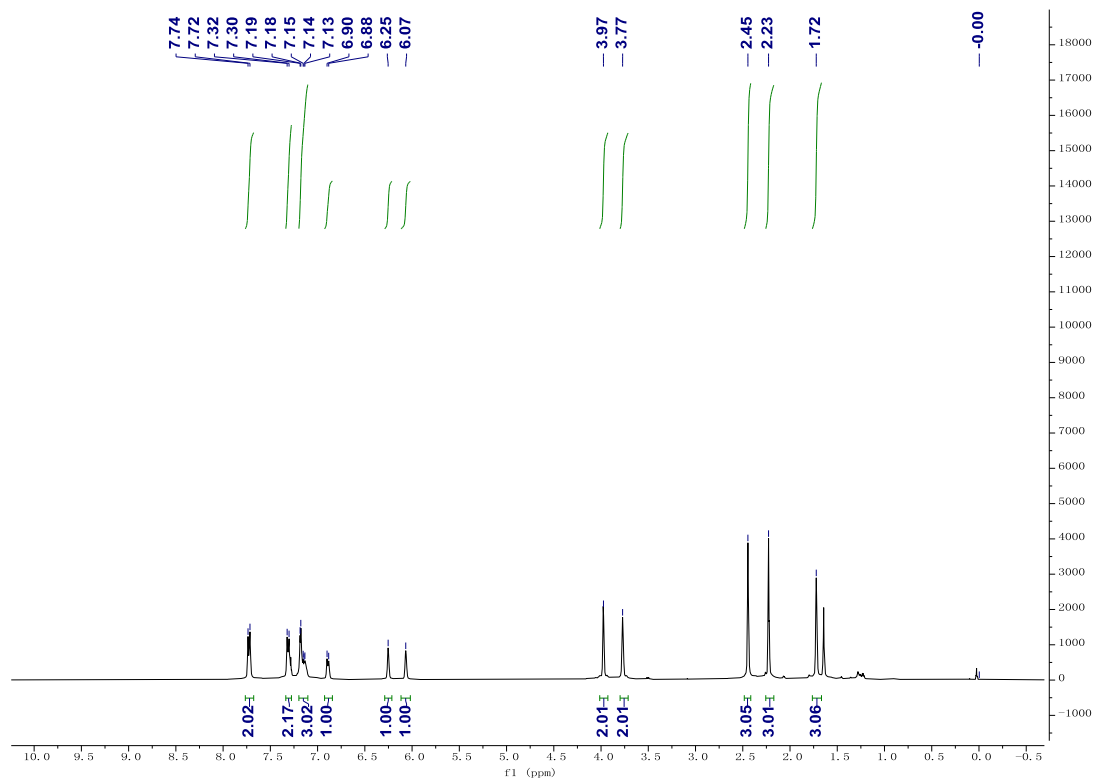


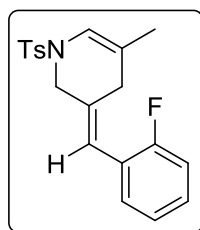
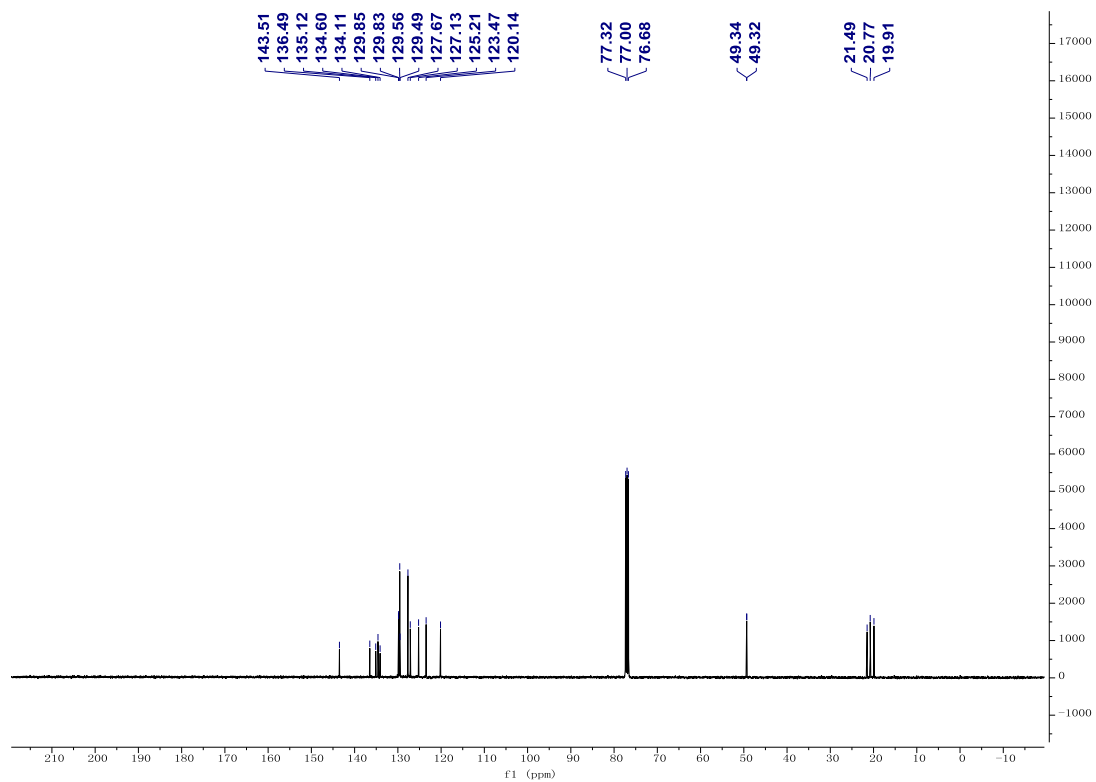
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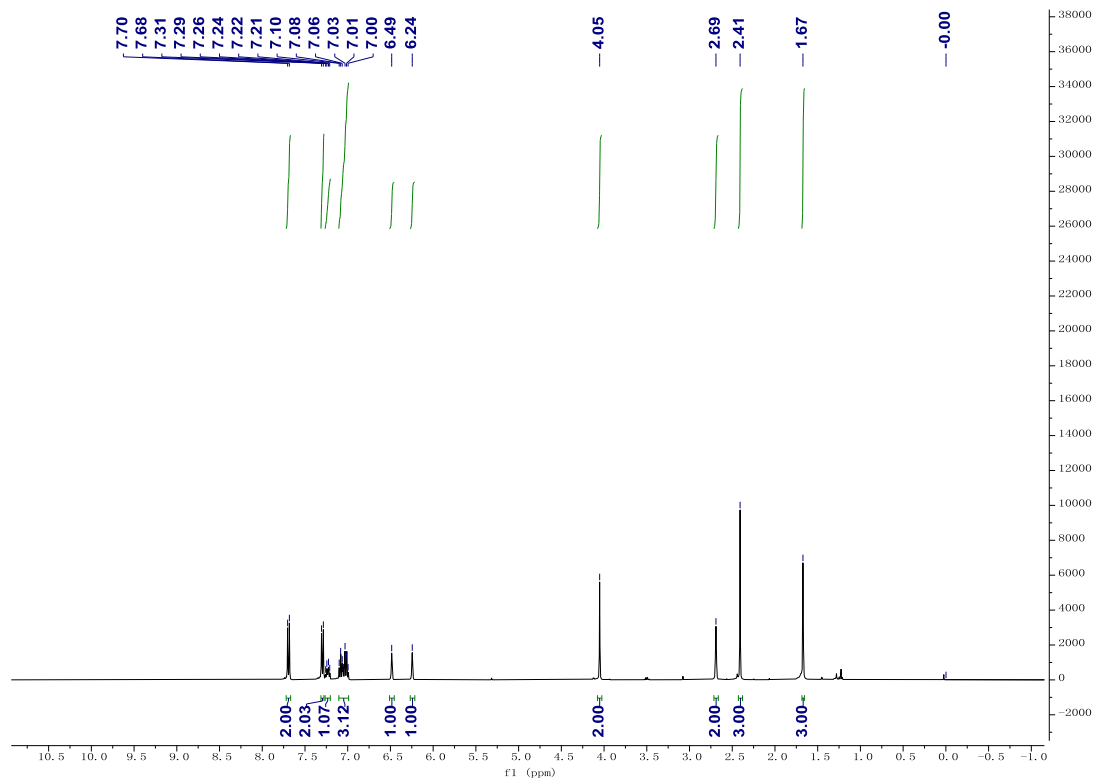


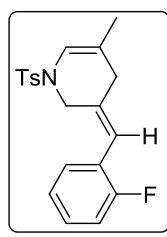
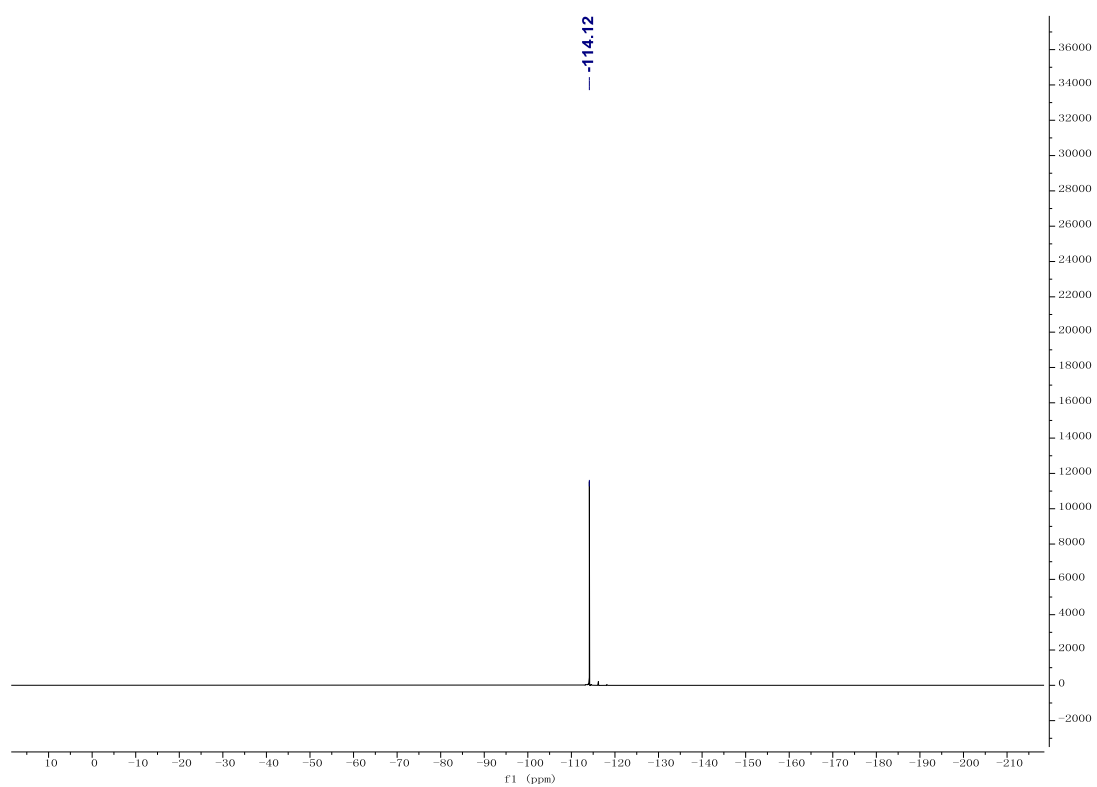
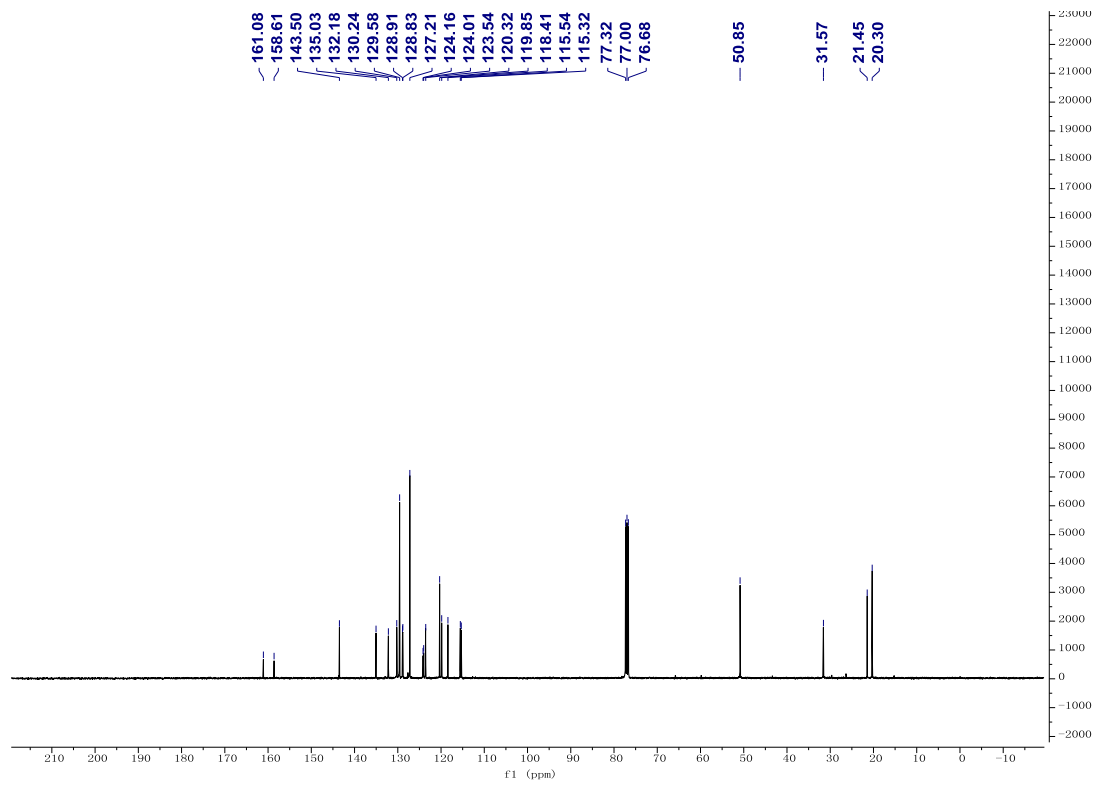
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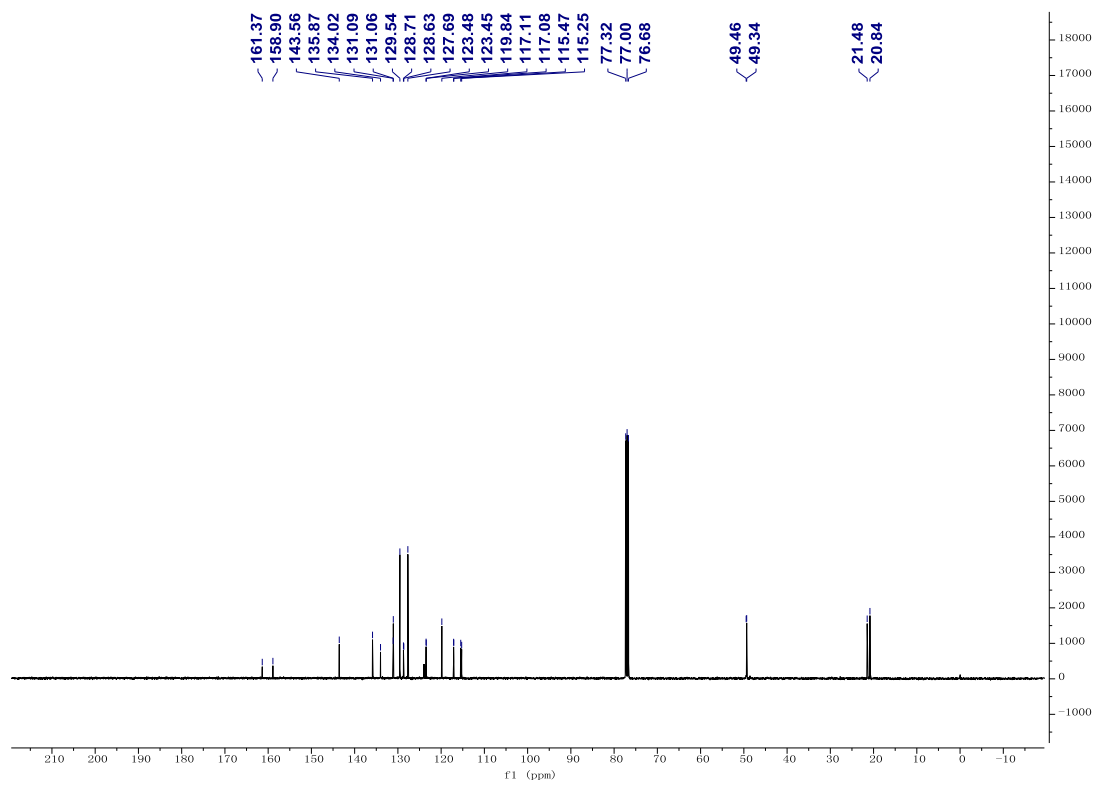
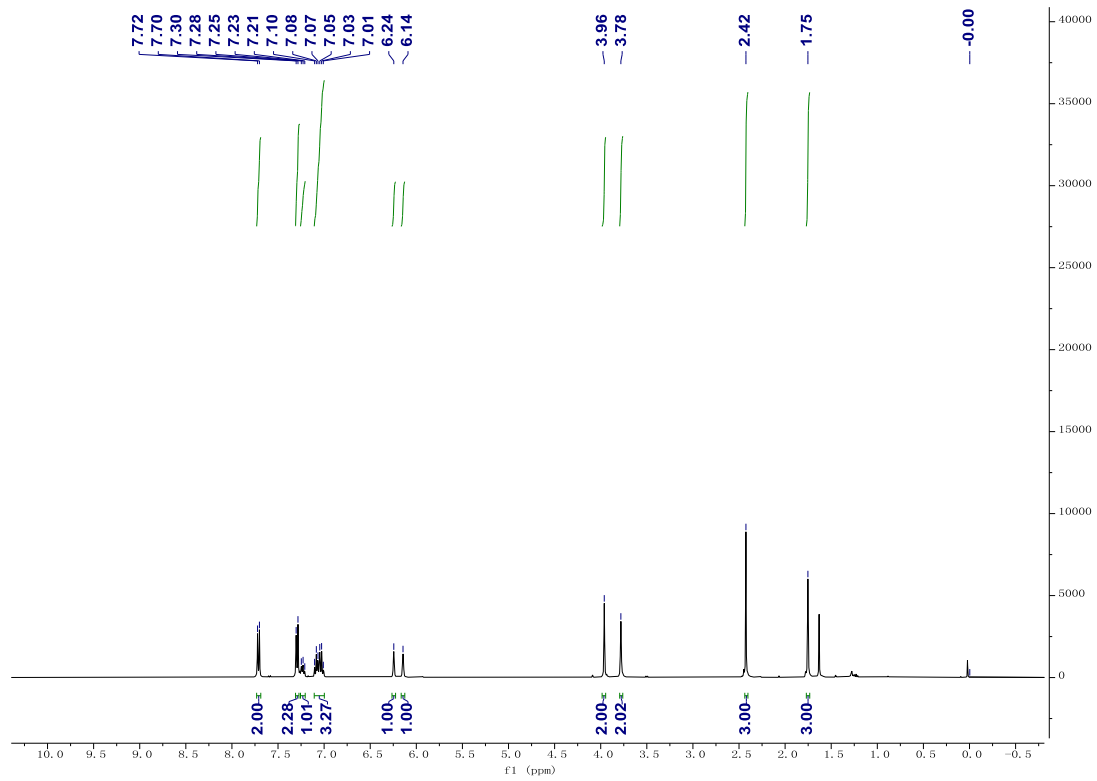


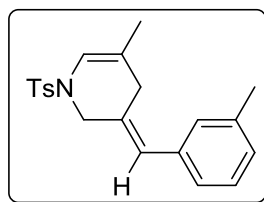
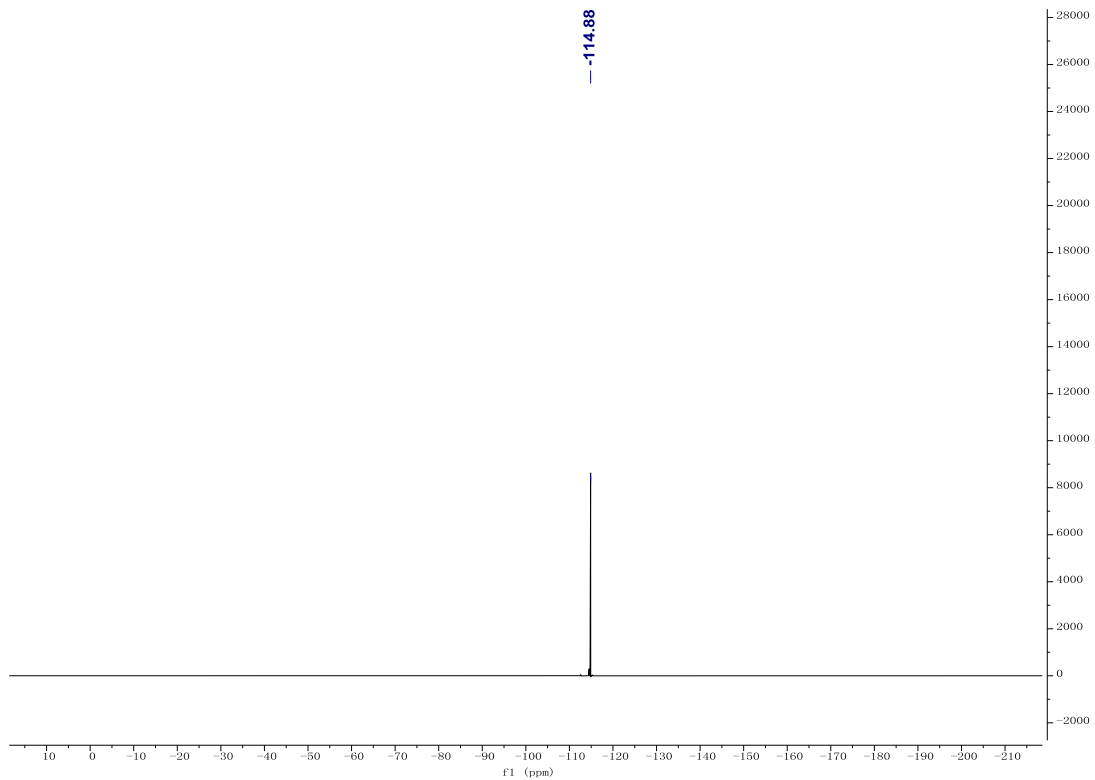
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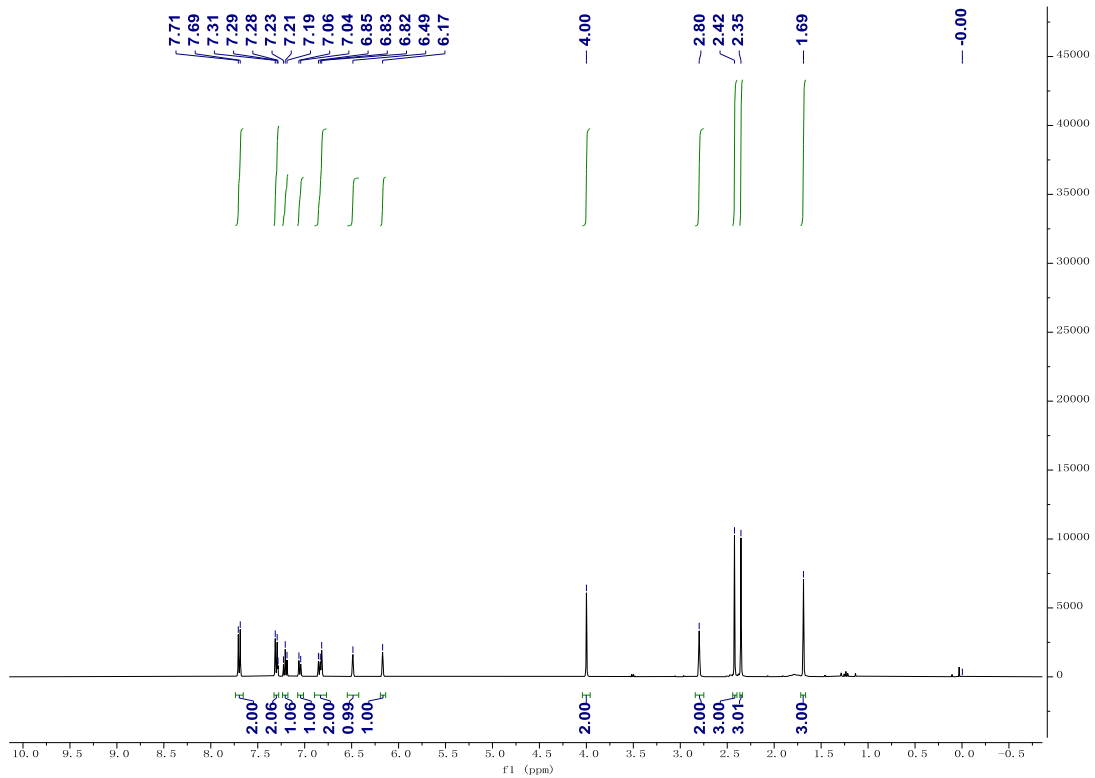


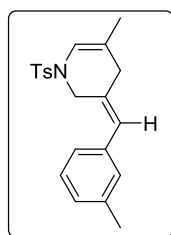
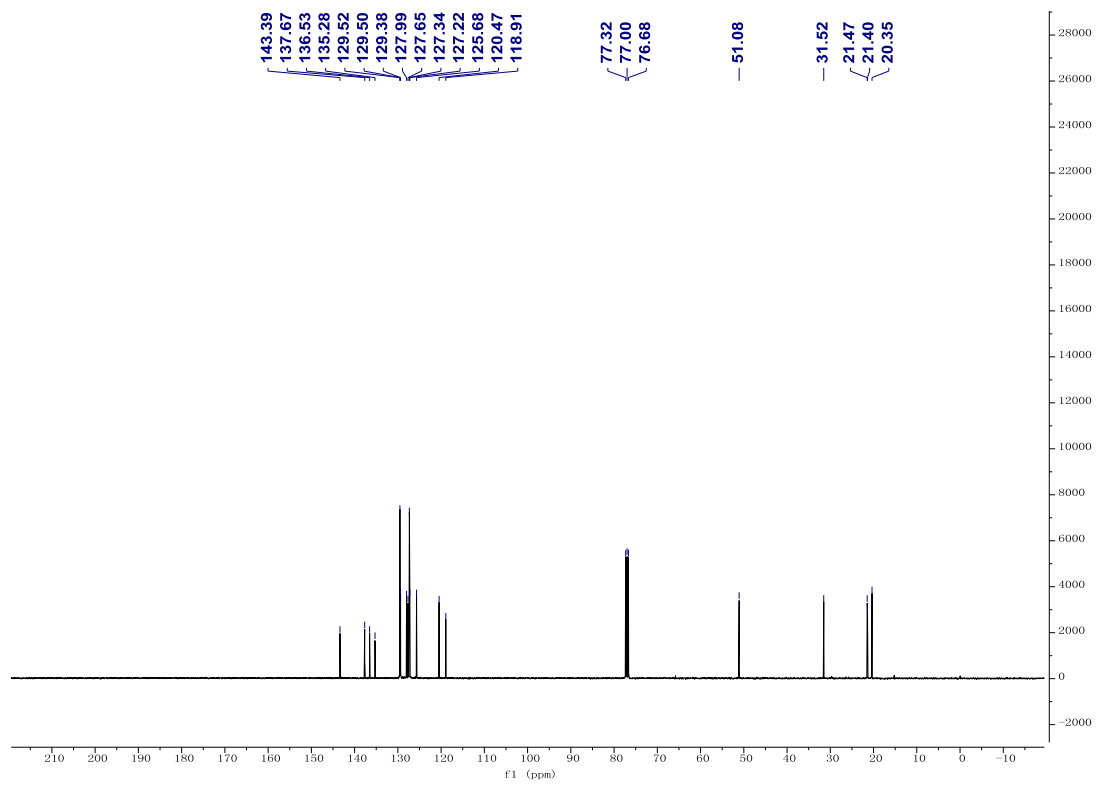
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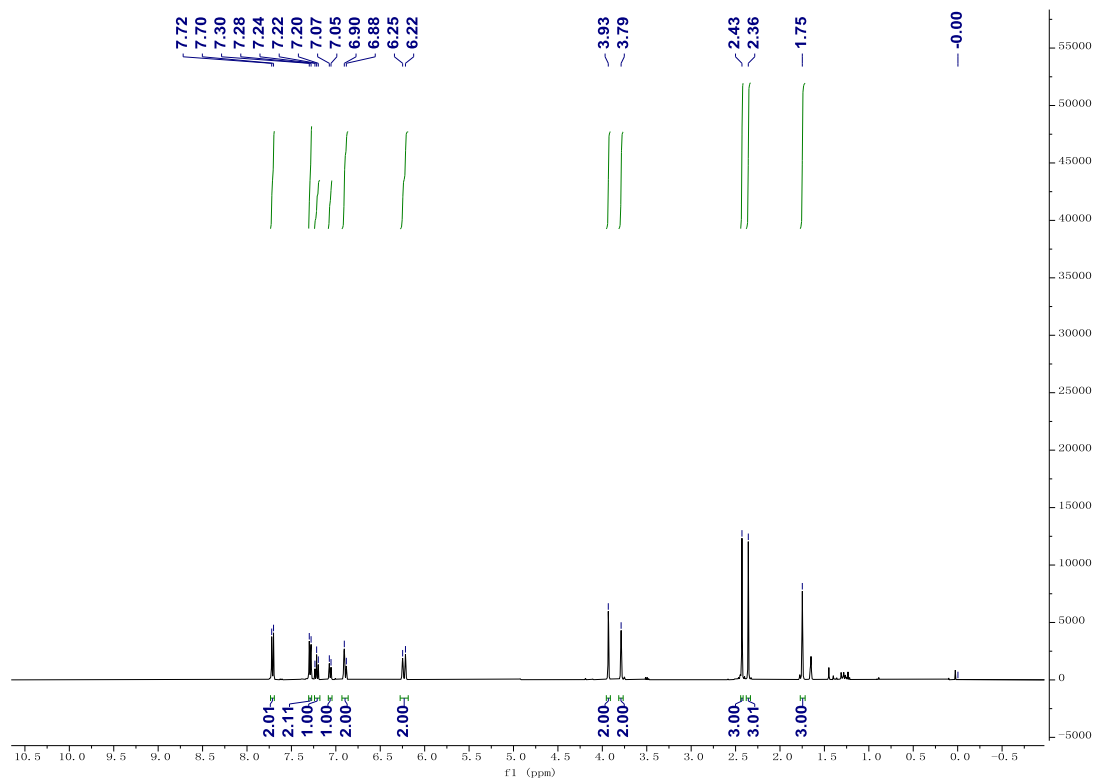


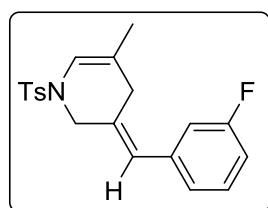
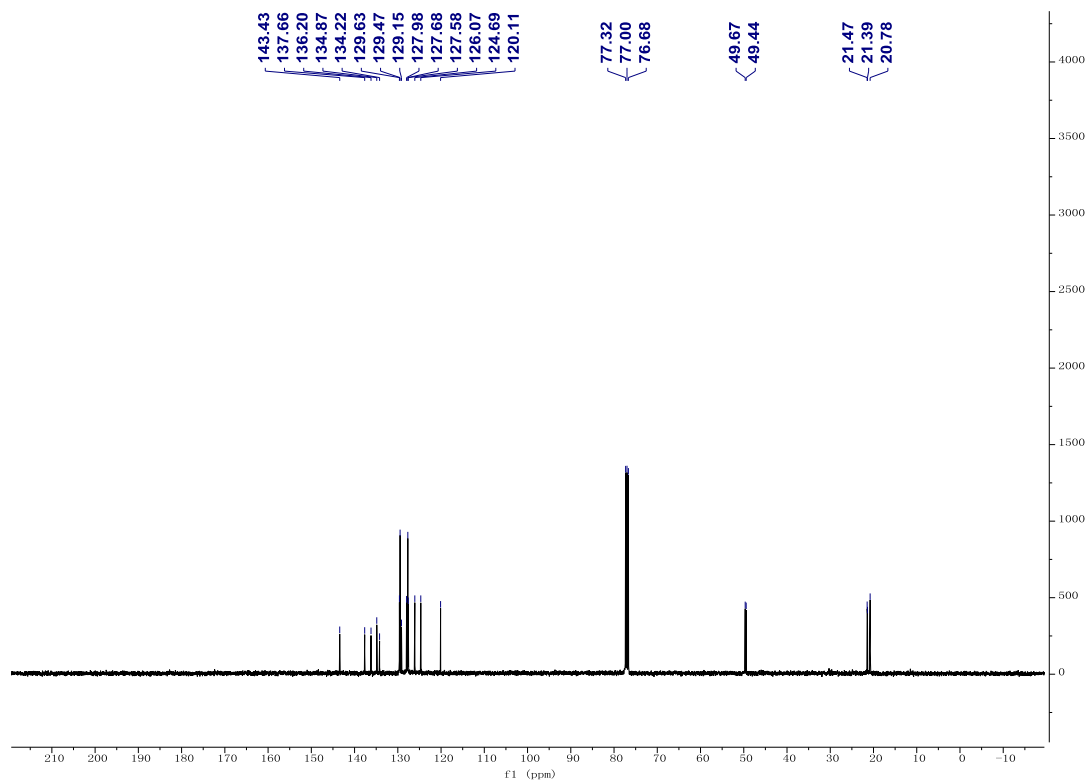
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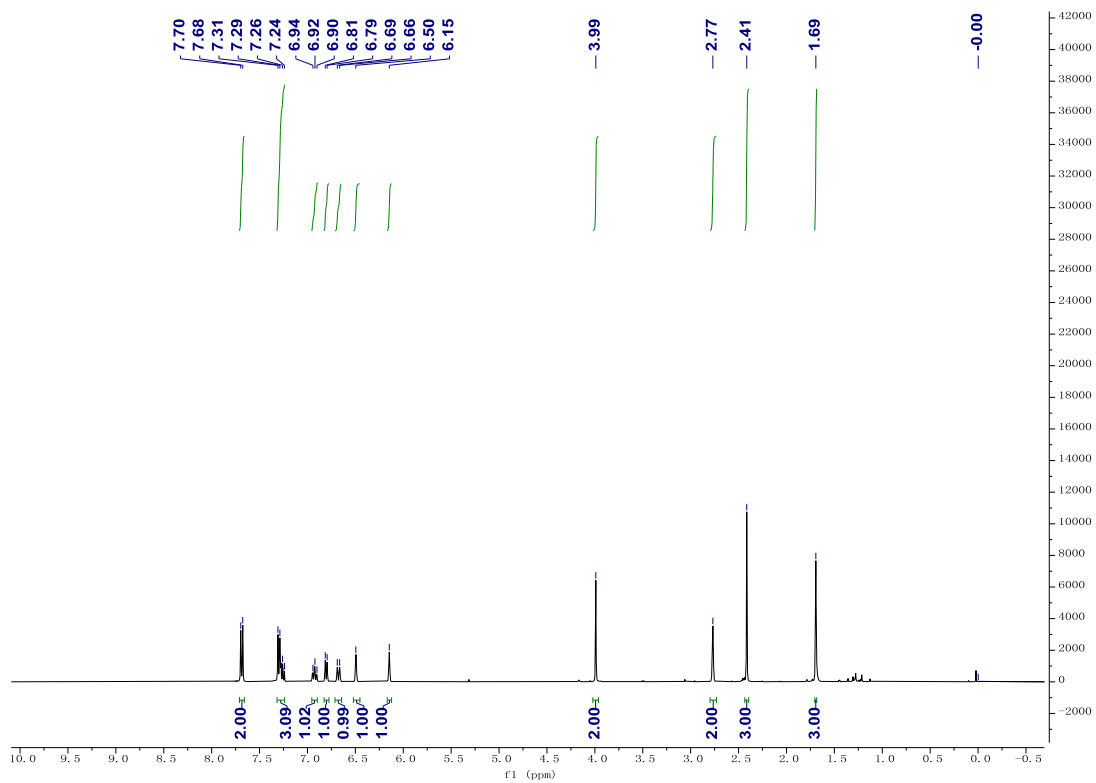


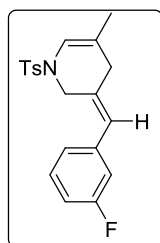
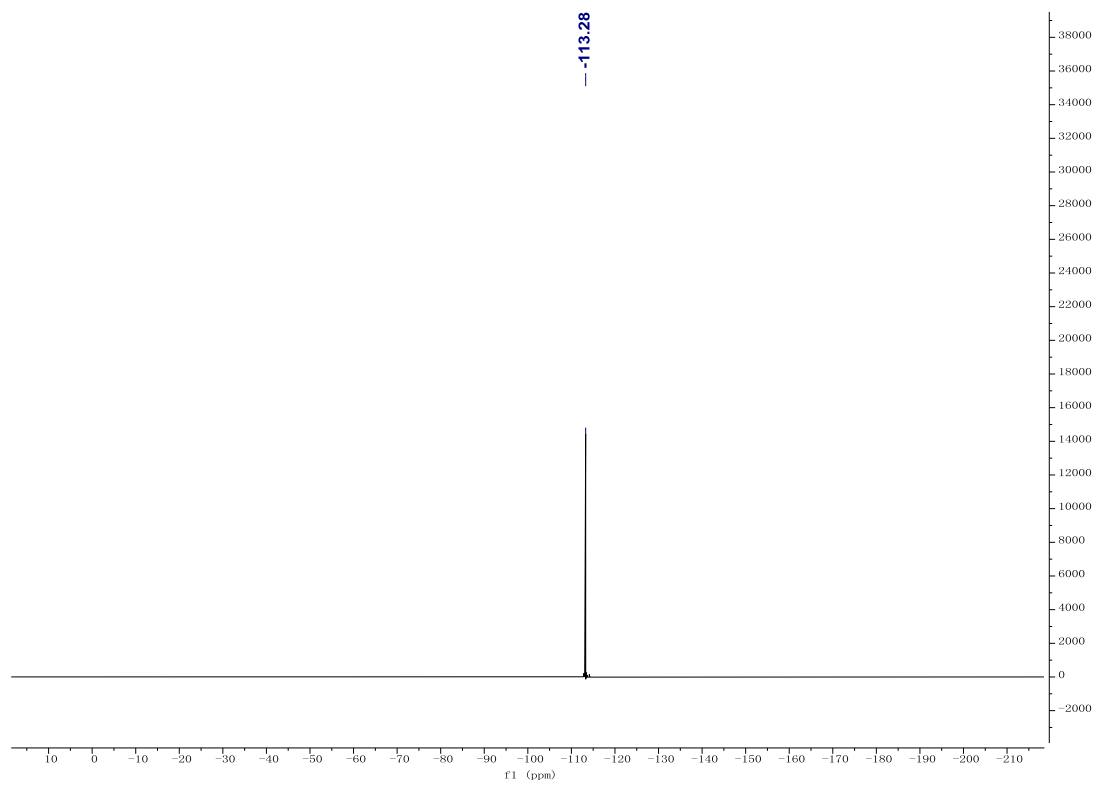
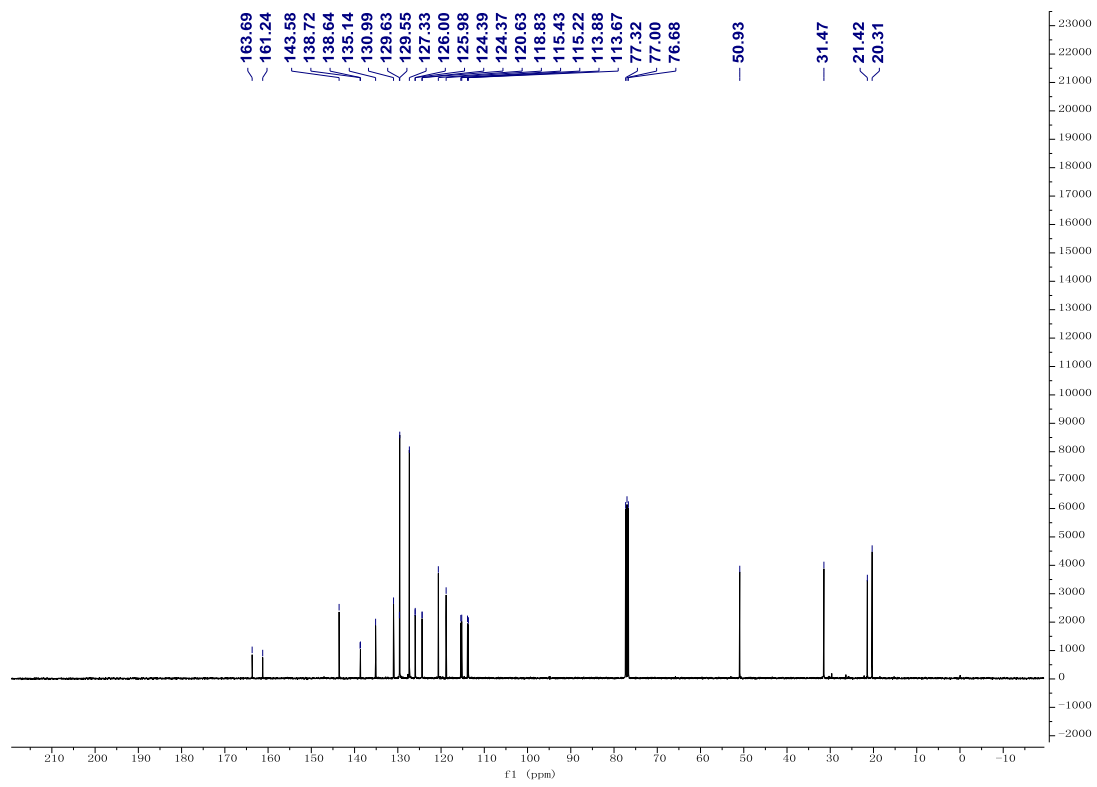
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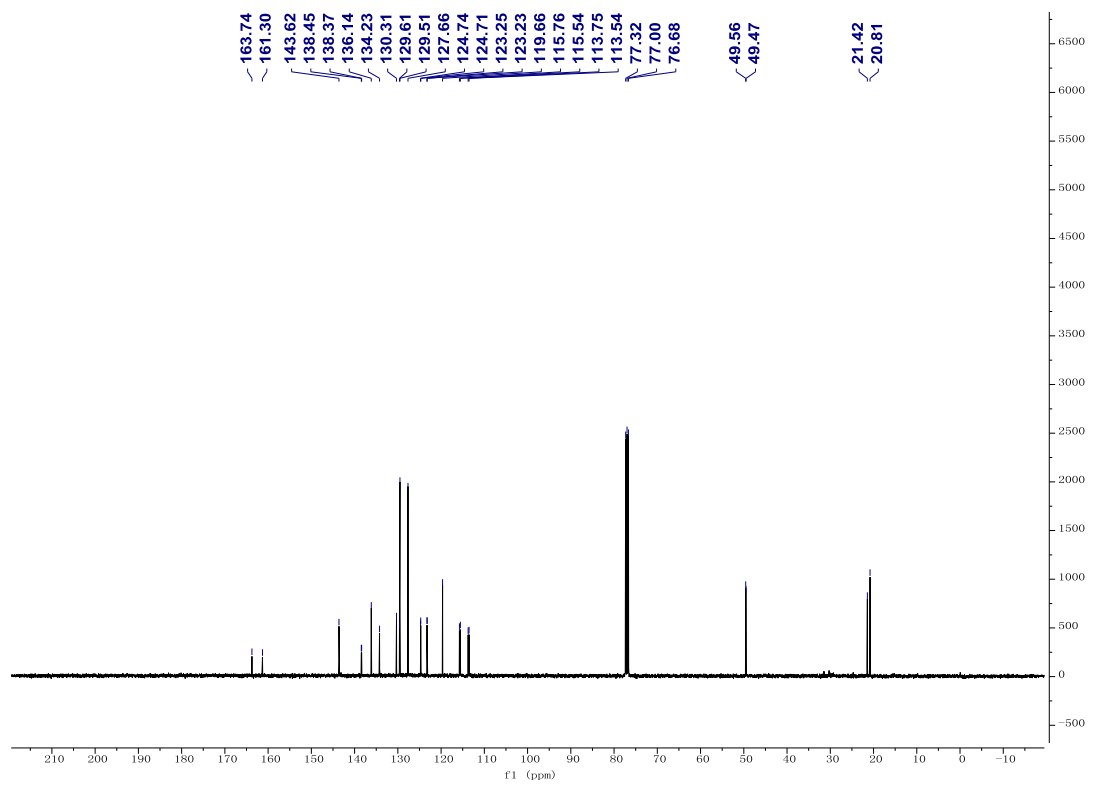
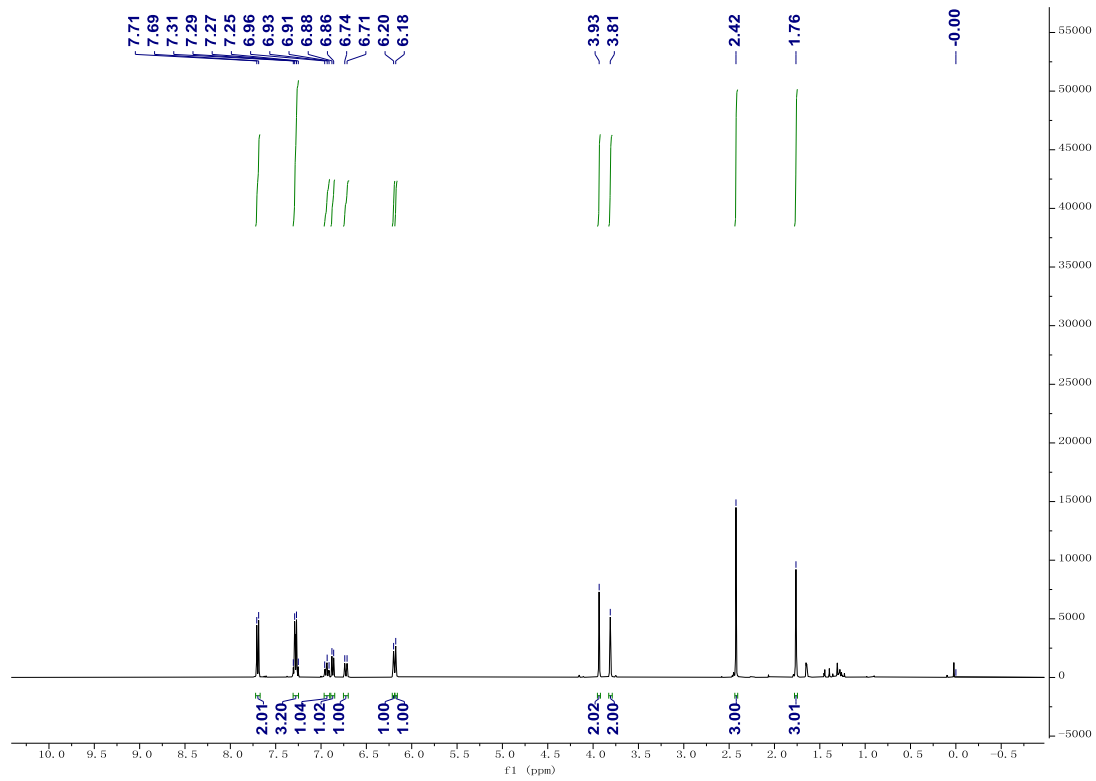


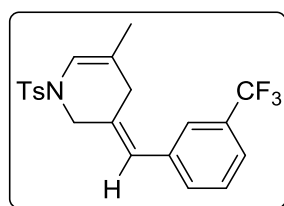
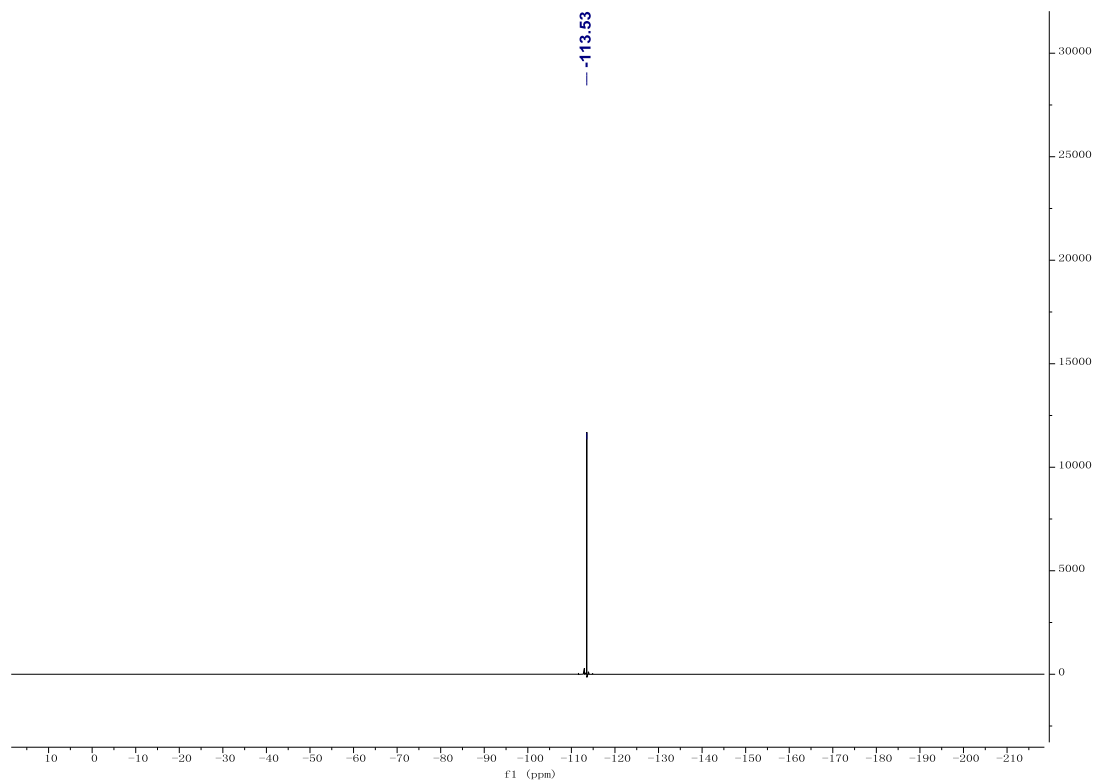
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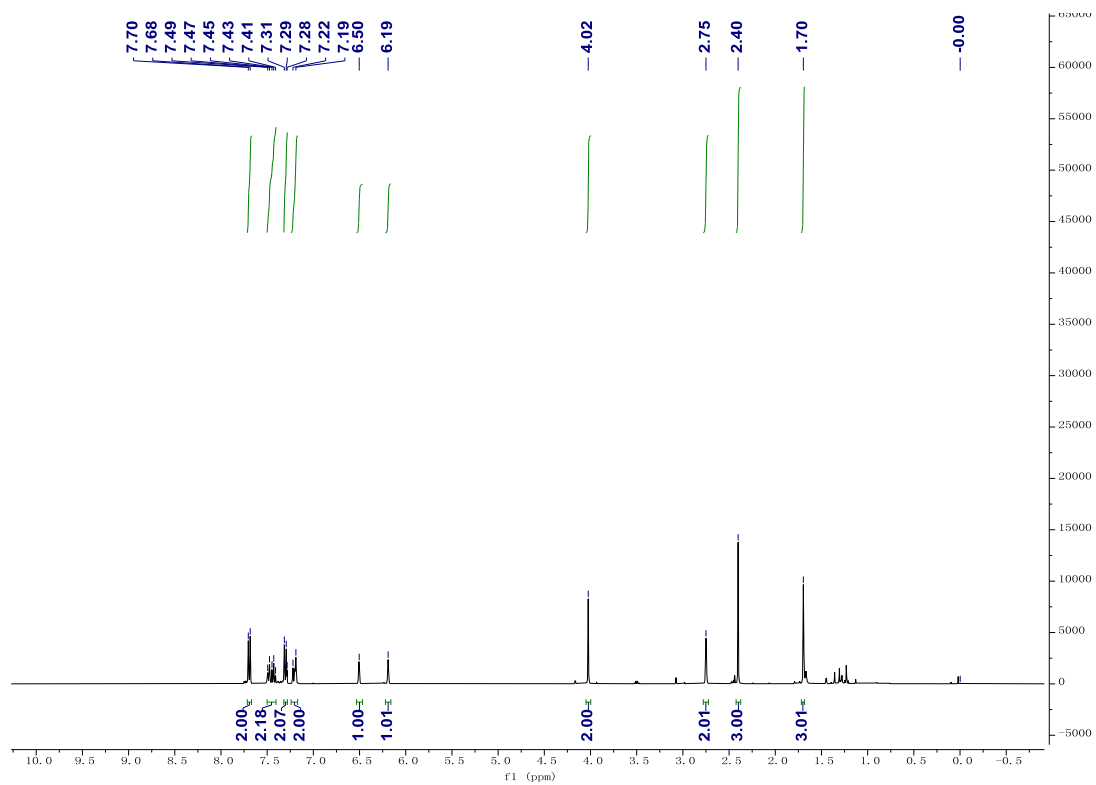


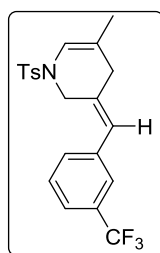
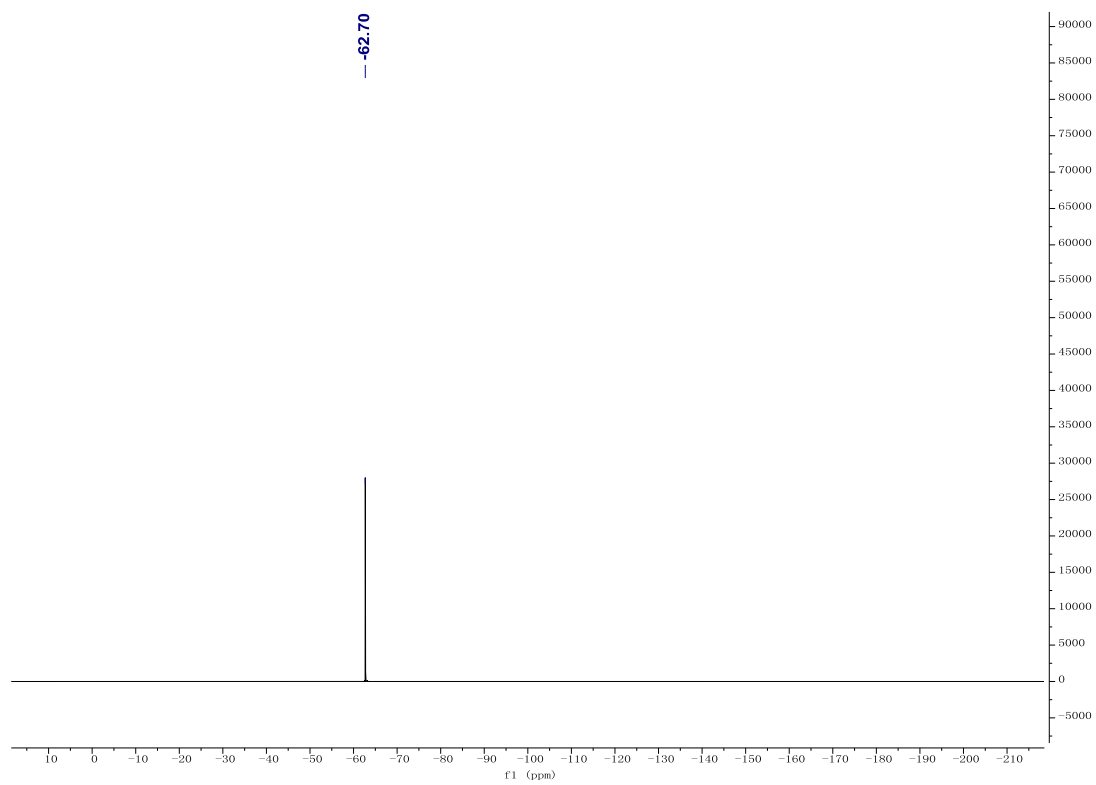
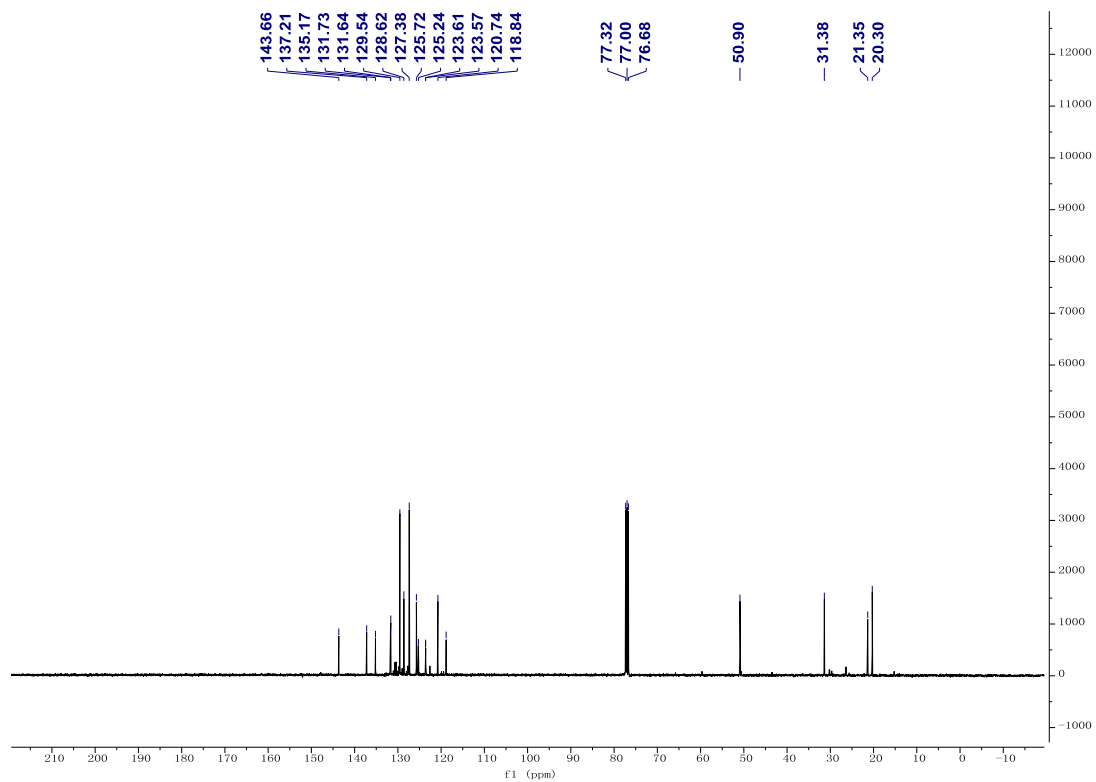
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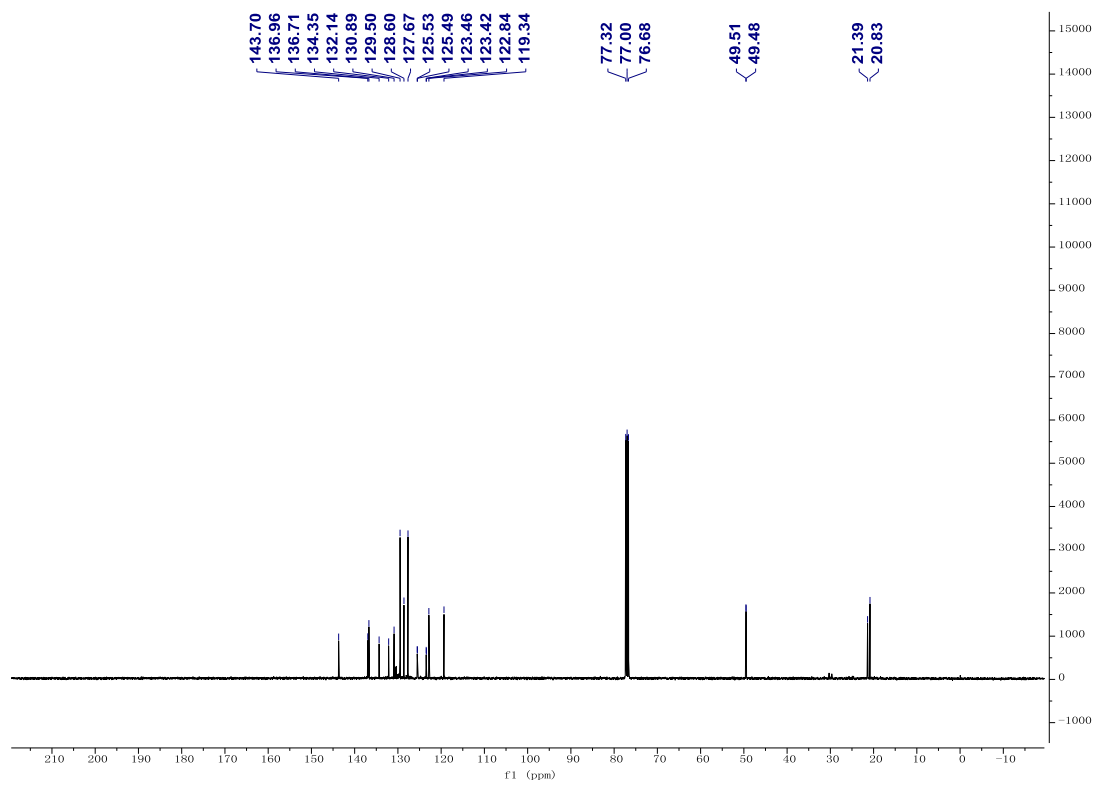
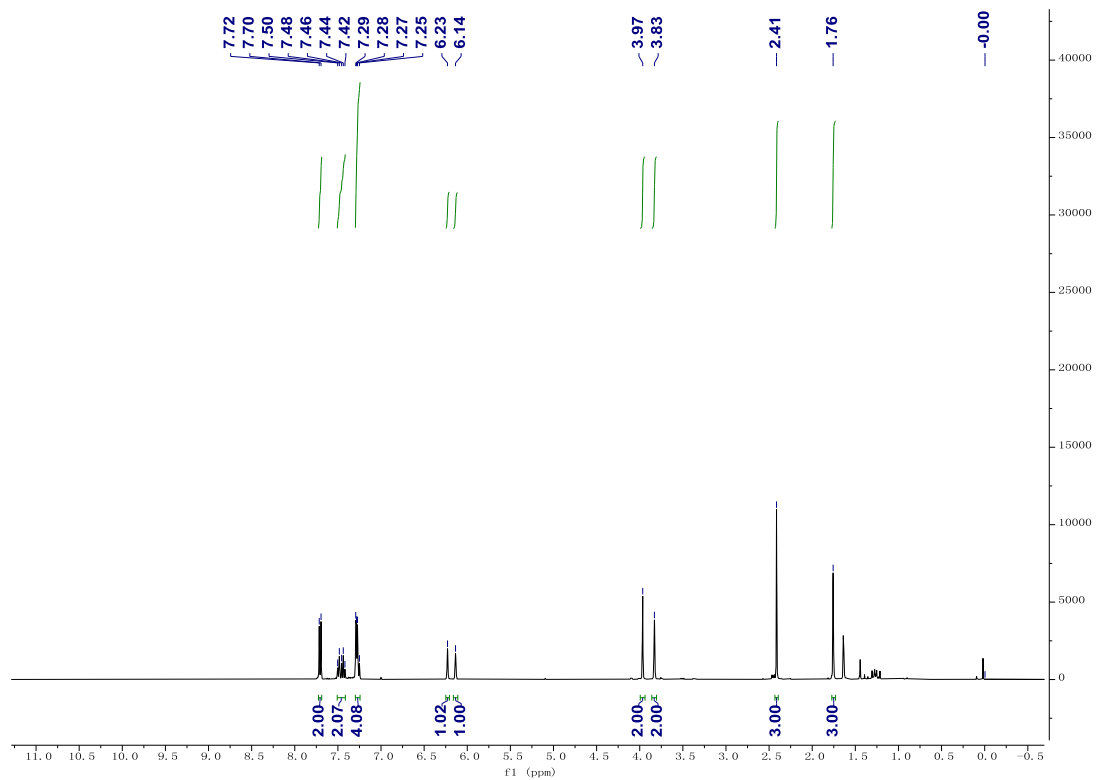


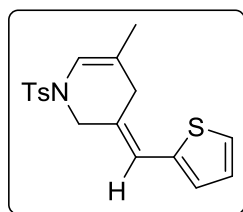
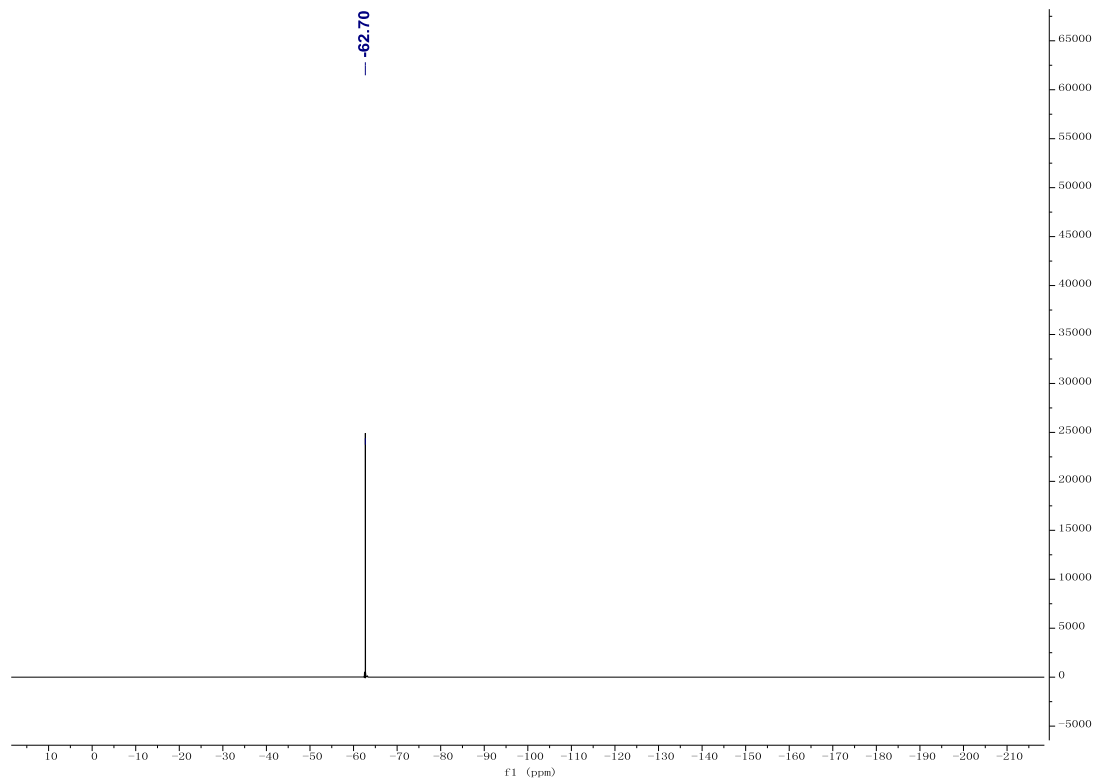
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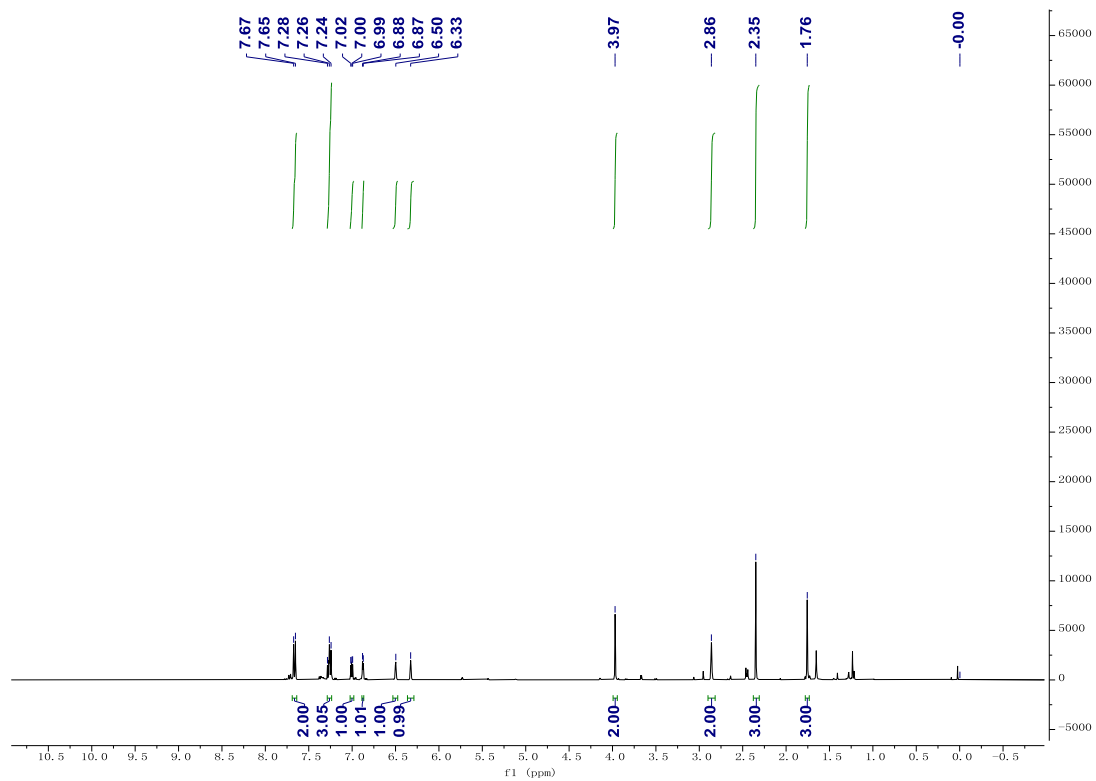


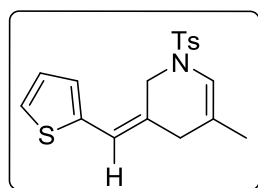
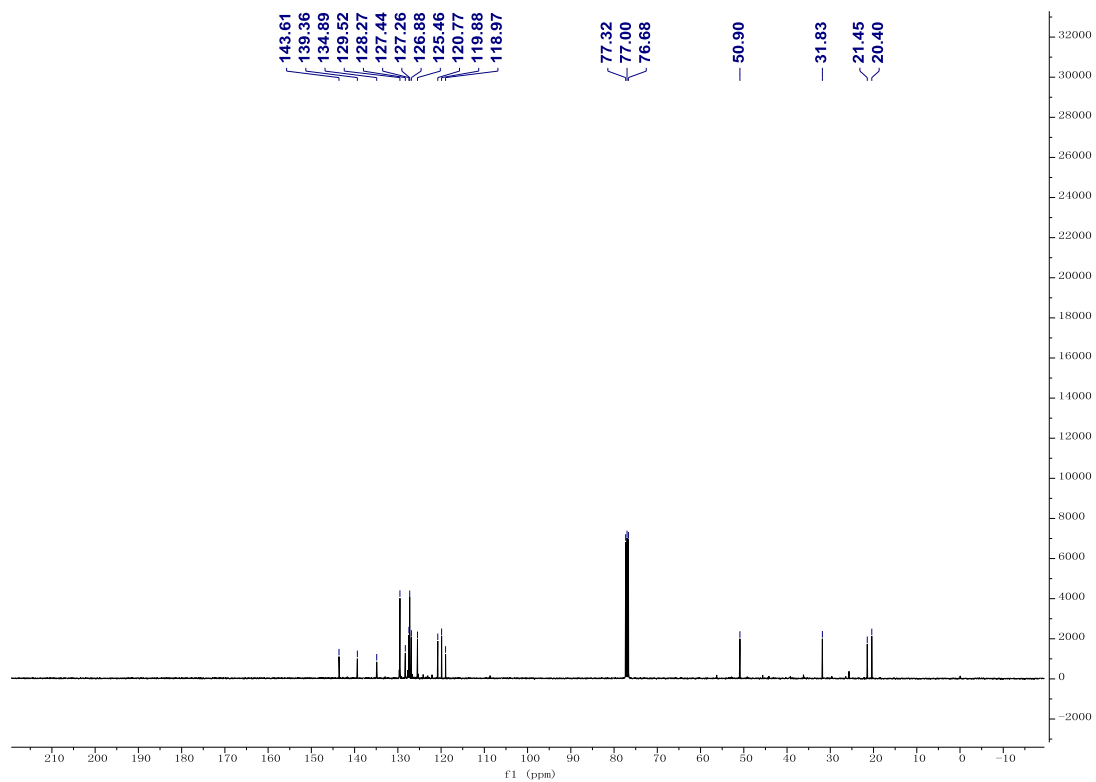
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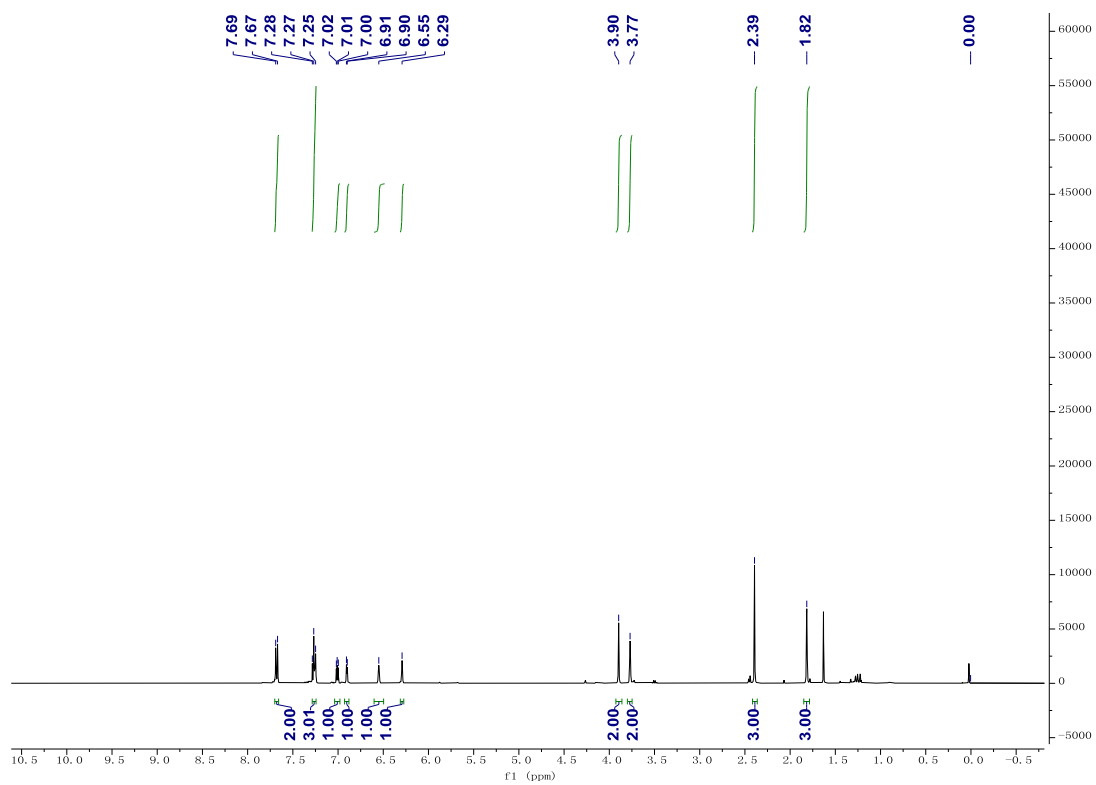


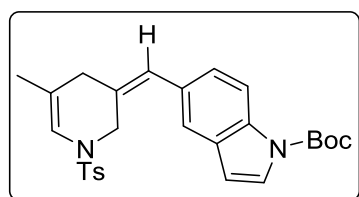
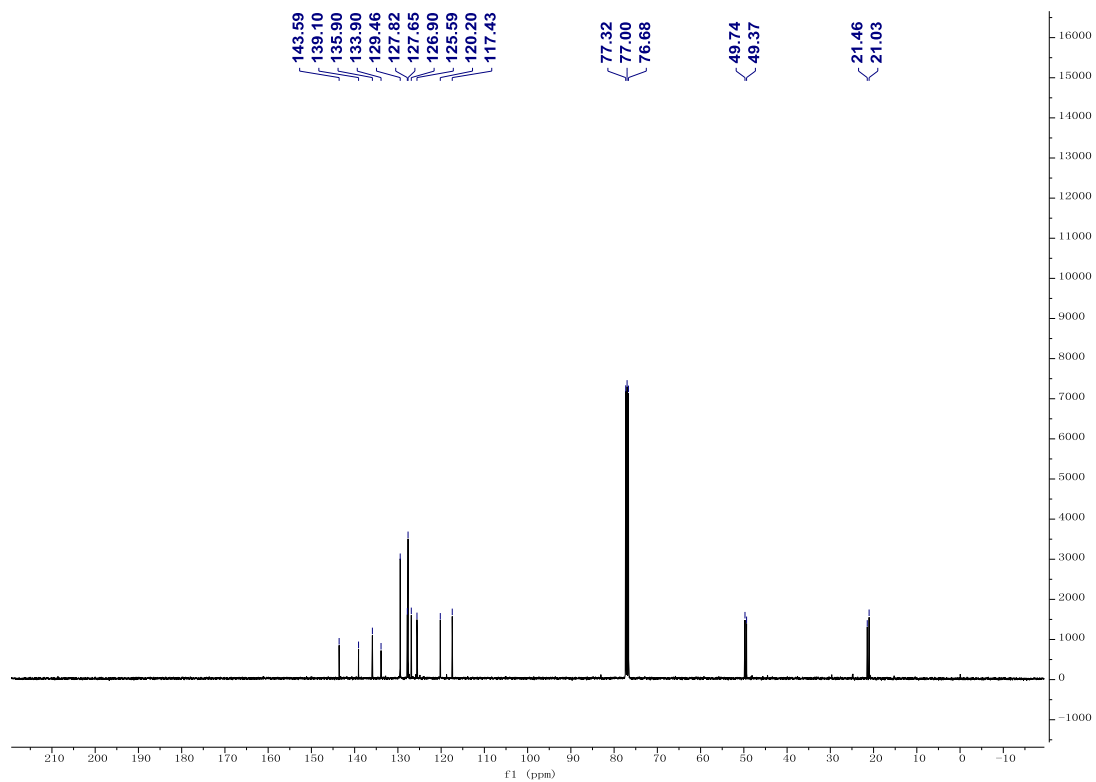
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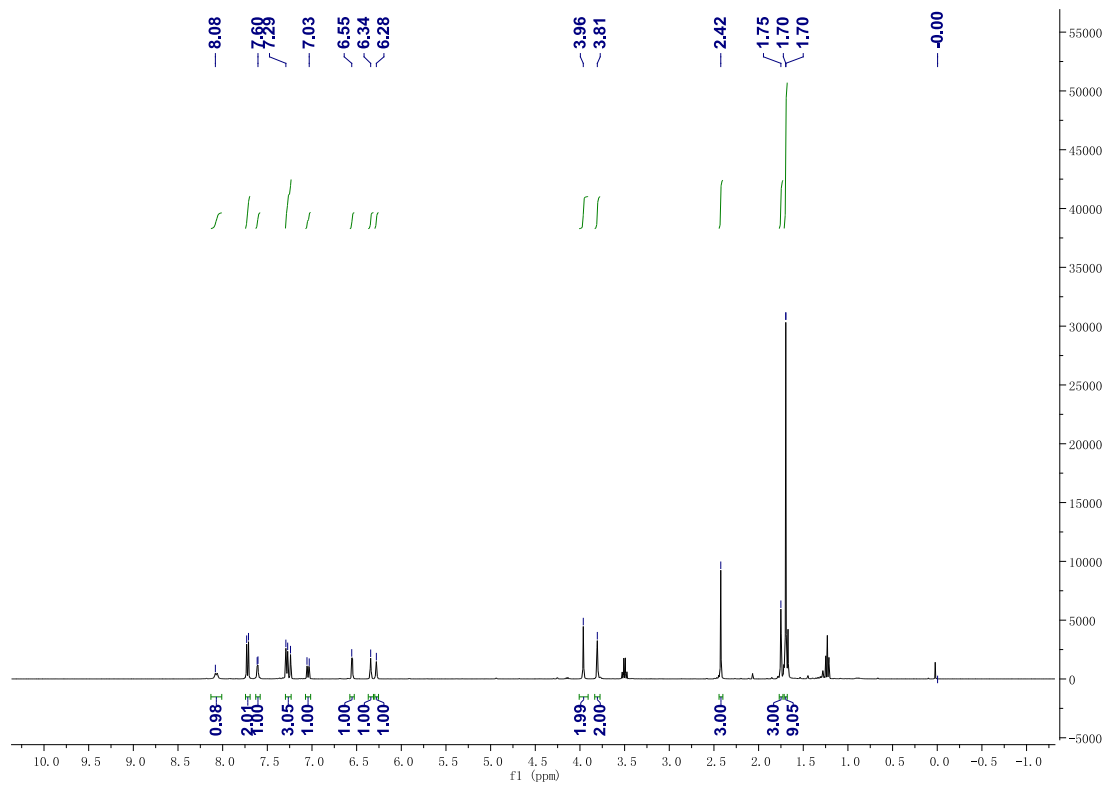


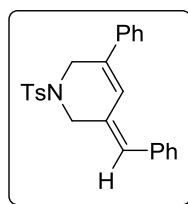
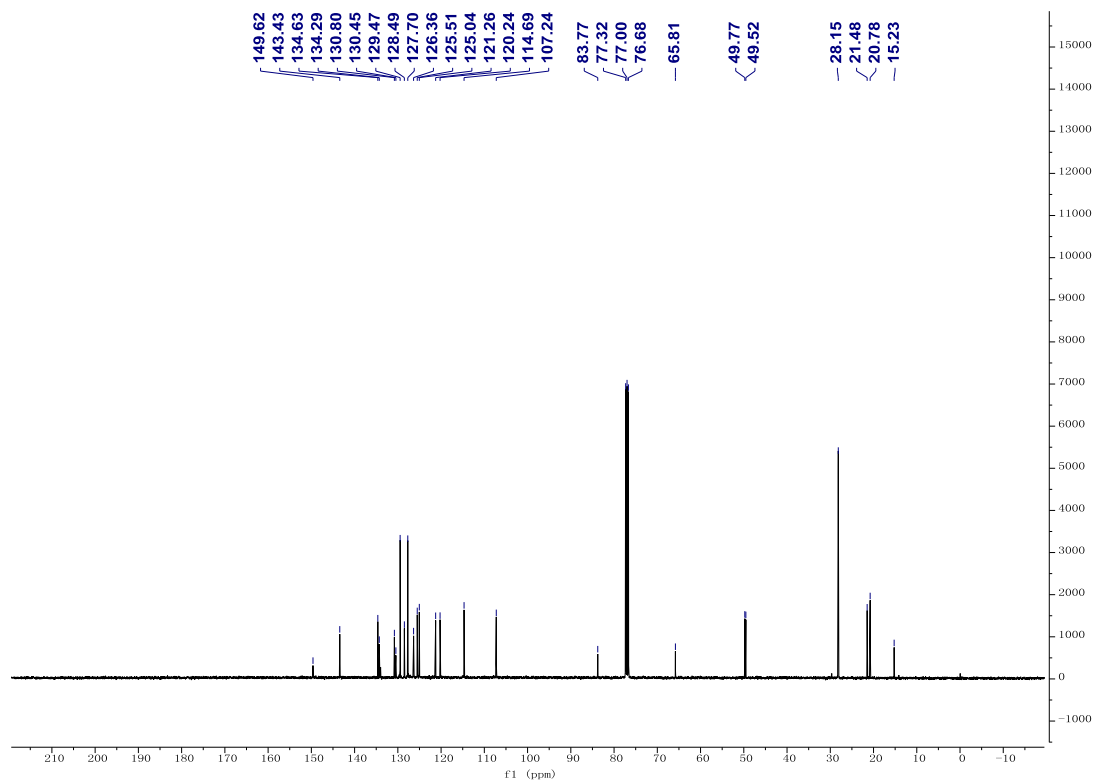
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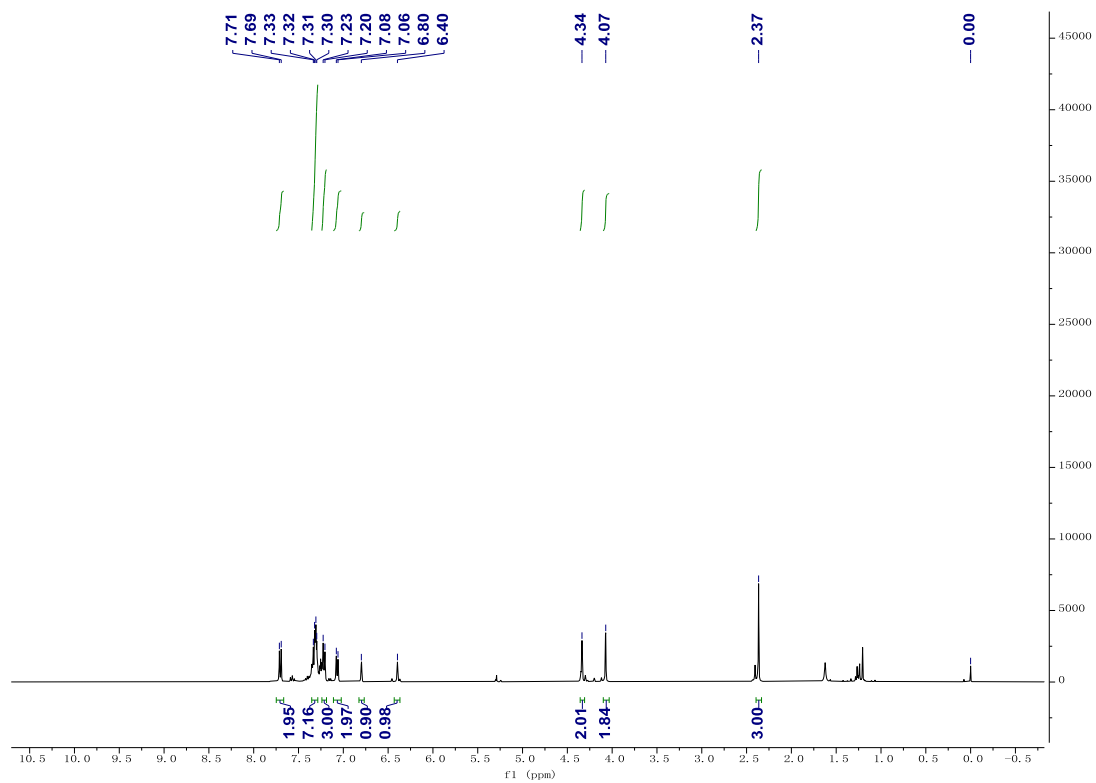


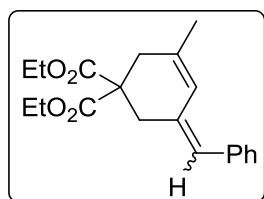
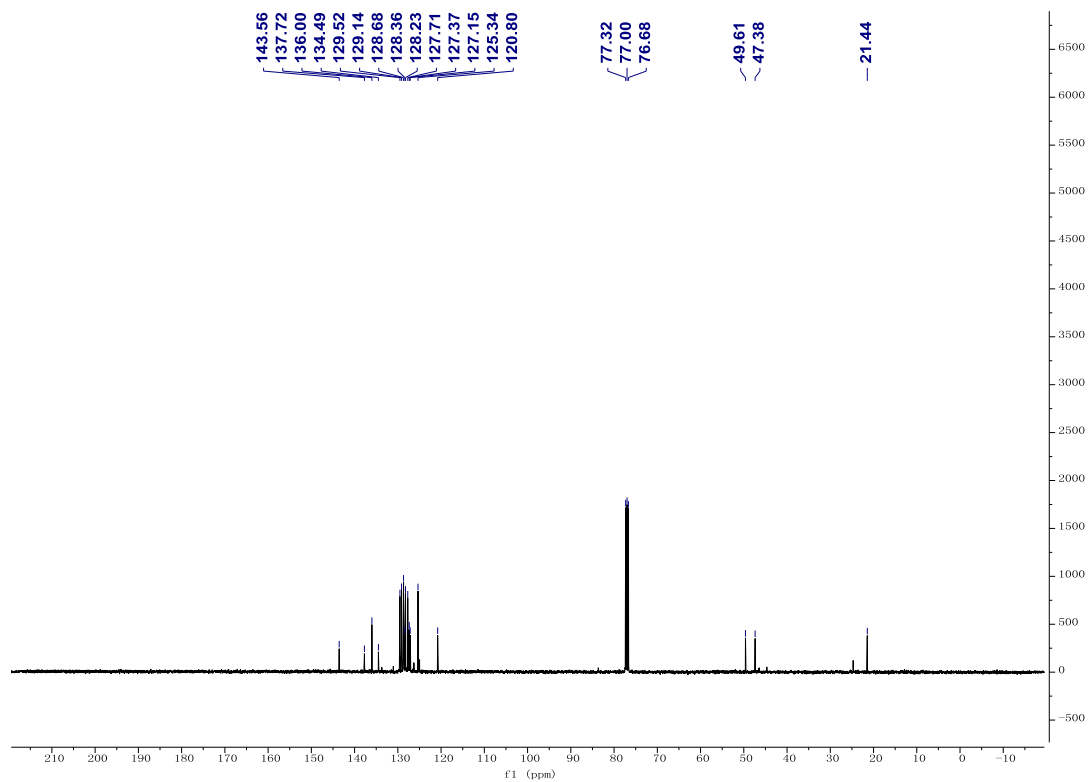
(Z)-6t





(E)-6u





6v

