Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

CO_2-Facilitated Radical Sequential (3+2) Annulation of 1,6-Enynes via Cooperation of Sulfinate Catalysis and Photocatalysis

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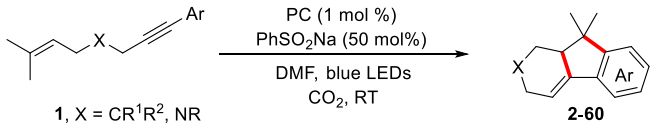
1. General Information

All reactions were conducted under an atmosphere of carbon dioxided. Unless otherwise noted, chemical reagents were purchased from commercial supplies (Accela, Acros Organics, Adamas-beta®, Alfa Aesar, Aladdin, Bidepharmatech Energy Chemical, TCI Chemicals, Innochem, J&K Chemicals, Laajoo, Leyan, Sigma-Aldrich, Sinocompound, and 3A Chemicals) and used directly without further purification. **The solvent DMF did not dry out the water.** Flash chromatography was performed with Sepaflash columns produced by Santai Technologies. Purification of products was performed by flash chromatography (FC) using silica gel or preparative thin layer chromatography. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE III spectrometer (400 MHz and 101 MHz, respectively). The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, td = triplet of doublet and m = multiplet. **To distinguish, some ^{13}C NMR chemical shifts retain two decimal places.** High-resolution mass spectra (HRMS) were obtained on an Impact II UHR-TOF mass spectrometry equipped with an ESI source from Bruker at Fujian Institute of Research on the Structure of Matter. The Blue LED strips (1 meter, 30W) were purchased from Prime LED Co., Ltd. (China). CO_2 gas (Purity: 99.995%) was purchased from Linde. The staring materials **1** were synthesized following the known procedures[S1], and all the products were identified by ^{1}H NMR, ^{13}C NMR and HRMS.

2. Experimental Section

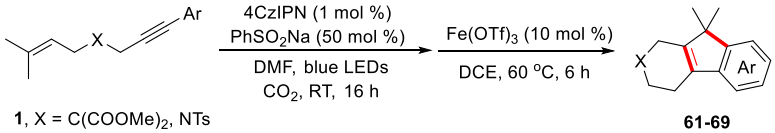
2.1 General procedures for the reactions reported herein

(a) (3+2) annulation of 1,6-enynes



The oven-dried Schlenk tube (38 mL) containing a stirring bar was charged with **1** (0.2 mmol), $PhSO_2Na$ (0.1 mmol, 50 mol%), 4CzIPN or $[Ir(ppy)_2(dtbbpy)]PF_6$ (0.002 mmol, 1 mmol%) and DMF (2 mL). The mixture was evacuated and back-filled with CO_2 for 3 times. The mixture was placed under a 30 W blue LED (λ_{max} = 465 nm, 7.5 cm away from the LEDs, with cooling fan to keep the reaction temperature at 25~30 ^{o}C) light source and stirred at ambient temperature for 16 h or 40 h. Upon completion of the reaction, all the solvents were removed under reduced pressure at high temperature. The crude reaction mixture was diluted with EtOAc (5 mL) and filtered through a short pad of Celite. The sealed tube and Celite pad were washed with an additional 25 mL of EtOAc. The filtrate was concentrated in vacuo, and crude ^{1}H NMR spectrum was taken using coumarin as internal standard. The resulting residue was purified by flash silica gel chromatography or preparative thin layer chromatography using petroleum ether/EtOAc (20:1-5:1) as the eluent to give the desired products.

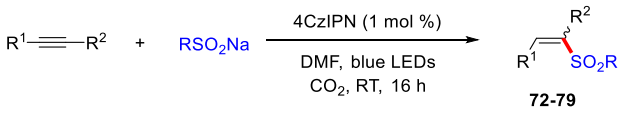
(b) One-pot two-step procedure for isomerization of the tetrahydrofluorenes



The oven-dried Schlenk tube (38 mL) containing a stirring bar was charged with **1** (0.2 mmol), $PhSO_2Na$ (0.1 mmol, 50 mol%), 4CzIPN or $[Ir(ppy)_2(dtbbpy)]PF_6$ (0.002 mmol, 1 mmol%) and DMF (2 mL). The mixture was evacuated and back-filled with CO_2 for 3 times. The mixture was placed under a 30 W blue LED (λ_{max} = 465 nm, 7.5 cm away from the LEDs, with cooling fan to keep the reaction temperature at 25~30 ^oC) light source and stirred at ambient temperature for 16 h or 40 h. Upon completion of the reaction, all the solvents were removed under reduced pressure at high temperature. The crude reaction mixture was diluted with EtOAc (5 mL) and filtered through a short pad of Celite. The sealed tube and Celite pad were washed with an additional 25 mL of EtOAc. The filtrate was concentrated in vacuo.

Then $Fe(OTf)_3$ (0.02 mmol, 10 mol %) and DCE (2 mL) were added to the crud products, and the mixture was stirred at 60 ^oC for 3 h (for products **61-66**, **68**, **69**) or 6 h (for product **67**) under Ar atmosphere. Upon completion of the reaction, the crude reaction mixture was diluted with EtOAc (5 mL) and filtered through a short pad of Celite. The sealed tube and Celite pad were washed with an additional 25 mL of EtOAc. The filtrate was concentrated in vacuo and crude ^1H NMR spectrum was taken using coumarin as internal standard. The resulting residue was purified by flash silica gel chromatography or preparative thin layer chromatography using petroleum ether/EtOAc (20:1-10:1) as the eluent to give the desired products.

(c) CO_2-facilitated addition of sulfonyl radicals to alkenes

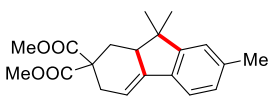


72-79

The oven-dried Schlenk tube (38 mL) containing a stirring bar was charged alkyne substrates (0.2 mmol), $PhSO_2Na$ (0.4 mmol, 2.0 equiv), 4CzIPN (0.002 mmol, 1 mmol%) and DMF (2 mL). The mixture was evacuated and back-filled with CO_2 for 3 times. The mixture was placed under a 30 W blue LED (λ_{max}=465 nm, 7.5 cm away from the LEDs, with cooling fan to keep the reaction temperature at 25~30 ^oC) light source and stirred at ambient temperature for 16 h. Upon completion of the reaction, all the solvents were removed under reduced pressure at high temperature. The crude reaction mixture was diluted with EtOAc (5 mL) and filtered through a short pad of Celite. The sealed tube and Celite pad were washed with an additional 25 mL of EtOAc. The filtrate was concentrated in vacuo, and crude ^1H NMR spectrum was taken using coumarin as internal standard. The resulting residue was purified by flash silica gel chromatography or preparative thin layer chromatography using petroleum ether/EtOAc (20:1-5:1) as the eluent to give the desired products**72-79**.

2.2 Characterization of products

dimethyl-7,9,9-trimethyl-1,3,9,9a-tetrahydro-2*H*-fluorene-2,2-dicarboxylate (2)



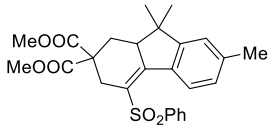
PC: 4CzIPN; Reaction time: 16 h; Yield: 57.7 mg, 88%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 20/1) as a white solid (m.p. = 70-71 ℃).

^1H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.1 Hz, 1H), 6.93 (s, 1H), 6.93 – 6.89 (m, 1H), 5.86 – 5.83 (m, 1H), 3.68 (s, 3H), 3.64 (s, 3H), 3.03 – 2.97 (m, 1H), 2.47 – 2.37 (m, 2H), 2.32 – 2.27 (m, 4H), 1.82

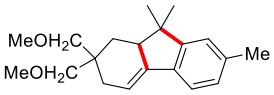
(t, *J* = 12.5 Hz, 1H), 1.30 (s, 3H), 0.87 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.0, 171.7, 154.3, 141.0, 138.0, 135.8, 127.7, 123.0, 120.2, 113.2, 54.1, 52.9, 52.9, 48.7, 44.4, 31.3, 28.7, 26.12, 26.08, 21.7. **HRMS (m/z, ESI-TOF):** Calcd for $C_{20}H_{24}O_4Na^+$ [M+Na^+] 351.1567, found 351.1570.

dimethyl-7,9,9-trimethyl-4-(phenylsulfonyl)-1,3,9,9a-tetrahydro-2H-fluorene-2,2-dicarboxylate (2')



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.1 Hz, 1H), 8.01 – 7.91 (m, 2H), 7.58 – 7.52 (m, 1H), 7.50 – 7.46 (m, 2H), 7.03 (s, 1H), 6.99 (d, *J* = 8.3 Hz, 1H), 3.77 (s, 3H), 3.66 (s, 3H), 3.48 (dt, *J* = 18.3, 2.0 Hz, 1H), 2.84 (dd, *J* = 18.2, 3.4 Hz, 1H), 2.57 – 2.44 (m, 2H), 2.35 (s, 3H), 1.94 – 1.81 (m, 1H), 1.36 (s, 3H), 0.94 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.5, 170.5, 157.5, 151.5, 141.8, 141.3, 133.0, 131.3, 129.0, 128.7, 127.5, 126.4, 126.3, 122.4, 53.8, 53.7, 53.2, 53.0, 44.2, 33.3, 27.4, 26.3, 25.4, 21.7. **HRMS (m/z, ESI-TOF):** Calcd for $C_{26}H_{28}O_6SNa^+$ [M+Na^+] 491.1499, found 491.1501.

2,2-bis(methoxymethyl)-7,9,9-trimethyl-2,3,9,9a-tetrahydro-1*H*-fluorene (3)

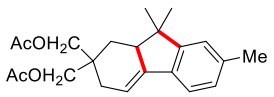


PC: 4CzIPN; Reaction time: 16 h; Yield: 43.2 mg, 72%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 15/1) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 7.6 Hz, 1H), 7.03 (s, 1H), 6.99 (d, *J* = 7.7 Hz, 1H), 5.90 (q, *J* = 3.0 Hz, 1H), 3.38 – 3.25 (m, 10H), 2.48 (dd, *J* = 7.7, 4.6 Hz, 1H), 2.35 (s, 3H), 2.15 – 1.98 (m, 2H), 1.83 (dd, *J* = 12.2, 5.0 Hz, 1H), 1.37 (s, 3H), 1.29 (t, *J* = 12.3 Hz, 1H), 0.90 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 154.6, 140.9, 137.4, 136.4, 127. 5, 123.0, 119.8, 114.9, 79.4, 74.0, 59.5, 59.4, 48.0, 44.2, 38.6, 30.9, 26.8, 26.1, 26.0, 21.7. **HRMS (m/z, ESI-TOF):** Calcd for $C_{20}H_{28}O_2Na^+$ [M+Na^+] 323.1982, found 323.1985.

(7,9,9-trimethyl-2,3,9,9a-tetrahydro-1*H*-fluorene-2,2-diyl)bis(methylene) diacetate (4)

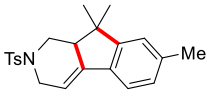


PC: 4CzIPN; Reaction time: 16 h; Yield: 54.1 mg, 76%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 10/1) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.23 (m, 1H), 7.02 (s, 1H), 7.00 (d, *J* = 7.7 Hz, 1H), 5.87 (q, *J* = 3.4 Hz, 1H), 4.13 – 3.99 (m, 4H), 2.50 – 2.44 (m, 1H), 2.35 (s, 3H), 2.16 – 2.11 (m, 2H), 2.10 (s, 3H), 2.06 (s, 3H), 1.85 (dd, *J* = 12.4, 5.1 Hz, 1H), 1.38 – 1.32 (m, 4H), 0.91 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.2, 171.1, 154.3, 141.2, 137.8, 135.9, 127.6, 123.0, 119.9, 113.3, 69.6, 64.7, 47.6, 44.2, 36.8, 30.5, 26.8, 26.0, 25.9, 21.7, 21.0, 20.9. **HRMS (m/z, ESI-TOF):** Calcd for $C_{22}H_{28}O_4Na^+$ [M+Na^+] 379.1880, found 379.1878.

7,9,9-trimethyl-2-tosyl-2,3,9,9a-tetrahydro-1*H*-indeno[2,1-c]pyridine (5)

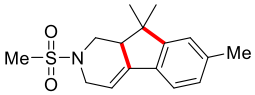


PC: 4CzIPN; Reaction time: 16 h; Yield: 57.3 mg, 78%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 20/1) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 7.3 Hz, 1H), 6.99 (s, 1H), 5.82 (q, *J* = 3.1 Hz, 1H), 4.25 (dt, *J* = 17.1, 3.5 Hz, 1H), 4.12 (dd, *J* = 11.0, 5.3 Hz, 1H), 3.40 (dt, *J* = 17.2, 3.2 Hz, 1H), 2.83 – 2.78 (m, 1H), 2.46 (t, *J* = 11.0 Hz, 1H), 2.42 (s, 3H), 2.35 (s, 3H), 1.42 (s, 3H), 0.87 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 154.2, 143.6, 141.0, 138.8, 134.9, 134.2, 129.8, 128.0, 127.6, 123.1, 120.4, 110.9, 50.8, 45.2, 44.2, 44.1, 26.8, 26.3, 21.8, 21.7. **HRMS (m/z, ESI-TOF):** Calcd for $C_{22}H_{26}NO_2S^+$ [M+H$^+$] 368.1679, found 368.1672.

7,9,9-trimethyl-2-(methylsulfonyl)-2,3,9,9a-tetrahydro-1*H*-indeno[2,1-c]pyridine (6)

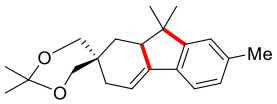


PC: 4CzIPN; Reaction time: 40 h; Yield: 41.9 mg, 72%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 15/1) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.2 Hz, 1H), 7.04 (d, *J* = 6.8 Hz, 2H), 5.95 – 5.87 (m, 1H), 4.24 (dd, *J* = 17.6, 3.1 Hz, 1H), 4.09 (d, *J* = 6.3 Hz, 1H), 3.75 (d, *J* = 17.3 Hz, 1H), 2.87 (s, 3H), 2.85 – 2.77 (m, 2H), 2.37 (s, 3H), 1.44 (s, 3H), 0.96 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 154.0, 141.1, 138.9, 134.8, 128.0, 123.1, 120.3, 111.0, 50.7, 44.9, 44.1, 43.9, 35.8, 26.8, 26.2, 21.7. **HRMS (m/z, ESI-TOF):** Calcd for $C_{16}H_{21}NO_2SNa^+$ [M+Na$^+$] 314.1185, found 314.1185.

2',2',7,9,9-pentamethyl-1,3,9,9a-tetrahydrospiro[fluorene-2,5'-[1,3]dioxane] (7)

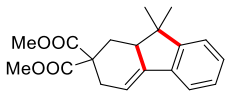


PC: 4CzIPN; Reaction time: 16 h; Yield: 41.8 mg, 67%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 20/1) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.3 Hz, 1H), 7.03 (s, 1H), 7.00 (d, *J* = 7.7 Hz, 1H), 5.93 – 5.90 (m, 1H), 3.77 (d, *J* = 11.6 Hz, 1H), 3.67 (d, *J* = 13.9 Hz, 3H), 2.53 – 2.41 (m, 2H), 2.35 (s, 3H), 2.01 – 1.90 (m, 2H), 1.47 (s, 3H), 1.45 (s, 3H), 1.38 (s, 3H), 1.21 (t, *J* = 12.2 Hz, 1H), 0.90 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 154.4, 140.7, 137.6, 136.1, 127.5, 123.0, 119.9, 114.4, 98.3, 71.5, 66.9, 47.7, 44.1, 32.6, 32.0, 28.0, 26.1, 25.9, 24.6, 23.1, 21.7. **HRMS (m/z, ESI-TOF):** Calcd for $C_{21}H_{29}O_2^+$ [M+H$^+$] 313.2162, found 313.2154.

dimethyl-9,9-dimethyl-1,3,9,9a-tetrahydro-2*H*-fluorene-2,2-dicarboxylate (8)

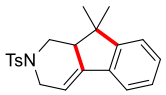


PC: 4CzIPN; Reaction time: 16 h; Yield: 45.8 mg, 73%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 20/1) as a white solid (m.p. = 105-106 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 7.1 Hz, 1H), 7.17 – 7.06 (m, 3H), 5.99 – 5.85 (m, 1H), 3.69 (s, 3H), 3.65 (s, 3H), 3.05 – 2.98 (m, 1H), 2.49 – 2.37 (m, 2H), 2.35 – 2.28 (m, 1H), 1.83 (t, *J* = 12.5 Hz, 1H), 1.32 (s, 3H), 0.88 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.0, 171.7, 154.1, 141.1, 138.4, 128.1, 126.8, 122.4, 120.5, 114.3, 54.1, 52.94, 52.88, 48.5, 44.6, 31.4, 28.7, 26.2, 26.1. **HRMS (m/z, ESI-TOF):** Calcd for $C_{19}H_{23}O_4^+$ [M+H$^+$] 315.1591, found 315.1596.

9,9-dimethyl-2-tosyl-2,3,9,9a-tetrahydro-1*H*-indeno[2,1-c]pyridine (9)

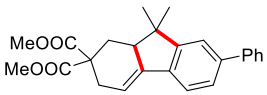


PC: 4CzIPN; Reaction time: 16 h; Yield: 47.3 mg, 67%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 20/1) as a yellow solid (m.p. = 65-66 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.1 Hz, 2H), 7.27 (dd, *J* = 10.7, 7.6 Hz, 3H), 7.19 – 7.09 (m, 3H), 5.82 (q, *J* = 3.1 Hz, 1H), 4.19 (dt, *J* = 17.2, 3.6 Hz, 1H), 4.06 (dd, *J* = 11.0, 5.3 Hz, 1H), 3.34 (dt, *J* = 17.3, 3.3 Hz, 1H), 2.80 – 2.71 (m, 1H), 2.40 (d, *J* = 11.0 Hz, 1H), 2.35 (s, 3H), 1.37 (s, 3H), 0.81 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 154.0, 143.6, 141.2, 129.9, 128.8, 127.6, 127.1, 122.5, 120.6, 112.0, 50.6, 45.2, 44.3, 44.2, 26.9, 26.3, 21.7. **HRMS (m/z, ESI-TOF):** Calcd for $C_{21}H_{24}NO_2S^+$ [M+H$^+$] 354.1522, found 354.1521.

dimethyl-9,9-dimethyl-7-phenyl-1,3,9,9a-tetrahydro-2*H*-fluorene-2,2-dicarboxylate (10)

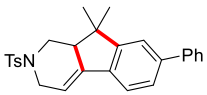


PC: 4CzIPN; Reaction time: 16 h; Yield: 51.5 mg, 66%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 20/1) as a yellow solid (m.p. = 120-121 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ7.61 (d, *J* = 6.9 Hz, 2H), 7.51 – 7.41 (m, 5H), 7.35 (t, *J* = 7.4 Hz, 1H), 6.06 (q, *J* = 3.6, 2.9 Hz, 1H), 3.80 (s, 3H), 3.76 (s, 3H), 3.17 – 3.12 (m, 1H), 2.62 – 2.43 (m, 3H), 1.96 (t, *J* = 12.4 Hz, 1H), 1.48 (s, 3H), 1.03 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.9, 171.6, 154.8, 141.6, 141.3, 140.7, 137.6, 128.8, 127.3, 126.1, 121.2, 120.8, 114.6, 54.1, 53.0, 52.9, 48.8, 44.7, 31.4, 28.7, 26.2. **HRMS (m/z, ESI-TOF):** Calcd for $C_{25}H_{26}O_4Na^+$ [M+Na$^+$] 413.1723, found 413.1722.

9,9-dimethyl-7-phenyl-2-tosyl-2,3,9,9a-tetrahydro-1*H*-indeno[2,1-c]pyridine (11)

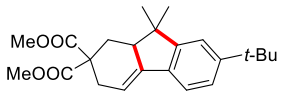


PC: 4CzIPN; Reaction time: 16 h; Yield: 54.1 mg, 63%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 20/1) as a yellow solid (m.p. = 170-171 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 7.2 Hz, 2H), 7.49 – 7.38 (m, 5H), 7.35 – 7.31 (m, 3H), 5.92 (q, *J* = 3.1 Hz, 1H), 4.29 (dt, *J* = 17.2, 3.5 Hz, 1H), 4.16 (dd, *J* = 11.0, 5.3 Hz, 1H), 3.43 (dt, *J* = 17.4, 3.1 Hz, 1H), 2.90 – 2.84 (m, 1H), 2.49 (t, *J* = 11.0 Hz, 1H), 2.42 (s, 3H), 1.49 (s, 3H), 0.93 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 154.6, 143.6, 142.0, 141.3, 140.7, 136.7, 134.1, 129.9, 128.9, 127.6, 127.5, 127.2, 126.4, 121.3, 120.9, 112.2, 50.9, 45.3, 44.4, 44.2, 26.9, 26.3, 21.7. **HRMS (m/z, ESI-TOF):** Calcd for $C_{27}H_{28}NO_2S^+$ [M+H$^+$] 430.1835, found 430.1826.

dimethyl-7-(tert-butyl)-9,9-dimethyl-1,3,9,9a-tetrahydro-2*H*-fluorene-2,2-dicarboxylate (12)

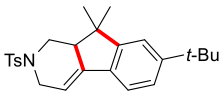


PC: 4CzIPN; Reaction time: 16 h; Yield: 55.5 mg, 75%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 20/1) as a white solid (m.p. = 125-126 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.7 Hz, 1H), 7.26 – 7.21 (m, 2H), 5.96 – 5.93 (m, 1H), 3.76 (s, 3H), 3.71 (s, 3H), 3.13 – 3.01 (m, 1H), 2.54 – 2.42 (m, 2H), 2.40 – 2.37 (m, 1H), 1.91 (t, *J* = 12.4 Hz, 1H), 1.41 (s, 3H), 1.32 (s, 9H), 0.96 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.0, 171.6, 153.9, 151.4, 140.8, 135.7, 124.0, 119.9, 118.9, 113.4, 54.0, 52.9, 52.8, 48.7, 44.6, 35.0, 31.6, 31.3, 28.6, 26.1, 26.1. **HRMS (m/z, ESI-TOF):** Calcd for $C_{23}H_{31}O_4^+$ [M+H$^+$] 371.2217, found 371.2219.

7-(tert-butyl)-9,9-dimethyl-2-tosyl-2,3,9,9a-tetrahydro-1*H*-indeno[2,1-c]pyridine (13)

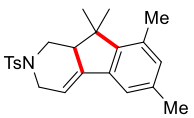


PC: 4CzIPN; Reaction time: 16 h; Yield: 63.8 mg, 78%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 20/1) as a yellow solid (m.p. = 98-99 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.34 – 7.28 (m, 3H), 7.24 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.20 (s, 1H), 5.84 (q, *J* = 2.8 Hz, 1H), 4.25 (dt, *J* = 17.0, 3.3 Hz, 1H), 4.13 (dd, *J* = 11.0, 5.3 Hz, 1H), 3.40 (dt, *J* = 17.0, 3.1 Hz, 1H), 2.83 – 2.80 (m, 1H), 2.49 – 2.42 (m, 4H), 1.45 (s, 3H), 1.31 (s, 9H), 0.88 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 153.7, 152.2, 143.5, 140.8, 134.8, 134.0, 129.8, 127.5, 124.3, 120.0, 119.0, 111.0, 50.8, 45.1, 44.3, 44.1, 35.0, 31.5, 26.8, 26.3, 21.6. **HRMS (m/z, ESI-TOF):** Calcd for $C_{25}H_{32}NO_2S^+$ [M+H$^+$] 410.2148, found 410.2150.

6,8,9,9-tetramethyl-2-tosyl-2,3,9,9a-tetrahydro-1*H*-indeno[2,1-c]pyridine (14)

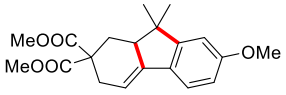


PC: 4CzIPN; Reaction time: 16 h; Yield: 51.4 mg, 67%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 20/1) as a white solid (m.p. = 170-171 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 6.96 (s, 1H), 6.74 (s, 1H), 5.75 (q, *J* = 3.1 Hz, 1H), 4.17 (dt, *J* = 17.1, 3.6 Hz, 1H), 4.02 (dd, *J* = 11.0, 5.3 Hz, 1H), 3.32 (dt, *J* = 17.0, 3.0 Hz, 1H), 2.77 – 2.63 (m, 1H), 2.38 (t, *J* = 10.9 Hz, 1H), 2.34 (s, 3H), 2.27 (s, 3H), 2.20 (s, 3H), 1.45 (s, 3H), 0.85 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 147.6, 143.6, 141.1, 138.3, 136.9, 134.1, 134.0, 132.7, 129.8, 127.6, 118.9, 111.1, 51.2, 45.3, 45.2, 43.8, 27.0, 23.1, 21.7, 21.1, 19.3. **HRMS (m/z, ESI-TOF):** Calcd for $C_{23}H_{27}NO_2SNa^+$ [M+Na^+] 404.1655, found 404.1648.

dimethyl-7-methoxy-9,9-dimethyl-1,3,9,9a-tetrahydro-2*H*-fluorene-2,2-dicarboxylate (15)

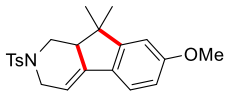


PC: 4CzIPN; Reaction time: 16 h; Yield: 53.0 mg, 77%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 20/1) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.19 (m, 1H), 6.71 – 6.62 (m, 2H), 5.78 – 5.76 (m, 1H), 3.73 (s, 3H), 3.68 (s, 3H), 3.65 (s, 3H), 3.06 – 2.93 (m, 1H), 2.48 – 2.35 (m, 2H), 2.35 – 2.25 (m, 1H), 1.82 (t, *J* = 12.5 Hz, 1H), 1.30 (s, 3H), 0.88 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.0, 171.7, 160.2, 155.9, 140.5, 131.3, 121.4, 112.7, 112.1, 107.8, 55.5, 54.1, 52.9, 52.9, 48.8, 44.7, 31.3, 28.7, 26.04, 26.01. **HRMS (m/z, ESI-TOF):** Calcd for $C_{20}H_{24}O_5Na^+$ [M+Na^+] 367.1516, found 367.1515.

7-methoxy-9,9-dimethyl-2-tosyl-2,3,9,9a-tetrahydro-1*H*-indeno[2,1-c]pyridine (16)

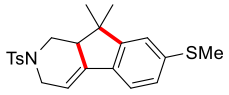


PC: 4CzIPN; Reaction time: 16 h; Yield: 59.7 mg, 78%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 20/1) as a yellow solid (m.p. = 105-106 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 1H), 6.74 (dd, *J* = 8.3, 2.4 Hz, 1H), 6.71 (d, *J* = 2.3 Hz, 1H), 5.74 (q, *J* = 3.2 Hz, 1H), 4.23 (dt, *J* = 16.9, 3.5 Hz, 1H), 4.12 (dd, *J* = 10.9, 5.3 Hz, 1H), 3.80 (s, 3H), 3.39 (dt, *J* = 17.0, 3.4 Hz, 1H), 2.85 – 2.78 (m, 1H), 2.46 (t, *J* = 10.9 Hz, 1H), 2.42 (s, 3H), 1.42 (s, 3H), 0.88 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 160.7, 155.8, 143.6, 140.5, 134.1, 130.4, 129.8, 127.6, 121.5, 113.1, 109.7, 107.7, 55.5, 51.0, 45.1, 44.3, 44.2, 26.7, 26.2, 21.6. **HRMS (m/z, ESI-TOF):** Calcd for $C_{22}H_{26}NO_3S^+$ [M+H^+] 384.1628, found 384.1621.

9,9-dimethyl-7-(methylthio)-2-tosyl-2,3,9,9a-tetrahydro-1*H*-indeno[2,1-c]pyridine (17)



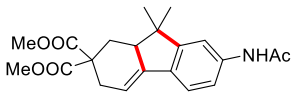
PC: 4CzIPN; Reaction time: 16 h; Yield: 43.0 mg, 54%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 20/1) as a yellow solid (m.p. = 127-128 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 1H), 7.08 (d, *J* = 7.0 Hz, 1H), 7.07 (s, 1H),5.84 (q, *J* = 3.0 Hz, 1H), 4.25 (dt, *J* = 17.2, 3.6 Hz, 1H),

4.12 (dd, *J* = 11.0, 5.3 Hz, 1H), 3.47 – 3.33 (m, 1H), 2.87 – 2.74 (m, 1H), 2.48 (s, 3H), 2.45 (t, *J* = 11.2 Hz, 1H), 2.42 (s, 3H),1.43 (s, 3H), 0.88 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 154.7, 143.6, 140.5, 139.1, 134.8, 134.1, 129.9, 127.6, 125.4, 120.9, 120.7, 111.5, 50.8, 45.2, 44.3, 44.1, 26.7, 26.2, 21.6, 16.2. **HRMS (m/z, ESI-TOF):** Calcd for $C_{22}H_{26}NO_2S_2^+$ [M+H$^+$] 400.1399, found 400.1396.

dimethyl-7-acetamido-9,9-dimethyl-1,3,9,9a-tetrahydro-2*H*-fluorene-2,2-dicarboxylate (18)

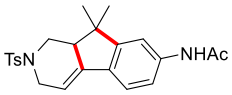


PC: 4CzIPN; Reaction time: 16 h; Yield: 53.4 mg, 72%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 3/1) as a yellow solid (m.p. = 181-182 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.52 (d, *J* = 1.8 Hz, 1H), 7.32 – 7.20 (m, 2H), 5.91 (q, *J* = 3.0 Hz, 1H), 3.77 (s, 3H), 3.74 (s, 3H), 3.14 – 3.03 (m, 1H), 2.52 – 2.46 (m, 2H), 2.41 – 2.31 (m, 1H), 2.17 (s, 3H), 1.90 (t, *J* = 12.5 Hz, 1H), 1.37 (s, 3H), 0.94 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.9, 171.7, 168.5, 155.1, 140.5, 138.2, 134.5, 120.8, 118.7, 114.0, 113.4, 54.0, 52.9, 52.9, 48.7, 44.7, 31.3, 28.6, 26.03, 25.96, 24.7. **HRMS (m/z, ESI-TOF):** Calcd for $C_{21}H_{26}NO_5^+$ [M+H$^+$] 372.1805, found 372.1804.

***N*-(9,9-dimethyl-2-tosyl-2,3,9,9a-tetrahydro-1*H*-indeno[2,1-c]pyridin-7-yl)acetamide (19)**

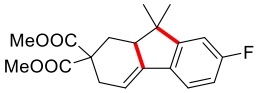


PC: 4CzIPN; Reaction time: 16 h; Yield: 66.4 mg, 81%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 3/1) as a yellow solid (m.p. = 190-191 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.63 (d, *J* = 8.1 Hz, 2H), 7.40 (s, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.22 – 7.14 (m, 2H), 5.71 (q, *J* = 3.1 Hz, 1H), 4.15 (dt, *J* = 17.1, 3.5 Hz, 1H), 4.01 (dd, *J* = 11.0, 5.4 Hz, 1H), 3.31 (dt, *J* = 16.2, 2.7 Hz, 1H), 2.71 – 2.64 (m, 1H), 2.38 – 2.33 (m, 4H), 2.07 (s, 3H), 1.30 (s, 3H), 0.77 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.7, 154.9, 143.8, 140.5, 138.8, 133.8, 133.4, 129.9, 127.6, 121.0, 119.0, 114.0, 111.0, 50.8, 45.2, 44.4, 44.1, 26.6, 26.1, 24.7, 21.6. **HRMS (m/z, ESI-TOF):** Calcd for $C_{23}H_{27}N_2O_3S^+$ [M+H$^+$] 411.1737, found 411.1732.

dimethyl-7-fluoro-9,9-dimethyl-1,3,9,9a-tetrahydro-2*H*-fluorene-2,2-dicarboxylate (20)



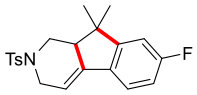
PC: [Ir(ppy)$_2$(dtbbpy)](PF_6); Reaction time: 16 h; Yield: 35.2 mg, 53%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 20/1) as a white solid (m.p. = 80-81 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (dd, *J* = 8.2, 5.2 Hz, 1H), 6.82 – 6.76 (m, 2H), 5.86 – 5.84 (m, 1H), 3.69 (s, 3H), 3.66 (s, 3H), 3.07 – 2.95 (m, 1H), 2.47 – 2.37 (m, 2H), 2.35 – 2.29 (m, 1H), 1.82 (t, *J* = 12.4 Hz, 1H), 1.30 (s, 3H), 0.87 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.8, 171.6, 163.2 (d, *J* = 246.1 Hz), 156.4 (d, *J* = 7.2 Hz), 140.0, 134.3 (d, *J* = 2.5 Hz), 121.7 (d, *J* = 8.8 Hz), 114.0 (d, *J* = 21.2

Hz), 113.9, 109.5 (d, *J* = 22.0 Hz), 53.9, 53.0, 52.9, 48.8, 44.8 (d, *J* = 1.9 Hz), 31.3, 28.6, 26.0, 25.9. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -113.73. **HRMS (m/z, ESI-TOF):** Calcd for $C_{19}H_{21}FO_4Na^+$ [M+Na^+] 355.1316, found 355.1324.

7-fluoro-9,9-dimethyl-2-tosyl-2,3,9,9a-tetrahydro-1*H*-indeno[2,1-c]pyridine (21)

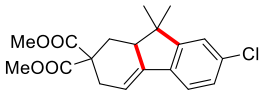


PC: 4CzIPN; Reaction time: 16 h; Yield: 54.9 mg, 74%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 20/1) as a yellow solid (m.p. = 96-97 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.31 – 7.20 (m, 3H), 6.86 – 6.75 (m, 2H), 5.76 (q, *J* = 3.1 Hz, 1H), 4.17 (dt, *J* = 17.2, 3.6 Hz, 1H), 4.05 (dd, *J* = 11.0, 5.3 Hz, 1H), 3.32 (dt, *J* = 17.1, 3.4 Hz, 1H), 2.81 – 2.74 (m, 1H), 2.40 – 2.35 (m, 4H), 1.35 (s, 3H), 0.81 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 163.6 (d, *J* = 247.3 Hz), 156.4 (d, *J* = 7.2 Hz), 143.7, 140.0, 134.0, 133.5 (d, *J* = 2.5 Hz), 129.9, 127.6, 121.9 (d, *J* = 8.9 Hz), 114.4 (d, *J* = 23.2 Hz), 111.6 (d, *J* = 2.2 Hz), 109.7 (d, *J* = 22.1 Hz), 51.0, 45.1, 44.5 (d, *J* = 1.9 Hz), 44.1, 26.7, 26.1, 21.7. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -112.50. **HRMS (m/z, ESI-TOF):** Calcd for $C_{21}H_{23}FNO_2S^+$ [M+H^+] 372.1428, found 372.1429.

dimethyl-7-chloro-9,9-dimethyl-1,3,9,9a-tetrahydro-2*H*-fluorene-2,2-dicarboxylate (22)

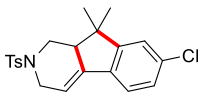


PC: 4CzIPN; Reaction time: 16 h; Yield: 55.7 mg, 80%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 20/1) as a yellow solid (m.p. = 74-75 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 7.9 Hz, 1H), 7.20 – 7.09 (m, 2H), 6.04 – 5.93 (m, 1H), 3.77 (s, 3H), 3.73 (s, 3H), 3.12 – 3.05 (m, 1H), 2.56 – 2.44 (m, 2H), 2.41 – 2.36 (m, 1H), 1.88 (t, *J* = 12.5 Hz, 1H), 1.38 (s, 3H), 0.95 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ172.8, 171.6, 155.9, 140.0, 136.9, 133.6, 127.1, 122.9, 121.6, 115.0, 53.9, 53.0, 52.9, 48.6, 44.8, 31.3, 28.5, 25.97, 25.95. **HRMS (m/z, ESI-TOF):** Calcd for $C_{19}H_{21}ClO_4Na^+$ [M+Na^+] 371.1021, found 371.1029.

7-chloro-9,9-dimethyl-2-tosyl-2,3,9,9a-tetrahydro-1*H*-indeno[2,1-c]pyridine (23)



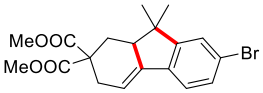
PC: 4CzIPN; Reaction time: 16 h; Yield: 51.1 mg, 66%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 20/1) as a yellow solid (m.p. = 81-82 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 1H), 7.17 – 7.15 (m, 2H), 5.88 (q, *J* = 3.2 Hz, 1H), 4.25 (dt, *J* = 17.3, 3.6 Hz, 1H), 4.12 (dd, *J* = 11.0, 5.3 Hz, 1H), 3.39 (dt, *J* = 17.3, 3.4 Hz, 1H), 2.85 – 2.80 (m, 1H), 2.47 – 2.41 (m, 4H), 1.43 (s, 3H), 0.88 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.7, 143.7, 140.1, 136.1, 134.4, 134.0, 129.9, 127.6,

127.4, 123.1, 121.7, 112.7, 50.8, 45.2, 44.5, 44.0, 26.7, 26.1, 21.7. **HRMS (m/z, ESI-TOF):** Calcd for $C_{21}H_{22}ClNO_2SNa^+$ [M+Na^+] 410.0952, found 410.0945.

dimethyl-7-bromo-9,9-dimethyl-1,3,9,9a-tetrahydro-2*H*-fluorene-2,2-dicarboxylate (24)

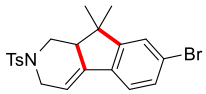


PC: 4CzIPN; Reaction time: 16 h; Yield: 56.4 mg, 72%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 20/1) as a yellow solid (m.p. = 92-93 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 1.7 Hz, 1H), 7.21 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.14 (d, *J* = 8.1 Hz, 1H), 5.94 – 5.91 (m, 1H), 3.69 (s, 3H), 3.66 (s, 3H), 3.03 – 2.97 (m, 1H), 2.47 – 2.36 (m, 2H), 2.36 – 2.27 (m, 1H), 1.80 (t, *J* = 12.5 Hz, 1H), 1.30 (s, 3H), 0.87 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.8, 171.6, 156.2, 140.1, 137.4, 129.9, 125.9, 122.0, 121.8, 115.2, 53.9, 53.00, 52.96, 48.5, 44.9, 31.3, 28.5, 26.0. **HRMS (m/z, ESI-TOF):** Calcd for $C_{19}H_{21}NaBrO_4Na^+$ [M+Na^+] 415.0515, found 415.0517.

7-bromo-9,9-dimethyl-2-tosyl-2,3,9,9a-tetrahydro-1*H*-indeno[2,1-c]pyridine (25)

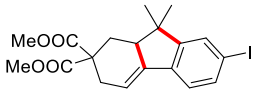


PC: 4CzIPN; Reaction time: 16 h; Yield: 52.6 mg, 61%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 20/1) as a yellow solid (m.p. = 91-92 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.29 – 7.21 (m, 4H), 7.14 (d, *J* = 8.5 Hz, 1H), 5.83 (q, *J* = 3.0 Hz, 1H), 4.17 (dt, *J* = 17.3, 3.6 Hz, 1H), 4.05 (dd, *J* = 11.0, 5.3 Hz, 1H), 3.31 (dt, *J* = 17.3, 3.5 Hz, 1H), 2.78 – 2.72 (m, 1H), 2.39 – 2.33 (m, 4H), 1.35 (s, 3H), 0.80 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 156.0, 143.7, 140.1, 136.5, 134.0, 130.3, 129.9, 127.6, 126.0, 122.5, 122.0, 112.9, 50.7, 45.2, 44.5, 44.0, 26.7, 26.2, 21.7. **HRMS (m/z, ESI-TOF):** Calcd for $C_{21}H_{22}BrNO_2SNa^+$ [M+Na^+] 454.0447, found 454.0446.

dimethyl-7-iodo-9,9-dimethyl-1,3,9,9a-tetrahydro-2*H*-fluorene-2,2-dicarboxylate (26)

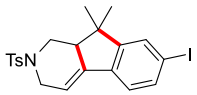


PC: 4CzIPN; Reaction time: 16 h; Yield: 64.2 mg, 73%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 20/1) as a yellow solid (m.p. = 105-106 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (s, 1H), 7.41 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 5.94 – 5.92 (m, 1H), 3.69 (s, 3H), 3.65 (s, 3H), 3.03 – 2.96 (m, 1H), 2.48 – 2.35 (m, 2H), 2.31 – 2.26 (m, 1H), 1.80 (t, *J* = 12.5 Hz, 1H), 1.29 (s, 3H), 0.87 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.7, 171.5, 156.4, 140.1, 138.0, 135.8, 131.9, 122.3, 115.4, 93.4, 53.9, 53.00, 52.96, 48.3, 44.8, 31.3, 28.4, 26.0. **HRMS (m/z, ESI-TOF):** Calcd for $C_{19}H_{21}IO_4Na^+$ [M+Na^+] 463.0377, found 463.0375.

7-iodo-9,9-dimethyl-2-tosyl-2,3,9,9a-tetrahydro-1*H*-indeno[2,1-c]pyridine (27)

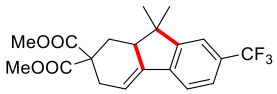


PC: 4CzIPN; Reaction time: 16 h; Yield: 48.9 mg, 51%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 20/1) as a yellow solid (m.p. = 114-115 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 7.4 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 1H), 5.93 (q, *J* = 3.0 Hz, 1H), 4.27 (dt, *J* = 17.3, 3.6 Hz, 1H), 4.14 (dd, *J* = 11.0, 5.4 Hz, 1H), 3.41 (dt, *J* = 17.4, 3.3 Hz, 1H), 2.86 – 2.79 (m, 1H), 2.48 – 2.42 (m, 4H), 1.43 (s, 3H), 0.89 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 156.1, 143.7, 140.2, 137.1, 136.1, 134.0, 132.0, 129.9, 127.6, 122.3, 113.1, 94.2, 50.5, 45.2, 44.4, 43.9, 26.7, 26.2, 21.7. **HRMS (m/z, ESI-TOF):** Calcd for $C_{21}H_{23}INO_2S^+$ [M+H$^+$] 480.0489, found 480.0484.

dimethyl-9,9-dimethyl-7-(trifluoromethyl)-1,3,9,9a-tetrahydro-2*H*-fluorene-2,2-dicarboxylate (28)

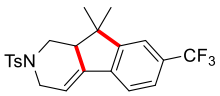


PC: 4CzIPN; Reaction time: 40 h; Yield: 46.6 mg, 61%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 20/1) as a white solid (m.p. = 92-93 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.34 (m, 3H), 6.06 – 6.04 (m, 1H), 3.70 (s, 3H), 3.66 (s, 3H), 3.05 (dt, *J* = 18.5, 3.8 Hz, 1H), 2.49 – 2.40 (m, 2H), 2.38 – 2.31 (m, 1H), 1.83 (t, *J* = 12.4 Hz, 1H), 1.35 (s, 3H), 0.90 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.7, 171.5, 154.6, 141.9 (d, *J* = 1.6 Hz), 140.1, 130.0 (q, *J* = 31.9 Hz), 124.6 (q, *J* = 273.2 Hz), 124.1 (q, *J* = 3.8 Hz), 120.7, 119.5 (q, *J* = 3.9 Hz), 117.2, 53.9, 53.0, 53.0, 48.6, 44.8, 31.4, 28.5, 26.01, 25.99. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -61.95. **HRMS (m/z, ESI-TOF):** Calcd for $C_{20}H_{22}F_3O_4^+$ [M+H$^+$] 383.1465, found 383.1468.

9,9-dimethyl-2-tosyl-7-(trifluoromethyl)-2,3,9,9a-tetrahydro-1*H*-indeno[2,1-c]pyridine (29)

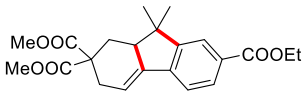


PC: 4CzIPN; Reaction time: 40 h; Yield: 53.9 mg, 64%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 20/1) as a white solid (m.p. = 138-139 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.61 (m, 2H), 7.35 (d, *J* = 7.9 Hz, 3H), 7.26 (d, *J* = 8.0 Hz, 2H), 5.95 (q, *J* = 3.1 Hz, 1H), 4.22 (dt, *J* = 17.5, 3.7 Hz, 1H), 4.08 (dd, *J* = 11.0, 5.4 Hz, 1H), 3.34 (dt, *J* = 17.6, 3.4 Hz, 1H), 2.85 – 2.72 (m, 1H), 2.39 (d, *J* = 11.0 Hz, 1H), 2.35 (s, 3H), 1.39 (s, 3H), 0.82 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 154.4, 143.8, 140.9 (d, *J* = 1.5 Hz), 140.0, 133.9, 130.7 (q, *J* = 31.9 Hz), 129.9, 127.6, 124.38 (q, *J* = 3.8 Hz), 124.37 (q, *J* = 273.3 Hz), 120.9, 119.6 (q, *J* = 3.9 Hz), 114.8, 50.7, 45.2, 44.5, 44.0, 26.6, 26.2, 21.6. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.04. **HRMS (m/z, ESI-TOF):** Calcd for $C_{22}H_{23}F_3NO_2S^+$ [M+H$^+$] 422.1396, found 422.1395.

7-ethyl 2,2-dimethyl-9,9-dimethyl-1,3,9,9a-tetrahydro-2*H*-fluorene-2,2,7-tricarboxylate (30)

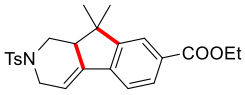


PC: $[Ir(ppy)_2(dtbbpy)](PF_6)$; Reaction time: 16 h; Yield: 47.1 mg, 61%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 15/1) as a yellow solid (m.p. = 90-91 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.77 (m, 2H), 7.32 (d, *J* = 8.5 Hz, 1H), 6.07 – 6.04 (m, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.70 (s, 3H), 3.66 (s, 3H), 3.08 – 3.01 (m, 1H), 2.50 – 2.39 (m, 2H), 2.39 – 2.29 (m, 1H), 1.83 (t, *J* = 12.5 Hz, 1H), 1.36 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H), 0.89 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.7, 171.5, 166.9, 154.2, 142.9, 140.5, 130.0, 128.6, 123.8, 120.2, 117.3, 61.0, 53.9, 53.00, 52.97, 48.5, 44.6, 31.5, 28.5, 26.1, 26.0, 14.5. **HRMS (m/z, ESI-TOF):** Calcd for $C_{22}H_{26}O_6Na^+$ [M+Na^+] 409.1622, found 409.1625.

ethyl (S)-9,9-dimethyl-2-tosyl-2,3,9,9a-tetrahydro-1*H*-indeno[2,1-c]pyridine-7-carboxylate (31)

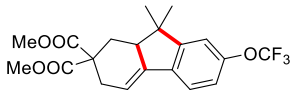


PC: 4CzIPN; Reaction time: 40 h; Yield: 53.6 mg, 63%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 15/1) as a yellow solid (m.p. = 132-133 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.9 Hz, 1H), 7.87 (s, 1H), 7.73 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 6.03 (q, *J* = 3.1 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 4.30 (dt, *J* = 17.5, 3.6 Hz, 1H), 4.16 (dd, *J* = 11.0, 5.3 Hz, 1H), 3.43 (dt, *J* = 17.7, 3.3 Hz, 1H), 2.89 – 2.84 (m, 1H), 2.46 (t, *J* = 10.9 Hz, 1H), 2.43 (s, 3H), 1.48 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H), 0.90 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.6, 154.0, 143.7, 141.9, 140.4, 133.9, 130.7, 129.9, 128.8, 127.6, 123.9, 120.3, 114.8, 61.1, 50.7, 45.2, 44.3, 44.0, 26.8, 26.1, 21.6, 14.5. **HRMS (m/z, ESI-TOF):** Calcd for $C_{24}H_{27}NO_4SNa^+$ [M+Na^+] 448.1553, found 448.1554.

dimethyl-9,9-dimethyl-7-(trifluoromethoxy)-1,3,9,9a-tetrahydro-2*H*-fluorene-2,2-dicarboxylate (32)

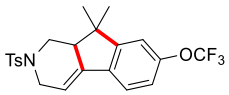


PC: 4CzIPN; Reaction time: 40 h; Yield: 61.3 mg, 77%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 20/1) as a white solid (m.p. = 60-61 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 9.0 Hz, 1H), 6.99 – 6.90 (m, 2H), 5.94 – 5.92 (m, 1H), 3.69 (s, 3H), 3.66 (s, 3H), 3.05 – 2.99 (m, 1H), 2.49 – 2.38 (m, 2H), 2.38 – 2.29 (m, 1H), 1.82 (t, *J* = 12.4 Hz, 1H), 1.32 (s, 3H), 0.88 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.8, 171.5, 156.0, 149.3 (q, *J* = 1.9 Hz), 139.8, 137.1, 121.5, 120.6 (q, *J* = 257.7 Hz), 119.8, 115.4, 115.4, 53.9, 53.00, 52.96, 48.7, 44.9, 31.3, 28.5, 25.95, 25.91. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -57.81. **HRMS (m/z, ESI-TOF):** Calcd for $C_{20}H_{22}F_3O_5^+$ [M+H^+] 399.1414, found 399.1412.

9,9-dimethyl-2-tosyl-7-(trifluoromethoxy)-2,3,9,9a-tetrahydro-1*H*-indeno[2,1-c]pyridine (33)

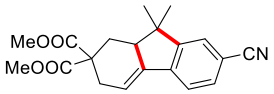


PC: 4CzIPN; Reaction time: 40 h; Yield: 54.2 mg, 62%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 20/1) as a yellow solid (m.p. = 100-101 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.27 (dd, *J* = 8.2, 4.0 Hz, 3H), 7.00 – 6.90 (m, 2H), 5.83 (q, *J* = 3.0 Hz, 1H), 4.19 (dt, *J* = 17.3, 3.6 Hz, 1H), 4.06 (dd, *J* = 11.0, 5.3 Hz, 1H), 3.32 (dt, *J* = 17.3, 4.1 Hz, 1H), 2.82 – 2.75 (m, 1H), 2.40 – 2.35 (m, 4H), 1.36 (s, 3H), 0.81 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.9, 149.7 (q, *J* = 1.9 Hz), 143.8, 139.9, 136.2, 134.0, 129.9, 127.6, 121.7, 120.6 (q, *J* = 258.1 Hz),120.0, 115.5, 113.0, 50.9, 45.1, 44.5, 44.0, 26.6, 26.1, 21.7. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -57.77. **HRMS (m/z, ESI-TOF):** Calcd for $C_{22}H_{23}F_3NO_3S^+$ [M+H$^+$] 438.1345, found 438.1347.

dimethyl-7-cyano-9,9-dimethyl-1,3,9,9a-tetrahydro-2*H*-fluorene-2,2-dicarboxylate (34)

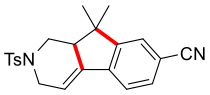


PC: [Ir(ppy)$_2$(dtbbpy)](PF$_6$); Reaction time: 16 h; Yield: 43.4 mg, 64%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 10/1) as a yellow solid (m.p. = 98-99 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.38 (m, 2H), 7.35 (d, *J* = 8.2 Hz, 1H), 6.11 – 6.09 (m, 1H), 3.71 (s, 3H), 3.67 (s, 3H), 3.12 – 3.01 (m, 1H), 2.50 – 2.40 (m, 2H), 2.37 – 2.30 (m, 1H), 1.81 (t, *J* = 12.5 Hz, 1H), 1.34 (s, 3H), 0.89 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.5, 171.4, 154.8, 142.9, 139.9, 131.1, 126.5, 121.2, 119.6, 118.8, 111.1, 53.8, 53.10, 53.06, 48.3, 44.9, 31.5, 28.4, 26.0, 25.9. **HRMS (m/z, ESI-TOF):** Calcd for $C_{20}H_{21}NO_4Na^+$ [M+Na$^+$] 362.1363, found 362.1370.

9,9-dimethyl-2-tosyl-2,3,9,9a-tetrahydro-1*H*-indeno[2,1-c]pyridine-7-carbonitrile (35)

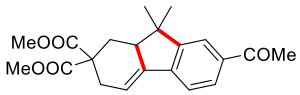


PC: 4CzIPN; Reaction time: 40 h; Yield: 43.8 mg, 58%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 10/1) as a yellow solid (m.p. = 109-110 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.3 Hz, 2H), 7.43 – 7.38 (m, 2H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 6.01 – 5.99 (m, 1H), 4.23 (dt, *J* = 17.8, 3.6 Hz, 1H), 4.08 (dd, *J* = 11.1, 5.4 Hz, 1H), 3.34 (dt, *J* = 17.8, 3.2 Hz, 1H), 2.84 – 2.73 (m, 1H), 2.39 – 2.33 (m, 4H), 1.39 (s, 3H), 0.82 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 154.6, 143.9, 141.9, 139.8, 133.8, 131.3, 129.9, 127.6, 126.6, 121.3, 119.3, 116.3, 111.8, 50.5, 45.2, 44.5, 43.9, 26.6, 26.1, 21.7. **HRMS (m/z, ESI-TOF):** Calcd for $C_{22}H_{22}N_2O_2SNa^+$ [M+Na$^+$] 401.1294, found 401.1297.

dimethyl-7-acetyl-9,9-dimethyl-1,3,9,9a-tetrahydro-2*H*-fluorene-2,2-dicarboxylate (36)

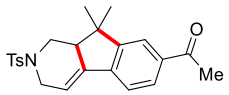


PC: 4CzIPN; Reaction time: 40 h; Yield: 34.2 mg, 48%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 10/1) as a white solid (m.p. = 126-127 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.69 (m, 2H), 7.35 (d, *J* = 8.0 Hz, 1H), 6.10 – 6.07 (m, 1H), 3.70 (s, 3H), 3.67 (s, 3H), 3.09 – 3.02 (m, 1H), 2.53 (s, 3H), 2.49 – 2.40 (m, 2H), 2.39 – 2.30 (m, 1H), 1.83 (t, *J* = 12.5 Hz, 1H), 1.37 (s, 3H), 0.90 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 198.1, 172.7, 171.5, 154.5, 143.2, 140.4, 137.0, 127.9, 122.3, 120.4, 117.8, 53.9, 53.04, 53.01, 48.6, 44.7, 31.5, 28.53, 26.9, 26.10, 26.06. **HRMS (m/z, ESI-TOF):** Calcd for $C_{21}H_{25}O_5^+$ [M+H$^+$] 357.1697, found 357.1692.

1-(9,9-dimethyl-2-tosyl-2,3,9,9a-tetrahydro-1*H*-indeno[2,1-c]pyridin-7-yl)ethan-1-one (37)

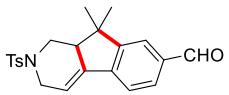


PC: 4CzIPN; Reaction time: 40 h; Yield: 40.3 mg, 51%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 10/1) as a yellow solid (m.p. = 108-109 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.5 Hz, 2H), 7.73 (d, *J* = 8.1 Hz, 2H), 7.43 (d, *J* = 8.1 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 6.06 (d, *J* = 3.0 Hz, 1H), 4.30 (dt, *J* = 17.6, 3.3 Hz, 1H), 4.16 (dd, *J* = 11.0, 5.3 Hz, 1H), 3.42 (dt, *J* = 17.6, 3.1 Hz, 1H), 2.91 – 2.81 (m, 1H), 2.60 (s, 3H), 2.48 – 2.43 (m, 4H), 1.49 (s, 3H), 0.90 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 197.8, 154.3, 143.7, 142.1, 140.2, 137.5, 133.7, 129.8, 128.0, 127.5, 122.4, 120.5, 115.2, 50.7, 45.2, 44.2, 44.0, 26.9, 26.7, 26.1, 21.6. **HRMS (m/z, ESI-TOF):** Calcd for $C_{23}H_{26}NO_3S^+$ [M+H$^+$] 396.1628, found 396.1626.

9,9-dimethyl-2-tosyl-2,3,9,9a-tetrahydro-1*H*-indeno[2,1-c]pyridine-7-carbaldehyde (38)

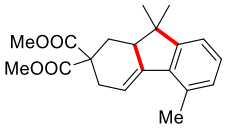


PC: 4CzIPN; Reaction time: 40 h; Yield: 28.2 mg, 37%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 10/1) as a yellow solid (m.p. = 89-90 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.74 – 7.71 (m, 4H), 7.50 (d, *J* = 8.3 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 6.11 (q, *J* = 2.8 Hz, 1H), 4.31 (dt, *J* = 17.7, 3.5 Hz, 1H), 4.17 (dd, *J* = 11.0, 5.4 Hz, 1H), 3.43 (dt, *J* = 17.8, 3.3 Hz, 1H), 2.96 – 2.84 (m, 1H), 2.48 – 2.44 (m, 4H), 1.50 (s, 3H), 0.91 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 191.9, 154.7, 143.8, 143.5, 140.2, 136.8, 133.7, 130.0, 129.9, 127.5, 123.3, 121.0, 116.0, 50.6, 45.2, 44.2, 43.9, 26.7, 26.1, 21.6. **HRMS (m/z, ESI-TOF):** Calcd for $C_{22}H_{24}NO_3S^+$ [M+H$^+$] 328.1471, found 328.1472.

dimethyl-5,9,9-trimethyl-1,3,9,9a-tetrahydro-2*H*-fluorene-2,2-dicarboxylate (39)

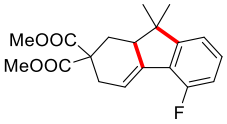


PC: 4CzIPN; Reaction time: 16 h; Yield: 38.0 mg, 58%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 20/1) as a yellow solid (m.p. = 85-86 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 – 6.96 (m, 2H), 6.90 (d, *J* = 7.1 Hz, 1H), 5.95 – 5.93 (m, 1H), 3.69 (s, 3H), 3.65 (s, 3H), 3.11 – 3.04 (m, 1H), 2.48 – 2.43 (m, 1H), 2.42 – 2.39 (m, 1H), 2.36 (s, 3H), 2.33 – 2.27 (m, 1H), 1.84 (t, *J* = 12.5 Hz, 1H), 1.30 (s, 3H), 0.89 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.1, 171.6, 154.8, 141.3, 136.4, 133.7, 128.9, 127.5, 119.8, 117.8, 53.7, 53.0, 52.9, 48.8, 44.2, 31.9, 28.7, 26.11, 26.05, 20.9. **HRMS (m/z, ESI-TOF):** Calcd for $C_{20}H_{24}O_4Na^+$ [M+Na$^+$] 351.1567, found 351.1575.

dimethyl-5-fluoro-9,9-dimethyl-1,3,9,9a-tetrahydro-2*H*-fluorene-2,2-dicarboxylate (40)

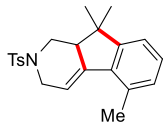


PC: 4CzIPN; Reaction time: 16 h; Yield: 41.8 mg, 63%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 20/1) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 – 7.12 (m, 1H), 6.98 (d, *J* = 7.5 Hz, 1H), 6.90 – 6.81 (m, 1H), 6.27 – 6.18 (m, 1H), 3.77 (s, 3H), 3.74 (s, 3H), 3.18 – 3.10 (m, 1H), 2.55 – 2.45 (m, 2H), 2.43 – 2.39 (m, 1H), 1.90 (t, *J* = 12.4 Hz, 1H), 1.39 (s, 3H), 0.96 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.8, 171.5, 158.6 (d, *J* = 251.8 Hz), 157.2 (d, *J* = 4.6 Hz), 137.2 (d, *J* = 3.2 Hz), 129.0 (d, *J* = 7.3 Hz), 125.3 (d, *J* = 14.5 Hz), 119.2 (d, *J* = 6.4 Hz), 117.9 (d, *J* = 3.3 Hz), 113.6 (d, *J* = 20.1 Hz), 53.6, 52.90, 52.86, 48.4, 45.1 (d, *J* = 1.5 Hz), 31.4, 28.4, 25.9. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -118.61. **HRMS (m/z, ESI-TOF):** Calcd for $C_{19}H_{22}FO_4^+$ [M+H$^+$] 333.1497, found 333.1504.

5,9,9-trimethyl-2-tosyl-2,3,9,9a-tetrahydro-1*H*-indeno[2,1-c]pyridine (41)

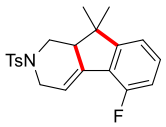


PC: 4CzIPN; Reaction time: 40 h; Yield: 16.9 mg, 23%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 20/1) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.13 (t, *J* = 7.7 Hz, 1H), 6.96 (d, *J* = 7.8 Hz, 1H), 6.92 (d, *J* = 7.5 Hz, 1H), 6.32 (q, *J* = 3.1 Hz, 1H), 4.27 (dt, *J* = 17.3, 3.6 Hz, 1H), 4.03 (dd, *J* = 11.0, 5.3 Hz, 1H), 3.32 (dt, *J* = 17.2, 3.3 Hz, 1H), 2.78 – 2.73 (m, 1H), 2.42 (s, 3H), 2.39 – 2.36 (m, 4H), 1.34 (s, 3H), 0.82 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.3, 143.7, 134.0, 134.9, 134.0, 129.9, 128.7, 127.7, 123.1, 118.6, 117.4, 50.8, 45.4, 44.1, 44.0, 26.8, 26.2, 21.7, 15.2. **HRMS (m/z, ESI-TOF):** Calcd for $C_{22}H_{25}NO_2SNa^+$ [M+Na$^+$] 390.1498, found 390.1510.

5-fluoro-9,9-dimethyl-2-tosyl-2,3,9,9a-tetrahydro-1*H*-indeno[2,1-c]pyridine (42)

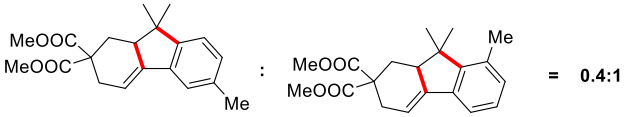


PC: 4CzIPN; Reaction time: 40 h; Yield: 32.6 mg, 44%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 20/1) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.9 Hz, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 7.11 (td, *J* = 7.7, 5.0 Hz, 1H), 6.90 (d, *J* = 7.5 Hz, 1H), 6.79 (t, *J* = 9.0 Hz, 1H), 6.05 (q, *J* = 3.3 Hz, 1H), 4.22 (dt, *J* = 18.5, 3.5 Hz, 1H), 4.06 (dd, *J* = 11.0, 5.3 Hz, 1H), 3.33 (dt, *J* = 17.4, 3.4 Hz, 1H), 2.80 – 2.73 (m, 1H), 2.40 (t, *J* = 11.0 Hz, 1H), 2.36 (s, 3H), 1.37 (s, 3H), 0.82 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.6 (d, *J* = 252.1 Hz), 157.0 (d, *J* = 4.3 Hz), 143.7, 137.2 (d, *J* = 3.0 Hz), 134.0, 129.89, 129.88 (d, *J* = 7.4 Hz), 127.6, 124.7 (d, *J* = 14.6 Hz), 118.1 (d, *J* = 3.4 Hz), 116.8 (d, *J* = 6.2 Hz), 113.9 (d, *J* = 19.9 Hz), 50.7, 45.2, 44.9 (d, *J* = 1.6 Hz), 44.0, 26.7, 26.2, 21.7. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -118.43. **HRMS (m/z, ESI-TOF):** Calcd for $C_{21}H_{23}FNO_2S^+$ [M+H$^+$] 372.1428, found 372.1432.

dimethyl-8,9,9-trimethyl-1,3,9,9a-tetrahydro-2*H*-fluorene-2,2-dicarboxylate (43)

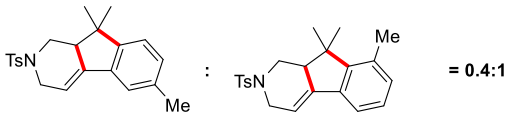


PC: 4CzIPN; Reaction time: 16 h; Yield: 43.3 mg, 66%.

The products were isolated by flash column chromatography (petroleum ether/EtOAc = 20/1) as a white oil (m.p. = 114-115 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.14 (m, 1H), 7.00 (q, *J* = 7.7 Hz, 1H), 6.88 (d, *J* = 7.4 Hz, 1H), 5.90 – 5.87 (m, 1H), 3.69 (s, 3H), 3.64 (s, 3H), 3.06 – 2.96 (m, 1H), 2.45 – 2.38 (m, 2H), 2.33 – 2.24 (m, 4H), 1.82 (t, *J* = 12.4 Hz, 1H), 1.36 (s, 3H), 0.90 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.0, 171.6, 150.5, 141.1, 139.0, 134.1, 131.0, 129.0, 126.9, 122.1, 121.0, 118.3, 114.0, 113.7, 54.2, 52.91, 52.85, 48.82, 48.75, 45.8, 31.5, 31.4, 28.7, 28.2, 26.4, 26.3, 26.1, 22.8, 19.6. **HRMS (m/z, ESI-TOF):** Calcd for $C_{20}H_{25}O_4^+$ [M+H$^+$] 329.1747, found 329.1745.

8,9,9-trimethyl-2-tosyl-2,3,9,9a-tetrahydro-1*H*-indeno[2,1-c]pyridine (44)

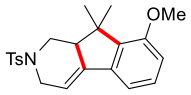


PC: 4CzIPN; Reaction time: 16 h; Yield: 48.4 mg, 66%.

The products were isolated by flash column chromatography (petroleum ether/EtOAc = 20/1) as a yellow solid (m.p. = 152-153 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.18 – 7.08 (m, 1H), 7.04 – 6.87 (m, 2H), 5.78 (q, *J* = 3.0 Hz, 1H), 4.17 (dt, *J* = 17.1, 3.6 Hz, 1H), 4.03 (dd, *J* = 11.1, 5.3 Hz, 1H), 3.36 – 3.29 (m, 1H), 2.75 – 2.68 (m, 1H), 2.41 – 2.34 (m, 4H), 2.31, 2.25 (s, 3H), 1.47, 1.34 (s, 3H), 0.86, 0.79 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 151.2, 150.3, 143.6, 141.14, 141.08, 138.1, 137.6, 136.8, 134.2, 134.1, 131.7, 129.8, 129.7, 127.6, 127.2, 122.2, 121.0, 118.4, 111.6, 111.4, 51.0, 50.8, 45.6, 45.3, 45.2, 44.2, 43.9, 43.8, 26.94, 26.92, 26.3, 23.0, 21.6, 21.4, 19.4. **HRMS (m/z, ESI-TOF):** Calcd for $C_{22}H_{26}NO_2S^+$ [M+H$^+$] 368.1679, found 368.1684.

8-methoxy-9,9-dimethyl-2-tosyl-2,3,9,9a-tetrahydro-1*H*-indeno[2,1-c]pyridine (45)

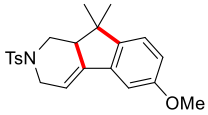


PC: $[Ir(ppy)_2(dtbbpy)](PF_6)$; Reaction time: 16 h; Yield: 36.0 mg, 47%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 20/1) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 7.9 Hz, 2H), 7.08 (t, *J* = 7.8 Hz, 1H), 6.89 (d, *J* = 7.6 Hz, 1H), 6.65 (d, *J* = 8.1 Hz, 1H), 5.77 (q, *J* = 3.2 Hz, 1H), 4.17 (dt, *J* = 17.2, 3.5 Hz, 1H), 4.03 (dd, *J* = 11.0, 5.3 Hz, 1H), 3.73 (s, 3H), 3.38 – 3.27 (m, 1H), 2.78 – 2.65 (m, 1H), 2.40 – 2.35 (m, 4H), 1.48 (s, 3H), 0.89 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.0, 143.6, 141.7, 139.8, 139.5, 134.1, 129.8, 128.6, 127.6, 112.9, 111.9, 110.8, 55.2, 50.8, 45.2, 45.0, 43.9, 26.9, 22.8, 21.7. **HRMS (m/z, ESI-TOF):** Calcd for $C_{22}H_{26}NO_3S^+$ [M+H$^+$] 384.1628, found 384.1629.

6-methoxy-9,9-dimethyl-2-tosyl-2,3,9,9a-tetrahydro-1*H*-indeno[2,1-c]pyridine (45')

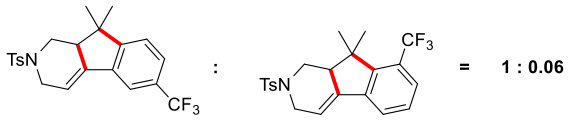


PC: $[Ir(ppy)_2(dtbbpy)](PF_6)$; Reaction time: 16 h; Yield: 10.7 mg, 14%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 20/1) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.3 Hz, 1H), 6.79 (d, *J* = 2.4 Hz, 1H), 6.74 (dd, *J* = 8.3, 2.4 Hz, 1H), 5.80 (q, *J* = 3.1 Hz, 1H), 4.19 (dt, *J* = 17.2, 3.6 Hz, 1H), 4.05 (dd, *J* = 11.0, 5.3 Hz, 1H), 3.72 (s, 3H), 3.34 (dt, *J* = 17.3, 3.2 Hz, 1H), 2.79 – 2.72 (m, 1H), 2.37 (d, *J* = 8.5 Hz, 4H), 1.34 (s, 3H), 0.79 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.2, 146.4, 143.7, 141.2, 138.8, 134.1, 129.9, 127.6, 123.3, 115.6, 112.1, 104.9, 55.6, 51.1, 45.2, 44.2, 43.7, 27.1, 26.4, 21.7. **HRMS (m/z, ESI-TOF):** Calcd for $C_{22}H_{26}NO_3S^+$ [M+H$^+$] 384.1628, found 384.1623.

9,9-dimethyl-2-tosyl-6-(trifluoromethyl)-2,3,9,9a-tetrahydro-1*H*-indeno[2,1-c]pyridine (46)

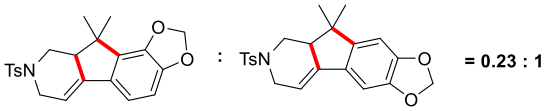


PC: 4CzIPN; Reaction time: 40 h; Yield: 44.6 mg, 53%.

The products were isolated by flash column chromatography (petroleum ether/EtOAc = 20/1) as a yellow solid (m.p. = 105-106 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.52 (s, 1H), 7.42 (d, *J* = 8.3 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 1H), 5.93 (q, *J* = 3.1 Hz, 1H), 4.22 (dt, *J* = 17.5, 3.7 Hz, 1H), 4.08 (dd, *J* = 11.0, 5.4 Hz, 1H), 3.40 – 3.30 (m, 1H), 2.83 – 2.76 (m, 1H), 2.42 – 2.34 (m, 4H), 1.39 (s, 3H), 0.82 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.5, 143.8, 140.0, 138.2, 134.0, 129.9, 128.5 (q, *J* = 220.5 Hz), 127.6, 125.7 (q, *J* = 4.2 Hz), 123.0, 117.7 (q, *J* = 4.1 Hz), 114.2, 50.7, 45.2, 44.5, 44.0, 26.6, 26.0, 21.7. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.16. **HRMS (m/z, ESI-TOF):** Calcd for $C_{22}H_{22}F_3NO_2SNa^+$ [M+Na$^+$] 444.1216, found 444.1219.

9,9-dimethyl-7-tosyl-7,8,8a,9-tetrahydro-6*H*-[1,3]dioxolo[4',5':5,6]indeno[2,1-c]pyridine (47)

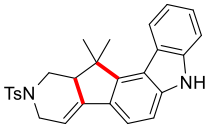


PC: 4CzIPN; Reaction time: 16 h; Yield: 59.6 mg, 75%.

The products were isolated by flash column chromatography (petroleum ether/EtOAc = 10/1) as a yellow solid (m.p. = 151-152 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 6.69 (s, 1H), 6.56 (s, 1H), 5.85 (d, *J* = 8.5 Hz, 2H), 5.60 (q, *J* = 3.1 Hz, 1H), 4.15 (dt, *J* = 17.0, 3.6 Hz, 1H), 4.02 (dd, *J* = 10.9, 5.3 Hz, 1H), 3.30 (dt, *J* = 17.0, 3.2 Hz, 1H), 2.77 – 2.71 (m, 1H), 2.39 – 2.33 (m, 4H), 1.30 (s, 3H), 0.78 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 148.7, 148.4, 147.3, 143.6, 140.8, 134.0, 131.1, 129.8, 127.6, 109.7, 103.0, 101.4, 100.7, 51.1, 45.1, 44.2, 44.1, 27.0, 26.3, 21.7. **HRMS (m/z, ESI-TOF):** Calcd for $C_{22}H_{23}NO_4SNa^+$ [M+Na^+] 420.1240, found 420.1243.

12,12-dimethyl-2-tosyl-1,2,3,7,12,12a-hexahydropyrido[3',4':4,5]cyclopenta[1,2-c]carbazole (48)

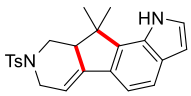


PC: 4CzIPN; Reaction time: 40 h; Yield: 56.6 mg, 64%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 5/1) as a yellow solid (m.p. = 269-271 ℃).

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.59 (s, 1H), 8.17 (d, *J* = 8.2 Hz, 1H), 7.77 (d, *J* = 7.9 Hz, 2H), 7.56 – 7.36 (m, 6H), 7.21 (t, *J* = 7.6 Hz, 1H), 5.82 (s, 1H), 4.29 – 4.07 (m, 2H), 3.34 (s, 1H), 2.84 – 2.71 (m, 1H), 2.48 (t, *J* = 11.0 Hz, 1H), 2.38 (s, 3H), 1.80 (s, 3H), 1.21 (s, 3H). **^{13}C NMR (101 MHz, DMSO-d_6)** δ 147.7, 144.0, 142.0, 141.7, 140.6, 133.8, 130.4, 129.1, 127.8, 125.6, 124.3, 120.8, 119.3, 118.9, 117.9, 111.8, 111.1, 108.8, 51.9, 45.4, 45.3, 44.3, 27.5, 22.4, 21.5. **HRMS (m/z, ESI-TOF):** Calcd for $C_{27}H_{26}N_2O_2SNa^+$ [M+Na^+] 465.1607, found 465.1612.

10,10-dimethyl-8-tosyl-1,7,8,9,9a,10-hexahydropyrido[3',*4*':4,5]cyclopenta[1,2-g]indole (49)

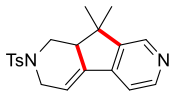


PC: 4CzIPN; Reaction time: 40 h; Yield: 32.9 mg, 42%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 5/1) as a brownness solid (m.p. = 118-119 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.26 – 7.20 (m, 3H), 6.63 (s, 1H), 5.74 (q, *J* = 2.9 Hz, 1H), 4.27 (dt, *J* = 16.8, 3.3 Hz, 1H), 4.17 (dd, *J* = 10.8, 5.2 Hz, 1H), 3.43 (dt, *J* = 16.7, 3.1 Hz, 1H), 2.93 – 2.89 (m, 1H), 2.54 (t, *J* = 11.0 Hz, 1H), 2.42 (s, 3H), 1.68 (s, 3H), 1.07 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 145.4, 143.5, 142.3, 136.9, 134.0, 129.7, 129.2, 127.6, 124.5, 122.9, 114.8, 110.5, 108.4, 100.8, 51.0, 45.3, 45.2, 44.0, 27.3, 24.3, 21.6. **HRMS (m/z, ESI-TOF):** Calcd for $C_{23}H_{24}N_2O_2SNa^+$ [M+Na^+] 415.1451, found 415.1451.

9,9-dimethyl-2-tosyl-2,3,9,9a-tetrahydro-1*H*-cyclopenta[1,2-c:4,3-c']dipyridine (50)

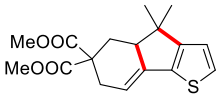


PC: $[Ir(ppy)_2(dtbbpy)](PF_6)$; Reaction time: 40 h; Yield: 36.8 mg, 52%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 10/1) as a brownness paste.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.37 (d, *J* = 5.1 Hz, 1H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 4.9 Hz, 1H), 6.06 (q, *J* = 3.0 Hz, 1H), 4.23 (dt, *J* = 17.8, 3.6 Hz, 1H), 4.08 (dd, *J* = 11.1, 5.4 Hz, 1H), 3.40 – 3.30 (m, 1H), 2.80 – 2.73 (m, 1H), 2.39 – 2.33 (m, 4H), 1.44 (s, 3H), 0.86 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 148.3, 148.2, 145.3, 145.0, 143.9, 139.7, 133.8, 129.9, 127.6, 117.3, 115.1, 50.5, 45.2, 43.9, 43.6, 26.7, 26.2, 21.7. **HRMS (m/z, ESI-TOF):** Calcd for $C_{20}H_{23}N_2O_2S^+$ [M+H$^+$] 355.1475, found 355.1482.

dimethyl-4,4-dimethyl-4,4a,5,7-tetrahydro-6*H*-indeno[1,2-b]thiophene-6,6-dicarboxylate (51)

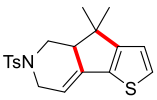


PC: 4CzIPN; Reaction time: 16 h; Yield: 42.2 mg, 66%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 20/1) as a brownness oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 4.9 Hz, 1H), 6.73 (d, *J* = 4.9 Hz, 1H), 5.55 (dt, *J* = 4.7, 2.9 Hz, 1H), 3.68 (s, 3H), 3.67 (s, 3H), 2.99 (dt, *J* = 19.3, 3.4 Hz, 1H), 2.60 (dtt, *J* = 11.2, 4.7, 2.6 Hz, 1H), 2.44 – 2.34 (m, 2H), 1.89 (t, *J* = 12.8 Hz, 1H), 1.28 (s, 3H), 0.93 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.8, 171.7, 159.5, 139.3, 137.3, 128.4, 120.7, 112.0, 53.9, 53.0, 52.9, 43.1, 31.0, 28.8, 26.8, 25.3. **HRMS (m/z, ESI-TOF):** Calcd for $C_{17}H_{20}O_4SNa^+$ [M+Na$^+$] 343.0975, found 343.0977.

4,4-dimethyl-6-tosyl-4a,5,6,7-tetrahydro-4*H*-thieno[2',3':3,4]cyclopenta[1,2-c]pyridine (52)

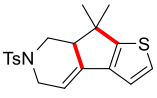


PC: 4CzIPN; Reaction time: 16 h; Yield: 40.2 mg, 56%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 20/1) as a yellow solid (m.p. = 88-89 ℃).

^{1}H NMR (400 MHz, $CDCl_3$)δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 4.9 Hz, 1H), 6.81 (d, *J* = 4.9 Hz, 1H), 5.54 (q, *J* = 3.1 Hz, 1H), 4.25 (dt, *J* = 17.1, 3.4 Hz, 1H), 4.11 (dd, *J* = 11.0, 5.1 Hz, 1H), 3.40 (dt, *J* = 17.1, 3.3 Hz, 1H), 3.16 – 3.09 (m, 1H), 2.55 (t, *J* = 11.1 Hz, 1H), 2.45 (s, 3H), 1.43 (s, 3H), 0.96 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.9, 143.7, 138.4, 137.1, 134.1, 129.9, 129.5, 127.6, 120.7, 109.5, 55.0, 44.8, 44.0, 42.7, 27.5, 25.5, 21.7. **HRMS (m/z, ESI-TOF):** Calcd for $C_{19}H_{21}NO_2S_2Na^+$ [M+Na$^+$] 382.0906, found 382.0912.

8,8-dimethyl-6-tosyl-6,7,7a,8-tetrahydro-5*H*-thieno[3',2':3,4]cyclopenta[1,2-c]pyridine (53)

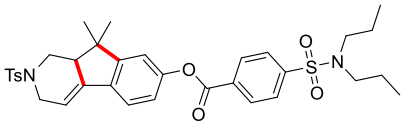


PC: 4CzIPN; Reaction time: 16 h; Yield: 41.6 mg, 58%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 20/1) as a brownness oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 5.0 Hz, 1H), 6.86 (d, *J* = 5.0 Hz, 1H), 5.54 (q, *J* = 2.8 Hz, 1H), 4.22 (dt, *J* = 16.8, 3.2 Hz, 1H), 4.08 (dd, *J* = 10.9, 5.2 Hz, 1H), 3.36 (dt, *J* = 16.8, 3.1 Hz, 1H), 3.16 – 3.10 (m, 1H), 2.52 (t, *J* = 11.1 Hz, 1H), 2.43 (s, 3H), 1.46 (s, 3H), 1.01 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.2, 143.6, 142.0, 137.3, 134.0, 129.8, 128.6, 127.5, 118.7, 109.3, 54.8, 44.7, 44.1, 43.9, 28.4, 26.5, 21.6. **HRMS (m/z, ESI-TOF):** Calcd for $C_{19}H_{22}NO_2S_2^+$ [M+H$^+$] 360.1086, found 360.1088.

9,9-dimethyl-2-tosyl-2,3,9,9a-tetrahydro-1*H*-indeno[2,1-c]pyridin-7-yl 4-(N,N-dipropylsulfamoyl)benzoate (55)

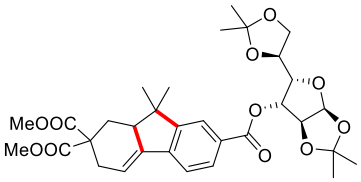


PC: [Ir(ppy)$_2$(dtbbpy)](PF$_6$); Reaction time: 40 h; Yield: 42.0 mg, 33%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 5/1) as a yellow solid (m.p. = 95-96 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.5 Hz, 2H), 7.95 (d, *J* = 8.5 Hz, 2H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 1H), 7.35 (d, *J* = 7.9 Hz, 2H), 7.08 – 7.01 (m, 2H), 5.91 (q, *J* = 2.9 Hz, 1H), 4.28 (dt, *J* = 17.2, 3.5 Hz, 1H), 4.15 (dd, *J* = 11.0, 5.3 Hz, 1H), 3.45 – 3.39 (m, 1H), 3.13 (dd, *J* = 8.7, 6.6 Hz, 4H), 2.90 – 2.85 (m, 1H), 2.46 (d, *J* = 14.8 Hz, 4H), 1.60 – 1.54 (m, 4H), 1.45 (s, 3H), 0.94 – 0.86 (m, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.0, 155.6, 151.1, 145.0, 143.7, 140.0, 135.6, 133.9, 132.8, 130.8, 129.8, 127.5, 127.2, 121.4, 120.4, 115.8, 112.4, 50.7, 49.9, 45.1, 44.4, 44.0, 26.6, 26.1, 21.9, 21.6, 11.2. **HRMS (m/z, ESI-TOF):** Calcd for $C_{34}H_{41}N_2O_6S_2$ [M+H$^+$] 637.2401, found 637.2404.

7-((3aS,5S,6R,6aS)-5-((S)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl) 2,2-dimethyl 9,9-dimethyl-1,3,9,9a-tetrahydro-2*H*-fluorene-2,2,7-tricarboxylate (56)

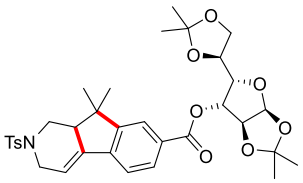


PC: 4CzIPN; Reaction time: 16 h; Yield: 78.2 mg, 65%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 5/1) as a yellow solid (m.p. = 105-106 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 7.4, 2.2 Hz, 2H), 7.39 – 7.30 (m, 1H), 6.09 (q, *J* = 3.1 Hz, 1H), 5.89 (t, *J* = 3.2 Hz, 1H), 5.42 (t, *J* = 3.0 Hz, 1H), 4.57 (dd, *J* = 3.7, 1.8 Hz, 1H), 4.32 – 4.25 (m, 2H), 4.07 – 4.01 (m, 2H), 3.70 (s, 3H), 3.66 (s, 3H), 3.05 (dt, *J* = 18.6, 3.8 Hz, 1H), 2.53 – 2.39 (m, 2H), 2.39 – 2.26 (m, 1H), 1.88 – 1.77 (m, 1H), 1.49 (s, 3H), 1.36 (d, *J* = 1.6 Hz, 3H), 1.34 (s, 3H), 1.25 (s, 3H), 1.19 (d, *J* = 1.5 Hz, 3H), 0.89 (d, *J* = 3.7 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.6, 165.5, 154.4, 143.6, 140.3, 128.7, 124.1, 120.4, 117.9, 112.4, 109.4, 105.2, 83.5, 80.1, 76.7, 76.7, 72.7, 67.3, 53.9, 53.00, 52.97, 48.5, 48.5, 44.6, 31.5, 28.5, 26.9, 26.8, 26.3, 26.10, 26.05, 25.3. **HRMS (m/z, ESI-TOF):** Calcd for $C_{32}H_{40}O_{11}Na^+$ [M+Na$^+$] 623.2463, found 623.2454.

(3aS,5S,6R,6aS)-5-((S)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl 9,9-dimethyl-2-tosyl-2,3,9,9a-tetrahydro-1*H*-indeno[2,1-c]pyridine-7-carboxylate (57)

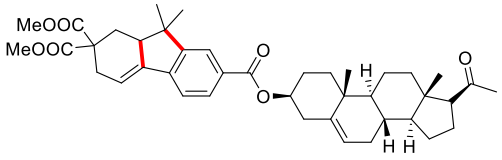


PC: 4CzIPN; Reaction time: 16 h; Yield: 96.0 mg, 75%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 5/1) as a luminous yellow solid (m.p. = 125-126 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (t, *J* = 6.0 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 2H), 6.07 (d, *J* = 2.9 Hz, 1H), 5.96 (d, *J* = 3.6 Hz, 1H), 5.49 (dd, *J* = 5.1, 2.1 Hz, 1H), 4.64 – 4.62 (m, 1H), 4.40 – 4.26 (m, 3H), 4.20 – 4.06 (m, 3H), 3.50 – 3.36 (m, 1H), 2.89 – 2.85 (m, 1H), 2.48 – 2.43 (m, 4H), 1.56 (s, 3H), 1.48 (s, 3H), 1.42 (s, 3H), 1.32 (s, 3H), 1.27 (s, 3H), 0.90 (d, *J* = 3.7 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.2, 154.2, 143.7, 142.5, 140.2, 133.8 (d, *J* = 3.1 Hz), 129.8, 129.6 (d, *J* = 4.1 Hz), 128.9, 127.5, 124.1 (d, *J* = 2.5 Hz), 120.5, 115.4, 112.4, 109.4, 105.1, 83.4, 79.9 (d, *J* = 3.0 Hz), 76.7 (d, *J* = 6.5 Hz), 72.6, 67.2, 50.6 (d, *J* = 4.0 Hz), 45.2, 44.2, 43.9, 26.8, 26.7, 26.7 (d, *J* = 4.0 Hz), 26.2, 26.1 (d, *J* = 7.6 Hz), 25.2, 21.6. **HRMS (m/z, ESI-TOF):** Calcd for $C_{34}H_{41}NO_9SNa^+$ [M+Na^+] 662.2394, found 662.2398.

7-((3S,8S,9S,10R,13S,14S,17R)-17-acetyl-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-3-yl) 2,2-dimethyl 9,9-dimethyl-1,3,9,9a-tetrahydro-2*H*-fluorene-2,2,7-tricarboxylate (58)

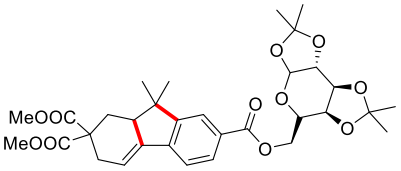


PC: 4CzIPN; Reaction time: 40 h; Yield: 70.8 mg, 54%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 3/1) as a yellow paste.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.83 (m, 2H), 7.39 (d, *J* = 7.9 Hz, 1H), 6.17 – 6.08 (m, 1H), 5.42 (d, *J* = 5.0 Hz, 1H), 4.90 – 4.82 (m, 1H), 3.78 (s, 3H), 3.74 (s, 3H), 3.16 – 3.08 (m, 1H), 2.57 – 2.46 (m, 5H), 2.44 – 2.37 (m, 1H), 2.23 – 2.17 (m, 1H), 2.14 (s, 3H), 2.08 – 1.99 (m, 3H), 1.97 – 1.86 (m, 2H), 1.79 – 1.65 (m, 4H), 1.52 – 1.47 (m, 2H), 1.44 (s, 3H), 1.28 – 1.18 (m, 6H), 1.08 (s, 3H), 0.97 (s, 3H), 0.64 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 209.6, 172.6, 171.5, 154.1, 142.8, 140.4, 139.8, 130.3, 128.5, 123.7, 122.4, 120.1, 117.1, 63.7, 56.9, 53.9, 52.9, 49.9, 48.5, 44.5, 44.0, 38.8, 38.2, 37.1, 36.7, 31.9, 31.8, 31.6, 31.4, 28.5, 27.9, 26.0, 25.9, 24.5, 22.9, 21.1, 19.4, 13.2. **HRMS (m/z, ESI-TOF):** Calcd for $C_{41}H_{52}O_7Na^+$ [M+Na^+] 679.3605, found 679.3605.

2,2-dimethyl 7-(((5S,5aS,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl) 9,9-dimethyl-1,3,9,9a-tetrahydro-2*H*-fluorene-2,2,7-tricarboxylate (59)

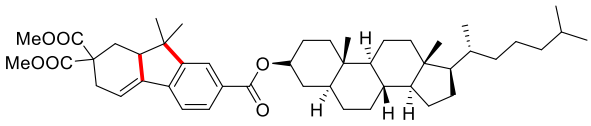


PC: 4CzIPN; Reaction time: 40 h; Yield: 74.5 mg, 62%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 5/1) as a yellow solid (m.p. = 102-103 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.86 (m, 2H), 7.40 (d, *J* = 8.4 Hz, 1H), 6.15 – 6.12 (m, 1H), 5.57 (dd, *J* = 5.0, 1.7 Hz, 1H), 4.66 (dd, *J* = 7.9, 2.4 Hz, 1H), 4.54 – 4.50 (m, 1H), 4.46 – 4.39 (m, 1H), 4.38 – 4.31 (m, 2H), 4.21 – 4.18 (m, 1H), 3.78 (s, 3H), 3.74 (s, 3H), 3.15 – 3.09 (m, 1H), 2.58 – 2.46 (m, 2H), 2.46 – 2.36 (m, 1H), 1.90 (t, *J* = 12.5 Hz, 1H), 1.52 (s, 3H), 1.48 (s, 3H), 1.43 (s, 3H), 1.36 (s, 3H), 1.34 (s, 3H), 0.96 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.6, 171.5, 166.6, 154.1, 143.0, 140.4, 129.5, 128.7, 124.0, 120.2, 117.3, 109.7, 108.9, 96.3, 71.2, 70.7, 70.6, 66.2, 63.91, 63.88, 53.8, 52.93, 52.91, 48.4, 44.5, 31.4, 28.4, 26.1, 26.0, 25.9, 25.0, 24.5. **HRMS (m/z, ESI-TOF):** Calcd for $C_{32}H_{40}O_{11}Na^+$ [M+Na^+] 623.2463, found 623.2455.

7-((3R,5S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl) 2,2-dimethyl 9,9-dimethyl-1,3,9,9a-tetrahydro-2*H*-fluorene-2,2,7-tricarboxylate (60)

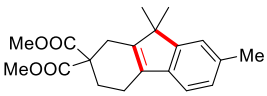


PC: 4CzIPN; Reaction time: 40 h; Yield: 61.3 mg, 42%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 10/1) as a yellow solid (m.p. = 94-95 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.82 (m, 2H), 7.38 (d, *J* = 7.8 Hz, 1H), 6.12 (dt, *J* = 4.4, 2.9 Hz, 1H), 5.00 – 4.85 (m, 1H), 3.77 (s, 3H), 3.74 (s, 3H), 3.12 (d, *J* = 18.4 Hz, 1H), 2.55 – 2.47 (m, 2H), 2.44 – 2.36 (m, 1H), 1.99 – 1.87 (m, 3H), 1.84 – 1.75 (m, 2H), 1.73 – 1.64 (m, 4H), 1.61 – 1.46 (m, 5H), 1.43 (s, 3H), 1.37 – 1.23 (m, 9H), 1.17 – 1.05 (m, 7H), 1.04 – 1.00 (m, 2H), 0.97 (s, 3H), 0.91 (d, *J* = 6.5 Hz, 3H), 0.87 (d, *J* = 2.0 Hz, 6H), 0.86 (d, *J* = 1.8 Hz, 3H), 0.66 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.6, 171.5, 166.3, 154.0, 142.7, 140.4, 130.4, 128.5, 123.7, 120.1, 117.0, 74.3, 56.4, 56.3, 54.2, 53.8, 52.91, 52.89, 48.5, 44.7, 44.5, 42.6, 40.0, 39.5, 36.8, 36.2, 35.8, 35.6, 35.5, 34.2, 32.0, 31.4, 28.7, 28.5, 28.3, 28.0, 27.6, 26.0, 25.9, 24.2, 23.9, 22.9, 22.6, 21.3, 18.7, 12.4, 12.1. **HRMS (m/z, ESI-TOF):** Calcd for $C_{47}H_{68}O_6Na^+$ [M+Na^+] 751.4908, found 751.4910.

dimethyl 7,9,9-trimethyl-1,3,4,9-tetrahydro-2*H*-fluorene-2,2-dicarboxylate (61)

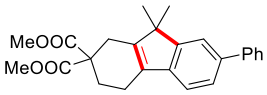


PC: 4CzIPN; Reaction time: 16 h; then $Fe(OTf)_3$ (10 mol %), 3 h. Yield: 53.1 mg, 81%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 20/1) as a yellow oil.

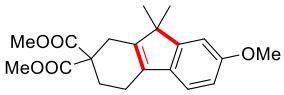
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (s, 1H), 6.95 (d, *J* = 1.1 Hz, 2H), 3.64 (s, 6H), 2.71 (t, *J* = 2.3 Hz, 2H), 2.45 – 2.40 (m, 2H), 2.31 (s, 3H), 2.28 (t, *J* = 6.3 Hz, 2H), 1.14 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.1, 153.9, 145.9, 140.0, 134.3, 131.2, 127.1, 122.2, 117.9, 54.3, 52.8, 48.8, 28.4, 28.0, 23.7, 21.7, 19.7. **HRMS (m/z, ESI-TOF):** Calcd for $C_{20}H_{24}O_4Na^+$ [M+Na^+] 351.1567, found 351.1569.

dimethyl 9,9-dimethyl-7-phenyl-1,3,4,9-tetrahydro-2*H*-fluorene-2,2-dicarboxylate (62)



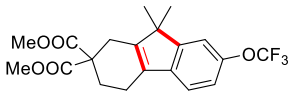
PC: 4CzIPN; Reaction time: 16 h; then $Fe(OTf)_3$ (10 mol %), 3 h. Yield: 49.1 mg, 63%.
The product was isolated by flash column chromatography (petroleum ether/EtOAc = 20/1) as a yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.53 (s, 1H), 7.49 – 7.39 (m, 3H), 7.35 – 7.29 (m, 1H), 7.21 (d, *J* = 7.7 Hz, 1H), 3.73 (s, 6H), 2.83 (d, *J* = 2.3 Hz, 2H), 2.57 – 2.53 (m, 2H), 2.38 (t, *J* = 6.4 Hz, 2H), 1.28 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.9, 154.2, 147.5, 142.0, 141.8, 137.9, 131.1, 128.7, 127.2, 126.8, 125.6, 120.1, 118.3, 54.2, 52.8, 49.1, 28.2, 28.1, 23.6, 19.6. **HRMS (m/z, ESI-TOF):** Calcd for $C_{25}H_{26}O_4Na^+$ [M+Na^+] 413.1723, found 413.1725.

dimethyl 7-methoxy-9,9-dimethyl-1,3,4,9-tetrahydro-2*H*-fluorene-2,2-dicarboxylate (63)



PC: 4CzIPN; Reaction time: 16 h; then $Fe(OTf)_3$ (10 mol %), 3 h. Yield: 42.0 mg, 61%.
The product was isolated by flash column chromatography (petroleum ether/EtOAc = 20/1) as a brownness oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (d, *J* = 8.1 Hz, 1H), 6.83 (d, *J* = 2.3 Hz, 1H), 6.68 (dd, *J* = 8.2, 2.4 Hz, 1H), 3.75 (s, 3H), 3.64 (s, 6H), 2.71 (s, 1H), 2.45 – 2.38 (m, 2H), 2.27 (t, *J* = 6.4 Hz, 2H), 1.14 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.1, 158.0, 155.6, 144.8, 135.8, 130.9, 118.4, 111.0, 108.6, 55.7, 54.3, 52.8, 49.0, 28.3, 28.0, 23.8, 19.7. **HRMS (m/z, ESI-TOF):** Calcd for $C_{20}H_{24}O_5Na^+$ [M+Na^+] 367.1516, found 367.1517.

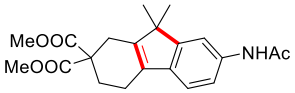
dimethyl 9,9-dimethyl-7-(trifluoromethoxy)-1,3,4,9-tetrahydro-2*H*-fluorene-2,2-dicarboxylate (64)



PC: 4CzIPN; Reaction time: 40 h; then $Fe(OTf)_3$ (10 mol %), 3 h. Yield: 49.3 mg, 62%.
The product was isolated by flash column chromatography (petroleum ether/EtOAc = 20/1) as a yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.13 (m, 1H), 7.12 – 7.05 (m, 2H), 3.73 (s, 6H), 2.80 (t, *J* = 2.2 Hz, 2H), 2.52 – 2.48 (m, 2H), 2.36 (t, *J* = 6.3 Hz, 2H), 1.23 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.8, 155.4, 148.1, 147.0, 141.1, 130.5, 121.9, 119.3, 118.5, 114.8, 54.0, 52.8, 49.2, 28.1, 28.0, 23.3,

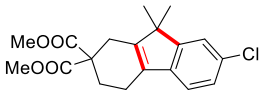
19.5. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -57.91. **HRMS (m/z, ESI-TOF):** Calcd for $C_{20}H_{21}F_3O_5Na^+$ [M+Na^+] 421.1233, found 421.1232.

dimethyl 7-acetamido-9,9-dimethyl-1,3,4,9-tetrahydro-2*H*-fluorene-2,2-dicarboxylate (65)



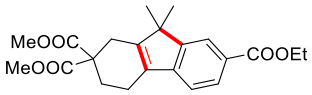
PC: 4CzIPN; Reaction time: 16 h; then $Fe(OTf)_3$ (10 mol %), 3 h. Yield: 48.1 mg, 65%.
The product was isolated by flash column chromatography (petroleum ether/EtOAc = 3/1) as a yellow solid (m.p. = 156-157 ℃).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 2.0 Hz, 2H), 7.21 – 7.16 (m, 1H), 6.96 (d, *J* = 7.9 Hz, 1H), 3.64 (s, 6H), 2.71 (s, 2H), 2.43 – 2.39 (m, 2H), 2.27 (t, *J* = 6.3 Hz, 2H), 2.09 (s, 3H), 1.13 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.0, 168.4, 154.6, 146.6, 139.0, 135.2, 130.9, 118.3, 118.2, 113.9, 54.2, 52.8, 49.1, 28.2, 28.1, 24.7, 23.6, 19.6. **HRMS (m/z, ESI-TOF):** Calcd for $C_{21}H_{26}NO_5^+$ [M+H^+] 372.1805, found 372.1806.

dimethyl 7-chloro-9,9-dimethyl-1,3,4,9-tetrahydro-2*H*-fluorene-2,2-dicarboxylate (66)



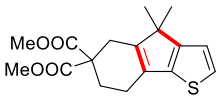
PC: 4CzIPN; Reaction time: 16 h; then $Fe(OTf)_3$ (10 mol %), 3 h. Yield: 46.5 mg, 67%.
The product was isolated by flash column chromatography (petroleum ether/EtOAc = 20/1) as a yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (s, 1H), 7.19 (dd, *J* = 7.9, 1.9 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 3.73 (s, 6H), 2.78 (t, *J* = 2.2 Hz, 2H), 2.50 – 2.46 (m, 2H), 2.35 (t, *J* = 6.3 Hz, 2H), 1.22 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.8, 155.3, 147.4, 140.9, 130.7, 130.6, 126.4, 121.8, 118.9, 54.0, 52.8, 49.1, 28.1, 27.9, 23.4, 19.5. **HRMS (m/z, ESI-TOF):** Calcd for $C_{19}H_{21}ClO_4Na^+$ [M+Na^+] 371.1021, found 371.1019.

7-ethyl 2,2-dimethyl 9,9-dimethyl-1,3,4,9-tetrahydro-2*H*-fluorene-2,2,7-tricarboxylate (67)



PC: $[Ir(ppy)_2(dtbbpy)](PF_6)$; Reaction time: 16 h; then $Fe(OTf)_3$ (10 mol %), 6 h. Yield: 32.3 mg, 42%.
The product was isolated by flash column chromatography (petroleum ether/EtOAc = 15/1) as a yellow solid (m.p. = 69-70 ℃).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.91 (m, 2H), 7.13 (d, *J* = 8.4 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 3.70 (s, 6H), 2.79 (t, *J* = 2.2 Hz, 2H), 2.52 – 2.48 (m, 2H), 2.34 (t, *J* = 6.3 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.23 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.8, 167.5, 153.5, 151.2, 147.2, 131.2, 128.9, 126.6, 122.1, 117.8, 60.9, 54.0, 52.9, 49.2, 28.2, 28.1, 23.3, 19.5, 14.5. **HRMS (m/z, ESI-TOF):** Calcd for $C_{22}H_{27}O_6^+$ [M+H^+] 387.1802, found 387.1803.

dimethyl 4,4-dimethyl-4,5,7,8-tetrahydro-6*H*-indeno[1,2-b]thiophene-6,6-dicarboxylate (68)

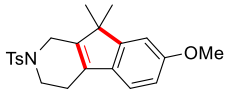


PC: 4CzIPN; Reaction time: 16 h; then $Fe(OTf)_3$ (10 mol %), 3 h. Yield: 18.0 mg, 28%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 20/1) as a brownness oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (d, *J* = 4.8 Hz, 1H), 6.88 (dd, *J* = 4.8, 1.4 Hz, 1H), 3.65 (s, 6H), 2.70 (d, *J* = 2.9 Hz, 2H), 2.49 – 2.39 (m, 2H), 2.25 (t, *J* = 6.5 Hz, 2H), 1.13 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.9, 156.9, 147.3, 142.5, 128.5, 123.8, 120.3, 53.9, 52.8, 47.5, 28.22, 28.18, 23.0, 20.9. **HRMS (m/z, ESI-TOF):** Calcd for $C_{17}H_{21}O_4S^+$ [M+H$^+$] 321.1155, found 321.1151.

7-methoxy-9,9-dimethyl-2-tosyl-2,3,4,9-tetrahydro-1*H*-indeno[2,1-c]pyridine (69)

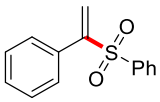


PC: 4CzIPN; Reaction time: 16 h; then $Fe(OTf)_3$ (10 mol %), 3 h. Yield: 38.6 mg, 44%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 20/1) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 8.1 Hz, 1H), 6.81 (d, *J* = 2.3 Hz, 1H), 6.68 (dd, *J* = 8.2, 2.4 Hz, 1H), 3.78 (t, *J* = 2.5 Hz, 2H), 3.74 (s, 3H), 3.30 (t, *J* = 5.7 Hz, 2H), 2.48 – 2.44 (m, 2H), 2.34 (s, 3H), 1.13 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.3, 155.3, 143.7, 142.3, 134.7, 134.03 130.7, 129.8, 127.7, 118.8, 111.1, 108.5, 55.7, 48.6, 43.3, 43.0, 24.4, 22.5, 21.7. **HRMS (m/z, ESI-TOF):** Calcd for $C_{22}H_{25}NO_3SNa^+$ [M+Na$^+$] 406.1447, found 406.1442.

(1-(phenylsulfonyl)vinyl)benzene (72)



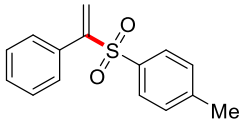
Yield: 30.7 mg, 63%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 10/1) as a white solid (m.p. = 73-74 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.57 (m, 2H), 7.48 – 7.42 (m, 1H), 7.33 (t, *J* = 7.8 Hz, 2H), 7.29 – 7.16 (m, 5H), 6.56 (s, 1H), 5.89 (s, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 151.0, 138.7, 133.4, 132.5, 129.4, 129.2, 128.9, 128.4, 128.3, 125.9.

NMR spectroscopic data was in good agreement with the literature.[S2]

1-methyl-4-((1-phenylvinyl)sulfonyl)benzene (73)

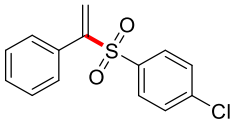


Yield: 28.3 mg, 55%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 10/1) as a yellow solid (m.p. = 62-63 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.9 Hz, 2H), 7.29 – 7.23 (m, 3H), 7.19 (dd, *J* = 9.0, 6.2 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.53 (s, 1H), 5.85 (s, 1H), 2.29 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 151.1, 144.4, 135.8, 132.6, 129.6, 129.3, 129.1, 128.4, 128.3, 125.6, 21.6.
NMR spectroscopic data was in good agreement with the literature.[S2]

1-chloro-4-((1-phenylvinyl)sulfonyl)benzene (74)

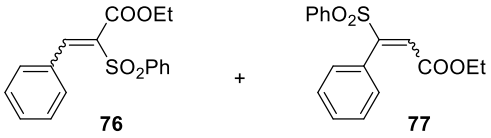


Yield: 21.2 mg, 38%.
The product was isolated by flash column chromatography (petroleum ether/EtOAc = 10/1) as a yellow solid (m.p. = 90-91 ℃).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.33 – 7.19 (m, 7H), 6.57 (s, 1H), 5.91 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 150.7, 140.1, 137.3, 132.2, 129.8, 129.6, 129.2, 129.2, 128.4, 126.4.
NMR spectroscopic data was in good agreement with the literature.[S2]

2-(1-(phenylsulfonyl)vinyl)benzonitrile (75)

Yield: 31.2 mg, 58%.
The product was isolated by flash column chromatography (petroleum ether/EtOAc = 8/1) as a yellow solid (m.p. = 116-117 ℃).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.68 – 7.62 (m, 2H), 7.62 – 7.55 (m, 2H), 7.52 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.48 – 7.39 (m, 3H), 6.91 (s, 1H), 6.12 (s, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 147.2, 137.6, 135.6, 134.2, 133.1, 132.4, 131.2, 129.9, 129.6, 129.3, 128.8, 116.5, 113.5.
NMR spectroscopic data was in good agreement with the literature.[S3]

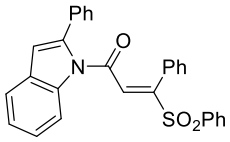
ethyl 3-phenyl-2-(phenylsulfonyl)acrylate (76), ethyl 3-phenyl-3-(phenylsulfonyl)acrylate (77)



76 **77**

Yield: 55.4 mg, 88%. (**76**, 55%; **77**, 33%. The yields of **76** and **77** were determined by ^{1}H NMR of the mixed products, and the NMR data of the mixture are provided.)
The products were isolated by flash column chromatography (petroleum ether/EtOAc = 10/1) as a white paste.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.90 (m, 3H), 7.66 – 7.50 (m, 5H), 7.46 – 7.35 (m, 7H), 7.22 (dd, *J* = 8.6, 1.1 Hz, 1H), 7.00 (dt, *J* = 8.4, 1.2 Hz, 1H), 4.20 (qd, *J* = 7.1, 1.0 Hz, 2H), 4.00 (qd, *J* = 7.1, 1.0 Hz, 1H), 1.13 (td, *J* = 7.1, 1.0 Hz, 3H), 1.01 (td, *J* = 7.1, 1.0 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 163.9, 163.2, 154.5, 143.9, 140.0, 137.1, 134.9, 134.1, 133.8, 131.62, 131.58, 130.1, 129.8, 129.7, 129.6, 129.2, 129.13, 129.06, 128.9, 128.6, 128.0, 127.3, 62.51, 61.47, 13.8, 13.7.
NMR spectroscopic data was in good agreement with the literature.[S4]

(*E*)-3-phenyl-1-(2-phenyl-1H-indol-1-yl)-3-(phenylsulfonyl)prop-2-en-1-one (78)

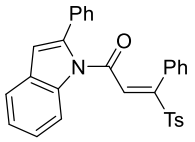


Yield: 81.3 mg, 88%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 10/1) as a yellow solid (m.p. = 175-176 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.59 – 7.55 (m, 3H), 7.52 – 7.48 (m, 1H), 7.46 – 7.40 (m, 3H), 7.34 – 7.28 (m, 4H), 7.26 – 7.19 (m, 2H), 7.16 – 7.11 (m, 1H), 7.09 (s, 1H), 7.07 – 6.98 (m, 4H), 6.51 (s, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.6, 149.1, 139.1, 137.6, 137.1, 133.9, 133.0, 131.0, 129.6, 129.4, 129.34, 129.29, 129.25, 129.1, 128.9, 128.8, 127.9, 125.3, 124.3, 120.6, 115.2, 111.6. **HRMS (m/z, ESI-TOF):** Calcd for $C_{29}H_{21}NO_3SNa^+$ [M+Na^+] 486.1134, found 486.1131.

(*E*)-3-phenyl-1-(2-phenyl-1H-indol-1-yl)-3-tosylprop-2-en-1-one (79)

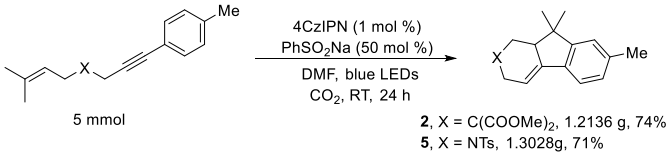


Yield: 71.4 mg, 75%.

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 10/1) as a yellow solid (m.p. = 165-166 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.59 – 7.53 (m, 3H), 7.47 – 7.39 (m, 3H), 7.25 – 7.20 (m, 2H), 7.19 – 7.08 (m, 5H), 7.06 – 6.98 (m, 5H), 6.50 (s, 1H), 2.35 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.7, 149.4, 145.0, 139.1, 137.6, 134.1, 133.0, 130.61 129.5, 129.3, 129.3, 129.2, 129.1, 128.9, 128.8, 127.8, 125.2, 124.2, 120.5, 115.2, 111.5, 21.8. **HRMS (m/z, ESI-TOF):** Calcd for $C_{30}H_{23}NO_3SNa^+$ [M+Na^+] 500.1291, found 500.1292.

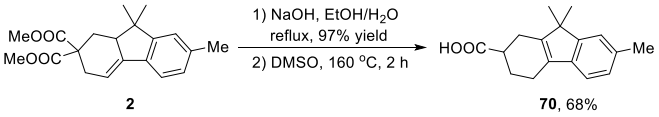
2.3 Gram-scale experiments



The oven-dried Schlenk tube (250 mL) containing a stirring bar was charged with 1,6-enynes (5 mmol), $PhSO_2Na$ (2.5 mmol, 50 mol %), 4CzIPN (1 mmol%) and anhydrous DMF (50 mL). N_2 gas in a balloon was bubbled into the mixture under stirring for 10 min through a needle and the tube was then evacuated and back-filled with CO_2 for 3 times. The mixture was placed under a 30 W blue LED (λ_{max} = 465 nm, 7.5 cm away from the LEDs, with cooling fan to keep the reaction temperature at 25~30 ^{o}C) light source and stirred at ambient temperature for 24 h. Upon completion of the reaction, all the solvents were removed under reduced pressure at high temperature. The crude reaction mixture was diluted with EtOAc (25 mL) and filtered through a short pad of Celite. The sealed tube and Celite pad were washed with an additional 125 mL of EtOAc. The filtrate was concentrated in vacuo, and crude

^{1}H NMR spectrum was taken using coumarin as internal standard. The resulting residue was purified by flash silica gel chromatography using petroleum ether/EtOAc (15:1) as the eluent to give the desired products.

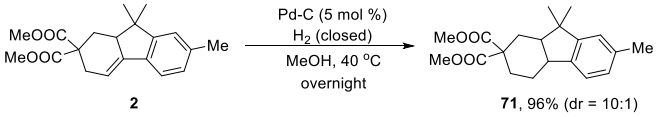
2.4 Further transformation of products



2 **70**, 68%

To a mixture of 1.50 mL of 6 M NaOH aq (9 mmol) and 5 mL of ethanol was added 1.0 mmol **2** under air and the mixture was heated to reflux for 15 h. After cooled to room temperature, the resulting mixture was neutralized by adding a 6 M solution of HCl and extracted three times with EtOAc. Combined organic portions were quickly dried over $MgSO_4$, filtered, and concentrated to obtain the dicarboxylic acid (0.97 mmol, 97% yield), which was used for the next step without further purification. The dicarboxylic acid (0.5 mmol) was heated at 160 ℃ for 2.0 h in DMSO (3 mL) to obtain isomerized monocarboxylic acid **70** in 68% yield. The product was isolated by flash column chromatography (petroleum ether/EtOAc = 5/1, 1% HOAc) as a brownness solid (m.p. = 85-86 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (s, 1H), 7.07 – 7.02 (m, 2H), 2.85 – 2.74 (m, 1H), 2.62 – 2.54 (m, 1H), 2.53 – 2.40 (m, 3H), 2.39 (s, 3H), 2.28 – 2.21 (m, 1H), 1.96 – 1.86 (m, 1H), 1.21 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 182.4, 154.0, 147.1, 140.3, 134.2, 131.8, 127.0, 122.2, 117.8, 48.7, 40.0, 25.4, 24.1, 24.0, 23.9, 21.7, 21.3. **HRMS (m/z, ESI-TOF):** Calcd for $C_{17}H_{19}O_2^-$ [M-H$^+$] 255.1391, found 255.1390.

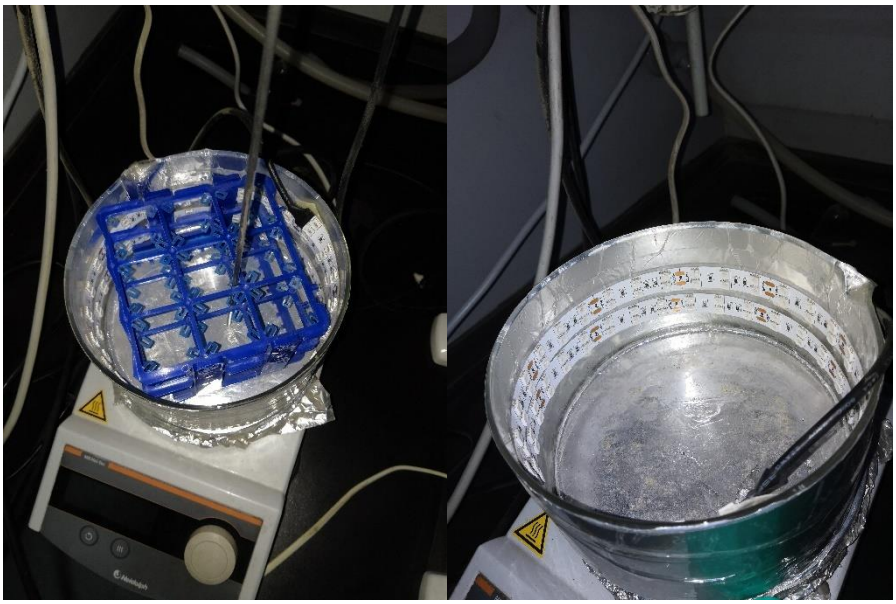


2 **71**, 96% (dr = 10:1)

The mixture of **2** (0.3 mmol), 10 % Pd-C (5 mol %) were dissolved in MeOH (5 mL), and the mixture was evacuated and back-filled with H_2 for 3 times. Then, the reaction mixture was vigorously stirred and heated to 40 ℃ under H_2 atmosphere for 18 h. Upon completion of the reaction, the reaction mixture was filtered through a short pad of Celite. The reaction tube and Celite pad were washed with an additional 25 mL of ethyl acetate. After all the solvents were removed under reduced pressure, the resulting residue was purified by preparative thin layer chromatography using petroleum ether/ethyl acetate (20:1) as the eluent to give the desired product **71** in 96% yield as a white solid (m.p. = 120-121 ℃).

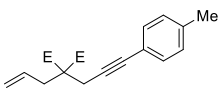
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (d, *J* = 1.1 Hz, 2H), 6.92 (s, 1H), 3.78 (s, 3H), 3.61 (s, 3H), 3.41 – 3.31 (m, 1H), 2.33 (s, 3H), 2.33 – 2.03 (m, 4H), 1.87 – 1.77 (m, 1H), 1.59 (td, *J* = 13.6, 3.9 Hz, 1H), 1.27 (s, 3H), 1.16 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.1, 171.7, 151.6, 139.7, 136.3, 127.3, 123.4, 122.3, 54.6, 52.7, 52.5, 48.0, 45.8, 38.9, 30.0, 28.4, 26.5, 22.0, 21.6, 21.5. **HRMS (m/z, ESI-TOF):** Calcd for $C_{20}H_{26}O_4Na^+$ [M+Na$^+$] 353.1723, found 353.1725.

2.5 General photoredox reaction setup

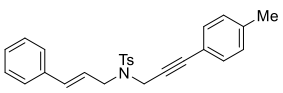


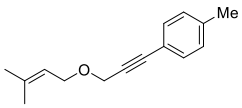
2.6 Unsuccessful examples

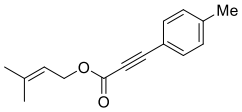
Unsuccessful examples:

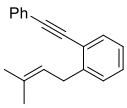


E = COOMe









3. Mechanistic studies

3.1 Stern-Volmer fluorescence quenching experiments

Fluorescence quenching experiments were measured on a Hitachi F7000 Spectrofluorophotometer. DMF was degassed by N_2 bubbling for 30 minutes before using. The complex $[Ir(ppy)_2(dtbbpy)]PF_6$ was excited at 465 nm and the emission spectrum λmax = 540 nm was recorded. In a typical experiment, 2.0 mL (5.0×10^{-5} M) solution of $[Ir(ppy)_2(dtbbpy)]PF_6$ in DMF was added into the 4.0 mL quartz cuvette (d = 1 cm) and covered with Teflon cap. Then the emission spectrum of the solution was collected at each addition. A stock solution of **1a** (0.5 mmol) or $PhSO_2Na$ (0.5 mmol) in 1 mL of DMF was prepared (0.5 M). Then, different amounts of these stock solutions were added to a solution of the photocatalyst $[Ir(ppy)_2(dtbbpy)]PF_6$ in DMF (5.0×10^{-5} M), respectively.

As shown, a significant decrease of $[Ir(ppy)_2(dtbbpy)]PF_6$ luminescence was observed, **suggesting that the mechanism might operate via a photo-redox cycle consisting of a reductive quenching with $PhSO_2Na$**.

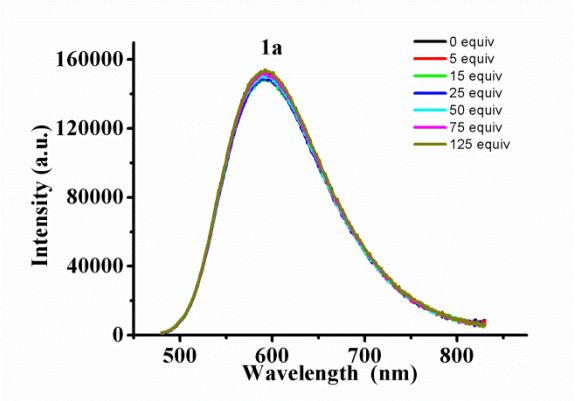


Figure S1. Fluorescence of $[Ir(ppy)_2(dtbbpy)]PF_6$ (50 μM) with **1a** (0-0.00667M) in DMF.

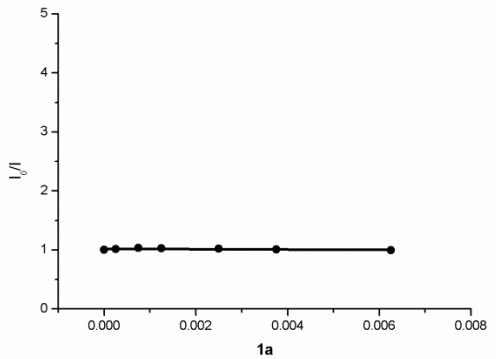


Figure S2. Stern-Volmer quenching plot of **1a**.

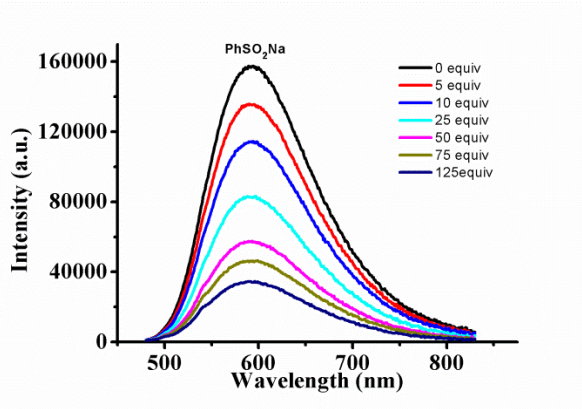


Figure S3. Fluorescence of $[Ir(ppy)_2(dtbbpy)]PF_6$ (50 μM) with $PhSO_2Na$ (0-0.00667M) in DMF.

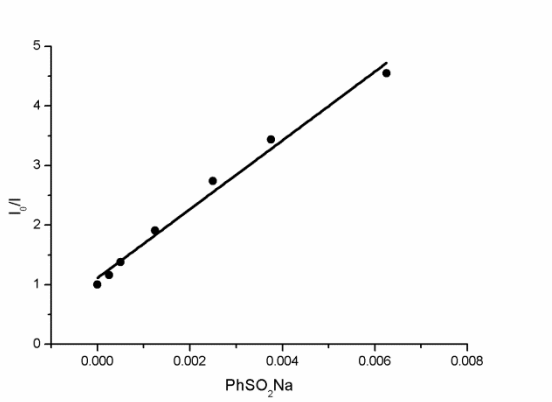
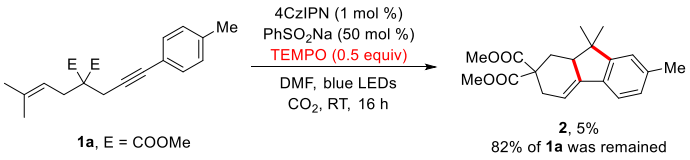
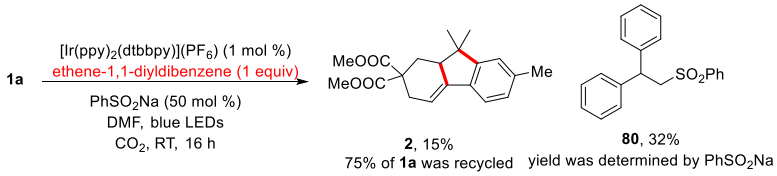


Figure S4. Stern-Volmerquenching plot of $PhSO_2Na$.

3.2 Control experiments with radical scavengers



The oven-dried Schlenk tube (38 mL) containing a stirring bar was charged with **1a** (0.2 mmol), $PhSO_2Na$ (0.1 mmol, 50 mol%), 4CzIPN (0.002 mmol, 1 mmol%), TEMPO (0.1 mmol, 0.5 equiv) and DMF (2 mL). N_2 gas in a balloon was bubbled into the mixture under stirring for 10 min through a needle and the tube was then evacuated and back-filled with CO_2 for 3 times. The mixture was placed under a 30 W blue LED (λ_{max} = 465 nm, 7.5 cm away from the LEDs, with cooling fan to keep the reaction temperature at 25~30 ^{o}C) light source and stirred at ambient temperature for 16 h. Upon completion of the reaction, all the solvents were removed under reduced pressure at high temperature. The crude reaction mixture was diluted with EtOAc (5 mL) and filtered through a short pad of Celite. The sealed tube and Celite pad were washed with an additional 25 mL of EtOAc. The filtrate was concentrated in vacuo, and crude ^{1}H NMR spectrum was taken using coumarin as internal standard. The result was detected by ^{1}H NMR spectrum.



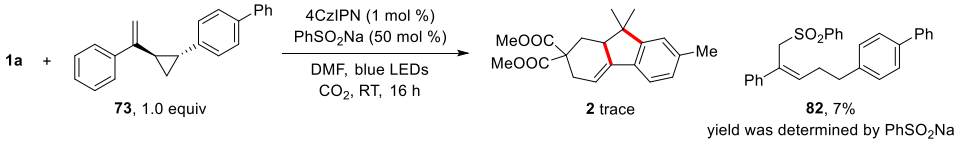
The oven-dried Schlenk tube (38 mL) containing a stirring bar was charged with **1** (0.2 mmol), $PhSO_2Na$ (0.1 mmol, 50 mol%), $[Ir(ppy)_2(dtbbpy)]PF_6$ (0.002 mmol, 1 mmol%), ethene-1,1-diyldibenzene (0.2 mmol, 1 equiv) and DMF (2 mL). N_2 gas in a balloon was bubbled into the mixture under stirring for 10 min through a needle and the tube was then evacuated and back-filled with CO_2 for 3 times. The mixture was placed under a 30 W blue LED (λ_{max}=465 nm, 7.5 cm away from the LEDs, with cooling fan to keep the reaction temperature at 25~30 ^oC) light source and stirred at ambient temperature for 16 h. Upon completion of the reaction, all the solvents were removed under reduced pressure at high temperature. The crude reaction mixture was diluted with EtOAc (5 mL) and filtered through a short pad of Celite. The sealed tube and Celite pad were washed with an additional 25 mL of EtOAc. The filtrate was concentrated in vacuo, and crude ^1H NMR spectrum was taken using coumarin as internal standard. The resulting residue was purified by flash silica gel chromatography to give the desired products (**2** and **80**).

(2-(phenylsulfonyl)ethane-1,1-diyl)dibenzene (80)

The product was isolated by flash column chromatography (petroleum ether/EtOAc = 10/1) as a white solid (m.p. = 164-165 ℃).

^1H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.53 (m, 2H), 7.44 – 7.38 (m, 1H), 7.27 (t, *J* = 7.8 Hz, 2H), 7.18 – 6.99 (m, 10H), 4.56 (t, *J* = 7.1 Hz, 1H), 3.85 (d, *J* = 7.1 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.5, 139.8, 133.4, 129.0, 128.9, 128.1, 127.7, 127.1, 61.6, 46.3. **HRMS (m/z, ESI-TOF):** Calcd for $C_{20}H_{18}O_2SNa^+$ [M+Na^+] 345.0920, found 345.0923.

3.3 Reaction with radical clock



The oven-dried Schlenk tube (38 mL) containing a stirring bar was charged with **1** (0.2 mmol), $PhSO_2Na$ (0.1 mmol, 50 mol%), 4CzIPN (0.002 mmol, 1 mmol%), **73** (0.2 mmol, 1 equiv) and DMF (2 mL). N_2 gas in a balloon was bubbled into the mixture under stirring for 10 min through a needle and the tube was then evacuated and back-filled with CO_2 for 3 times. The mixture was placed under a 30 W blue LED (λ_{max}=465 nm, 7.5 cm away from the LEDs, with cooling fan to keep the reaction temperature at 25~30 ^oC) light source and stirred at ambient temperature for 16 h. Upon completion of the reaction, all the solvents were removed under reduced pressure at high temperature. The crude reaction mixture was diluted with EtOAc (5 mL) and filtered through a short pad of Celite. The sealed tube and Celite pad were washed with an additional 25 mL of EtOAc. The filtrate was concentrated in vacuo, and crude ^1H NMR spectrum was taken using coumarin as internal standard. The resulting residue was purified by flash silica gel chromatography to give the desired product **82**.

4-(4-phenyl-5-(phenylsulfonyl)pent-3-en-1-yl)-1,1'-biphenyl (82)

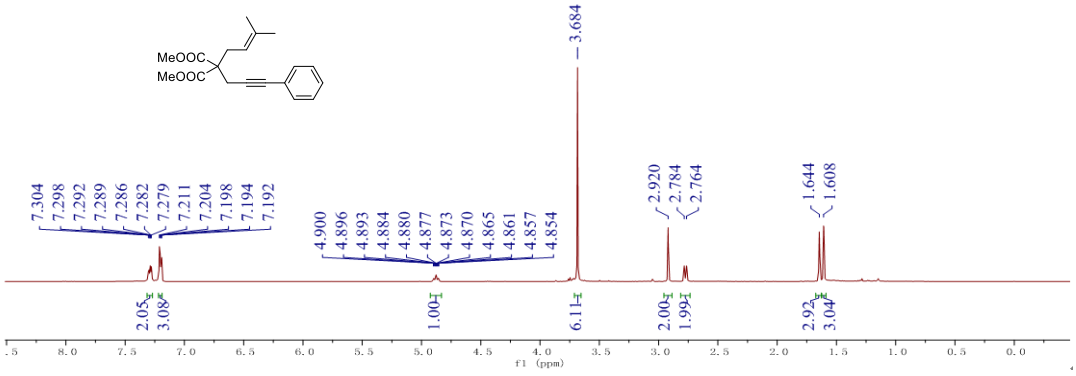
The product was isolated by flash column chromatography (petroleum ether/EtOAc = 10/1) as a yellow solid (m.p. = 105-106 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.69 (m, 2H), 7.62 – 7.56 (m, 2H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.49 (d, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.38 – 7.32 (m, 3H), 7.23 (s, 1H), 7.21 – 7.10 (m, 5H), 6.04 (t, *J* = 7.4 Hz, 1H), 4.28 (s, 2H), 2.74 (t, *J* = 7.6 Hz, 2H), 2.47 (q, *J* = 7.5 Hz, 2H), 2.17 (s, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.0, 140.8, 140.3, 139.1, 139.0, 137.5, 133.5, 129.0, 128.9, 128.8, 128.6, 128.5, 128.3, 127.3, 127.2, 127.0, 126.4, 57.7, 34.8, 31.2. **HRMS (m/z, ESI-TOF):** Calcd for $C_{29}H_{26}O_2SNa^+$ [M+Na^+] 461.1546, found 461.1544.

3.4 Investigation of using d_5-1g

***d*$_5$-1g**, E = COOMe ***d*$_4$-8**, 63%

The oven-dried Schlenk tube (38 mL) containing a stirring bar was charged with ***d*$_5$-1g** (0.2 mmol), $PhSO_2Na$ (0.1 mmol, 50 mol%), 4CzIPN (0.002 mmol, 1 mmol%) and DMF (2 mL). N_2 gas in a balloon was bubbled into the mixture under stirring for 10 min through a needle and the tube was then evacuated and back-filled with CO_2 for 3 times. The mixture was placed under a 30 W blue LED (λ_{max} = 465 nm, 7.5 cm away from the LEDs, with cooling fan to keep the reaction temperature at 25~30 ^oC) light source and stirred at ambient temperature for 16 h. Upon completion of the reaction, all the solvents were removed under reduced pressure at high temperature. The crude reaction mixture was diluted with EtOAc (5 mL) and filtered through a short pad of Celite. The sealed tube and Celite pad were washed with an additional 25 mL of EtOAc. The filtrate was concentrated in vacuo, and crude ^{1}H NMR spectrum was taken using coumarin as internal standard. The resulting residue was purified by preparative thin layer chromatography using petroleum ether/EtOAc (20:1) as the eluent to give the desired product ***d*$_4$-8** in 63% yield.


MeOOC
MeOOC
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7.298
7.292
7.289
7.286
7.282
7.279
7.211
7.204
7.198
7.194
7.192
4.900
4.896
4.893
4.884
4.880
4.877
4.873
4.870
4.865
4.861
4.857
4.854
3.684
2.920
2.784
2.764
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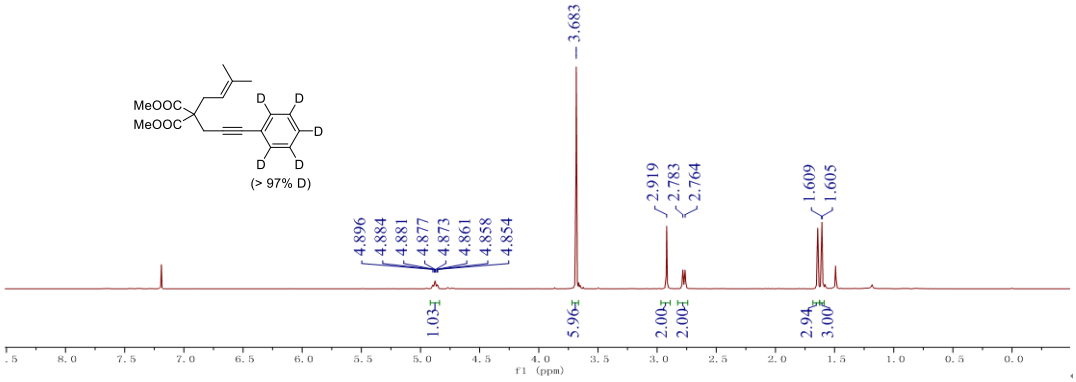
1.00
6.11
2.00
1.99
2.92
3.04
f1 (ppm)


MeOOC
MeOOC
D
(> 97% D)
4.896
4.884
4.881
4.877
4.873
4.861
4.858
4.854
3.683
2.919
2.783
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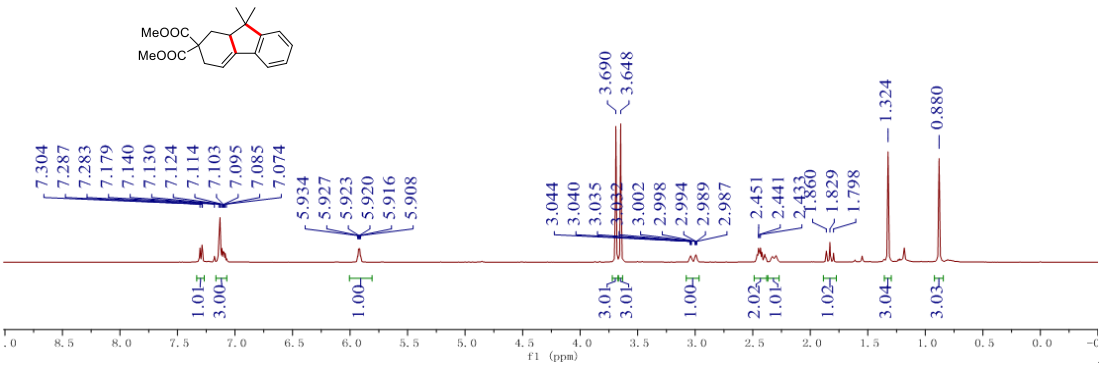
5.96
2.00
2.00
2.94
3.00
f1 (ppm)


MeOOC
MeOOC
7.304
7.287
7.283
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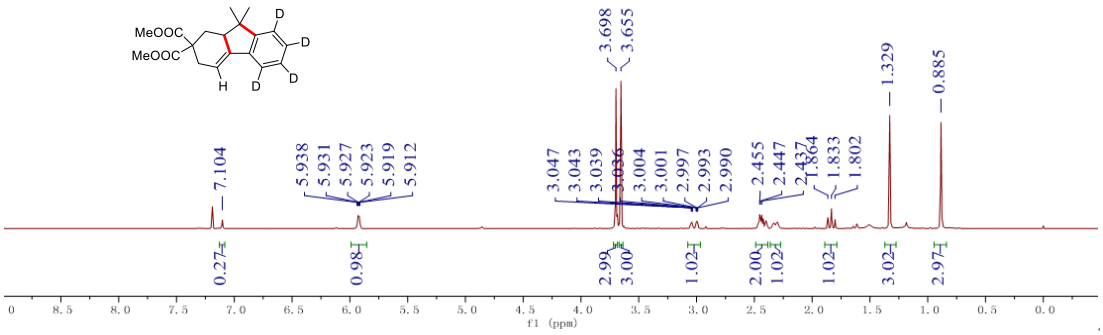
7.140
7.130
7.124
7.114
7.103
7.095
7.085
7.074
5.934
5.927
5.923
5.920
5.916
5.908
3.690
3.648
3.044
3.040
3.035
3.033
3.002
2.998
2.994
2.989
2.987
2.451
2.441
2.433
1.860
1.829
1.798
1.324
0.880
1.01
3.00
1.00
3.01
3.01
1.00
2.02
1.01
1.02
3.04
3.03
f1 (ppm)


MeOOC
MeOOC
D
H
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5.938
5.931
5.927
5.923
5.919
5.912
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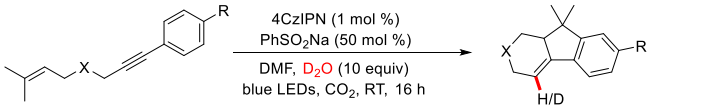
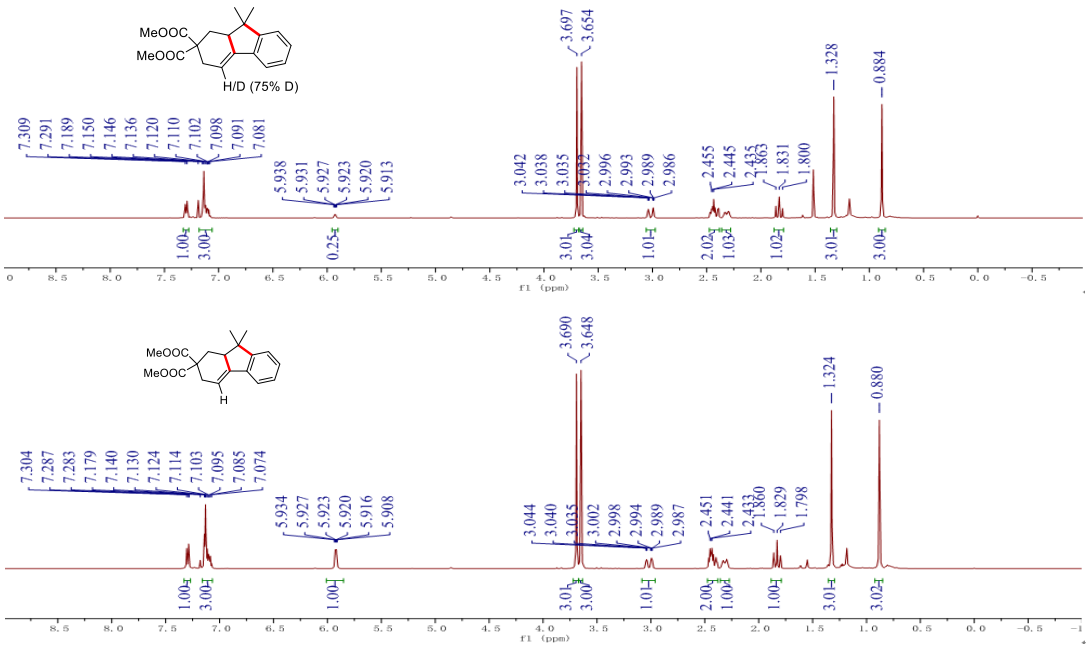
3.655
3.047
3.043
3.039
3.036
3.004
3.001
2.997
2.993
2.990
2.455
2.447
2.437
1.864
1.833
1.802
1.329
0.885
0.27
0.98
2.99
3.00
1.02
2.00
1.02
1.02
3.02
2.97
f1 (ppm)

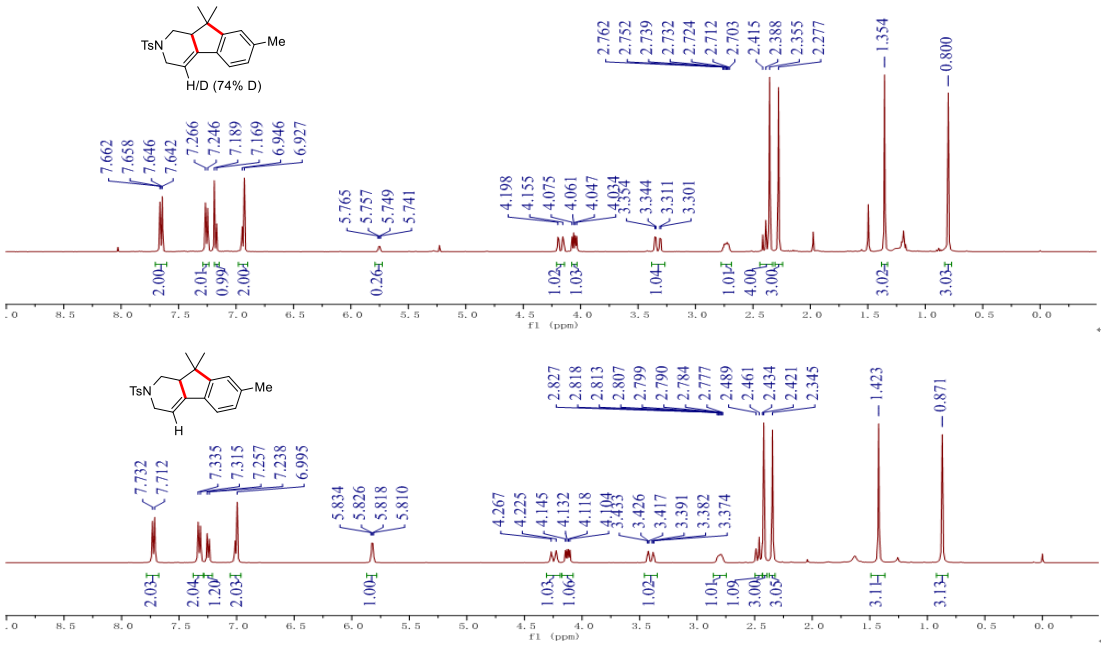
3.5 Isotope-labelling studies

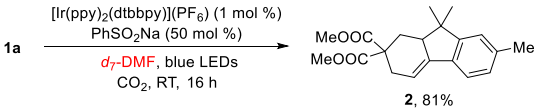


***d*-8**, X = $C(COOMe)_2$, R = H, 68% (75% D)
***d*-5**, X = NTs, R = Me, 73% (74% D)

The oven-dried Schlenk tube (38 mL) containing a stirring bar was charged with 1,6-enynes (0.2 mmol), $PhSO_2Na$ (0.1 mmol, 50 mol%), 4CzIPN (0.002 mmol, 1 mmol%), D_2O (2 mmol, 10 equiv) and DMF (2 mL). N_2 gas in a balloon was bubbled into the mixture under stirring for 10 min through a needle and the tube was then evacuated and back-filled with CO_2 for 3 times. The mixture was placed under a 30 W blue LED (λ_{max} = 465 nm, 7.5 cm away from the LEDs, with cooling fan to keep the reaction temperature at 25~30 ^{o}C) light source and stirred at ambient temperature for 16 h. Upon completion of the reaction, all the solvents were removed under reduced pressure at high temperature. The crude reaction mixture was diluted with EtOAc (5 mL) and filtered through a short pad of Celite. The sealed tube and Celite pad were washed with an additional 25 mL of EtOAc. The filtrate was concentrated in vacuo, and crude ^{1}H NMR spectrum was taken using coumarin as internal standard. The resulting residue was purified by preparative thin layer chromatography using petroleum ether/EtOAc (20:1 or 15:1) as the eluent to give the desired products ***d*-8** or ***d*-5**.

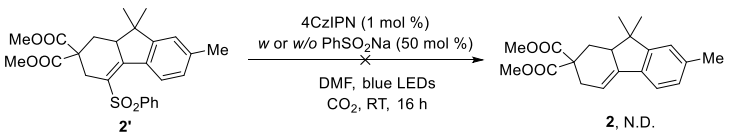






The oven-dried Schlenk tube (38 mL) containing a stirring bar was charged with **1a** (0.2 mmol), $PhSO_2Na$ (0.1 mmol, 50 mol%), 4CzIPN (0.002 mmol, 1 mmol%) and d_7-DMF (1.4 mL). N_2 gas in a balloon was bubbled into the mixture under stirring for 10 min through a needle and the tube was then evacuated and back-filled with CO_2 for 3 times. The mixture was placed under a 30 W blue LED (λ_{max}=465 nm, 7.5 cm away from the LEDs, with cooling fan to keep the reaction temperature at 25~30 ^oC) light source and stirred at ambient temperature for 16 h. Upon completion of the reaction, all the solvents were removed under reduced pressure at high temperature. The crude reaction mixture was diluted with EtOAc (5 mL) and filtered through a short pad of Celite. The sealed tube and Celite pad were washed with an additional 25 mL of EtOAc. The filtrate was concentrated in vacuo, and crude ^1H NMR spectrum was taken using coumarin as internal standard. The resulting residue was purified by preparative thin layer chromatography using petroleum ether/EtOAc (20:1) as the eluent to give the desired product **2**.

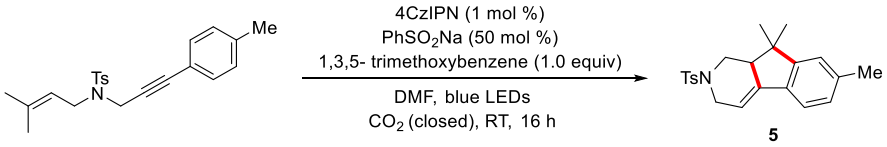
3.6 Investigation of using 2'



The oven-dried Schlenk tube (38 mL) containing a stirring bar was charged with **2'** (0.1 mmol), *w* or *w/o* $PhSO_2Na$ (0.05 mmol, 50 mol%), 4CzIPN (0.001 mmol, 1 mmol%) and DMF (1 mL). N_2 gas in a balloon was bubbled into the mixture under stirring for 10 min through a needle and the tube was then evacuated and back-filled with CO_2 for 3 times. The mixture was placed under a 30 W blue LED (λ_{max}

= 465 nm, 7.5 cm away from the LEDs, with cooling fan to keep the reaction temperature at 25~30 °C) light source and stirred at ambient temperature for 16 h. Upon completion of the reaction, all the solvents were removed under reduced pressure at high temperature. The crude reaction mixture was diluted with EtOAc (5 mL) and filtered through a short pad of Celite. The sealed tube and Celite pad were washed with an additional 25 mL of EtOAc. The filtrate was concentrated in vacuo, and crude ^{1}H NMR spectrum was taken using coumarin as internal standard. The result was detected by crud ^{1}H NMR spectrum.

3.7 Light On-Off Experiment



5

Light on-off experiment following the standard procedure: the reaction of 1,6-enyne (73.4 mg, 0.2 mmol, 1.0 equiv), $PhSO_2Na$ (0.1 mmol, 50 mol%), 4CzIPN (0.002 mmol, 1 mmol%), 1,3,5-trimethoxybenzene (33.6 mg, 0.2 mmol, 1.0 equiv) and DMF (2 mL) was evacuated and back-filled with CO_2 for 3 times and stirred at ambient temperature. Yield was determined by ^{1}H NMR of the crude mixture using 1,3,5- trimethoxybenzene as internal standard.

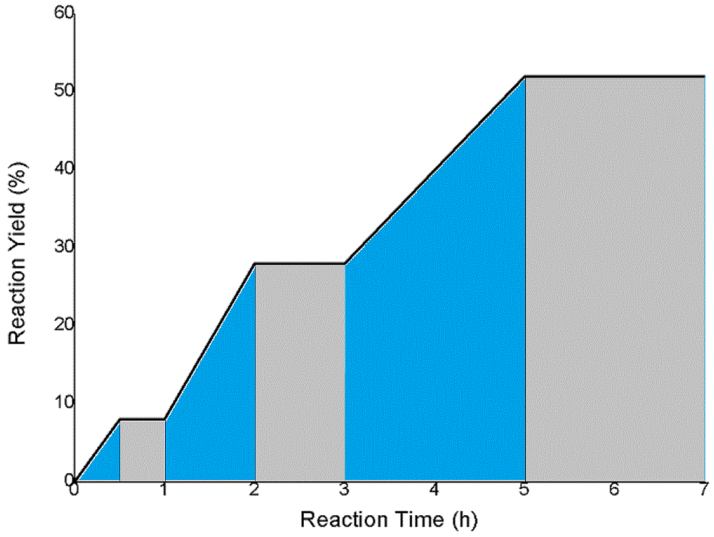
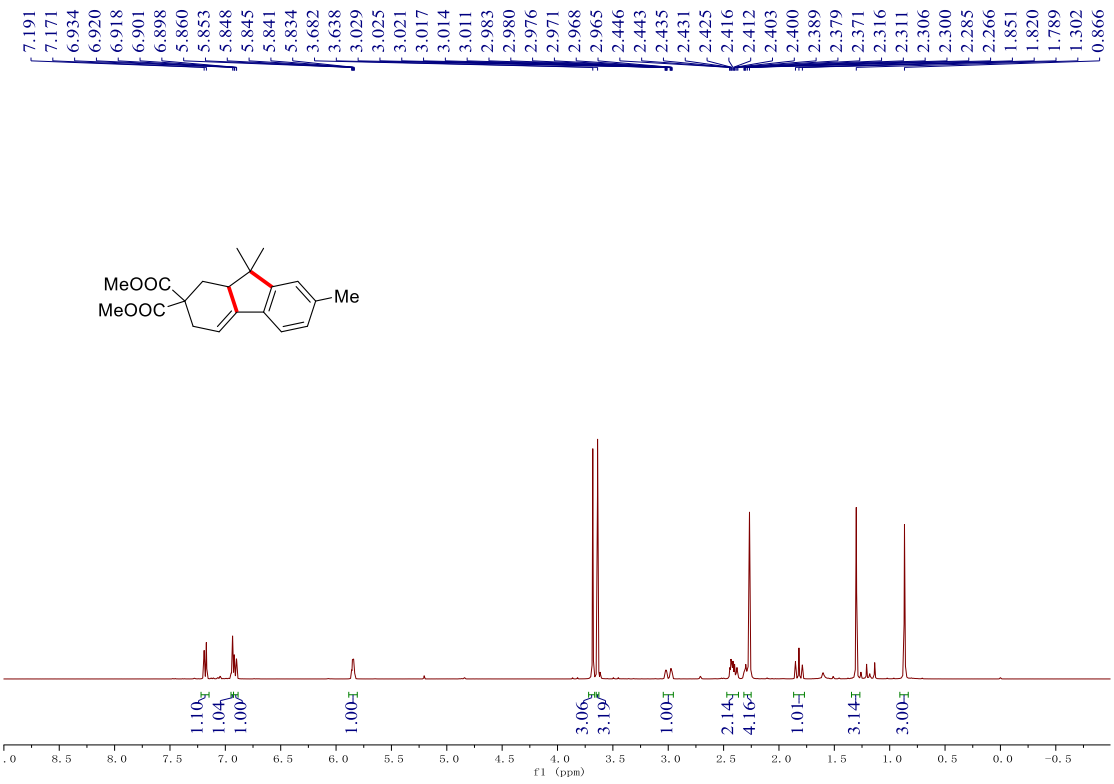


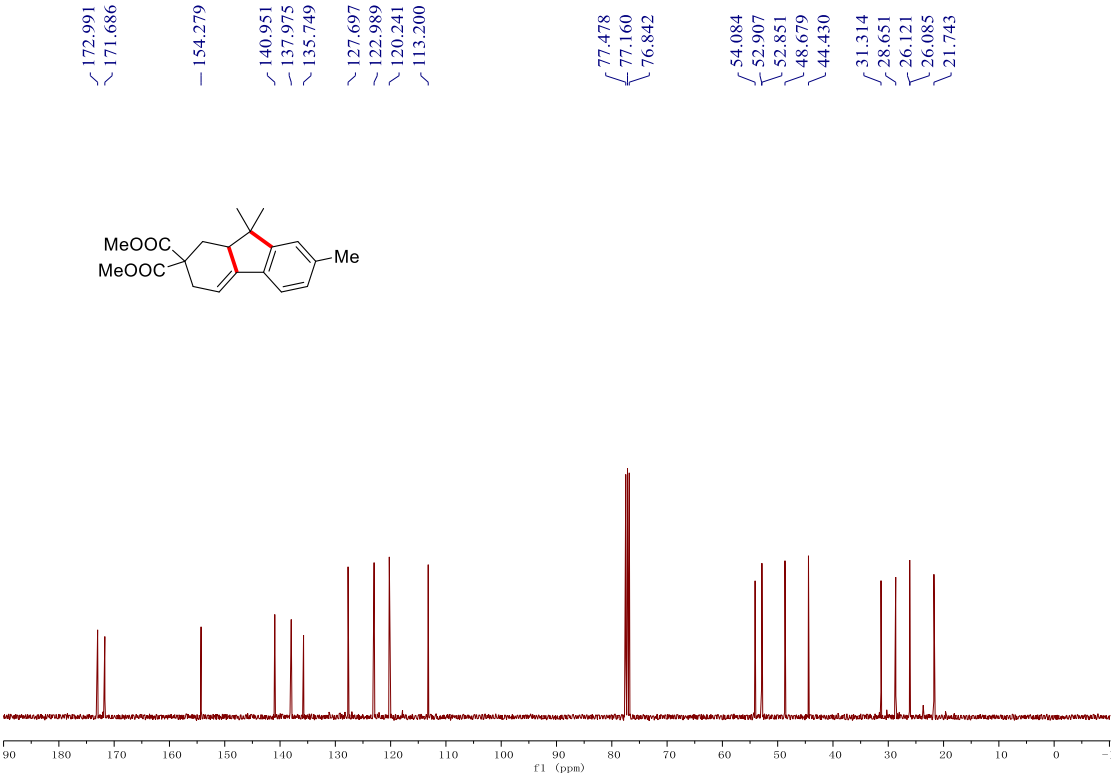
Figure S5. Light on-off experiment. The blue area indicates the blue LED irradiation, while the grey area indicates the dark treatment. The x axis is the reaction time, and the y axis is the reaction yield of **5**.

4. NMR Spectra of Compounds

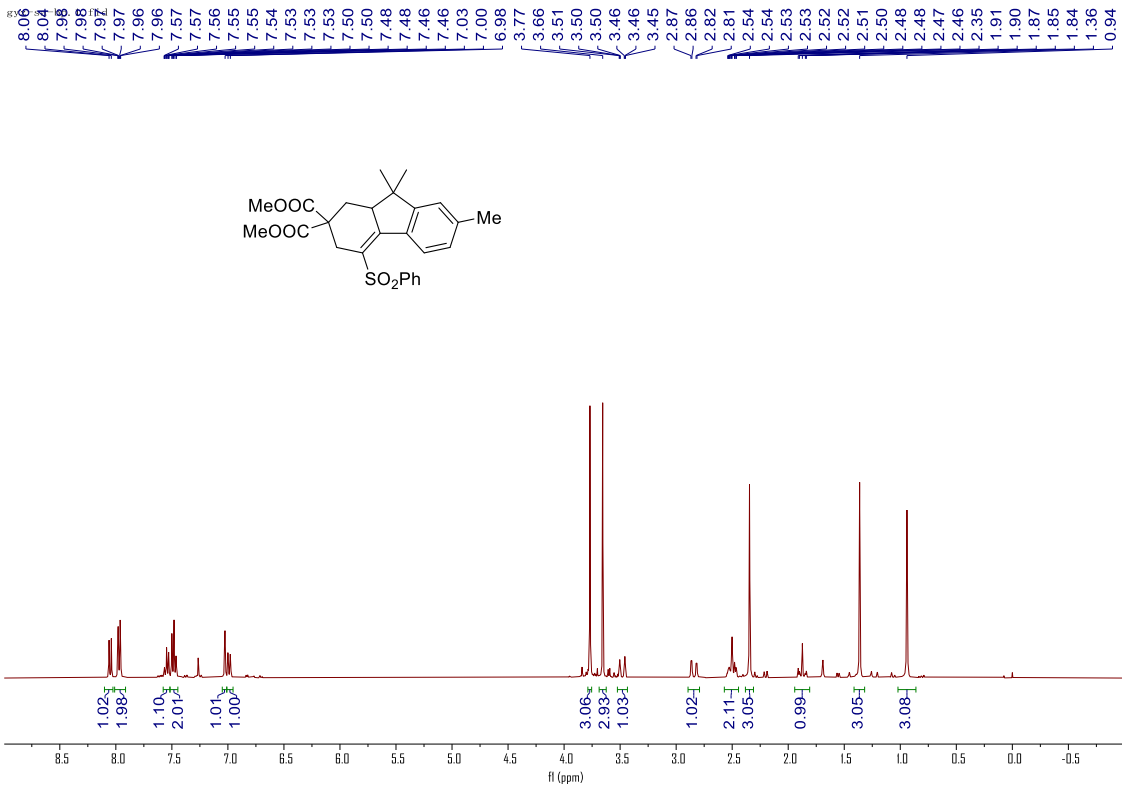
^{1}H NMR Spectrum of 2 ($CDCl_3$ as solvent, 400 MHz)



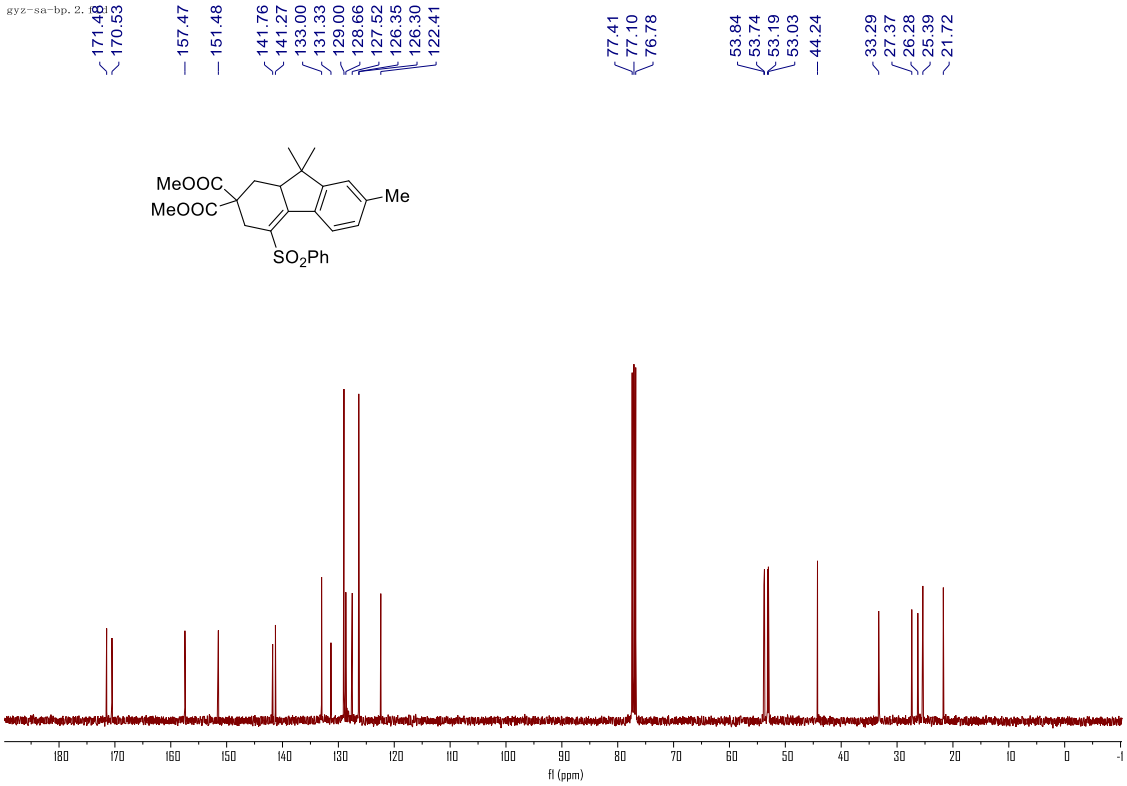
^{13}C {^{1}H} NMR Spectrum of 2 ($CDCl_3$ as solvent, 101 MHz)



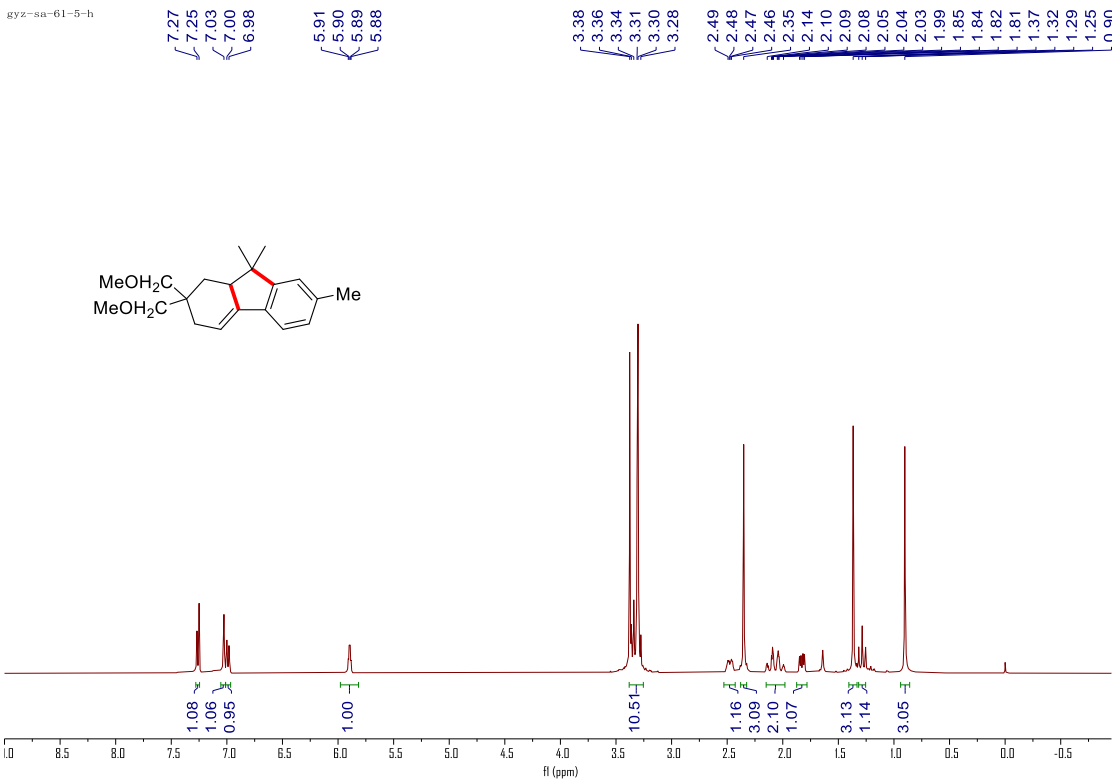
^{1}H NMR Spectrum of 2a' ($CDCl_3$ as solvent, 400 MHz)



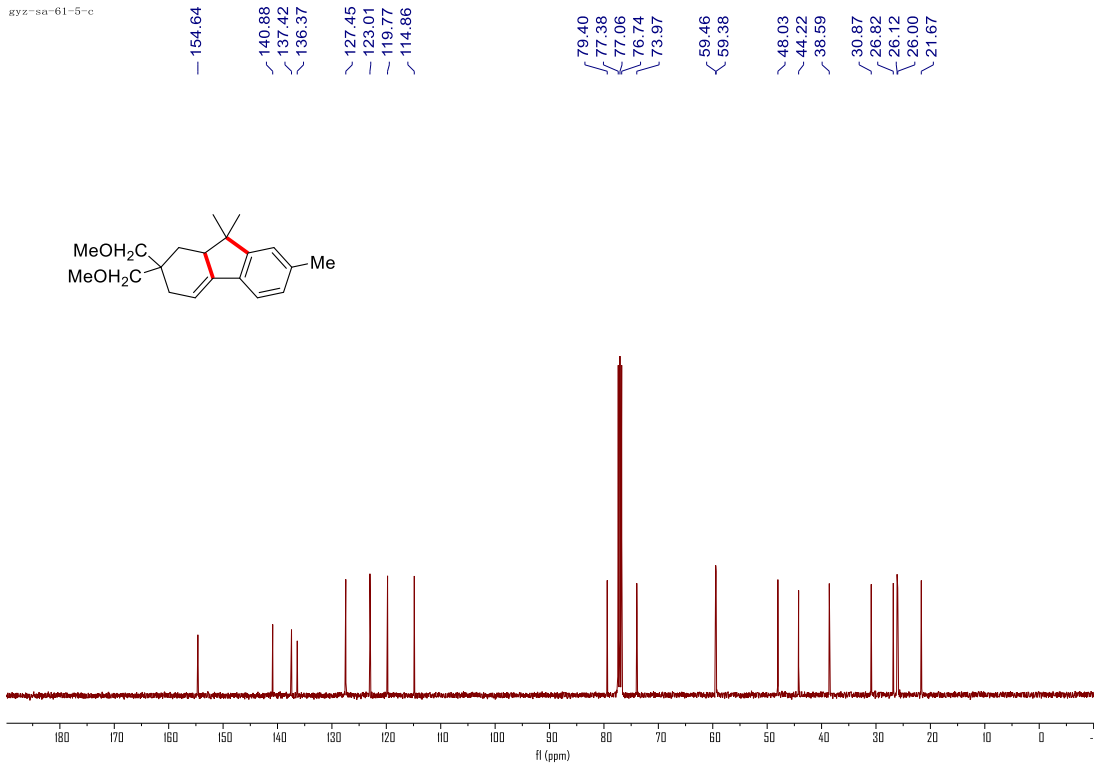
^{13}C {^{1}H} NMR Spectrum of 2' ($CDCl_3$ as solvent, 101 MHz)



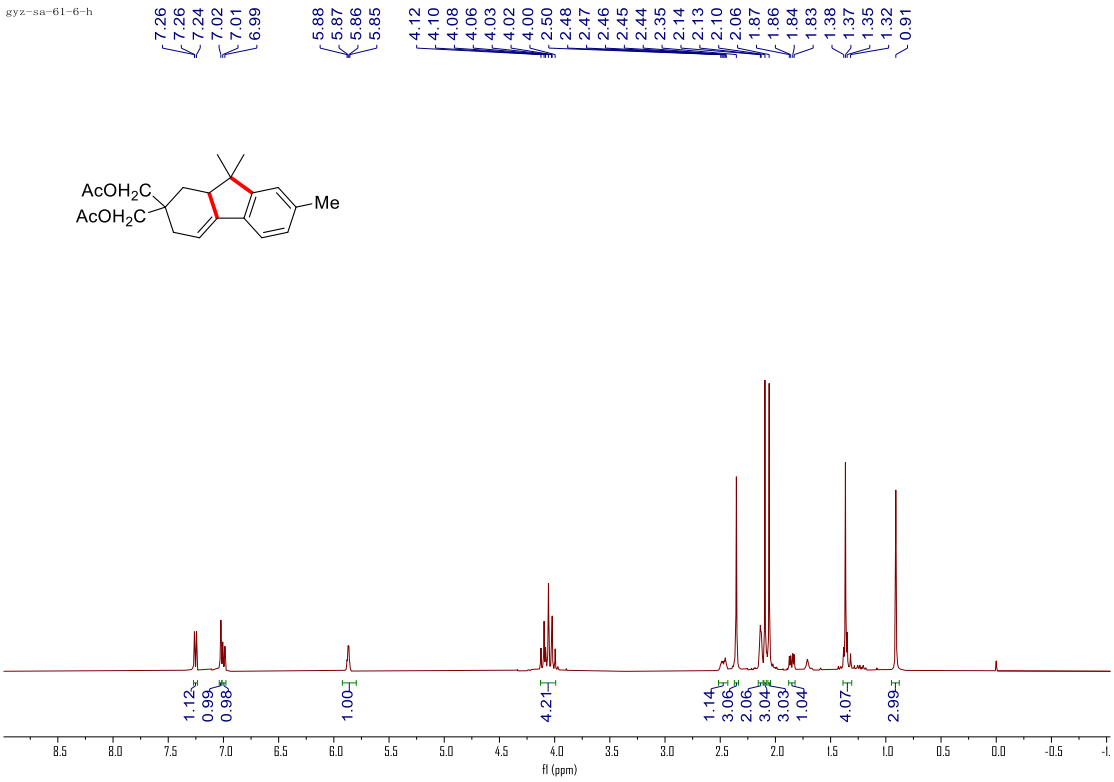
^{1}H NMR Spectrum of 3 ($CDCl_3$ as solvent, 400 MHz)



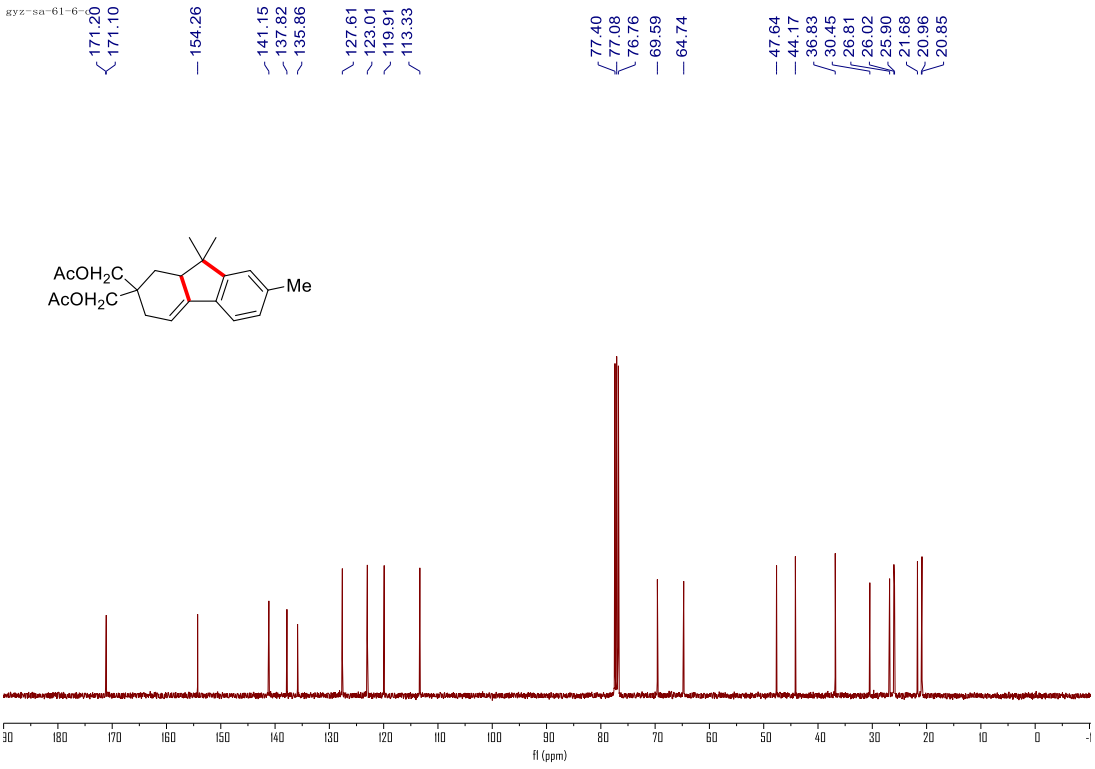
^{13}C {^{1}H} NMR Spectrum of 3 ($CDCl_3$ as solvent, 101 MHz)



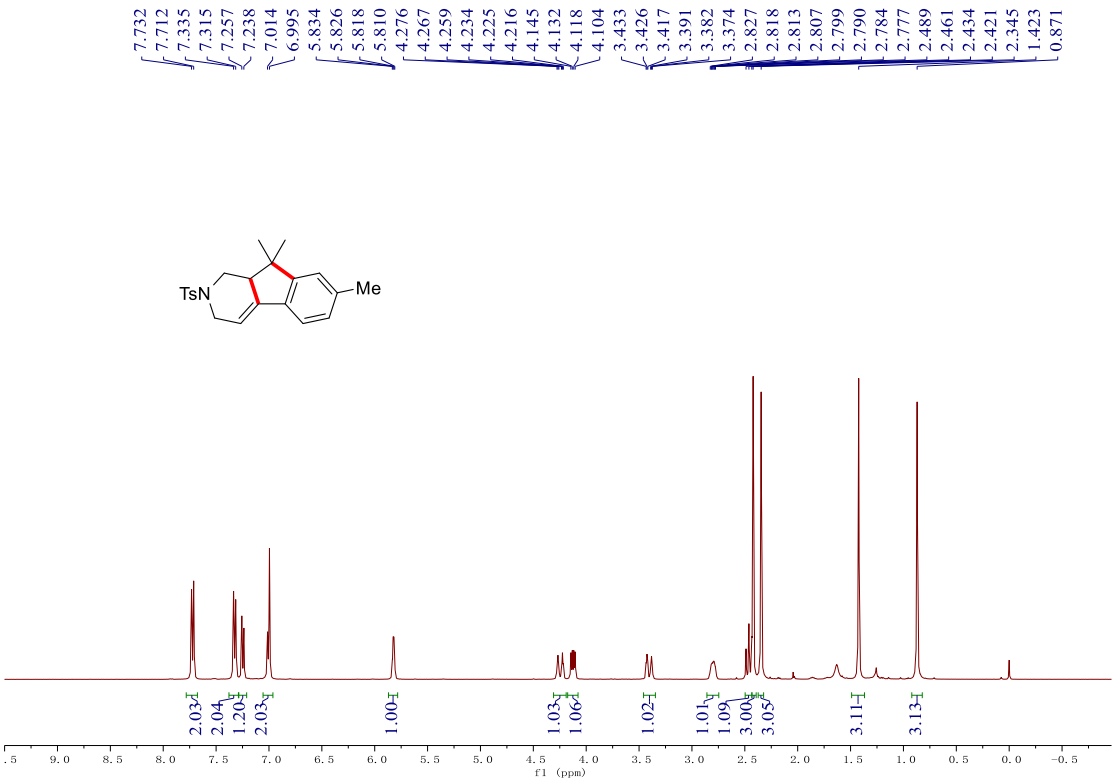
^{1}H NMR Spectrum of 4 ($CDCl_3$ as solvent, 400 MHz)



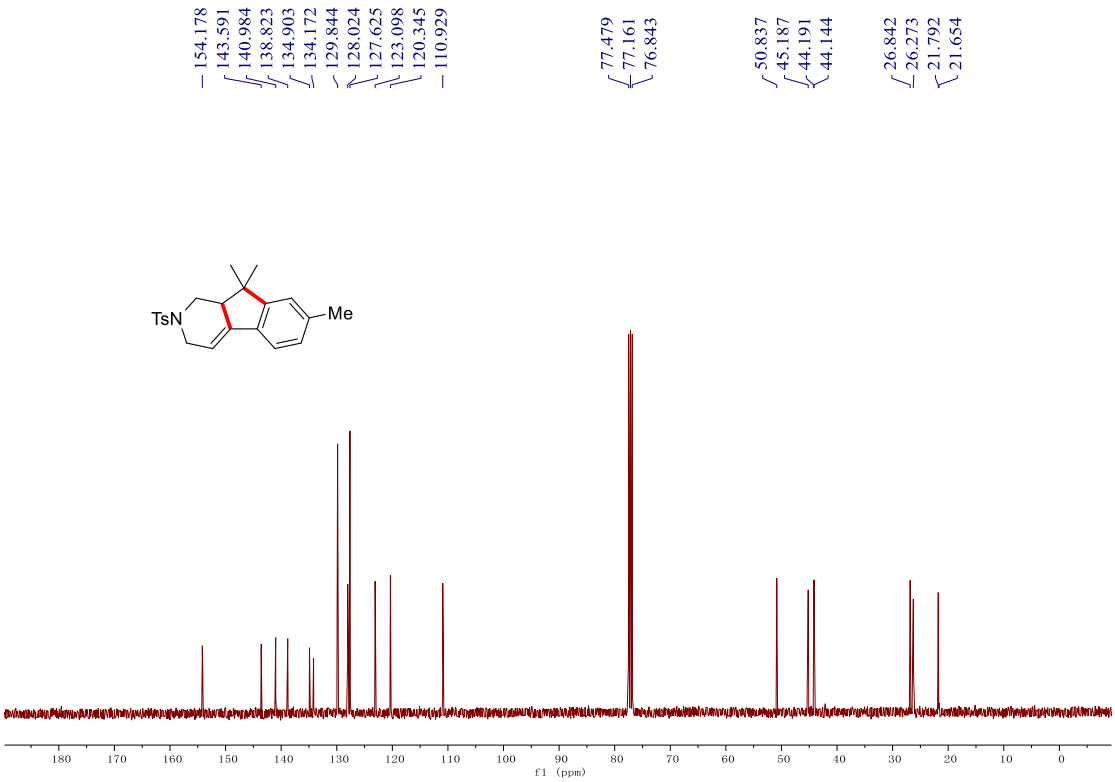
^{13}C {^{1}H} NMR Spectrum of 4 ($CDCl_3$ as solvent, 101 MHz)



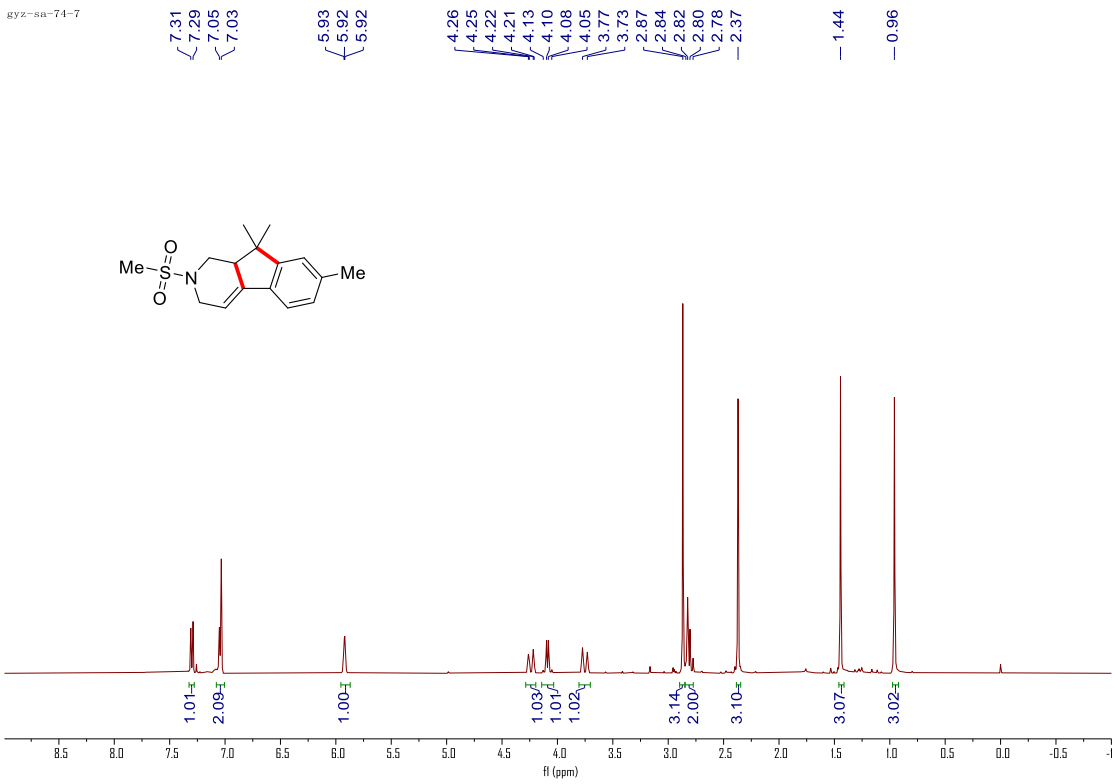
^{1}H NMR Spectrum of 5 ($CDCl_3$ as solvent, 400 MHz)



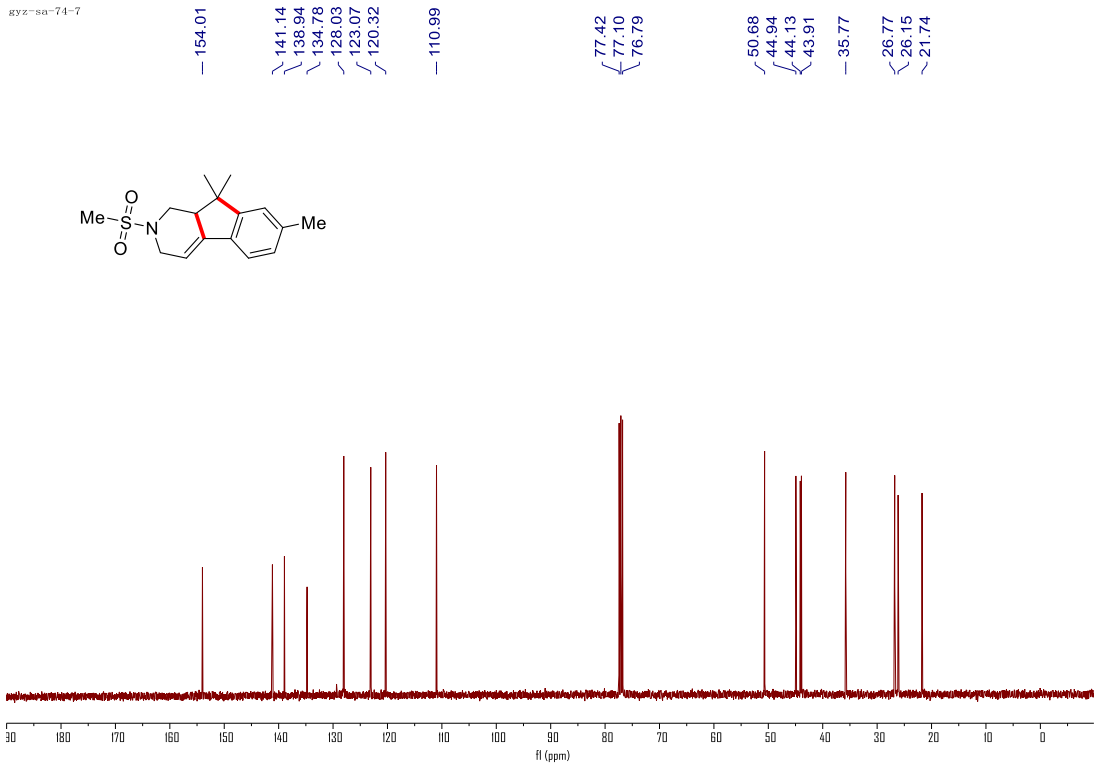
^{13}C {^{1}H} NMR Spectrum of 5 ($CDCl_3$ as solvent, 101 MHz)



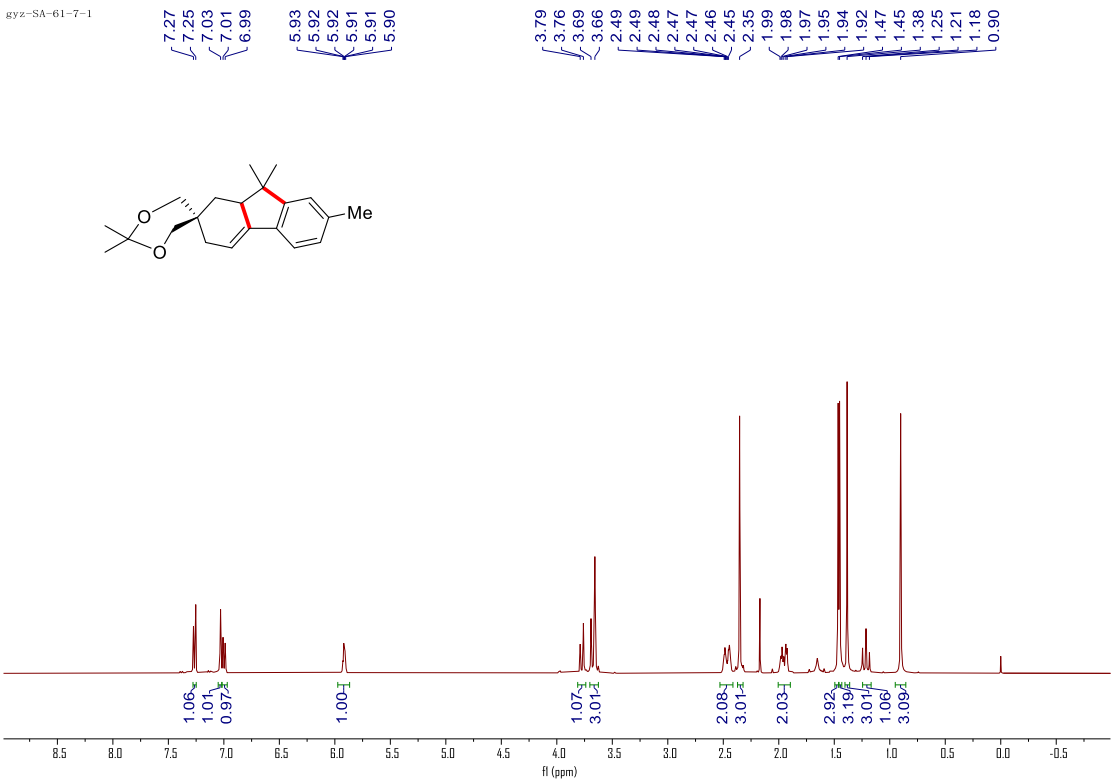
^{1}H NMR Spectrum of 6 ($CDCl_3$ as solvent, 400 MHz)



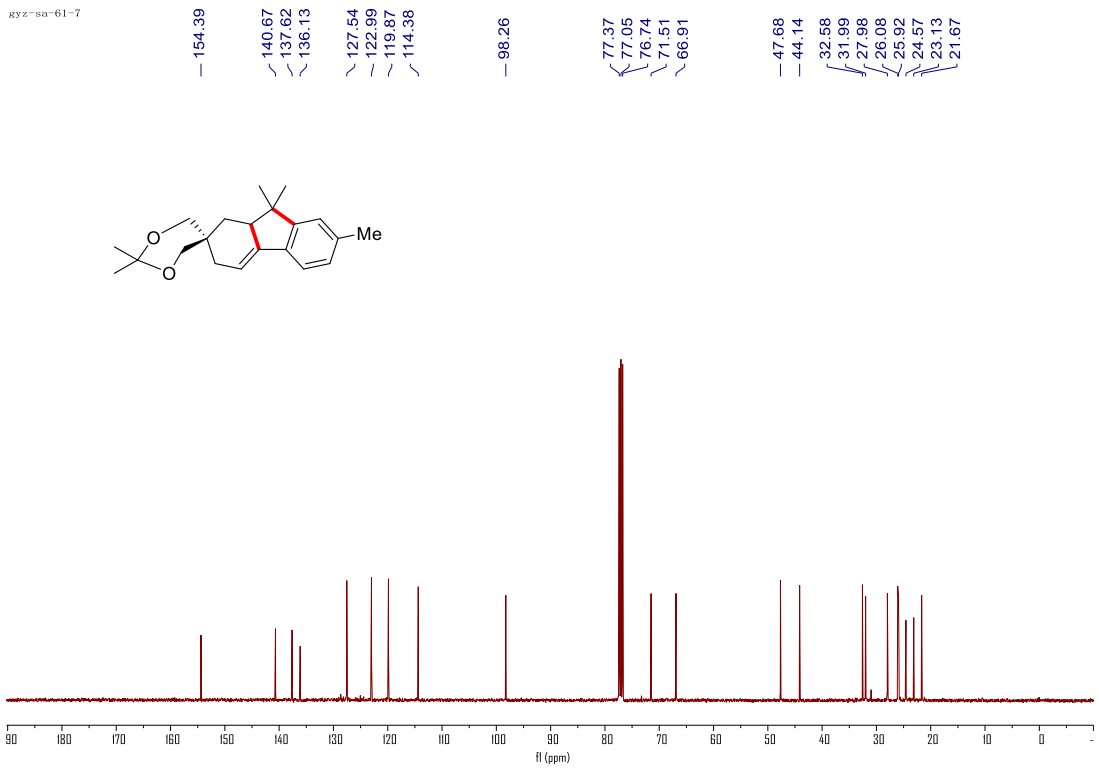
^{13}C {^{1}H} NMR Spectrum of 6 ($CDCl_3$ as solvent, 101 MHz)



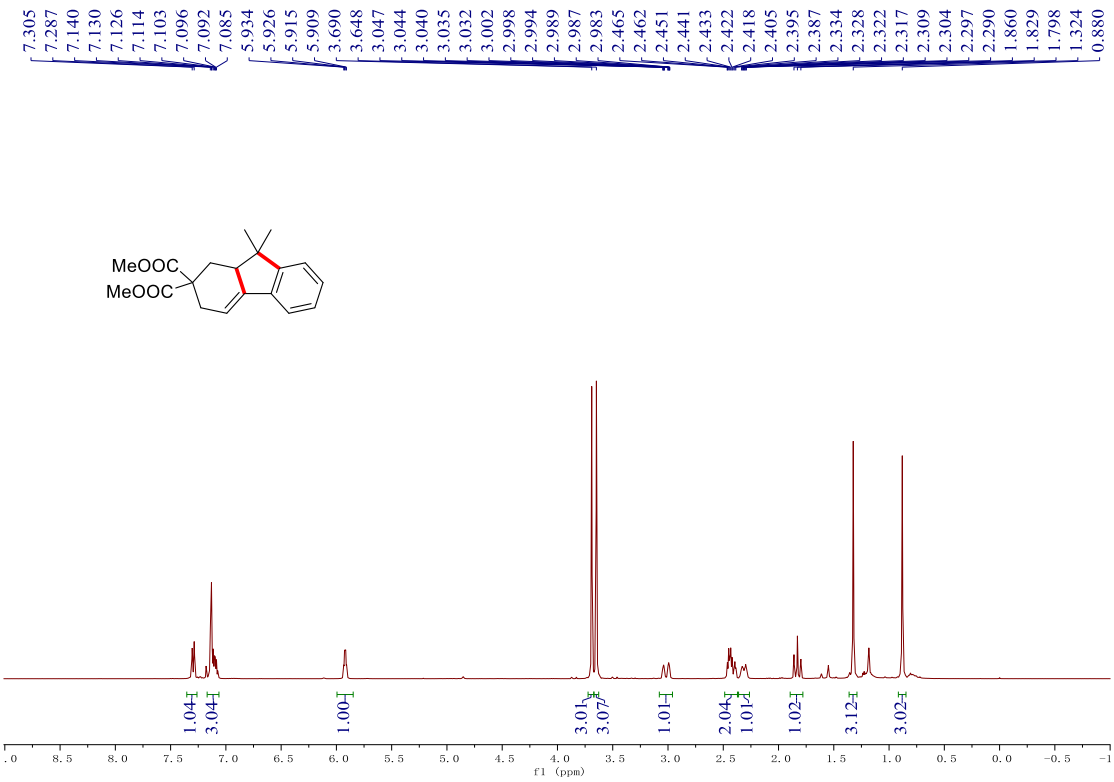
^{1}H NMR Spectrum of 7 ($CDCl_3$ as solvent, 400 MHz)



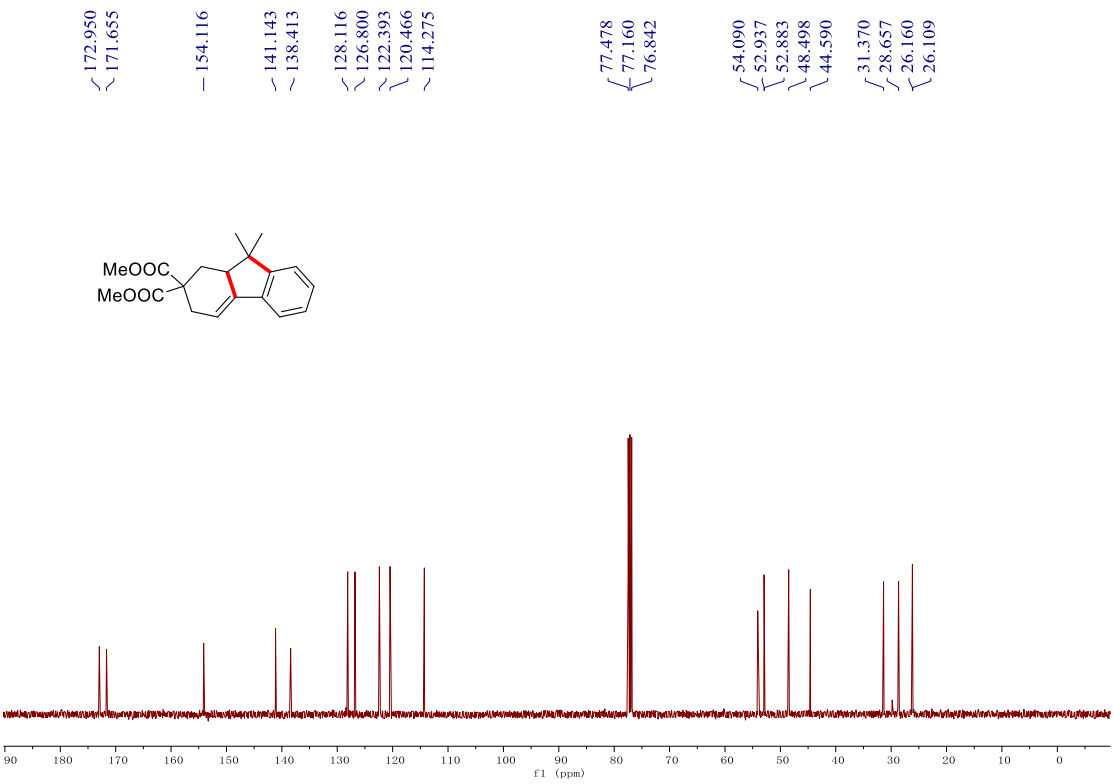
^{13}C {^{1}H} NMR Spectrum of 7 ($CDCl_3$ as solvent, 101 MHz)



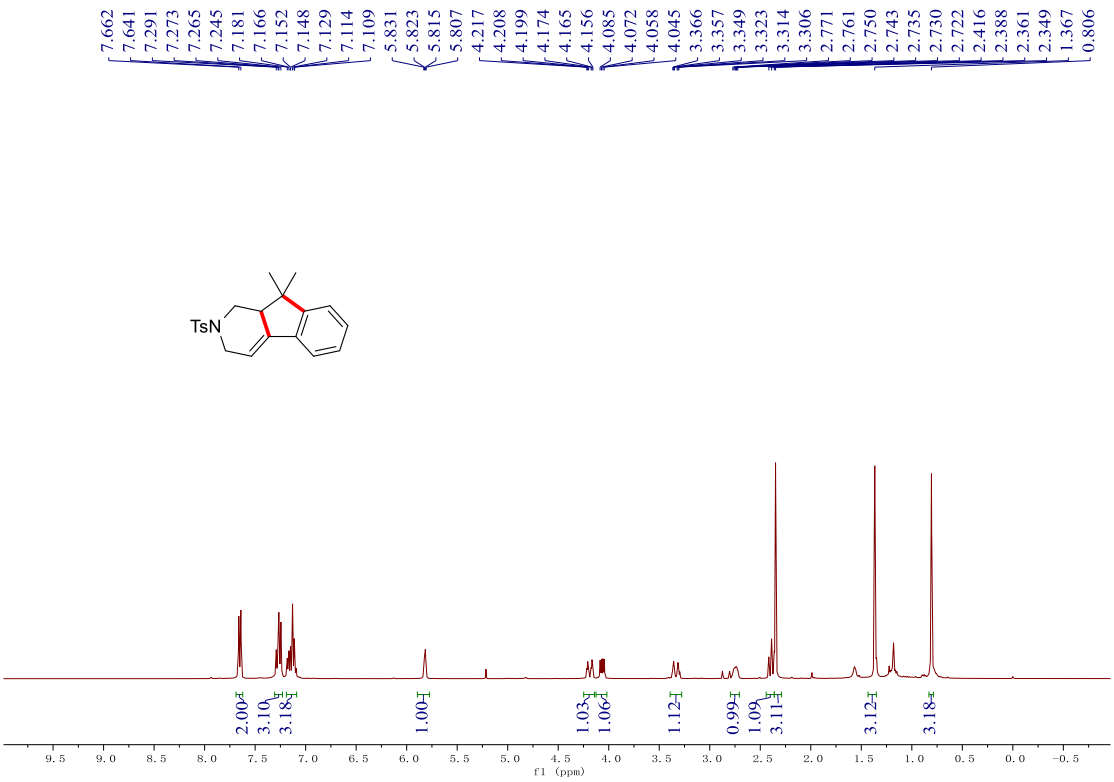
^{1}H NMR Spectrum of 8 ($CDCl_3$ as solvent, 400 MHz)



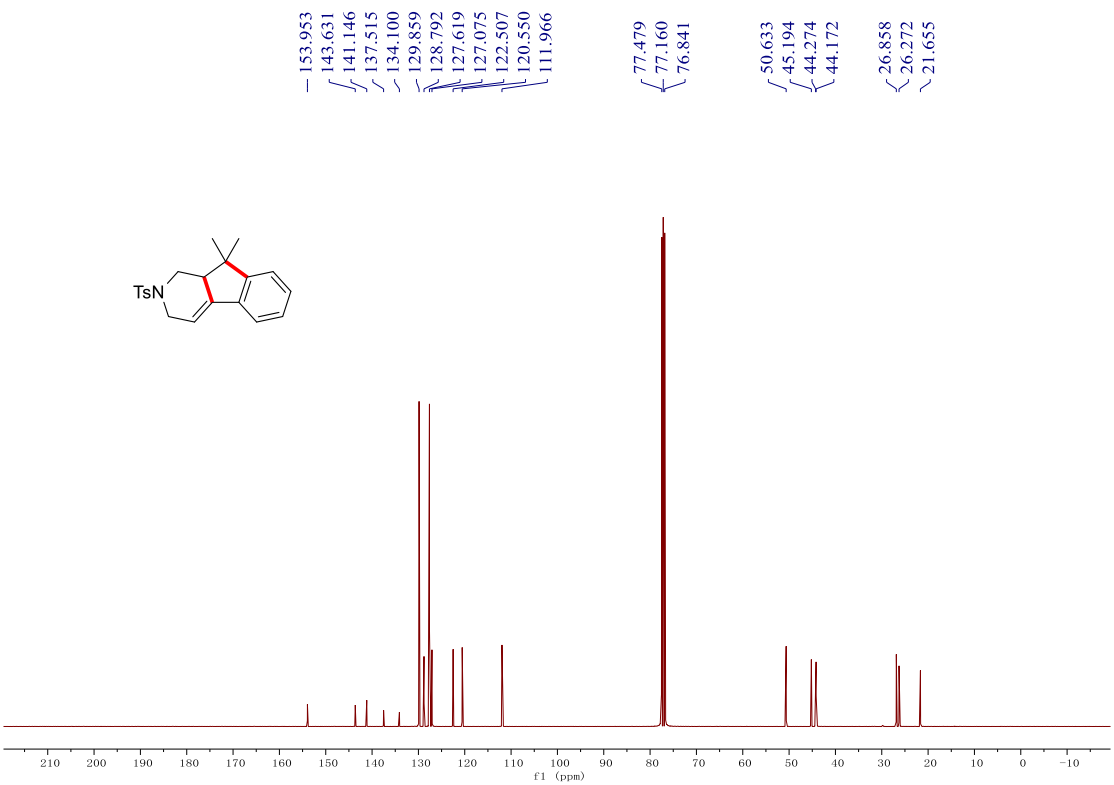
^{13}C {^{1}H} NMR Spectrum of 8 ($CDCl_3$ as solvent, 101 MHz)



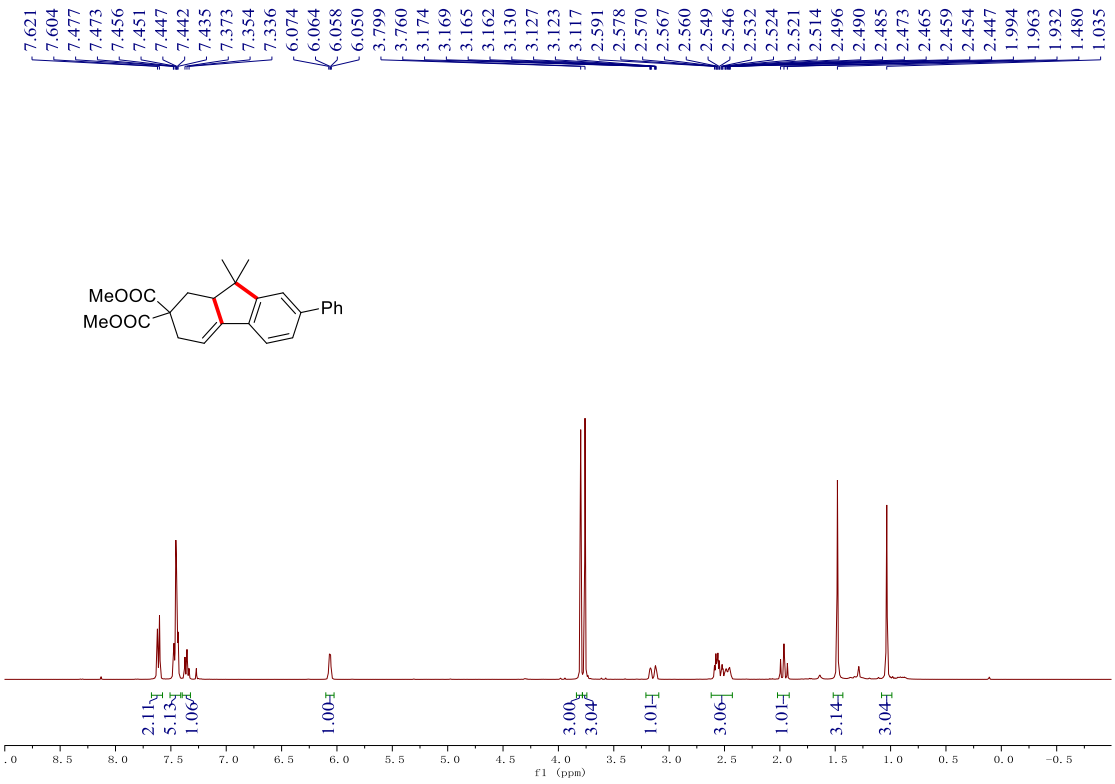
^{1}H NMR Spectrum of 9 ($CDCl_3$ as solvent, 400 MHz)



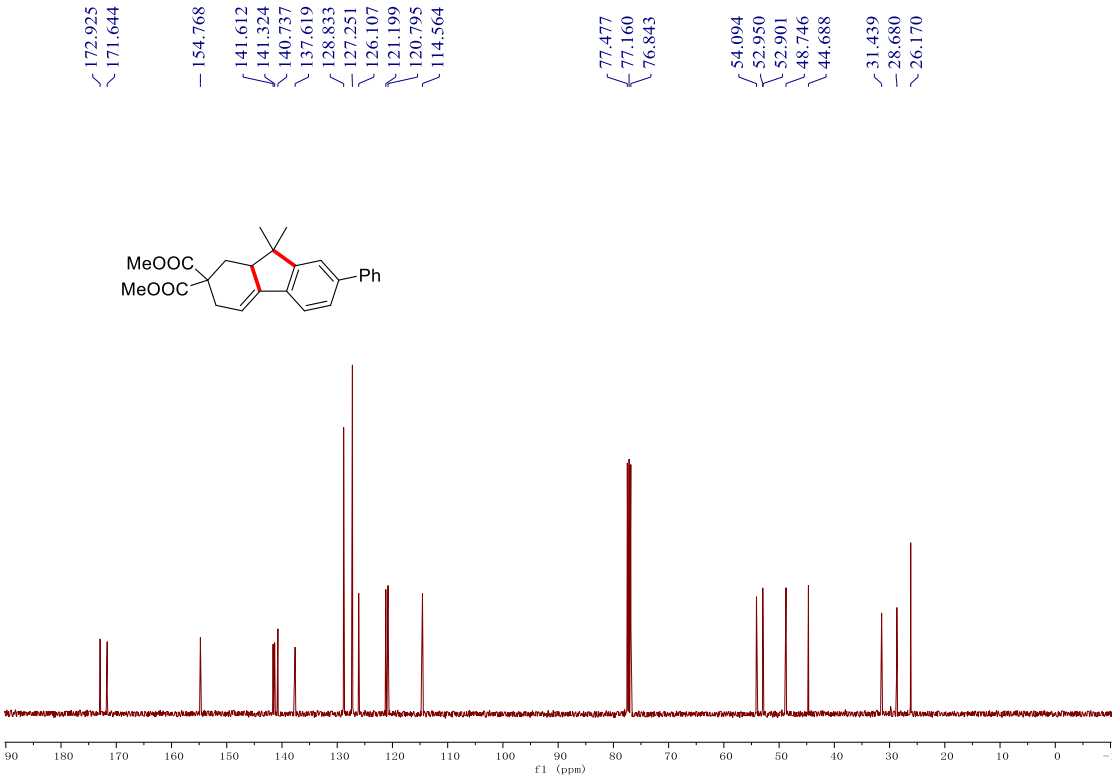
^{13}C {^{1}H} NMR Spectrum of 9 ($CDCl_3$ as solvent, 101 MHz)



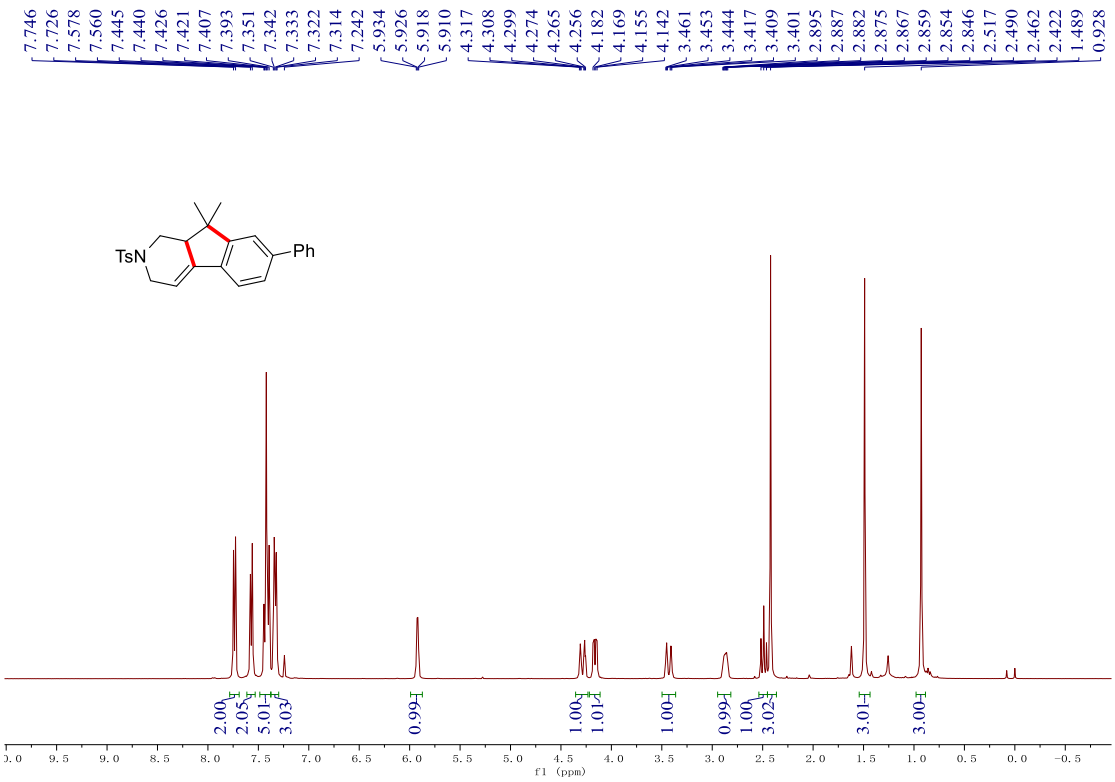
^{1}H NMR Spectrum of 10 ($CDCl_3$ as solvent, 400 MHz)



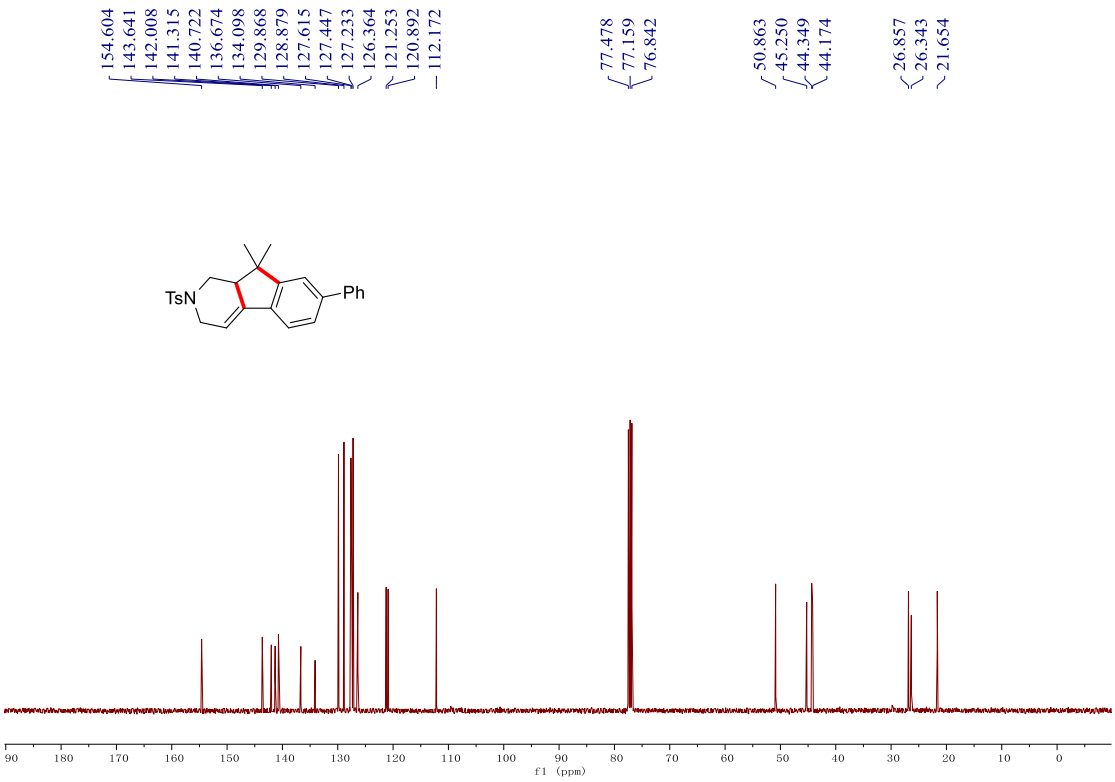
^{13}C {^{1}H} NMR Spectrum of 10 ($CDCl_3$ as solvent, 101 MHz)



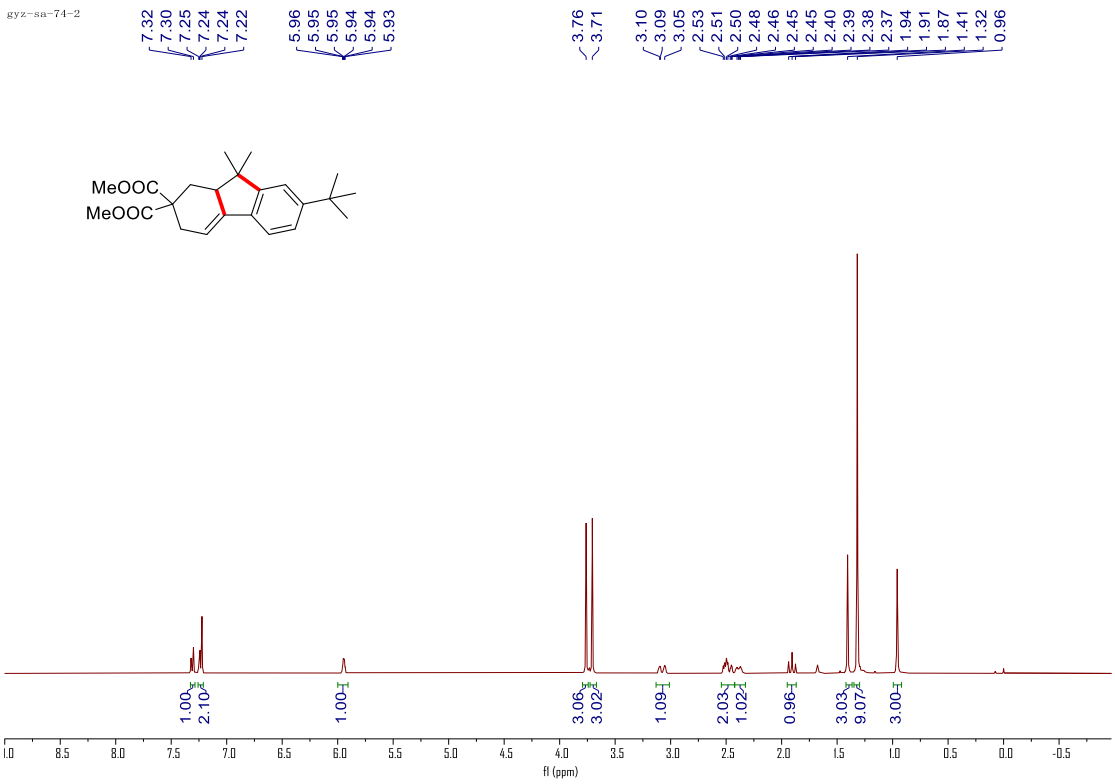
^{1}H NMR Spectrum of 11 ($CDCl_3$ as solvent, 400 MHz)



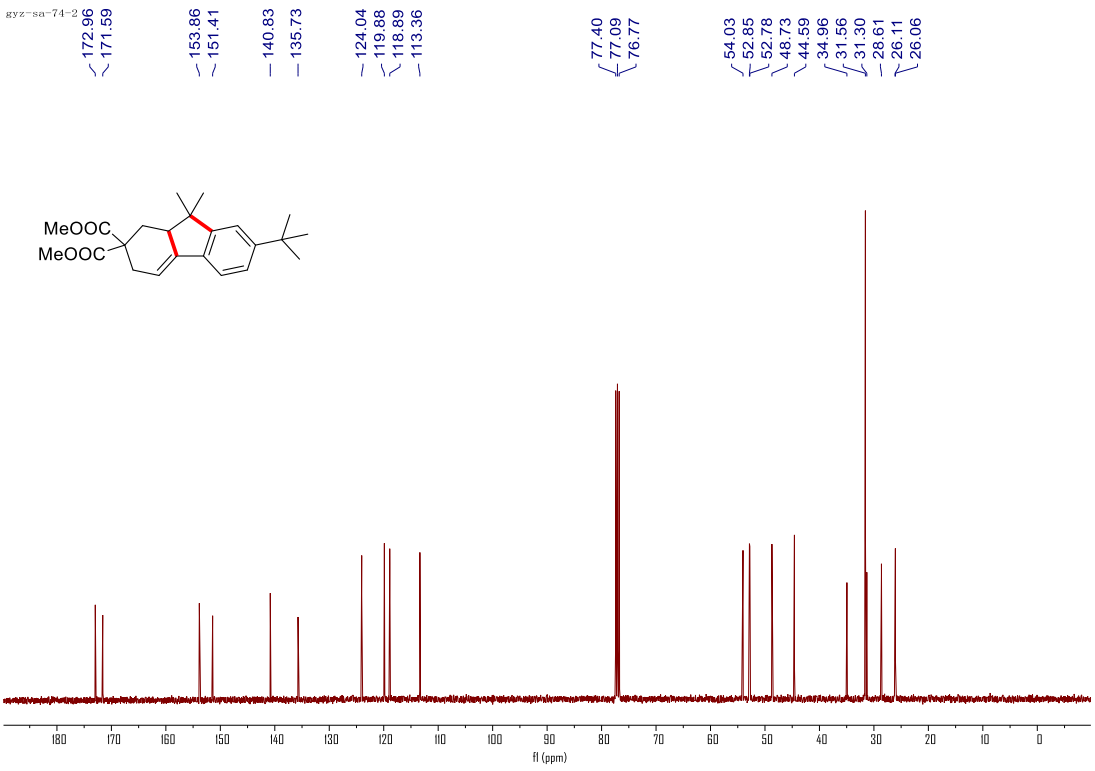
^{13}C {^{1}H} NMR Spectrum of 11 ($CDCl_3$ as solvent, 101 MHz)



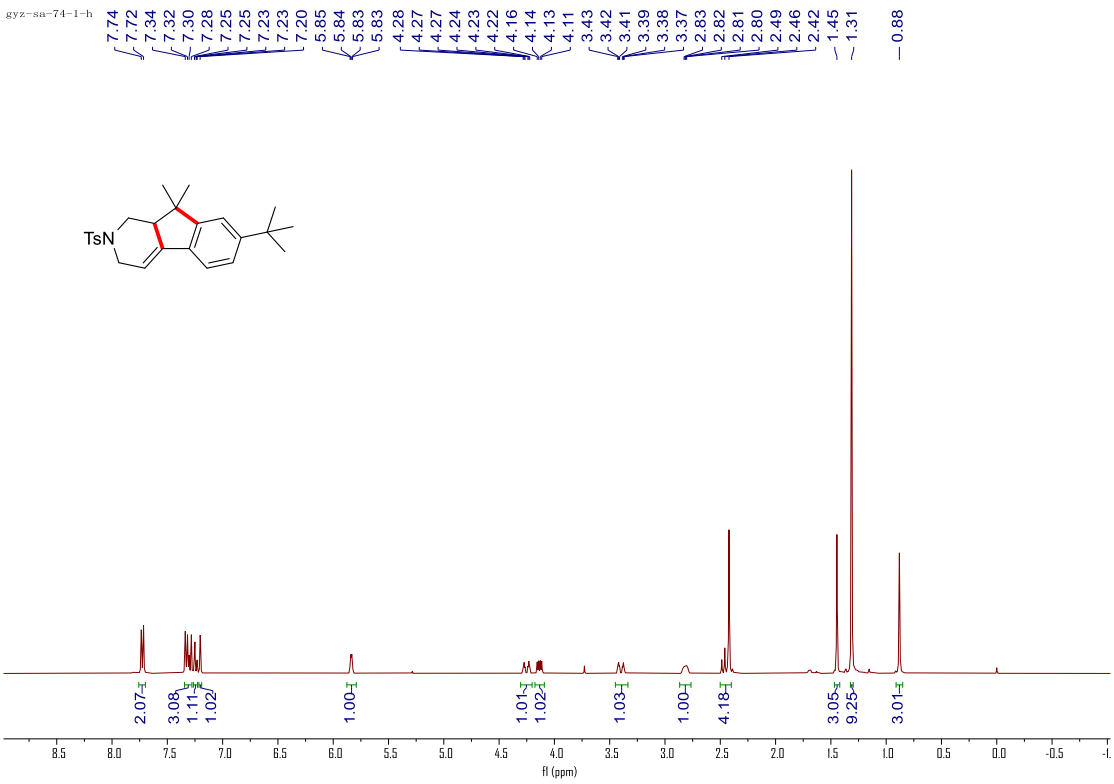
^{1}H NMR Spectrum of 12 ($CDCl_3$ as solvent, 400 MHz)



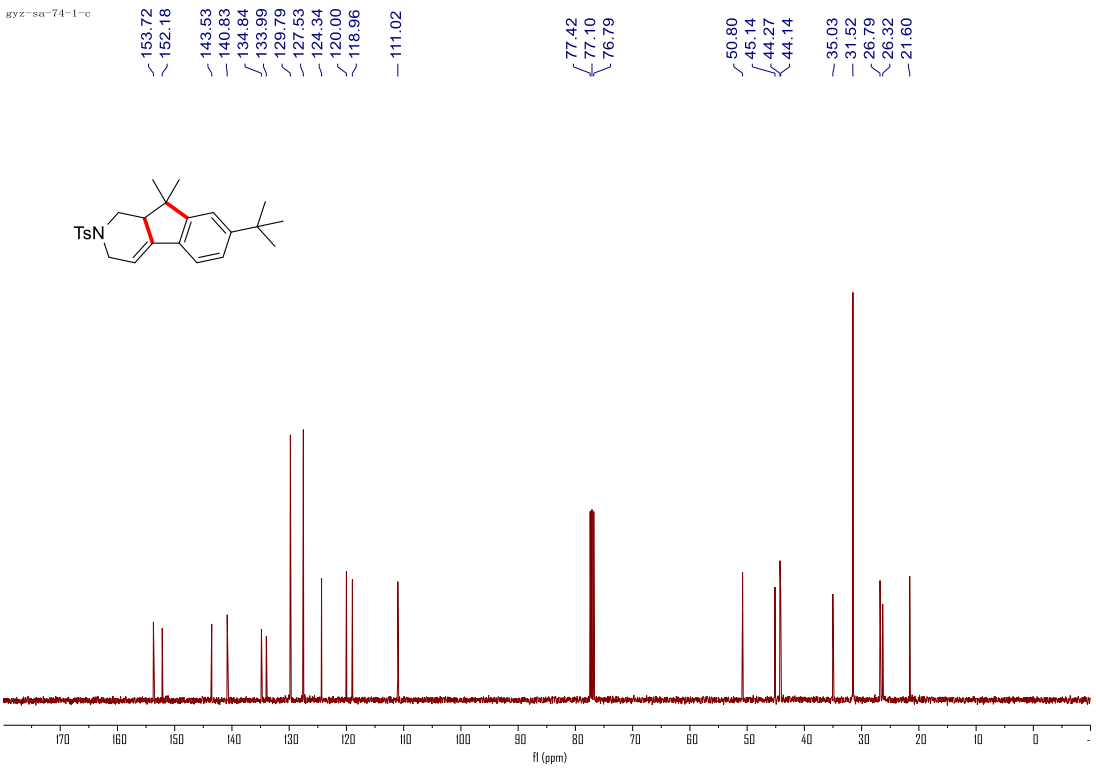
^{13}C {^{1}H} NMR Spectrum of 12 ($CDCl_3$ as solvent, 101 MHz)



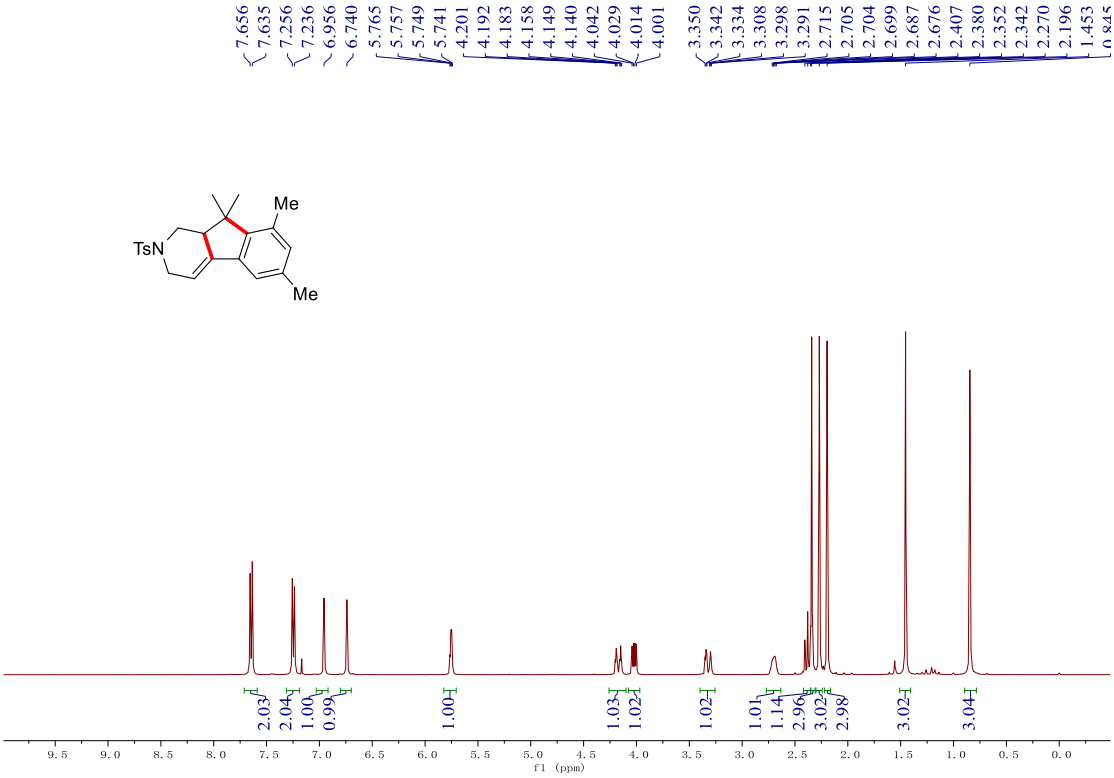
^{1}H NMR Spectrum of 13 ($CDCl_3$ as solvent, 400 MHz)



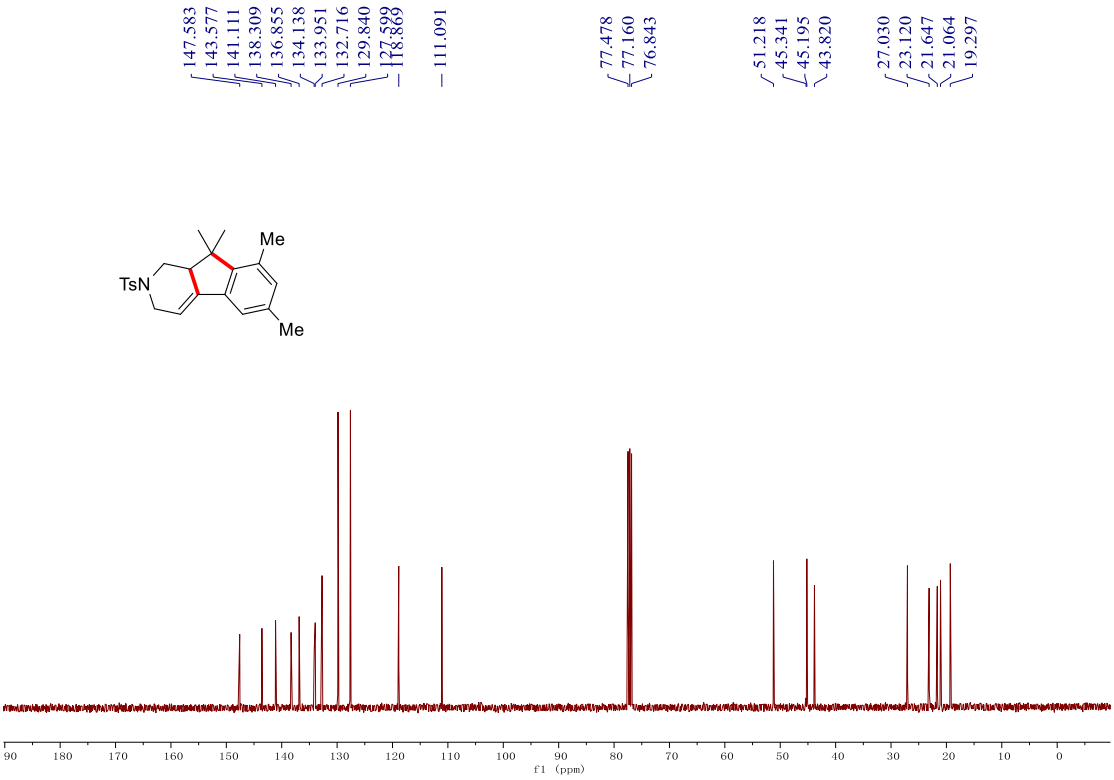
^{13}C {^{1}H} NMR Spectrum of 13 ($CDCl_3$ as solvent, 101 MHz)



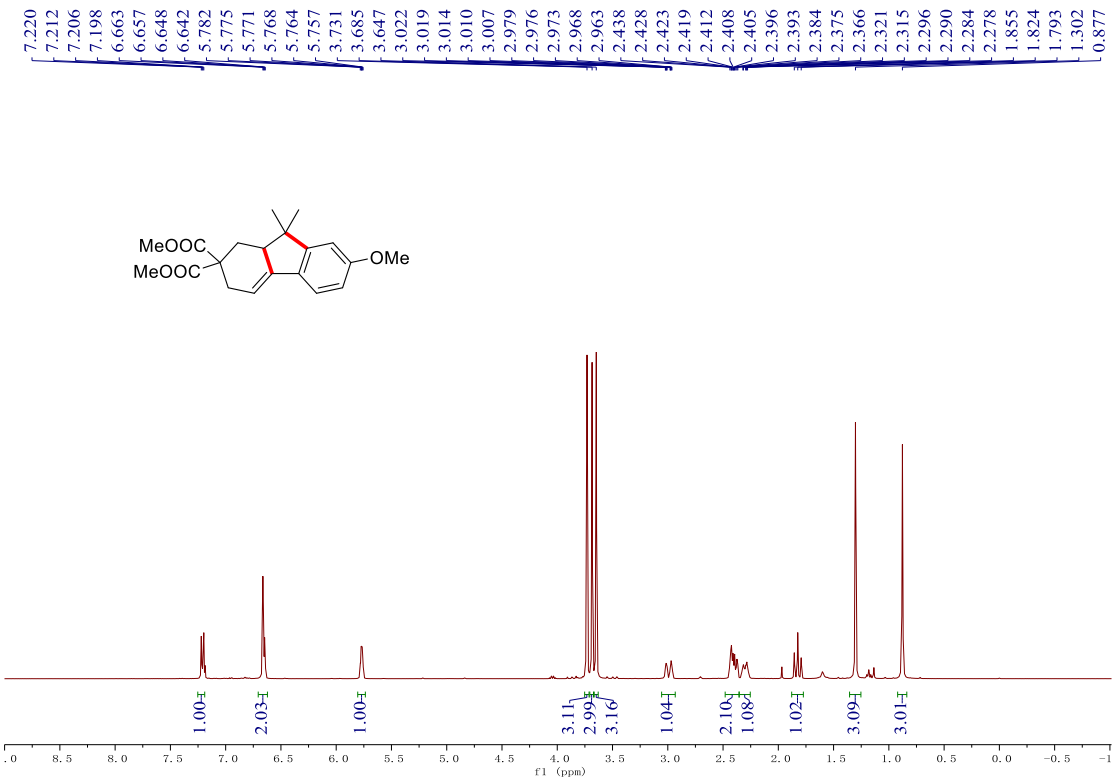
^{1}H NMR Spectrum of 14 ($CDCl_3$ as solvent, 400 MHz)



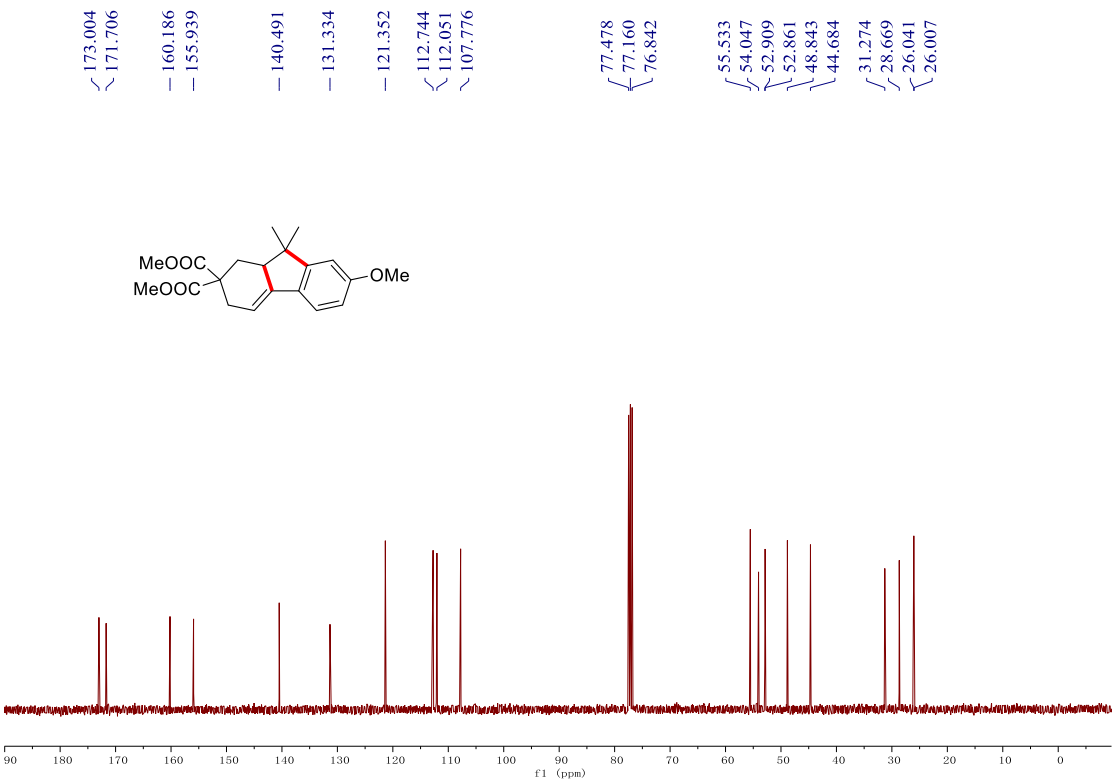
^{13}C {^{1}H} NMR Spectrum of 14 ($CDCl_3$ as solvent, 101 MHz)



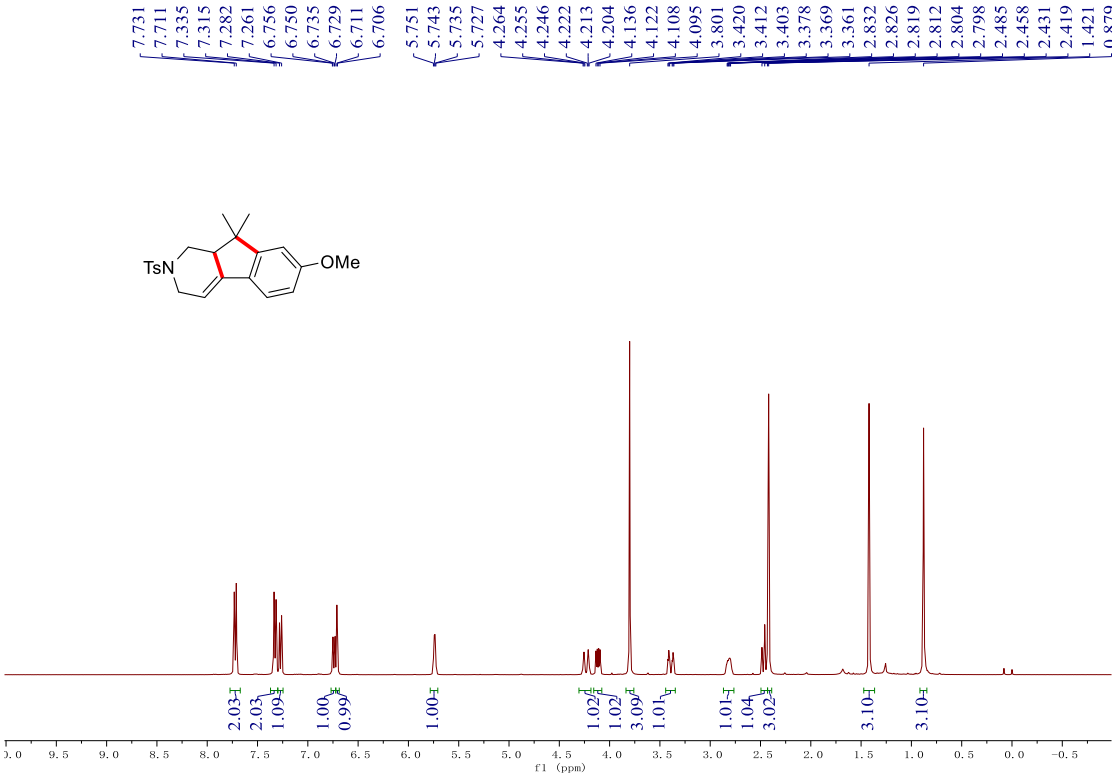
^{1}H NMR Spectrum of 15 ($CDCl_3$ as solvent, 400 MHz)



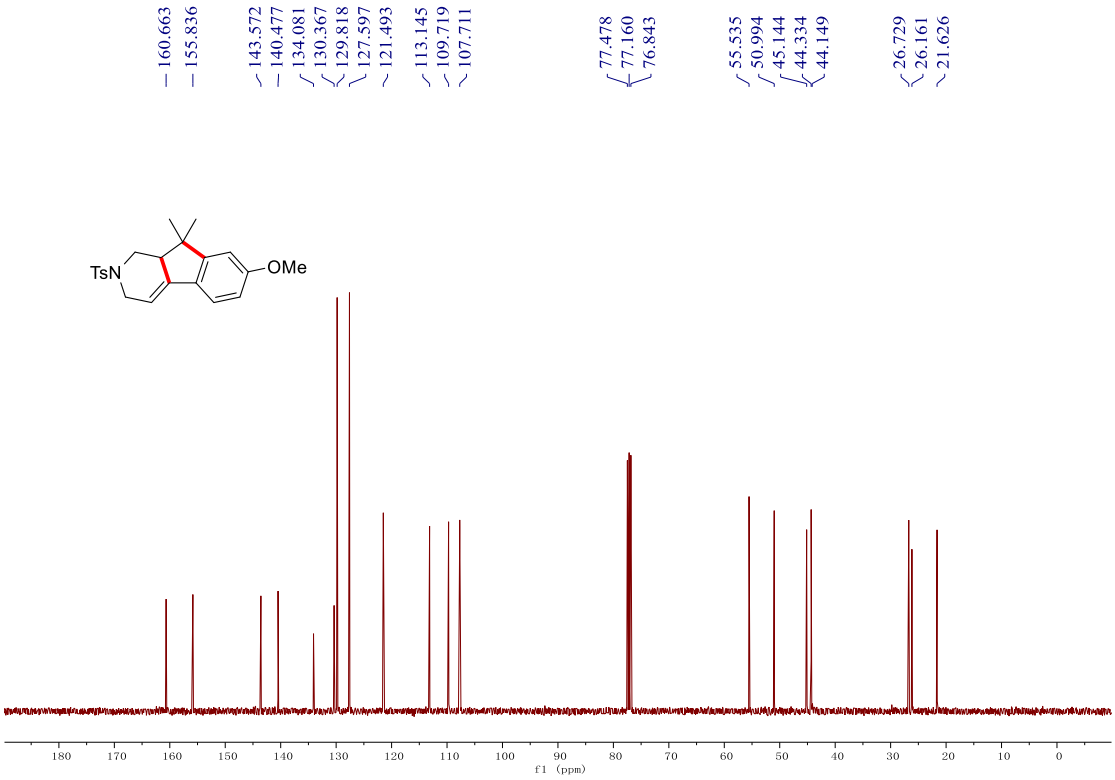
^{13}C {^{1}H} NMR Spectrum of 15 ($CDCl_3$ as solvent, 101 MHz)



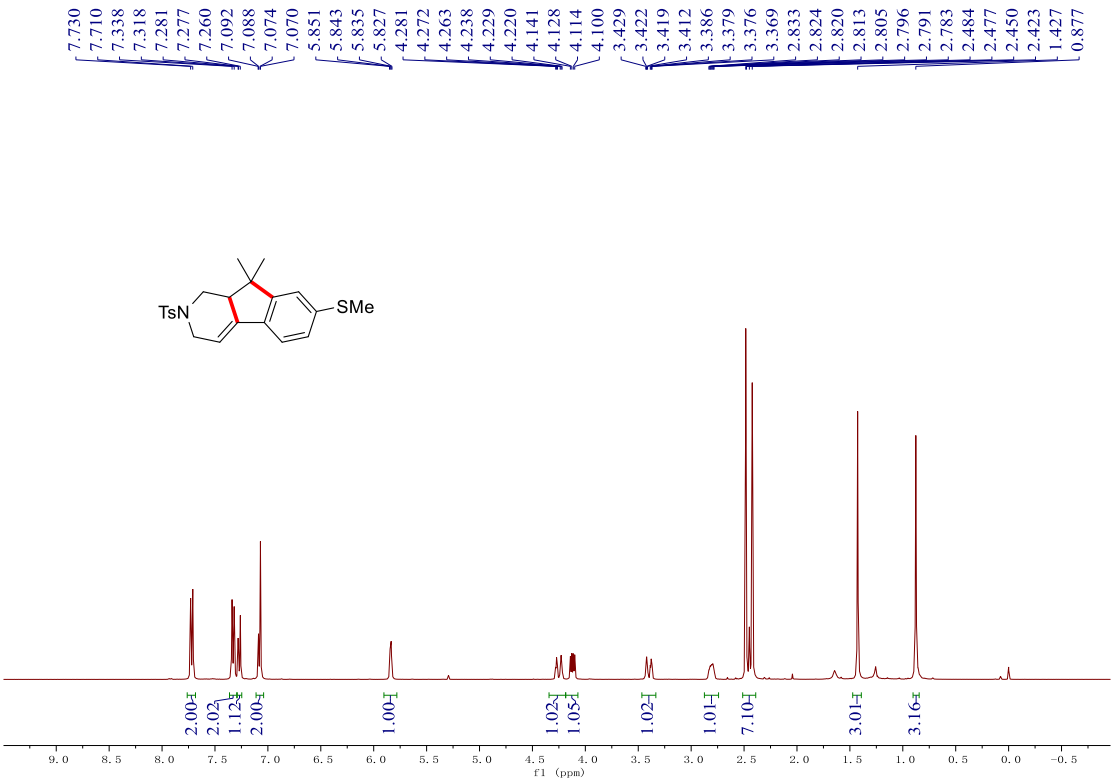
^{1}H NMR Spectrum of 16 ($CDCl_3$ as solvent, 400 MHz)



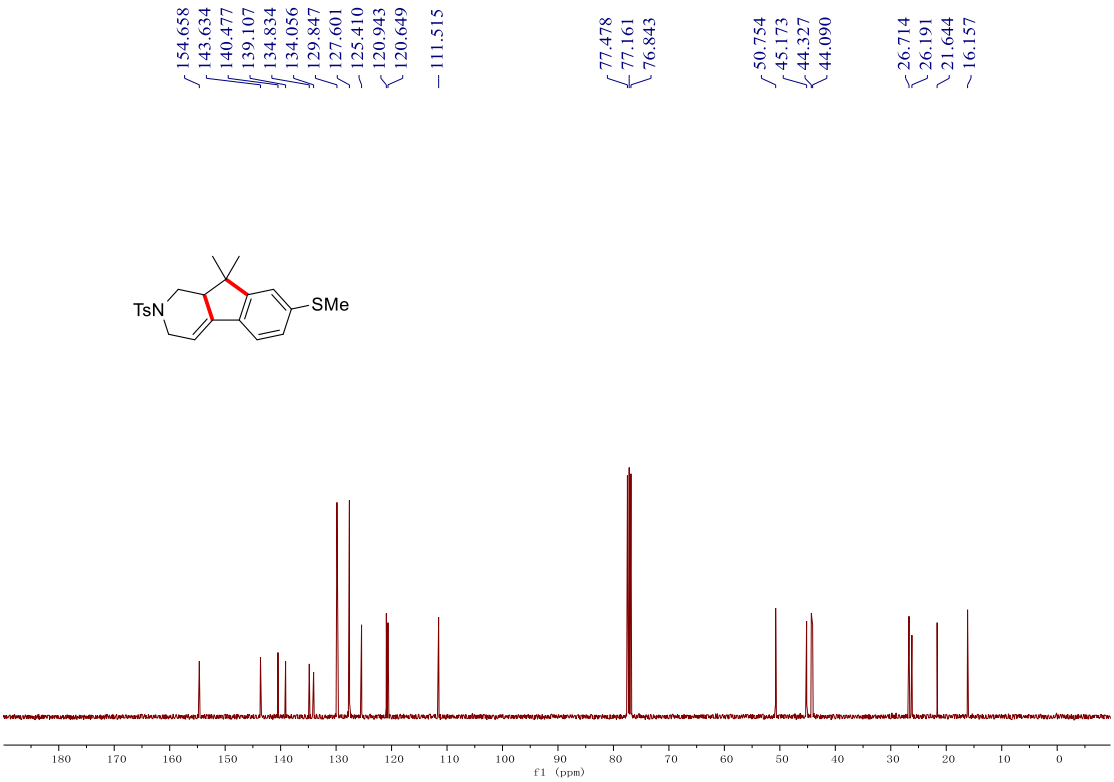
^{13}C {^{1}H} NMR Spectrum of 16 ($CDCl_3$ as solvent, 101 MHz)



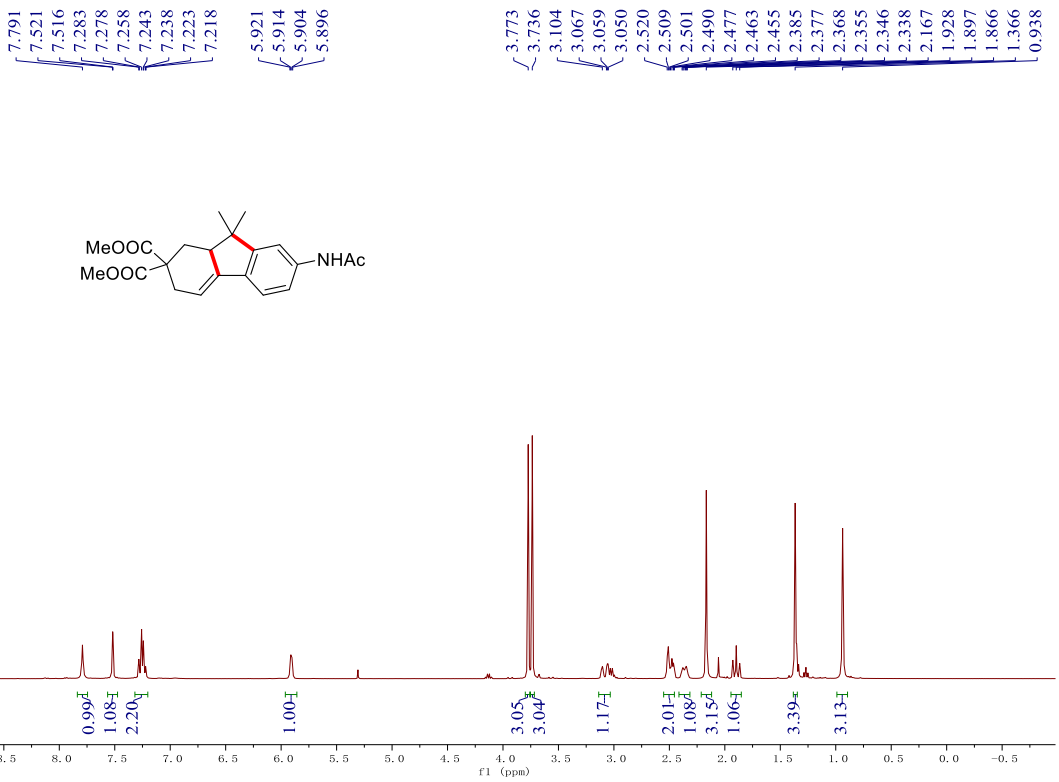
^{1}H NMR Spectrum of 17 ($CDCl_3$ as solvent, 400 MHz)



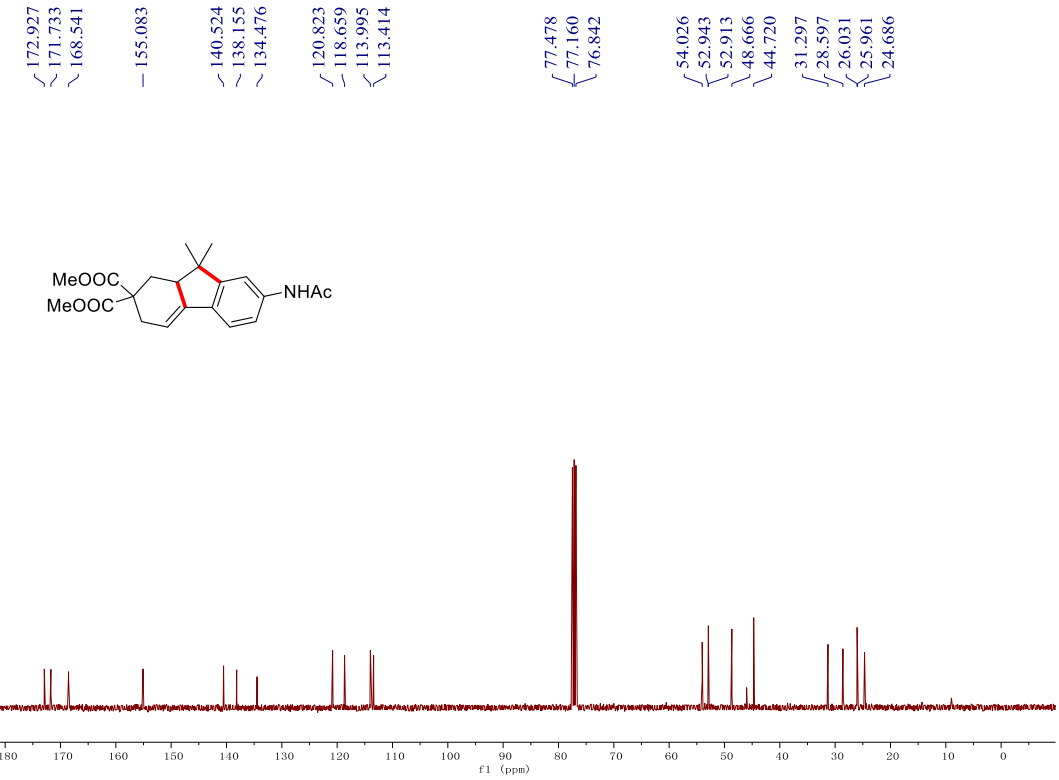
^{13}C {^{1}H} NMR Spectrum of 17 ($CDCl_3$ as solvent, 101 MHz)



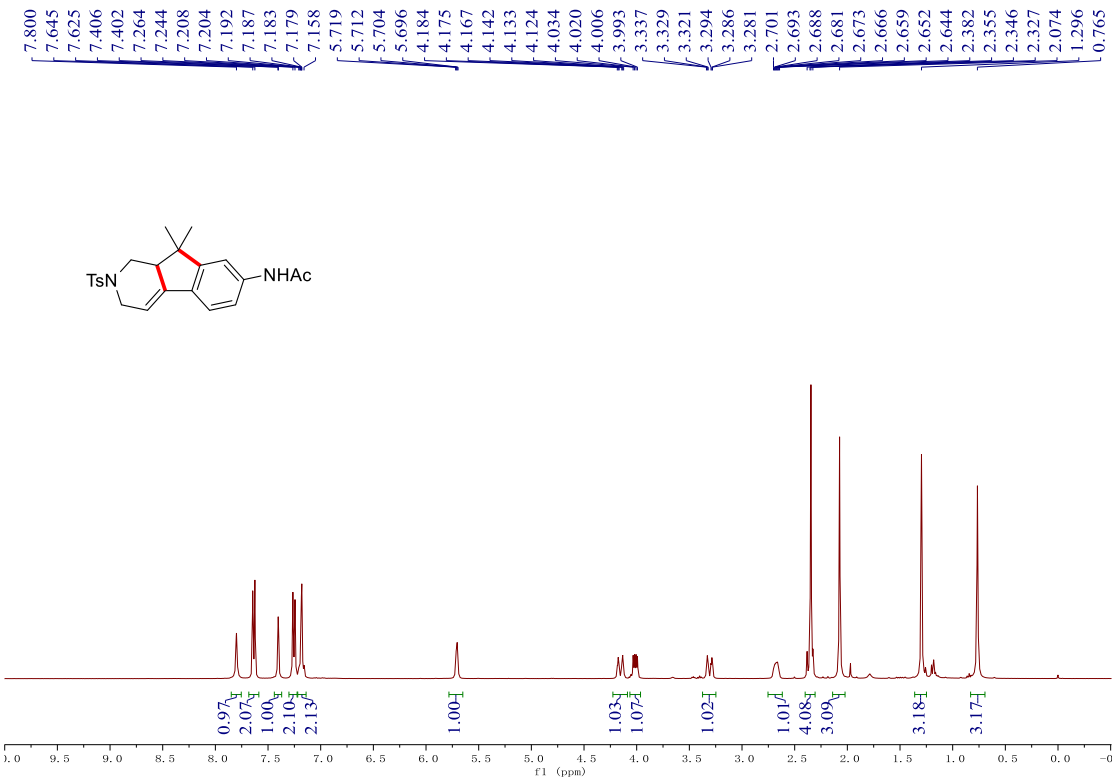
^{1}H NMR Spectrum of 18 ($CDCl_3$ as solvent, 400 MHz)



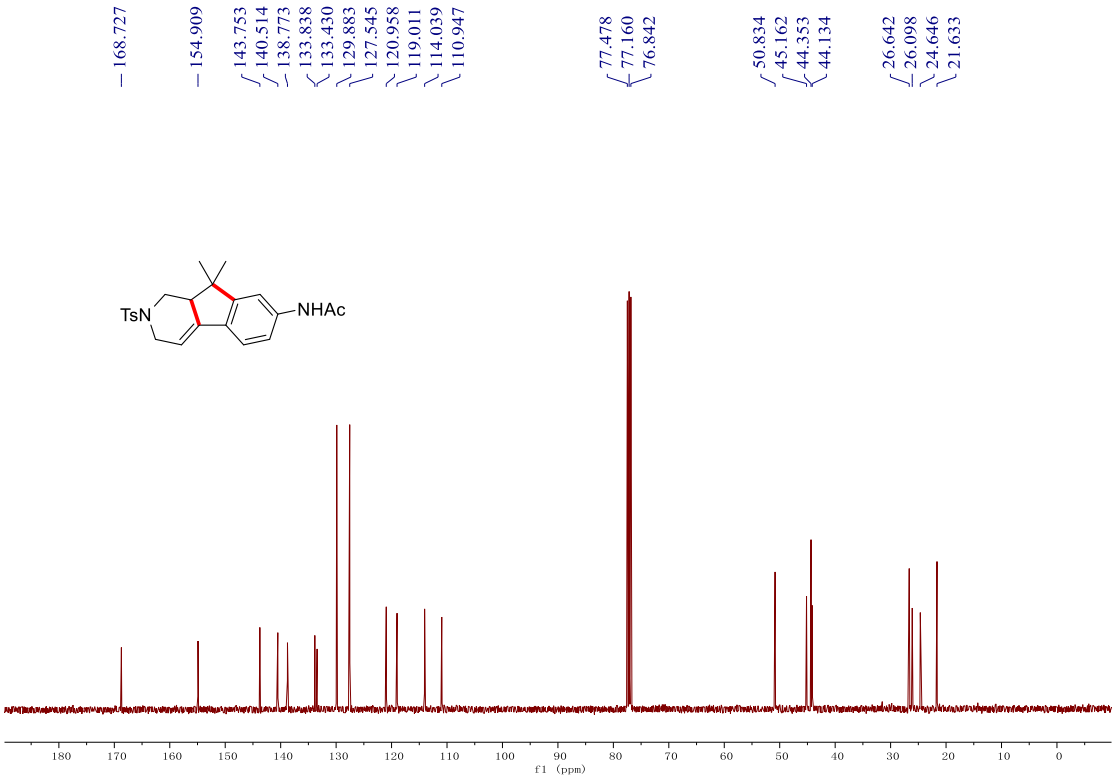
^{13}C {^{1}H} NMR Spectrum of 18 ($CDCl_3$ as solvent, 101 MHz)



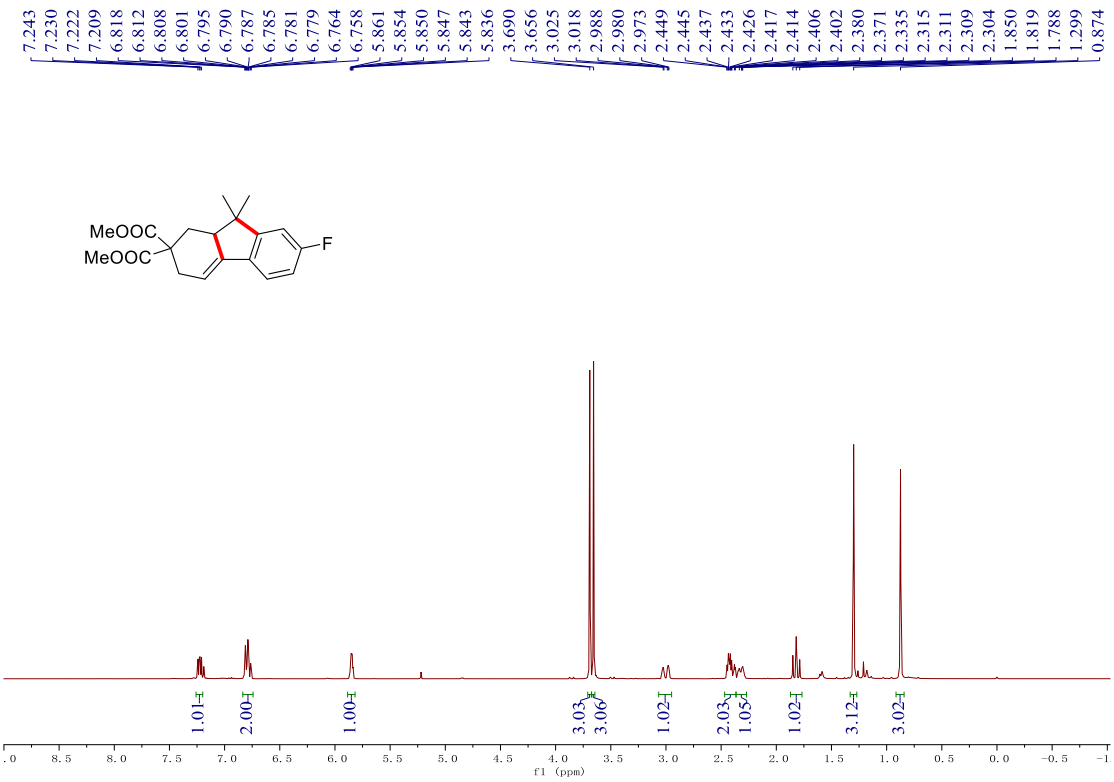
^{1}H NMR Spectrum of 19 ($CDCl_3$ as solvent, 400 MHz)



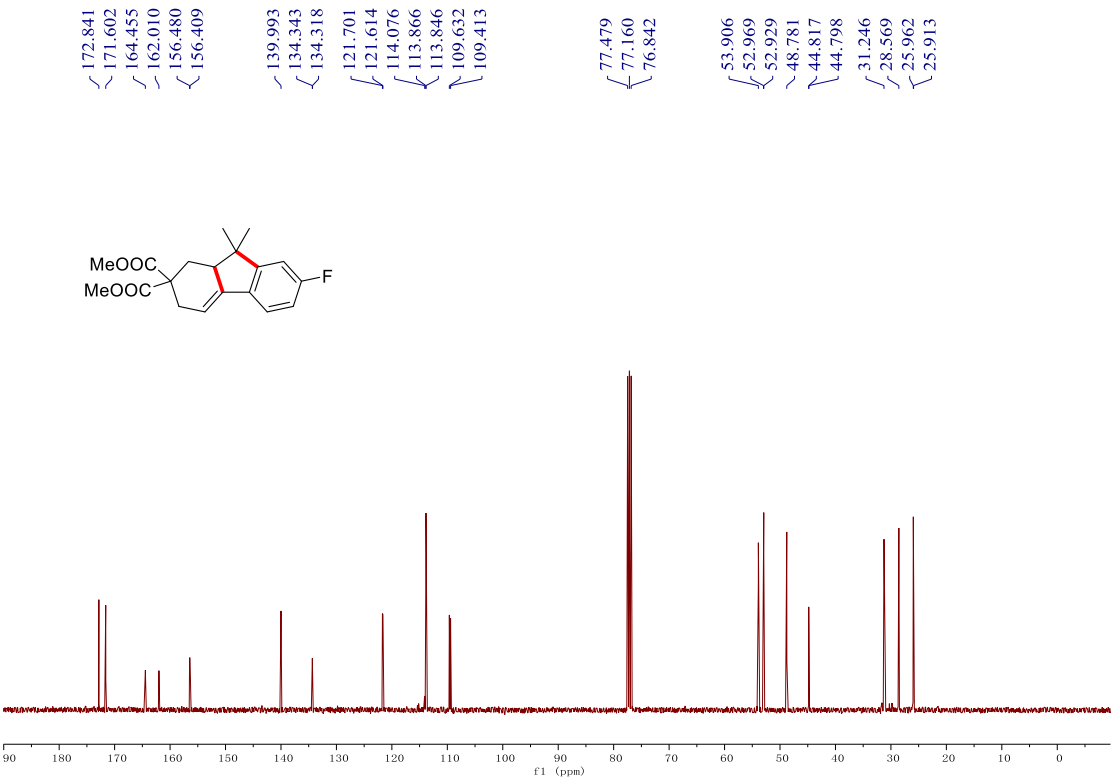
^{13}C {^{1}H} NMR Spectrum of 19 ($CDCl_3$ as solvent, 101 MHz)



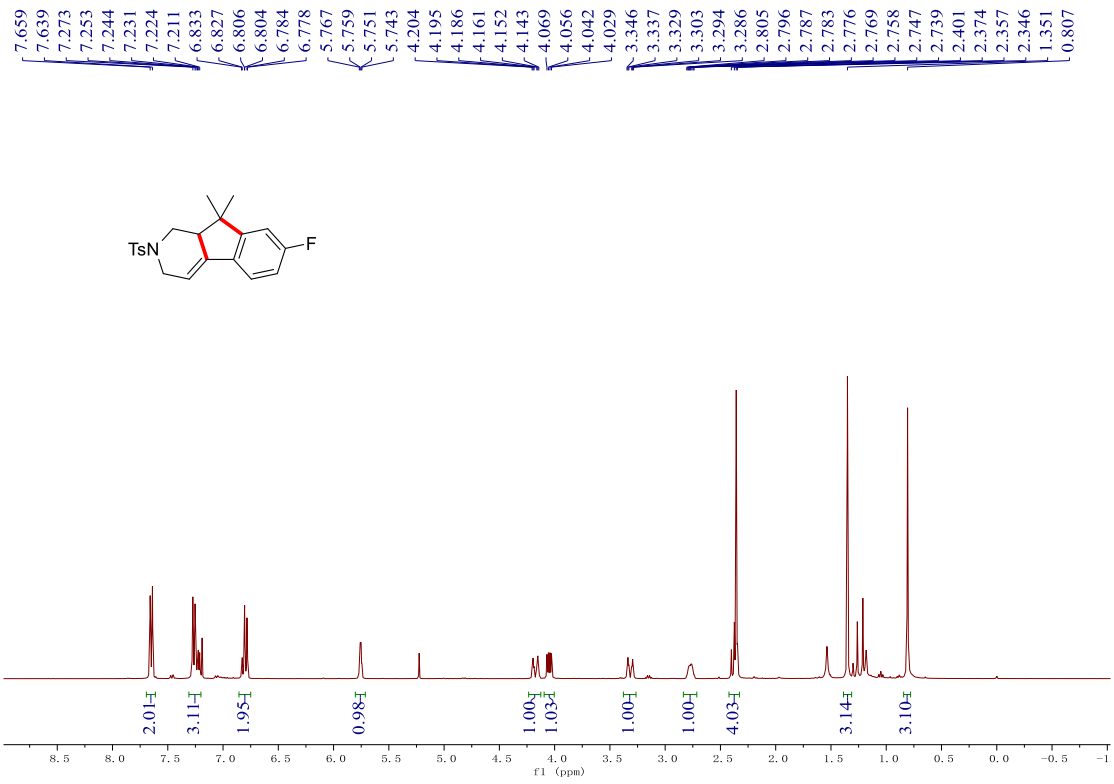
^{1}H NMR Spectrum of 20 ($CDCl_3$ as solvent, 400 MHz)



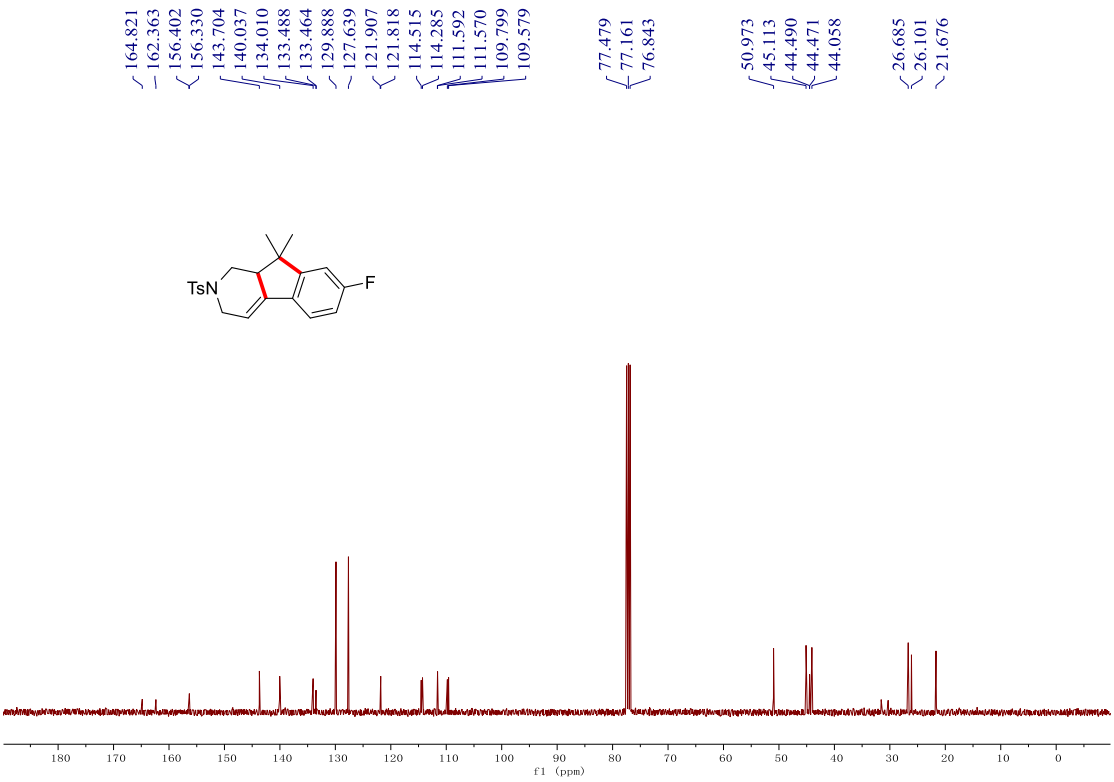
^{13}C {^{1}H} NMR Spectrum of 20 ($CDCl_3$ as solvent, 101 MHz)



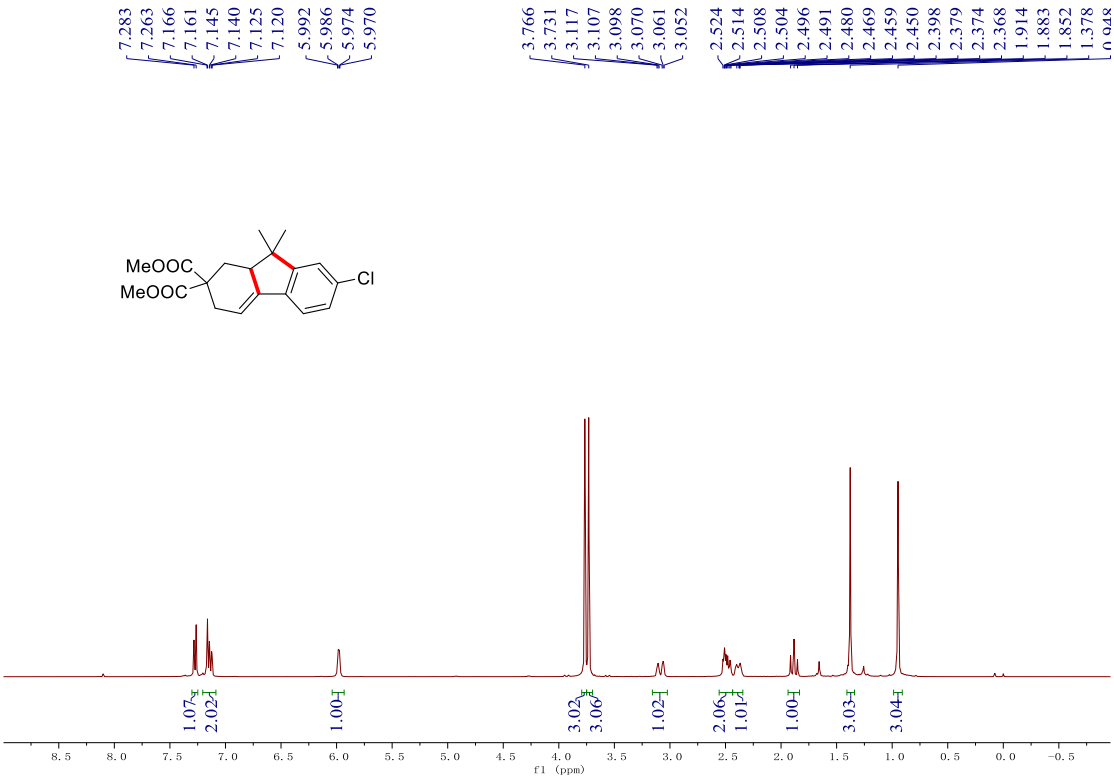
^{1}H NMR Spectrum of 21 ($CDCl_3$ as solvent, 400 MHz)



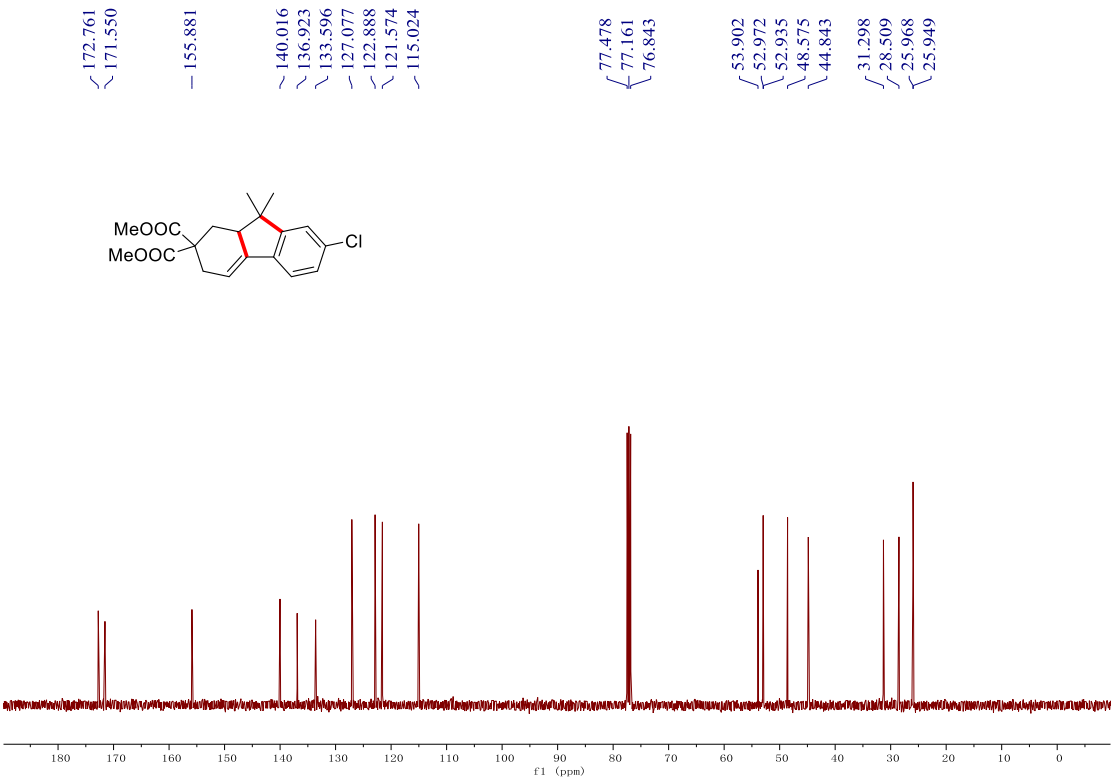
^{13}C {^{1}H} NMR Spectrum of 21 ($CDCl_3$ as solvent, 101 MHz)



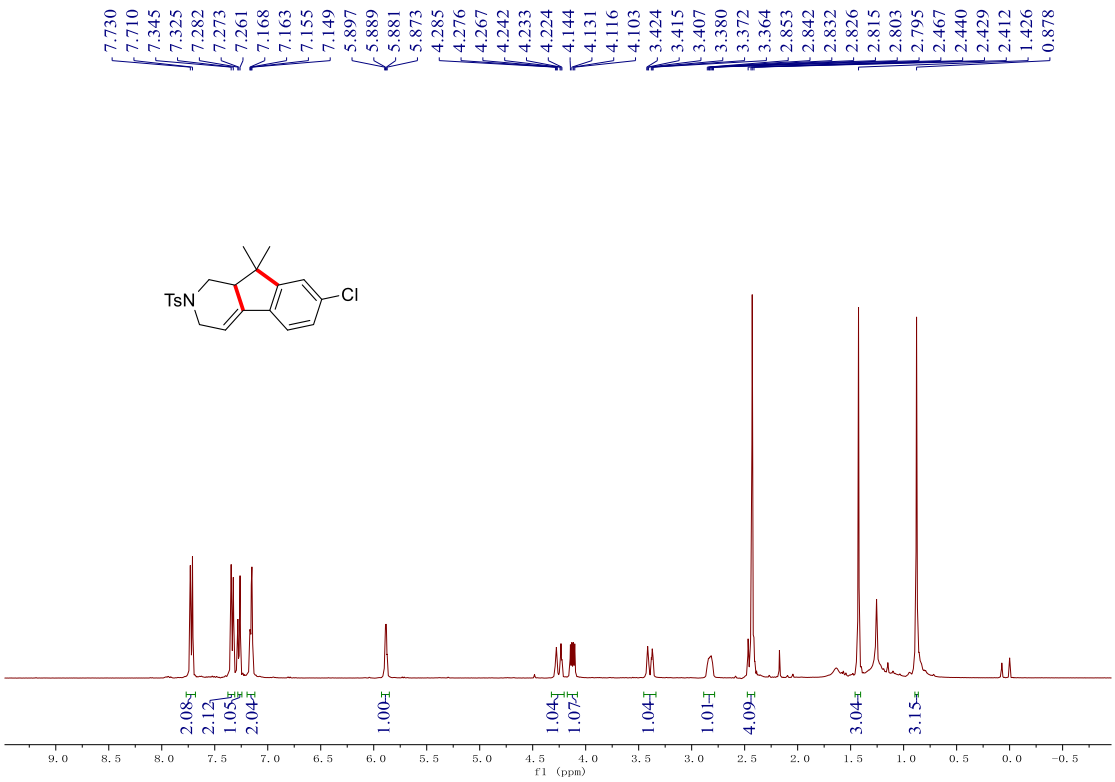
^{1}H NMR Spectrum of 22 ($CDCl_3$ as solvent, 400 MHz)



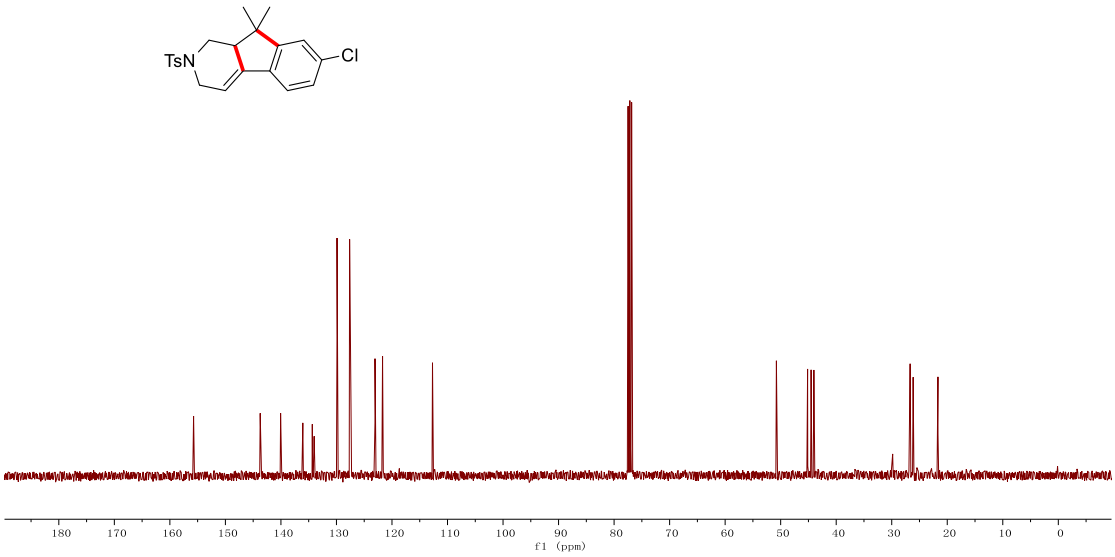
^{13}C {^{1}H} NMR Spectrum of 22 ($CDCl_3$ as solvent, 101 MHz)



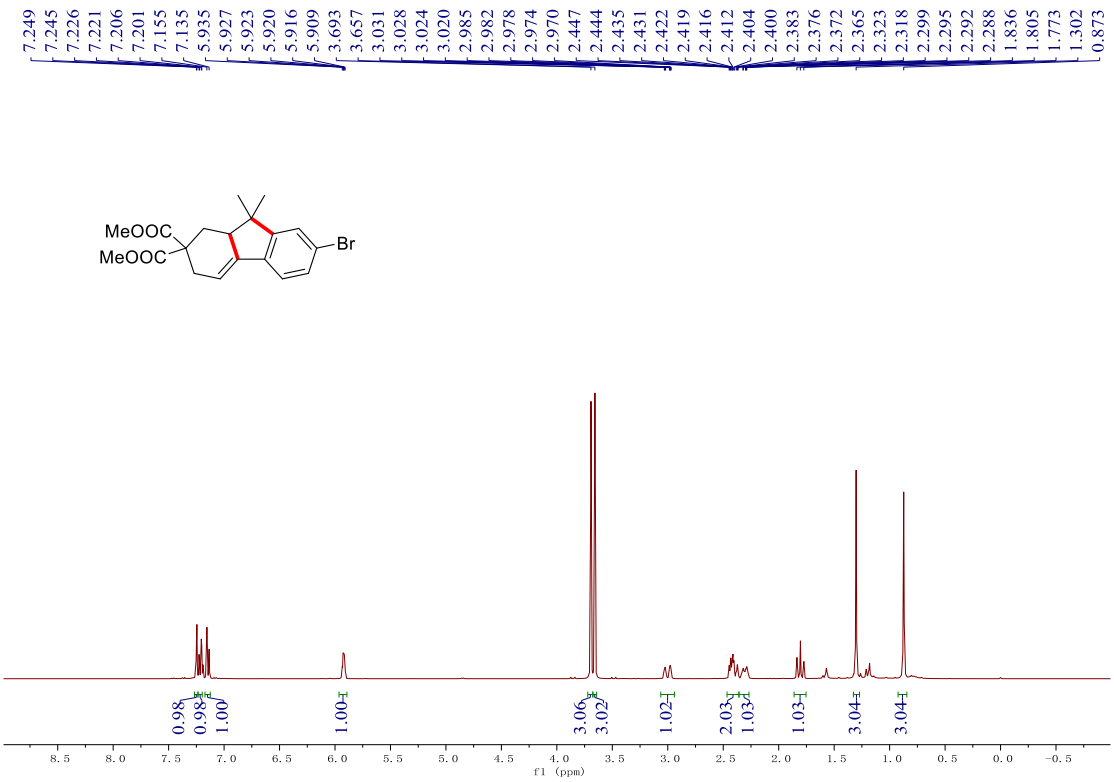
^{1}H NMR Spectrum of 23 ($CDCl_3$ as solvent, 400 MHz)



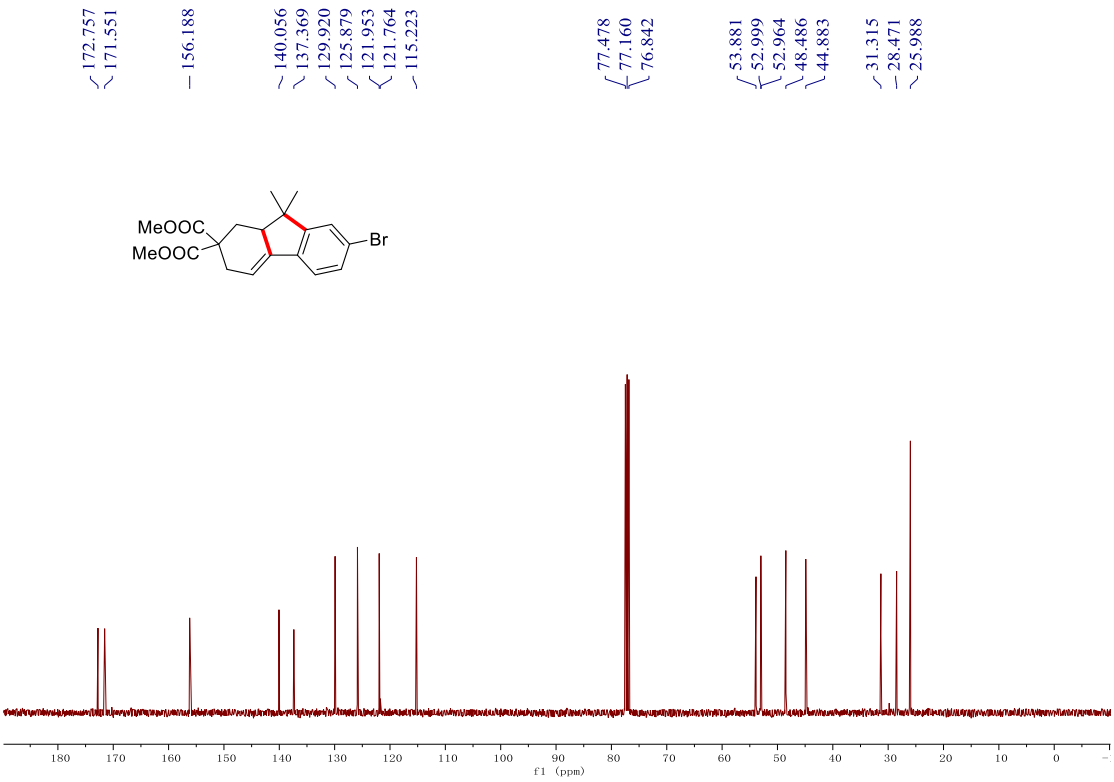
^{13}C {^{1}H} NMR Spectrum of 23 ($CDCl_3$ as solvent, 101 MHz)



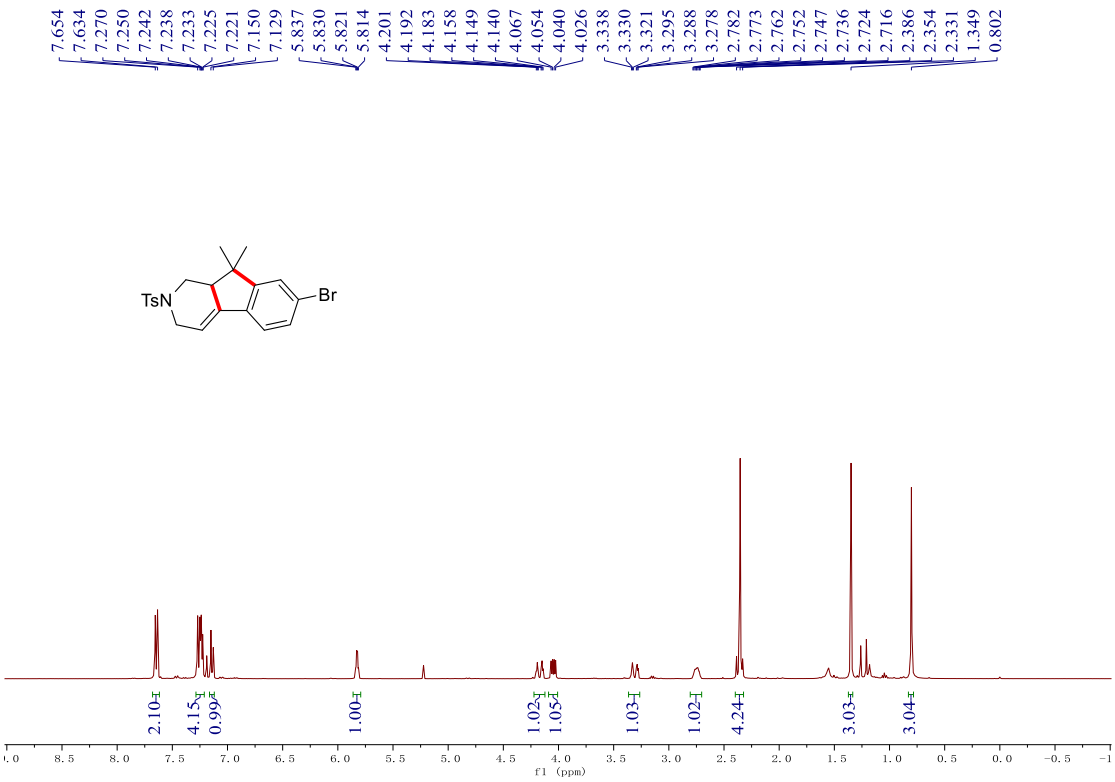
^{1}H NMR Spectrum of 24 ($CDCl_3$ as solvent, 400 MHz)



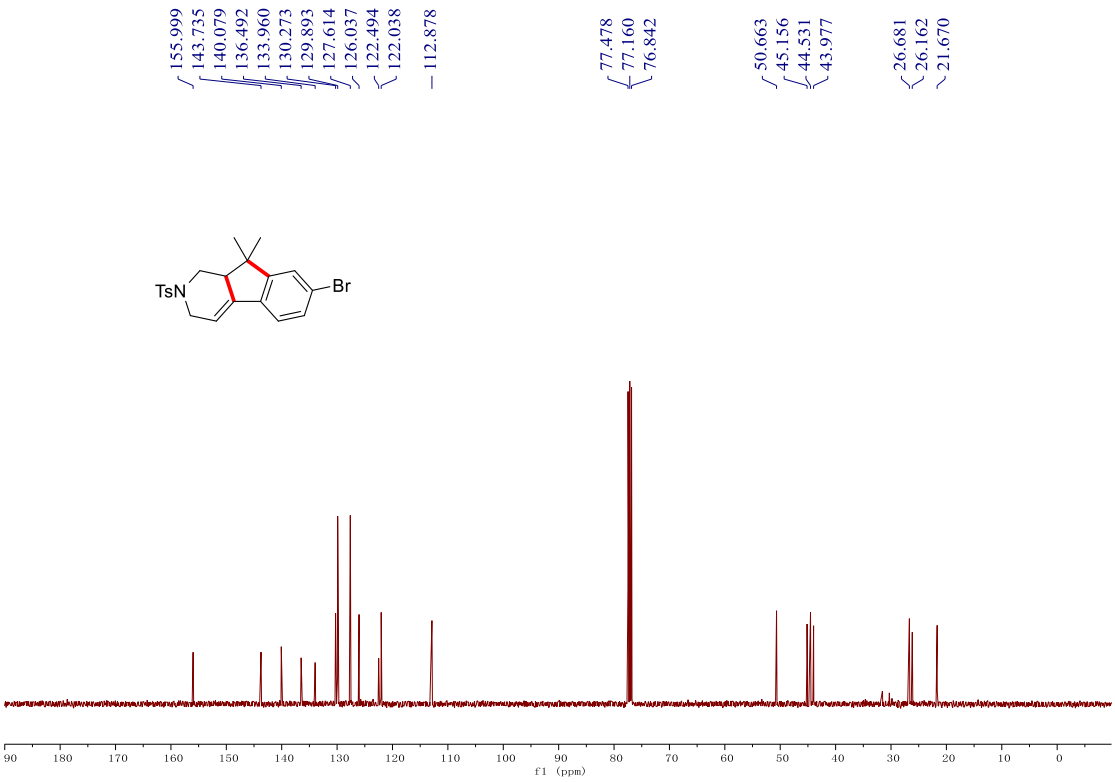
^{13}C {^{1}H} NMR Spectrum of 24 ($CDCl_3$ as solvent, 101 MHz)



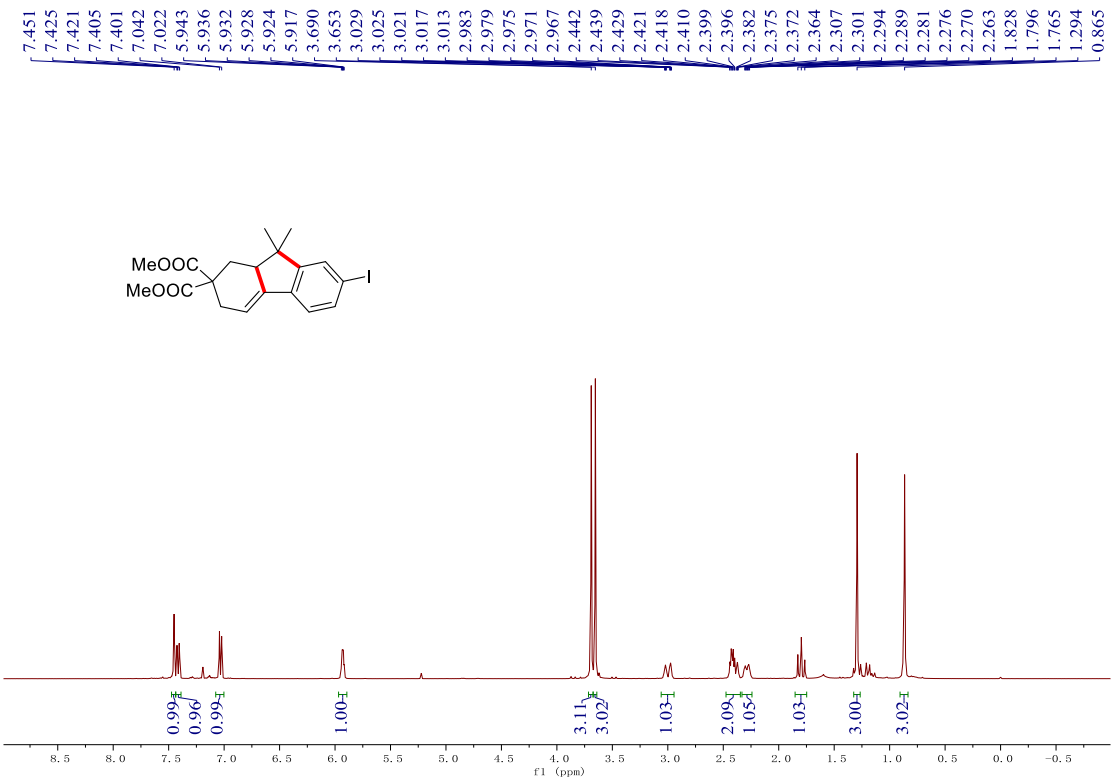
^{1}H NMR Spectrum of 25 ($CDCl_3$ as solvent, 400 MHz)



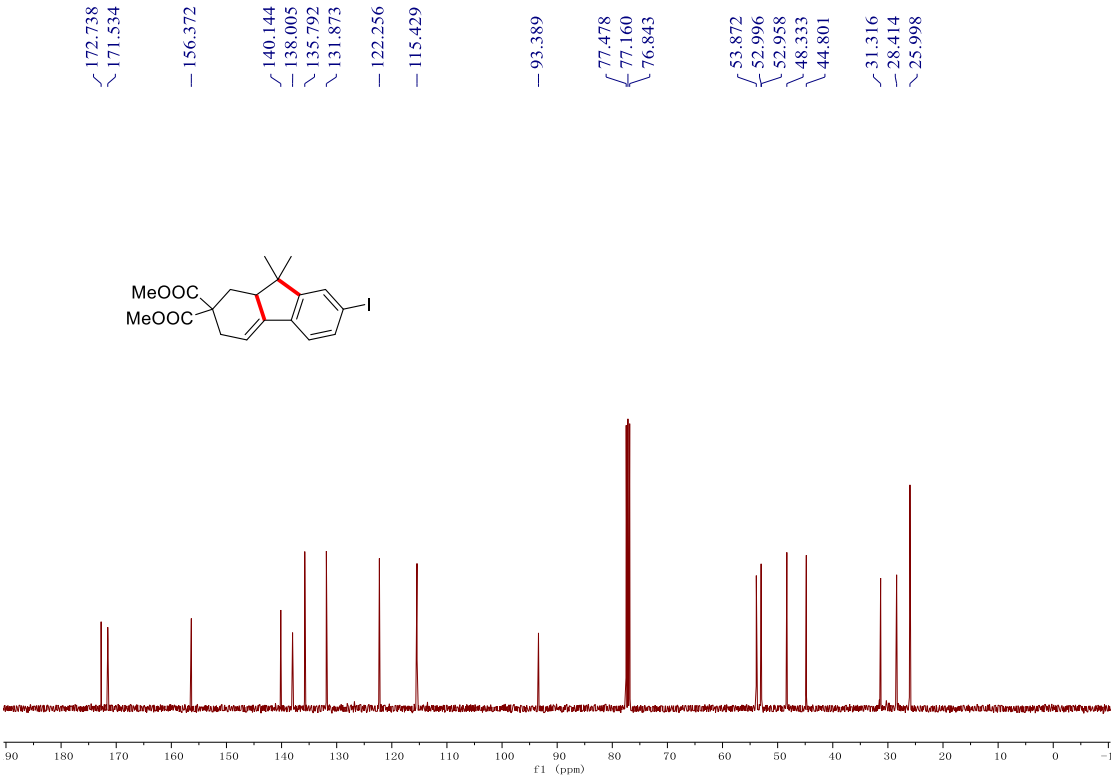
^{13}C {^{1}H} NMR Spectrum of 25 ($CDCl_3$ as solvent, 101 MHz)



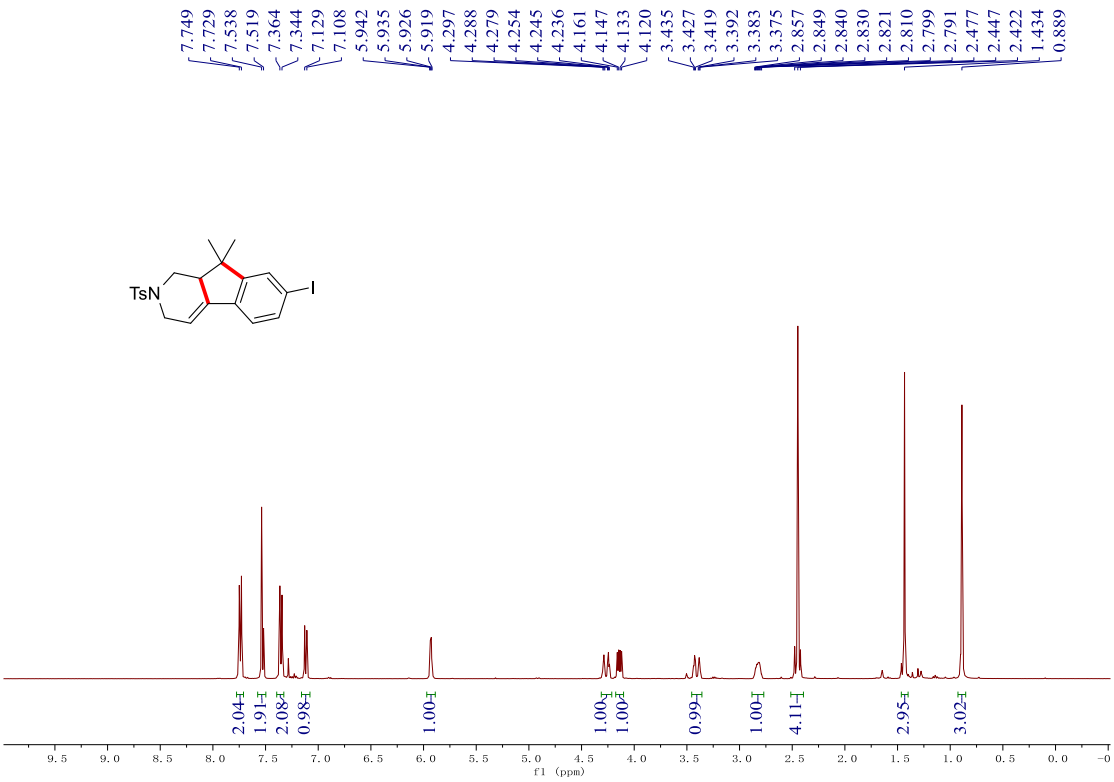
^{1}H NMR Spectrum of 26 ($CDCl_3$ as solvent, 400 MHz)



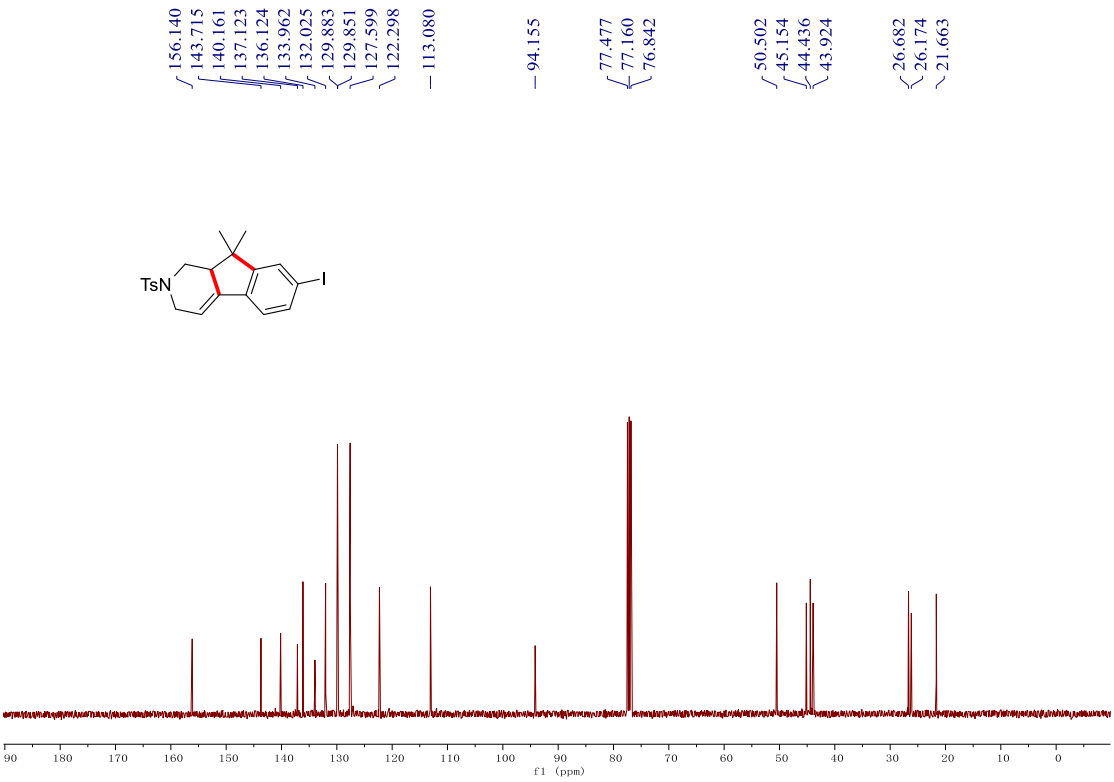
^{13}C {^{1}H} NMR Spectrum of 26 ($CDCl_3$ as solvent, 101 MHz)



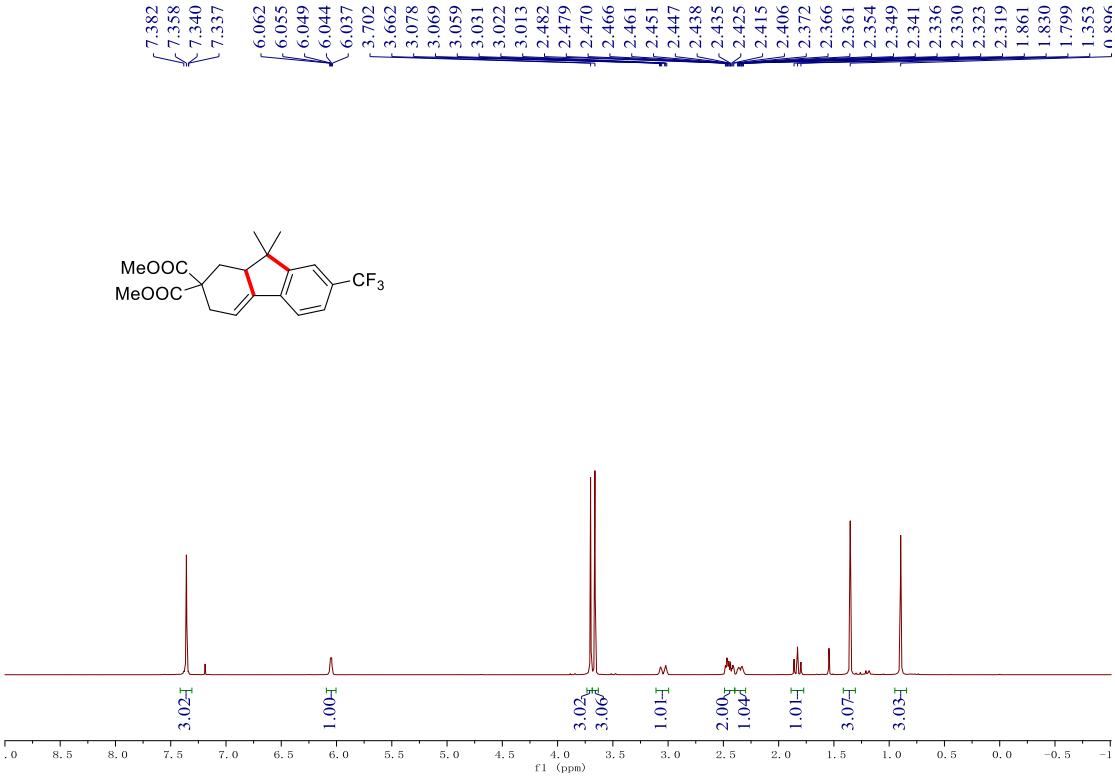
^{1}H NMR Spectrum of 27 ($CDCl_3$ as solvent, 400 MHz)



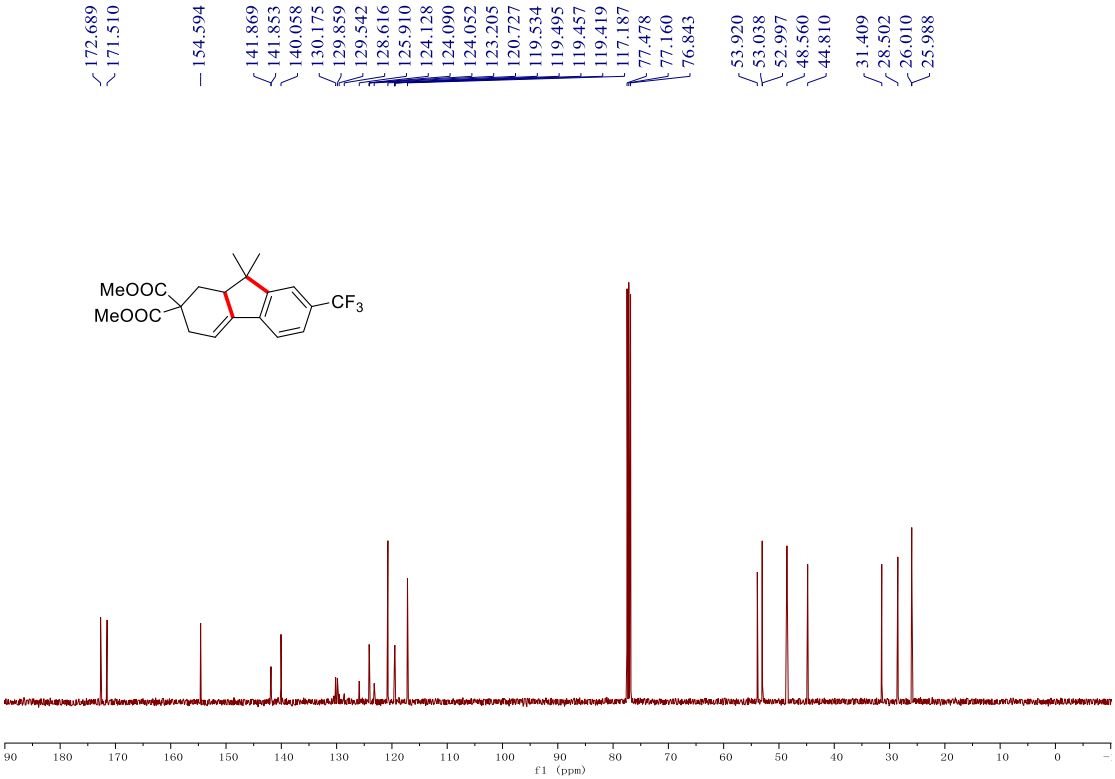
^{13}C {^{1}H} NMR Spectrum of 27 ($CDCl_3$ as solvent, 101 MHz)



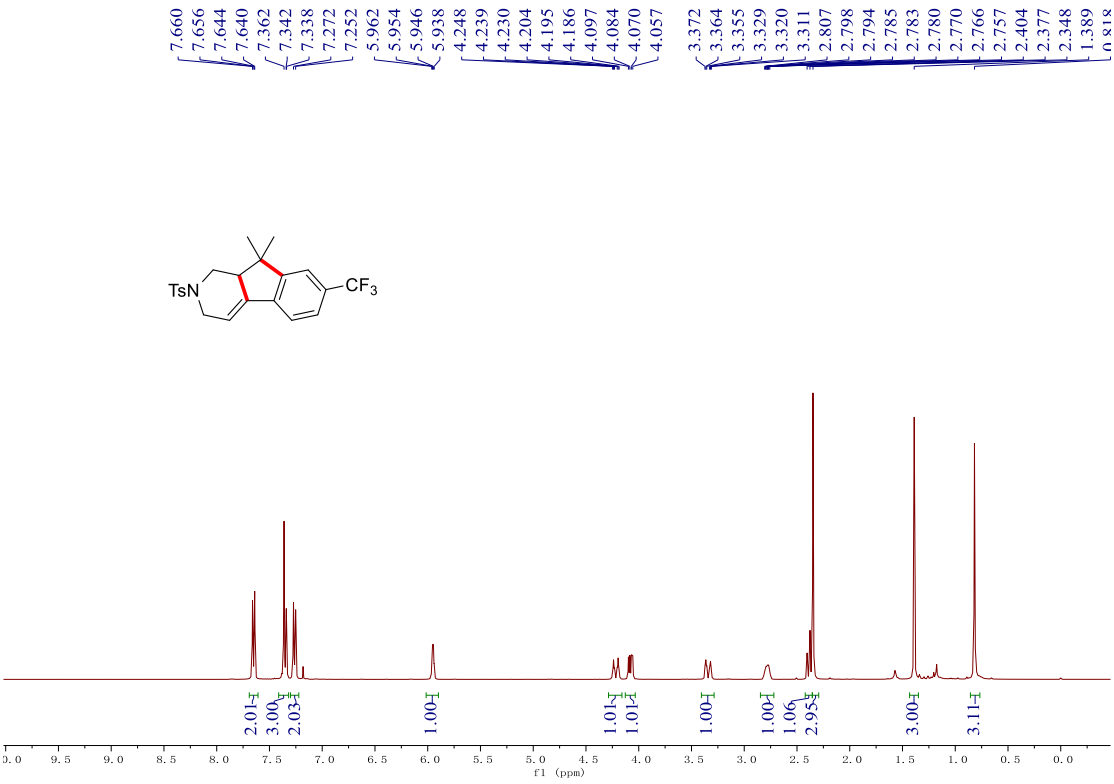
^{1}H NMR Spectrum of 28 ($CDCl_3$ as solvent, 400 MHz)



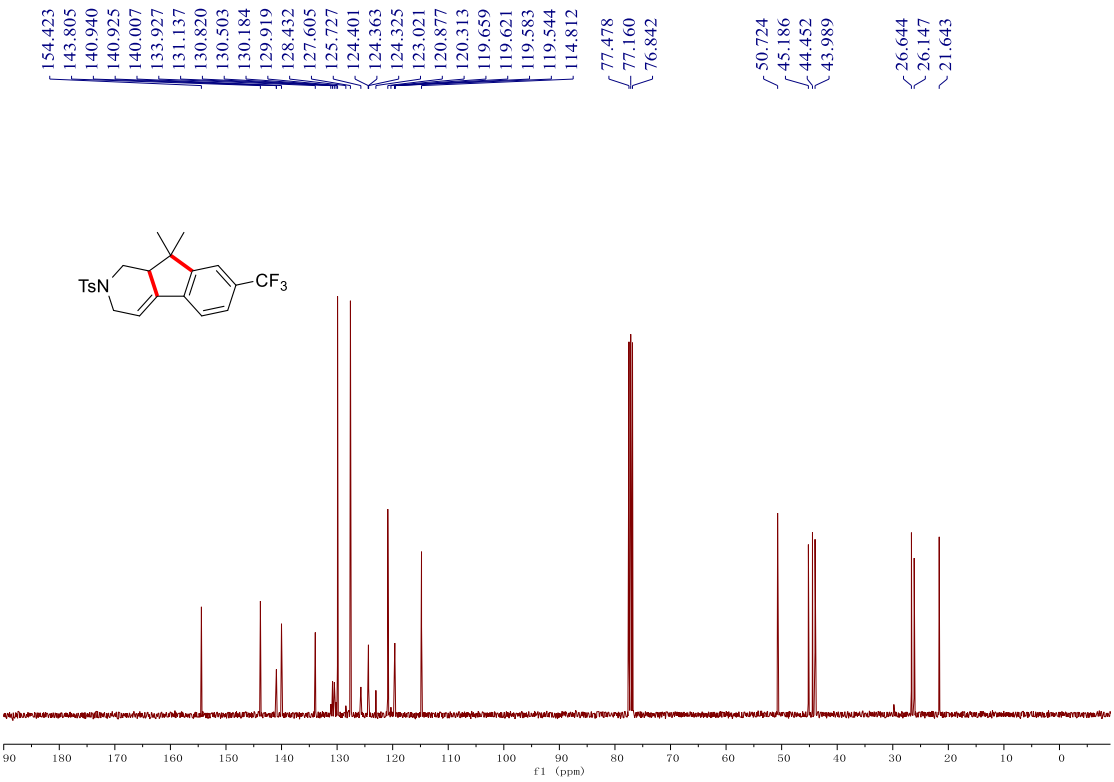
^{13}C {^{1}H} NMR Spectrum of 28 ($CDCl_3$ as solvent, 101 MHz)



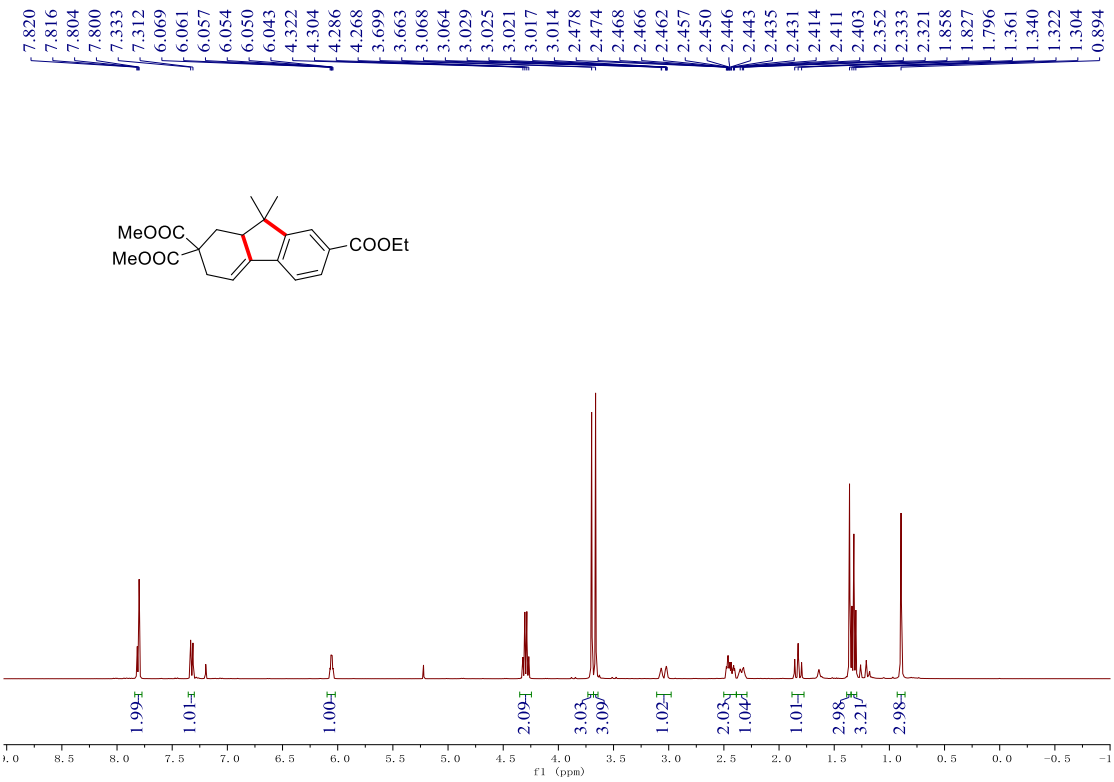
^{1}H NMR Spectrum of 29 ($CDCl_3$ as solvent, 400 MHz)



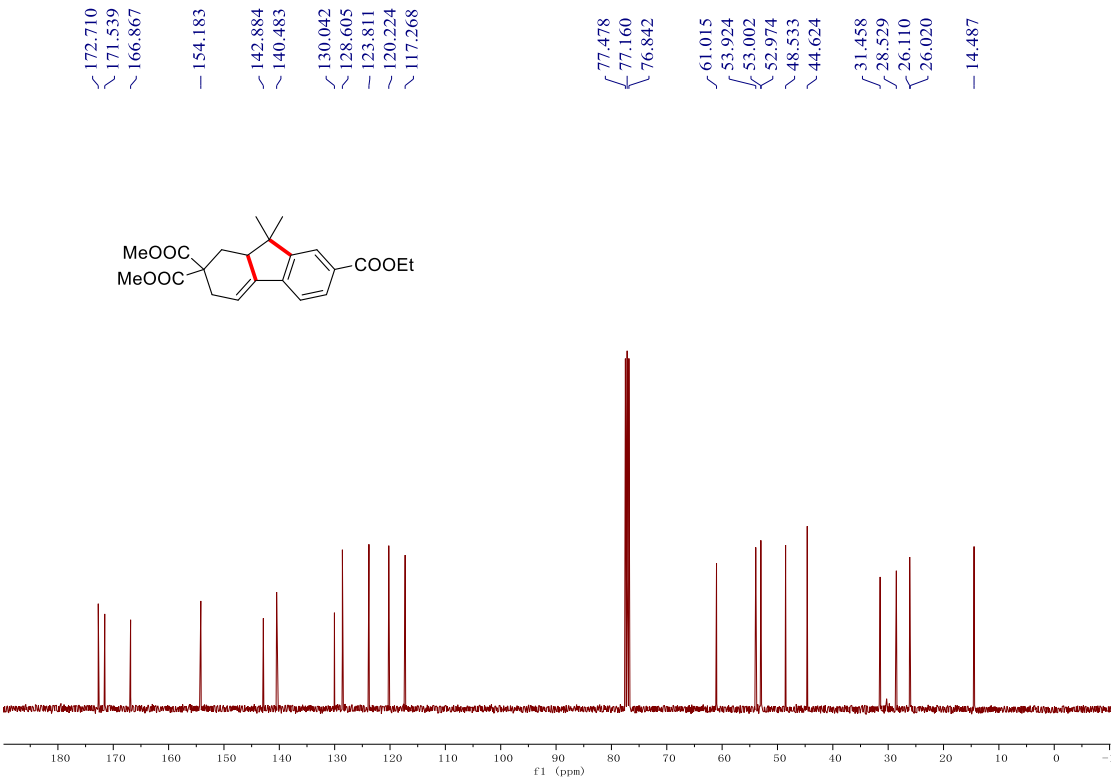
^{13}C {^{1}H} NMR Spectrum of 29 ($CDCl_3$ as solvent, 101 MHz)



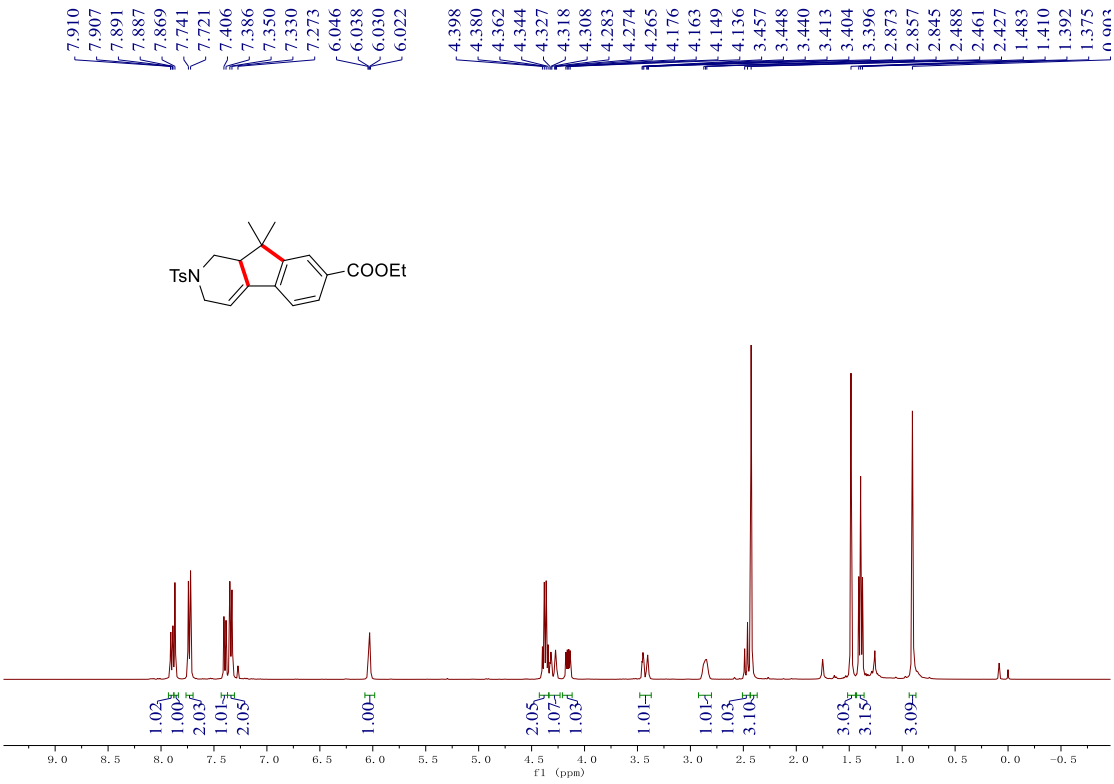
^{1}H NMR Spectrum of 30 ($CDCl_3$ as solvent, 400 MHz)



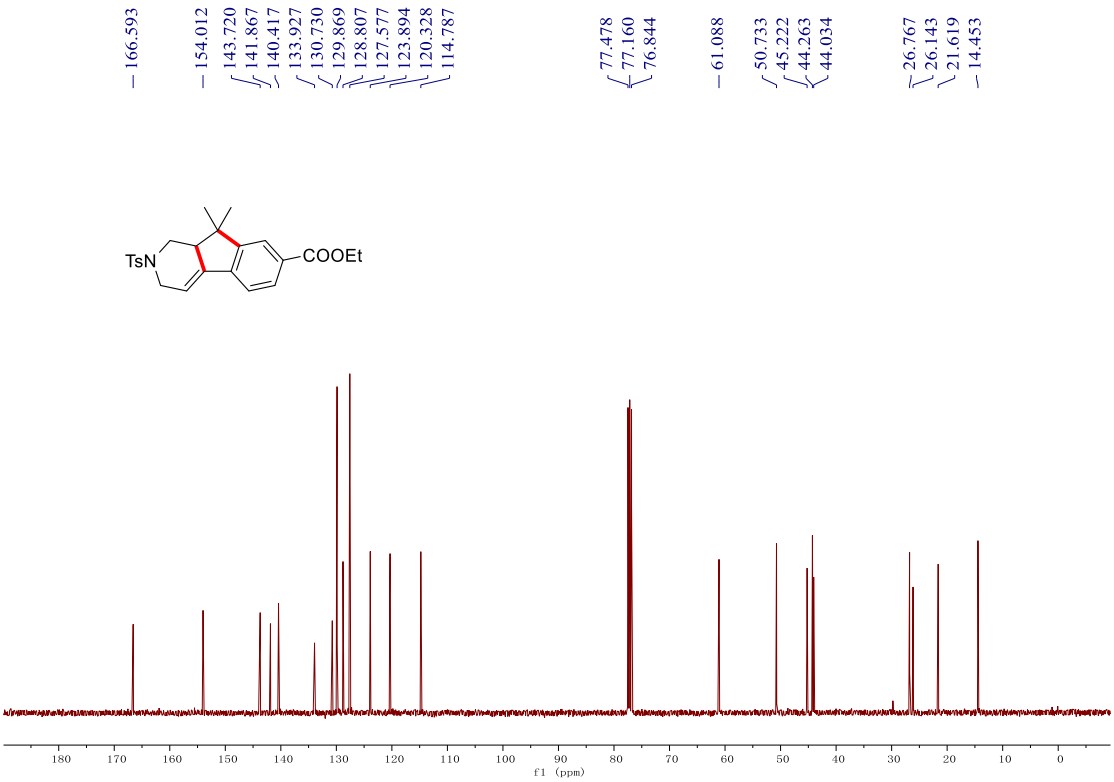
^{13}C {^{1}H} NMR Spectrum of 30 ($CDCl_3$ as solvent, 101 MHz)



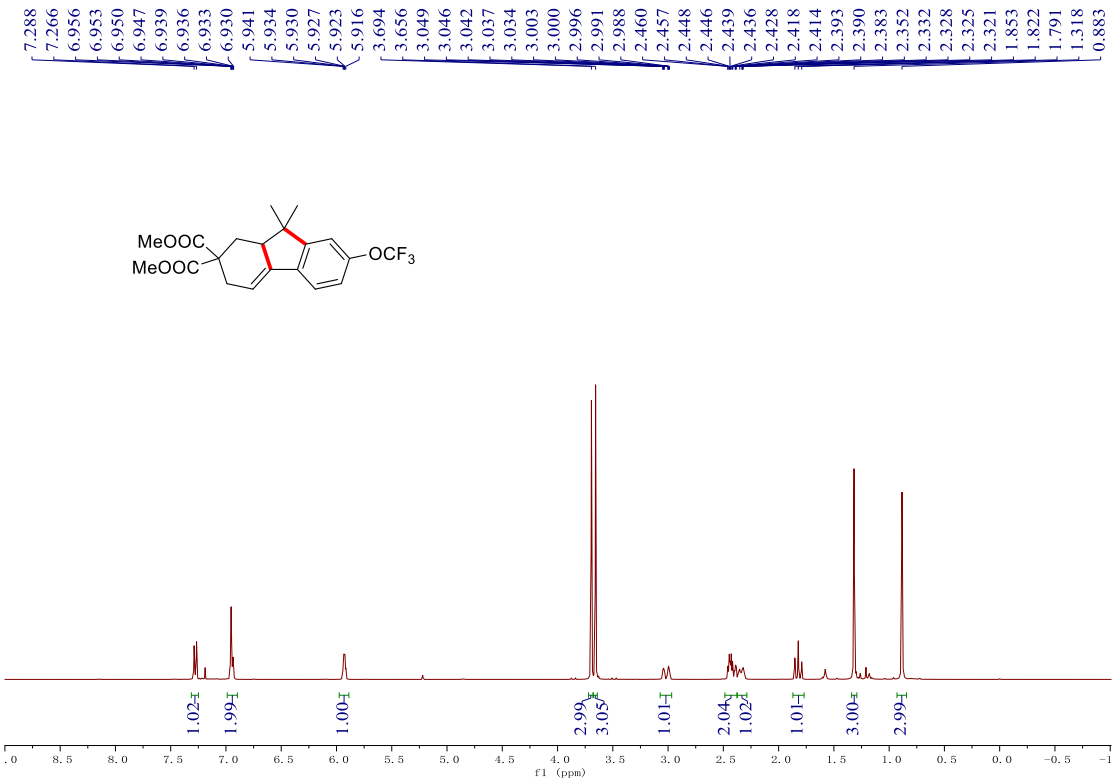
^{1}H NMR Spectrum of 31 ($CDCl_3$ as solvent, 400 MHz)



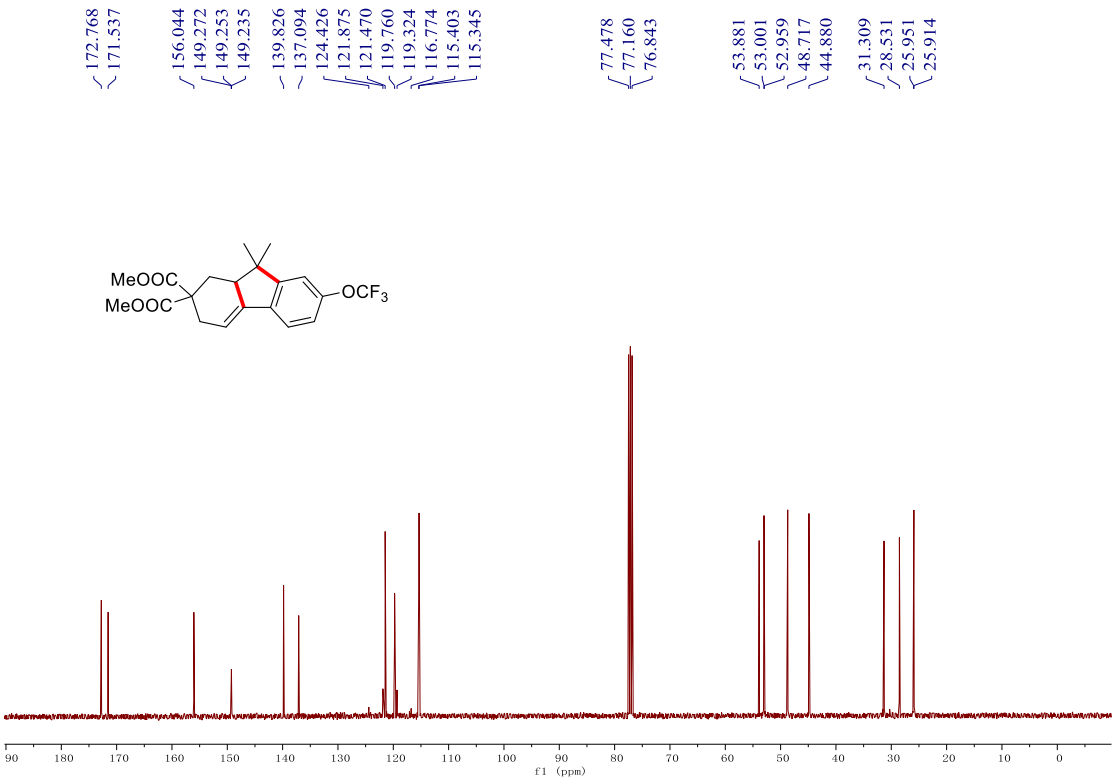
^{13}C {^{1}H} NMR Spectrum of 31 ($CDCl_3$ as solvent, 101 MHz)



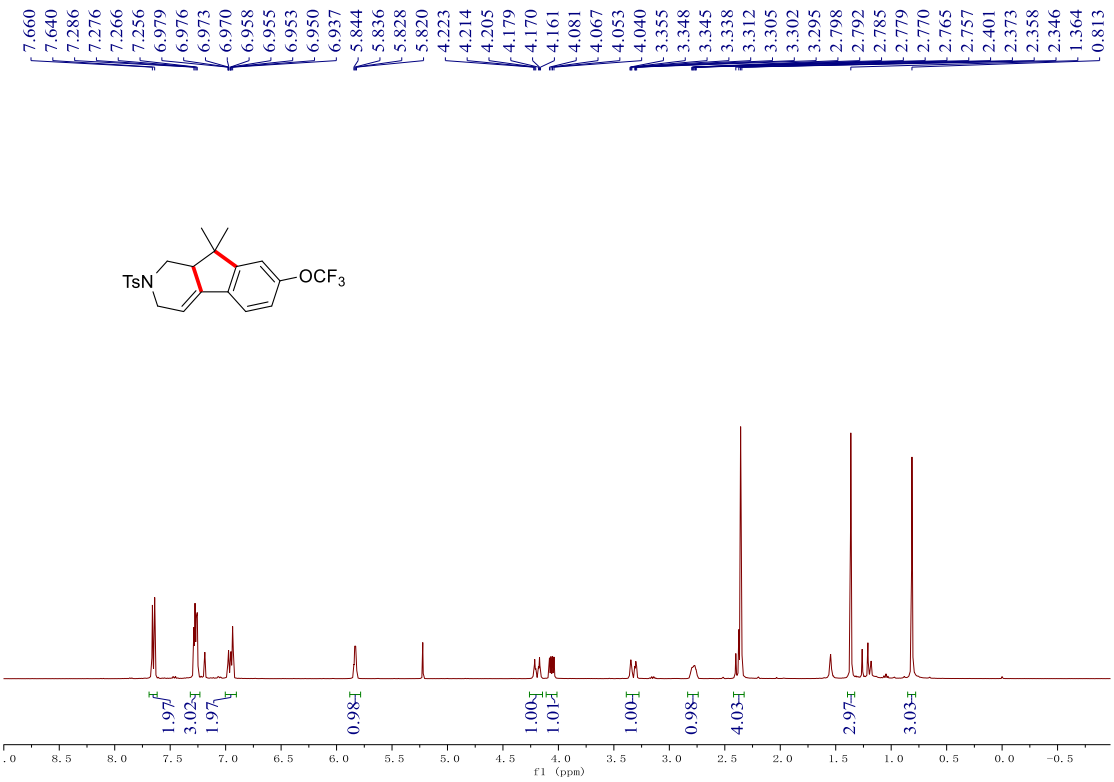
^{1}H NMR Spectrum of 32 ($CDCl_3$ as solvent, 400 MHz)



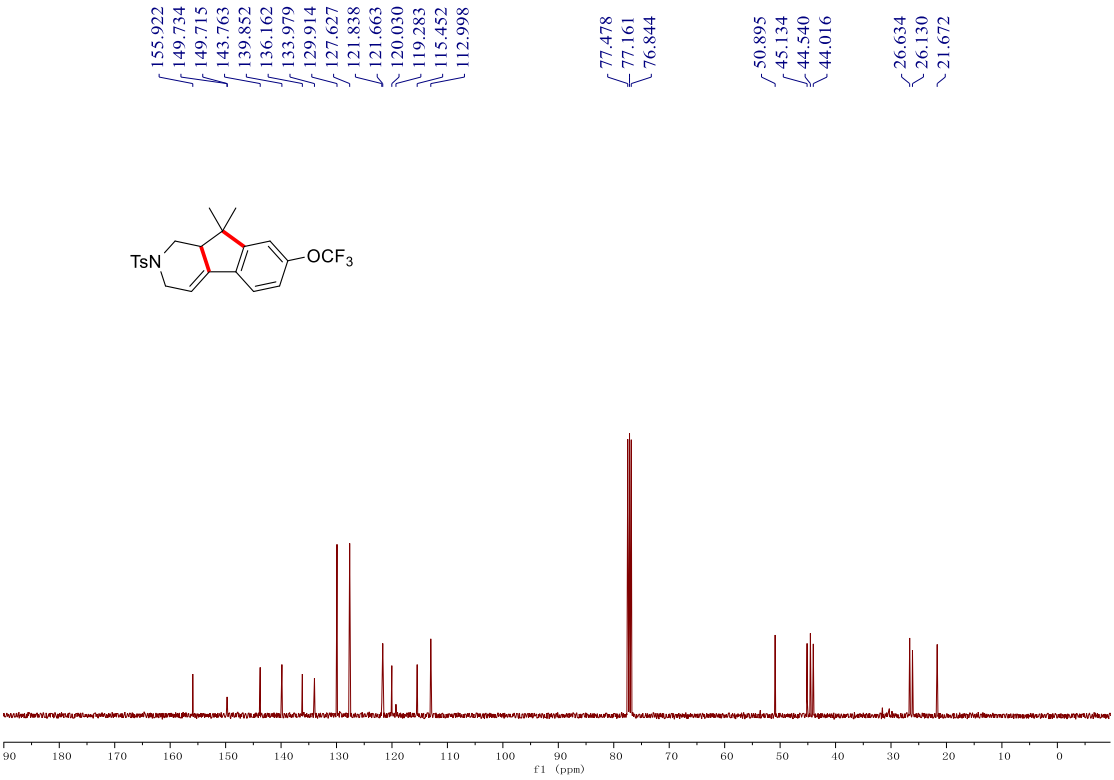
^{13}C {^{1}H} NMR Spectrum of 32 ($CDCl_3$ as solvent, 101 MHz)



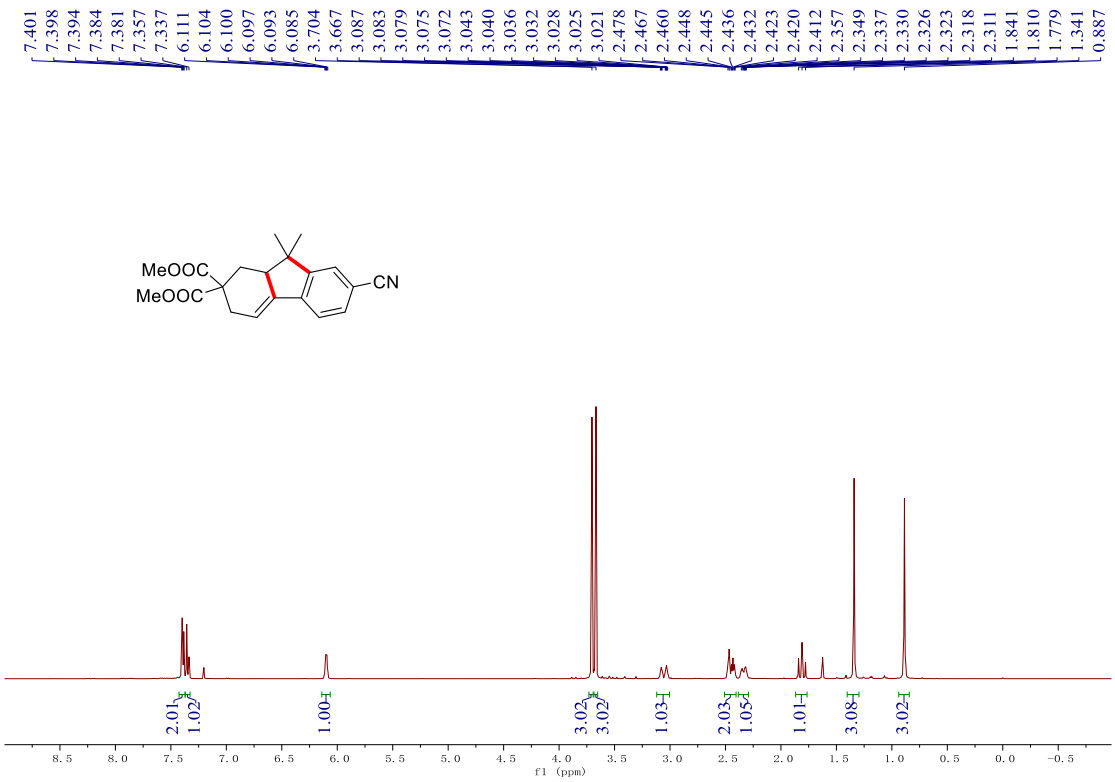
^{1}H NMR Spectrum of 33 ($CDCl_3$ as solvent, 400 MHz)



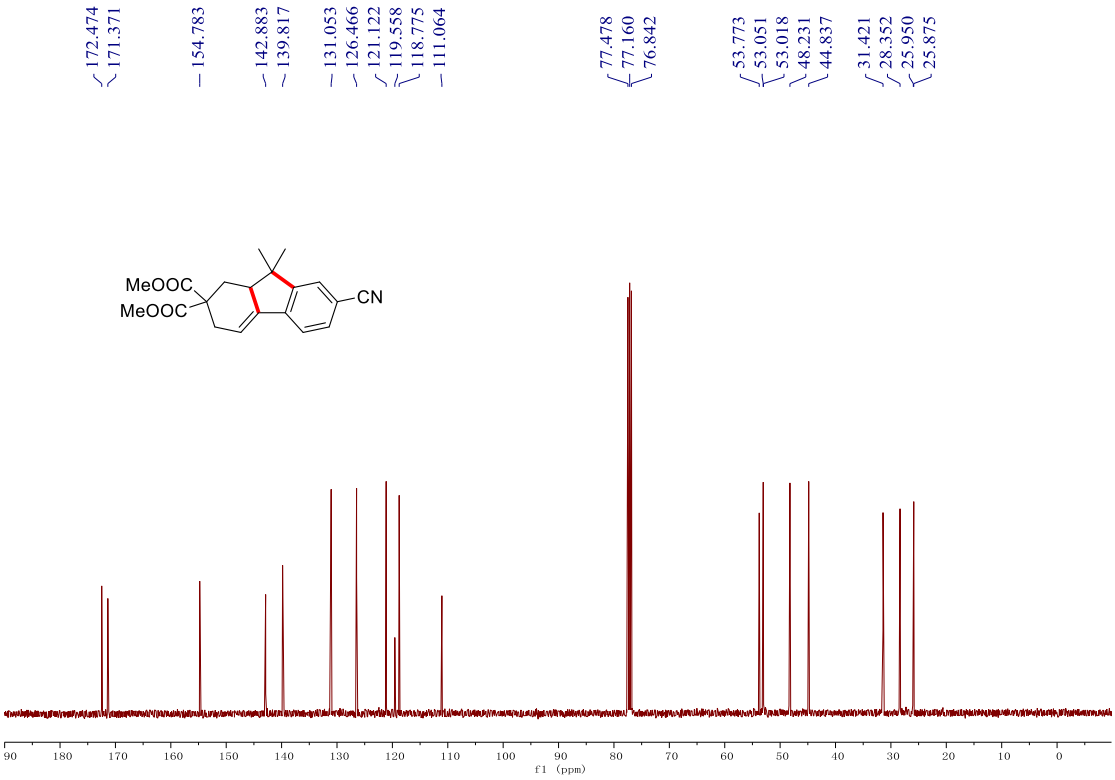
^{13}C {^{1}H} NMR Spectrum of 33 ($CDCl_3$ as solvent, 101 MHz)



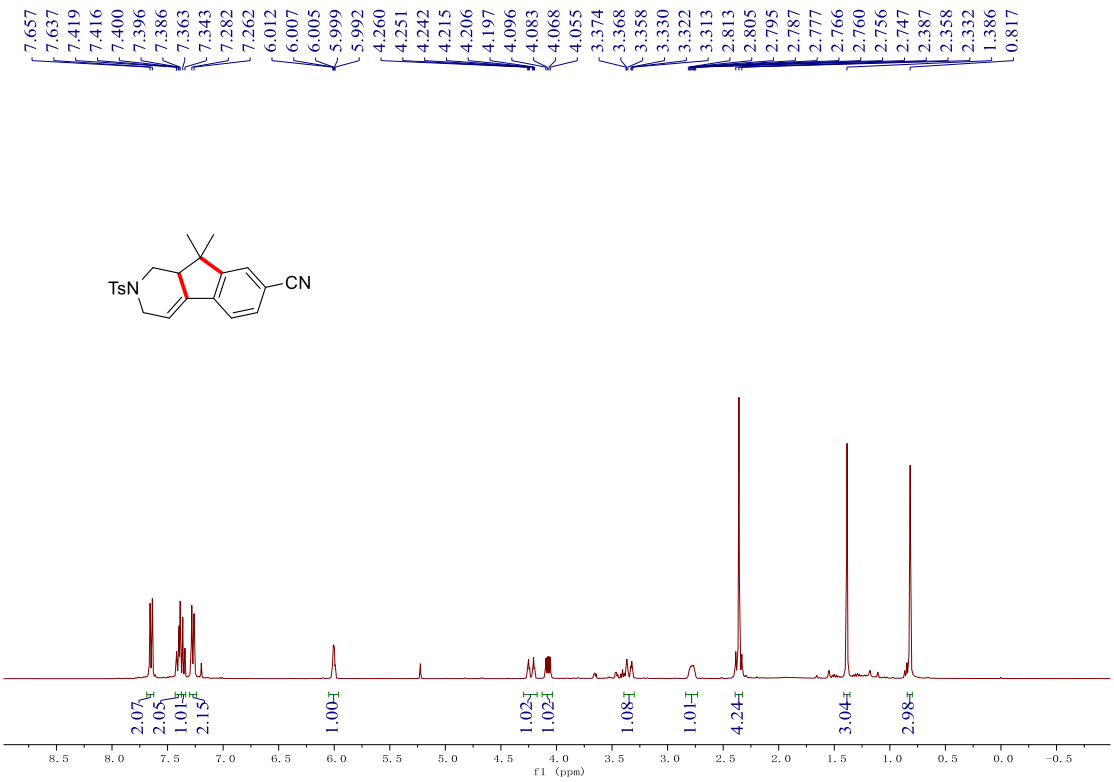
^{1}H NMR Spectrum of 34 ($CDCl_3$ as solvent, 400 MHz)



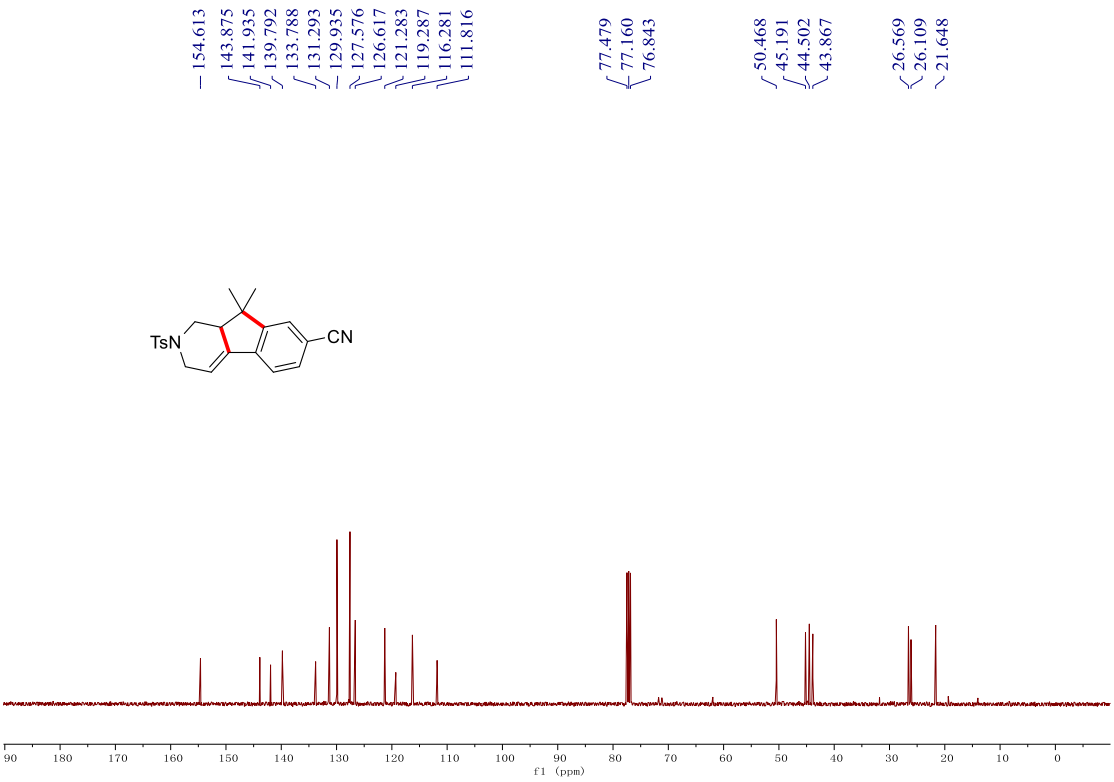
^{13}C {^{1}H} NMR Spectrum of 34 ($CDCl_3$ as solvent, 101 MHz)



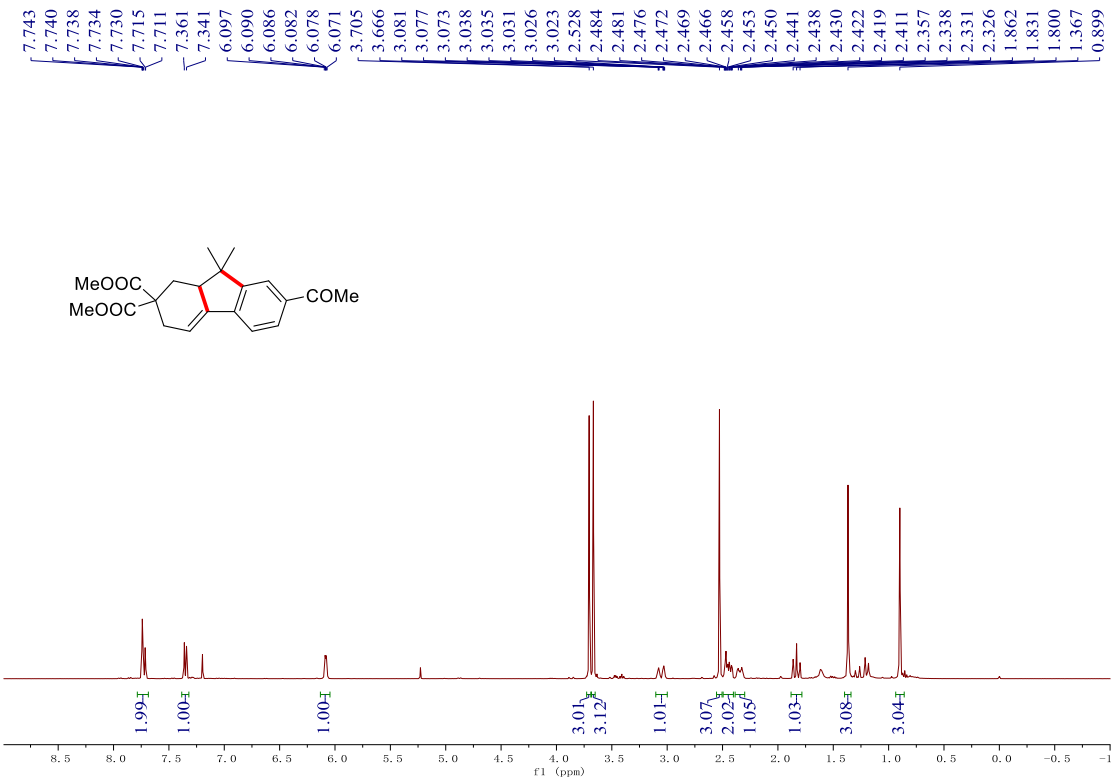
^{1}H NMR Spectrum of 35 ($CDCl_3$ as solvent, 400 MHz)



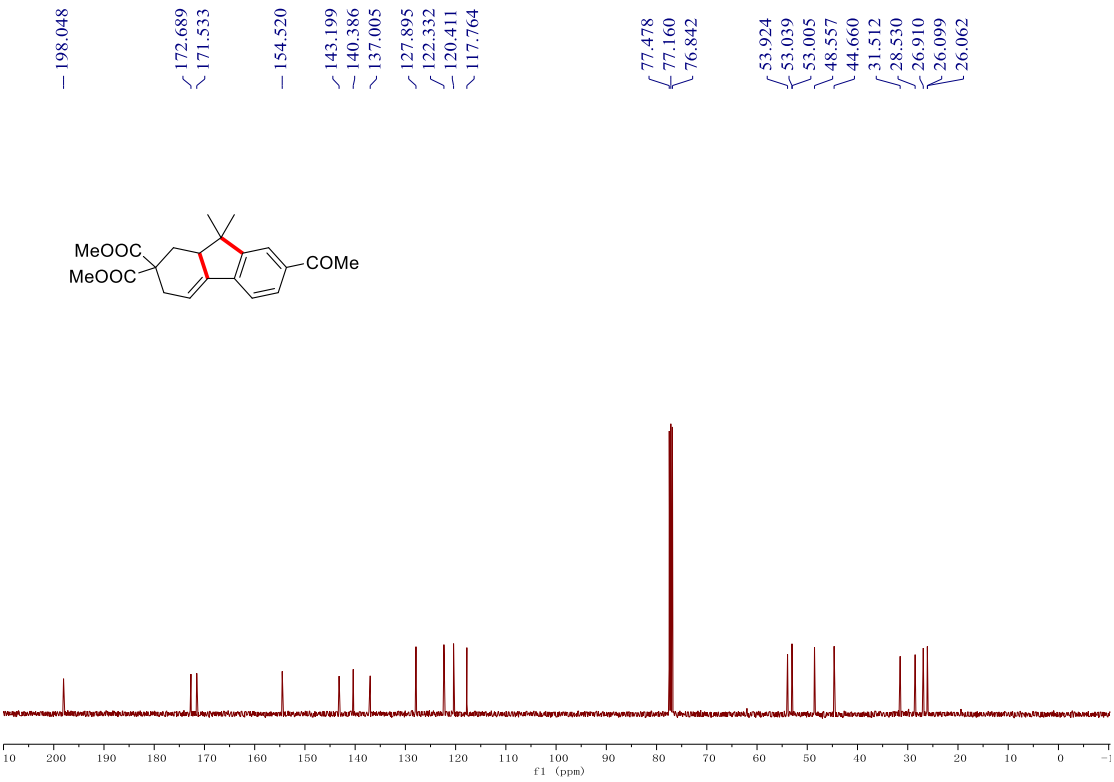
^{13}C {^{1}H} NMR Spectrum of 35 ($CDCl_3$ as solvent, 101 MHz)



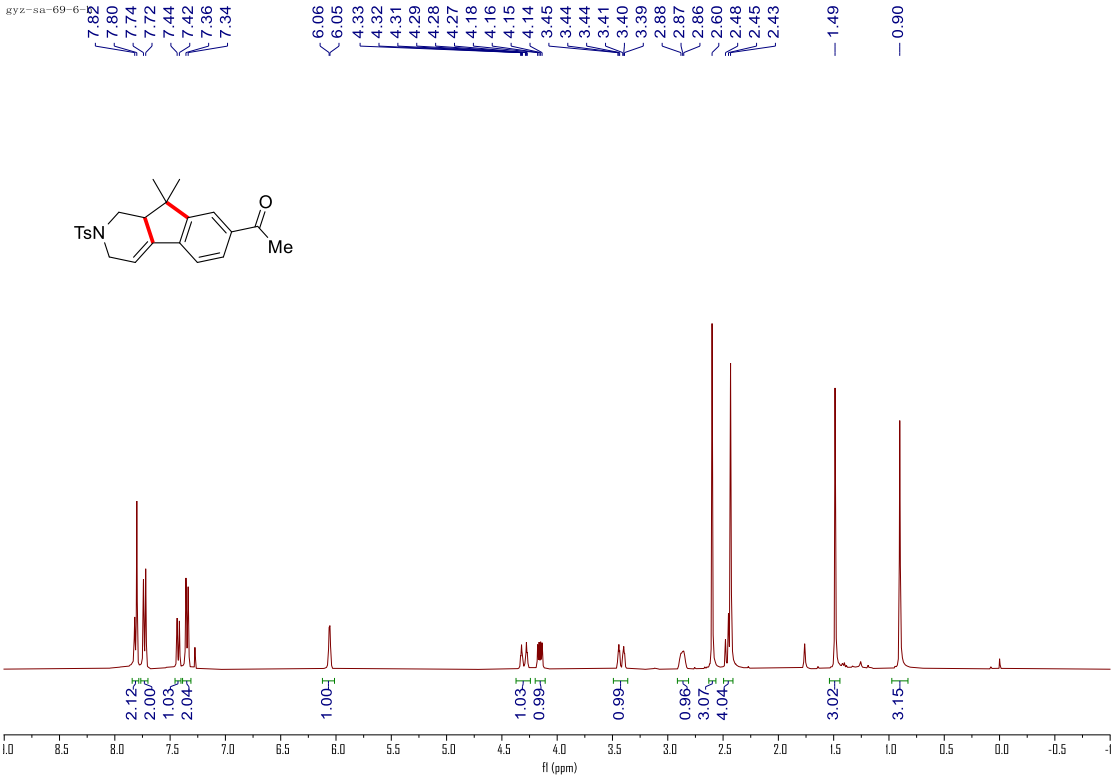
^{1}H NMR Spectrum of 36 ($CDCl_3$ as solvent, 400 MHz)



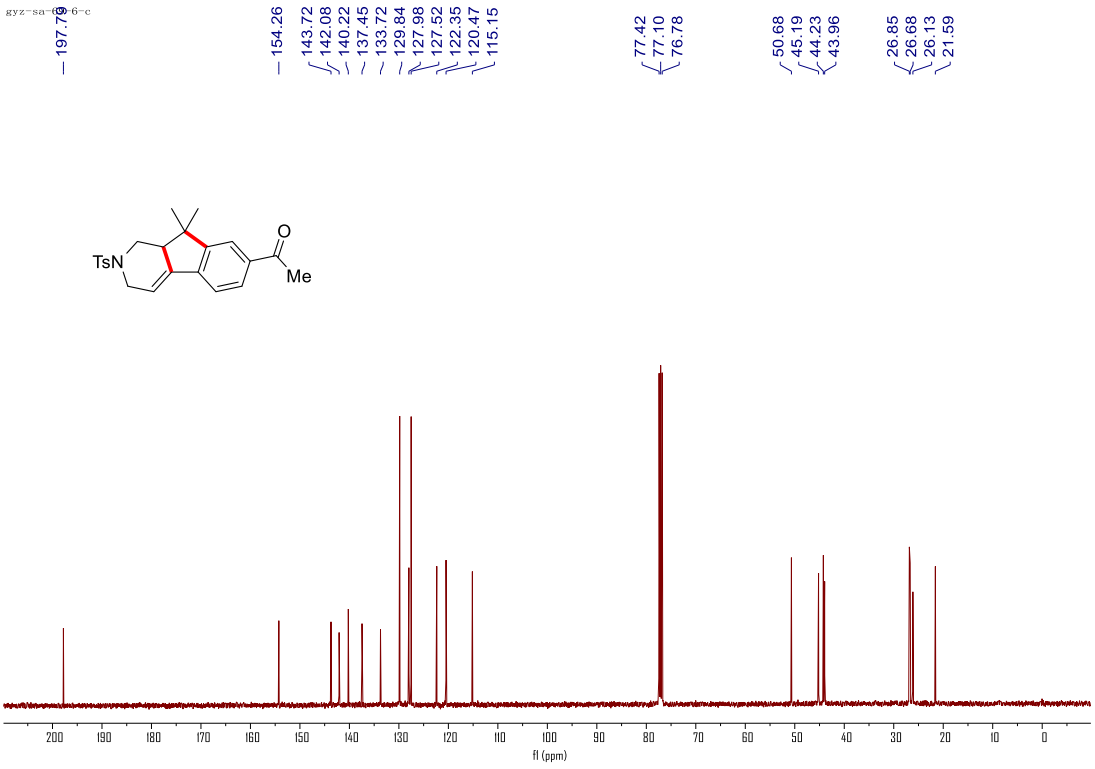
^{13}C {^{1}H} NMR Spectrum of 36 ($CDCl_3$ as solvent, 101 MHz)



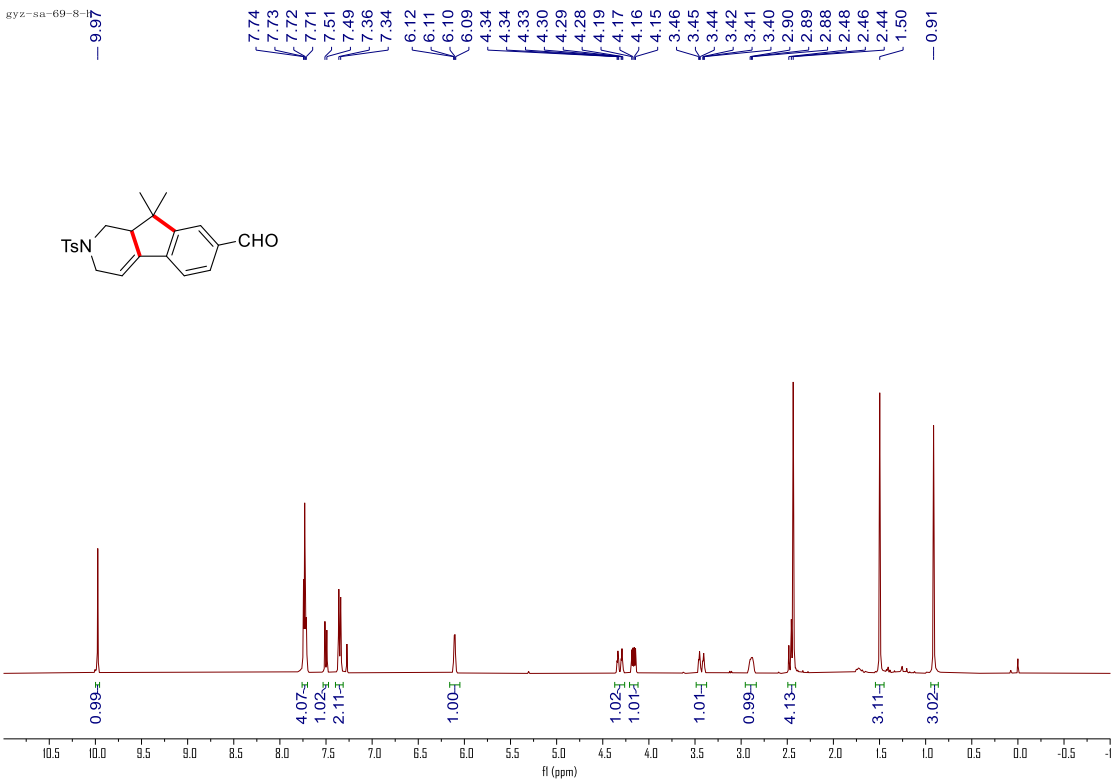
^{1}H NMR Spectrum of 37 ($CDCl_3$ as solvent, 400 MHz)



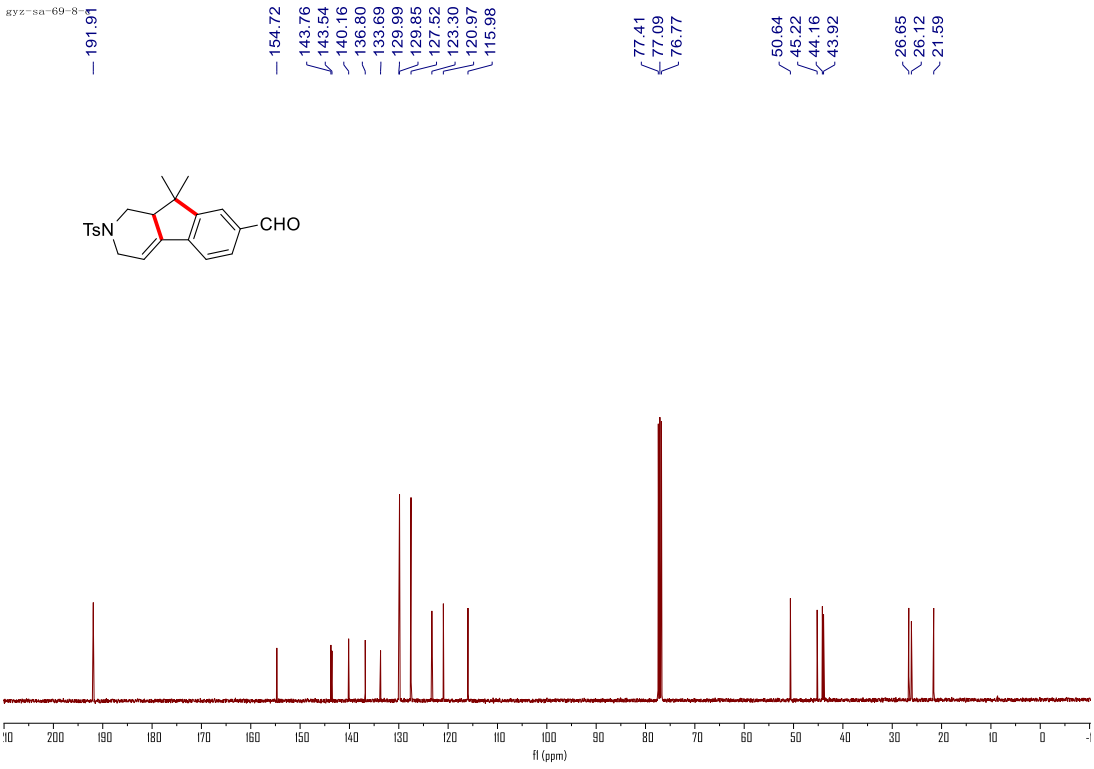
^{13}C {^{1}H} NMR Spectrum of 37 ($CDCl_3$ as solvent, 101 MHz)



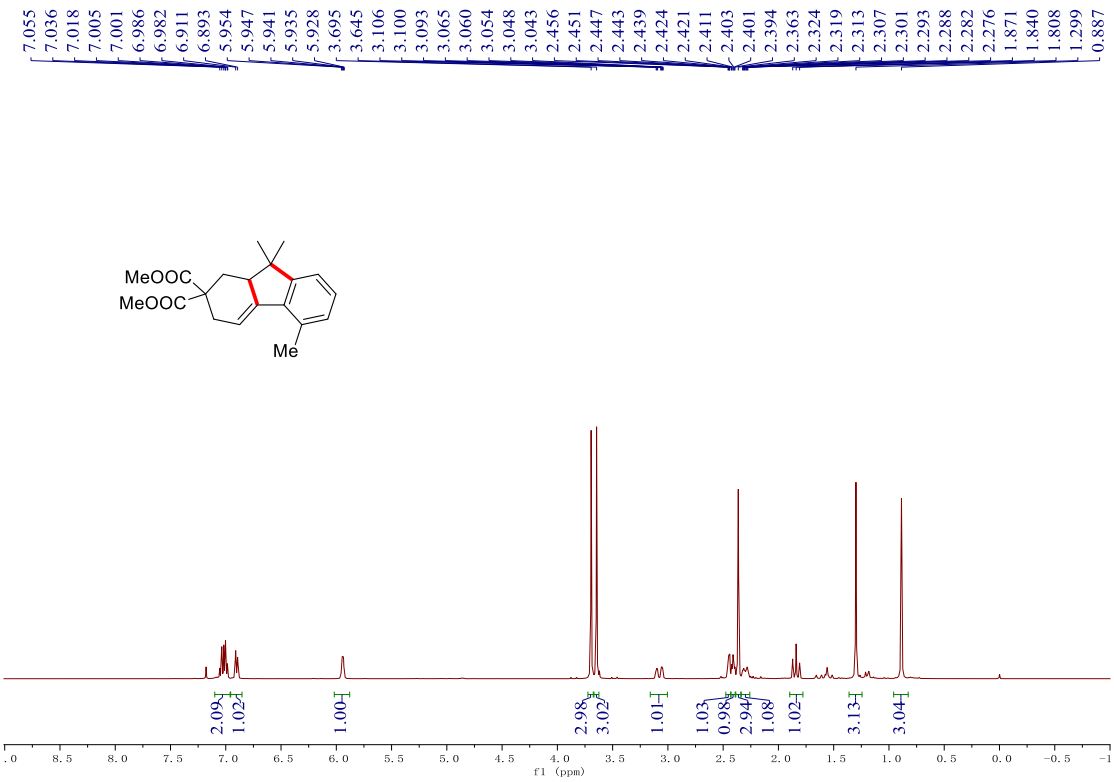
^{1}H NMR Spectrum of 38 ($CDCl_3$ as solvent, 400 MHz)



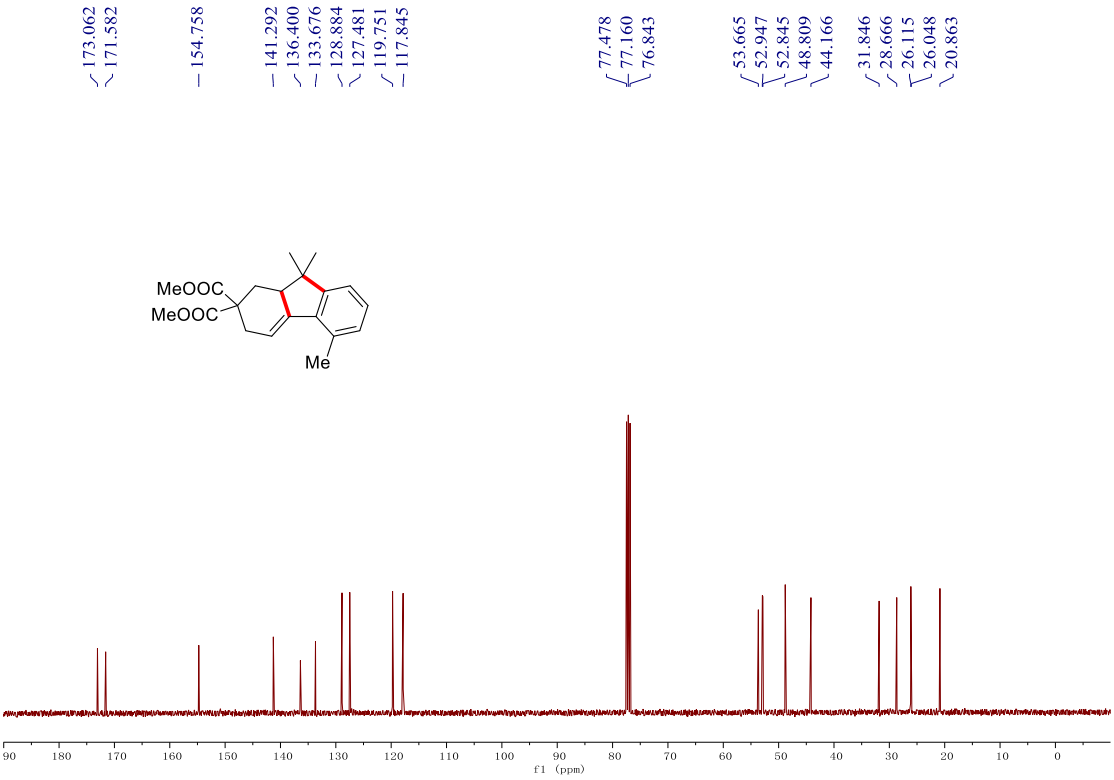
^{13}C {^{1}H} NMR Spectrum of 38 ($CDCl_3$ as solvent, 101 MHz)



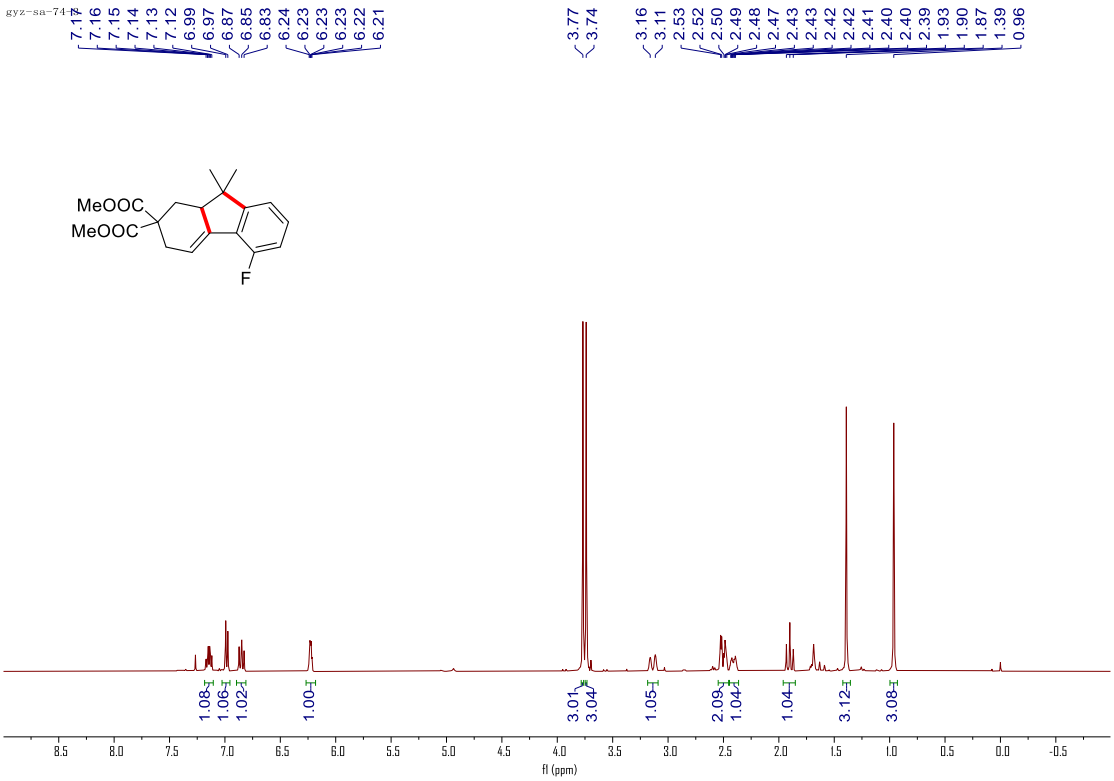
^{1}H NMR Spectrum of 39 ($CDCl_3$ as solvent, 400 MHz)



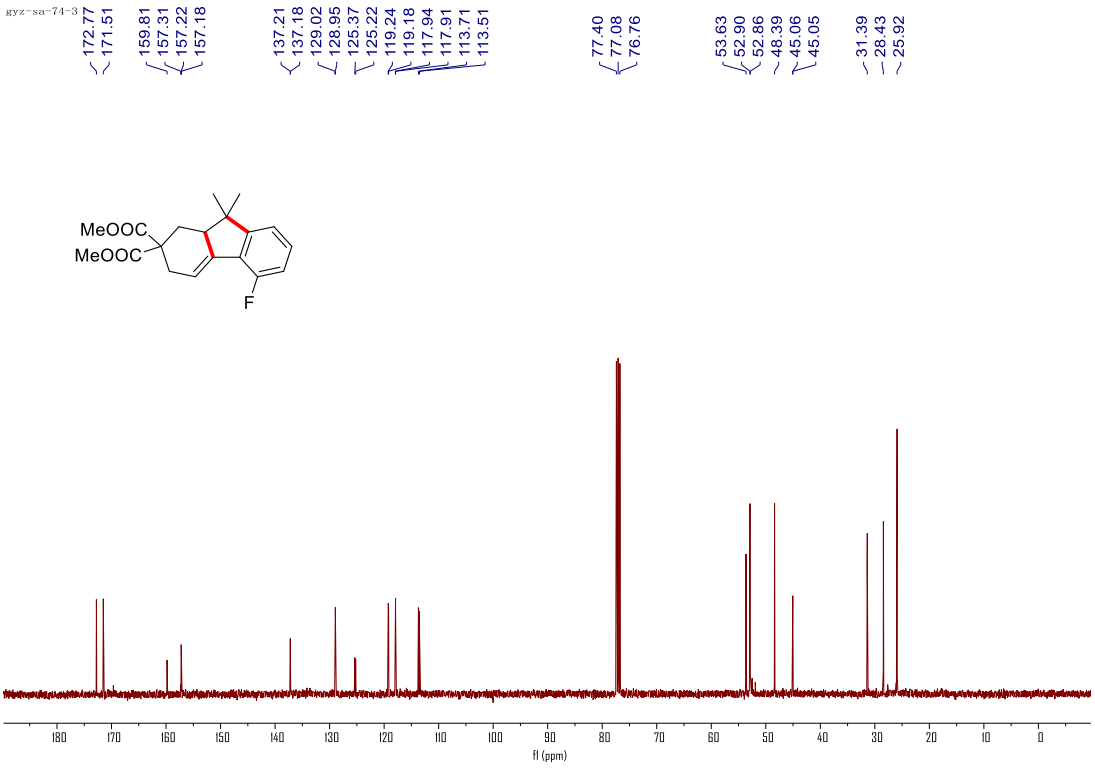
^{13}C {^{1}H} NMR Spectrum of 39 ($CDCl_3$ as solvent, 101 MHz)



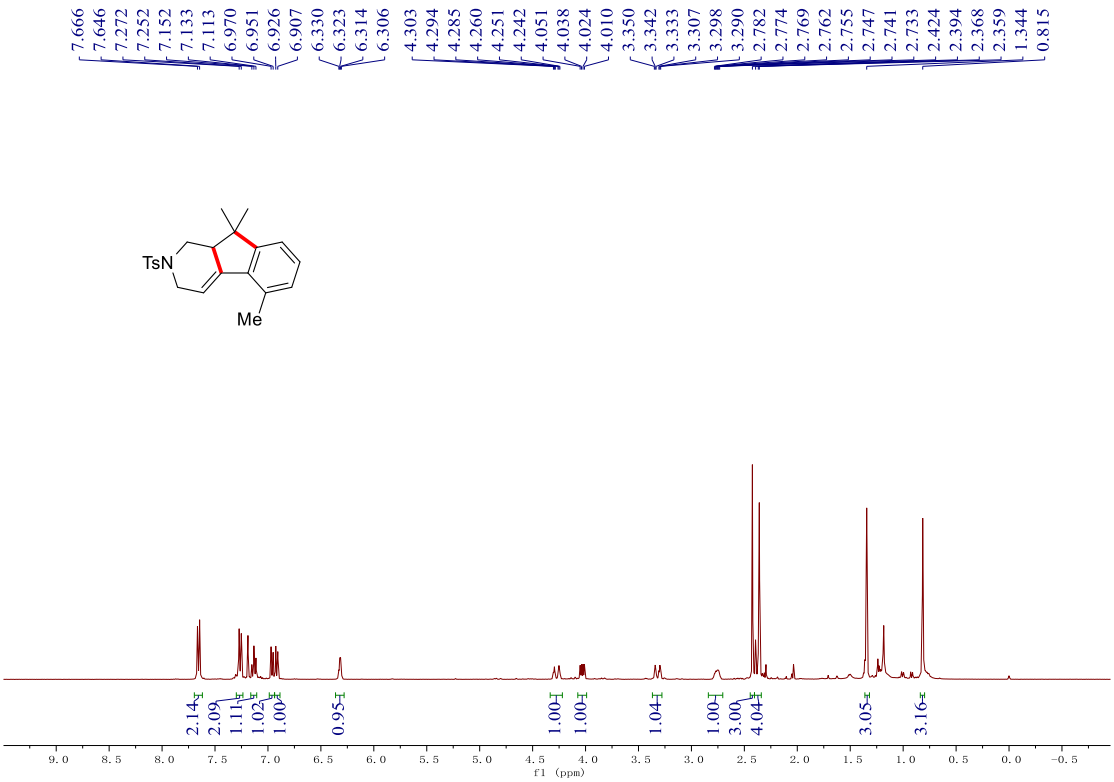
^{1}H NMR Spectrum of 40 ($CDCl_3$ as solvent, 400 MHz)



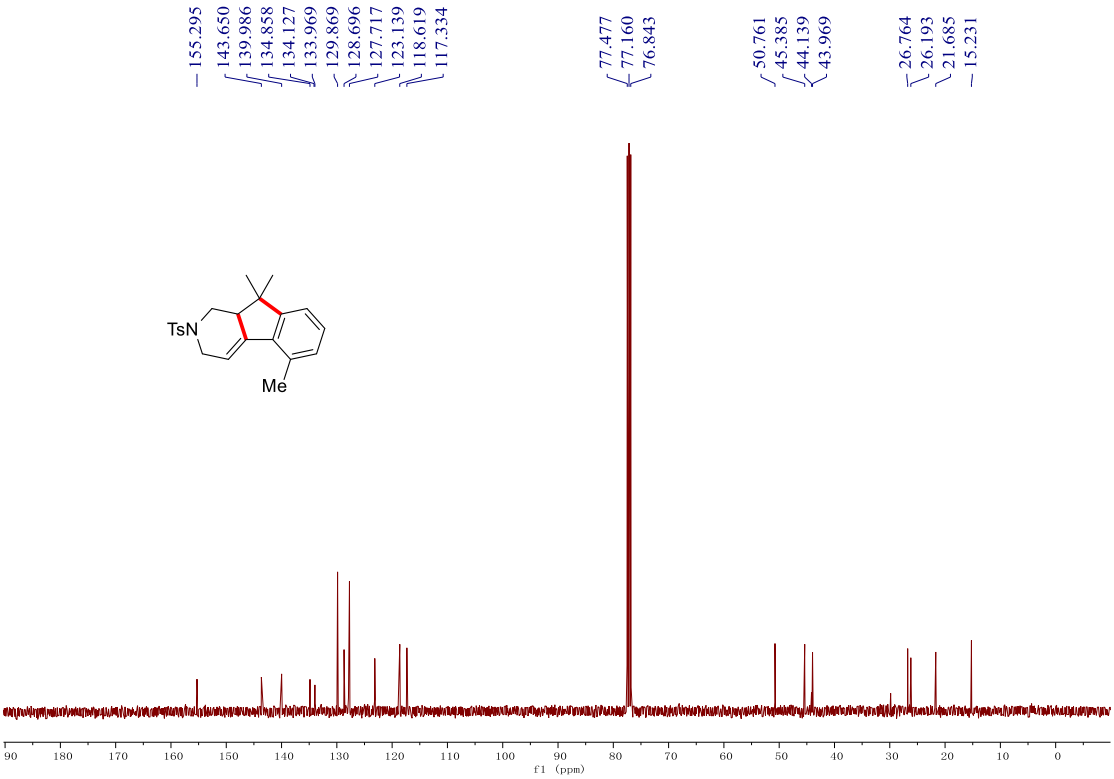
^{13}C {^{1}H} NMR Spectrum of 40 ($CDCl_3$ as solvent, 101 MHz)



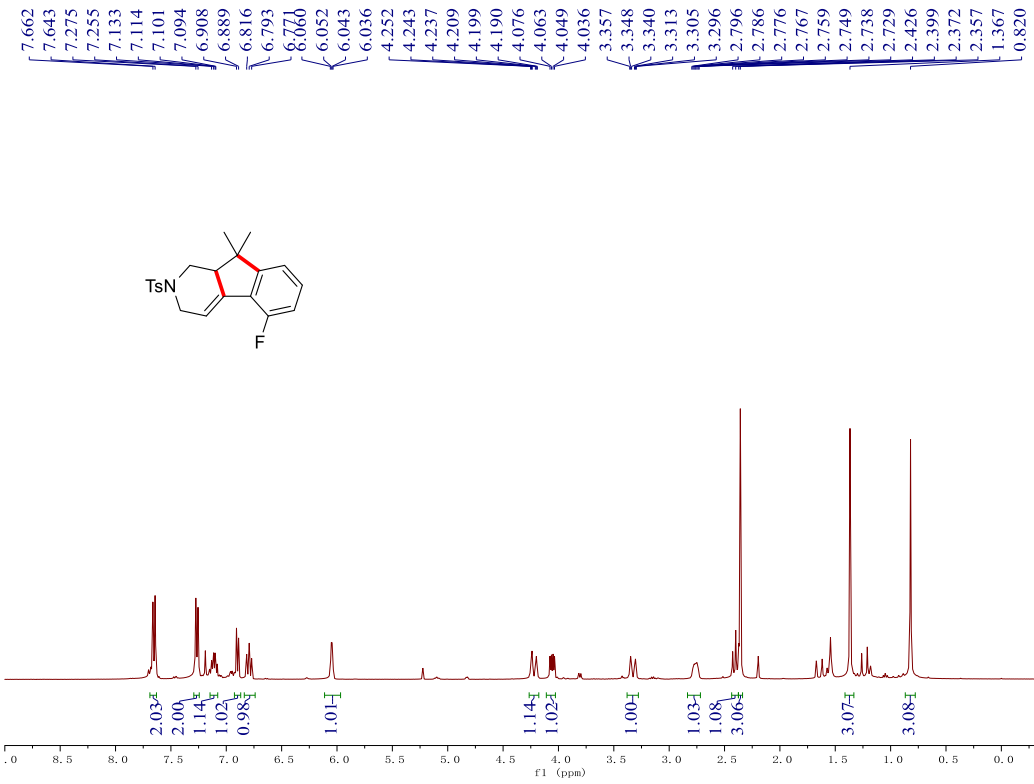
^{1}H NMR Spectrum of 41 ($CDCl_3$ as solvent, 400 MHz)



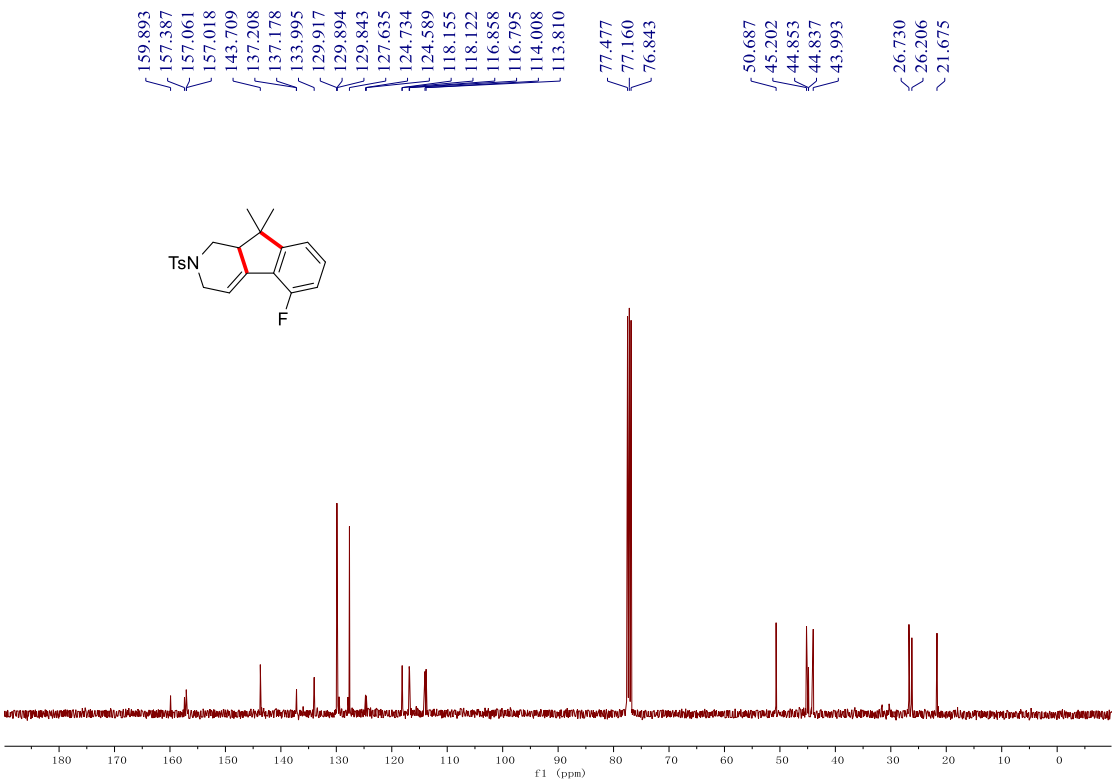
^{13}C {^{1}H} NMR Spectrum of 41 ($CDCl_3$ as solvent, 101 MHz)



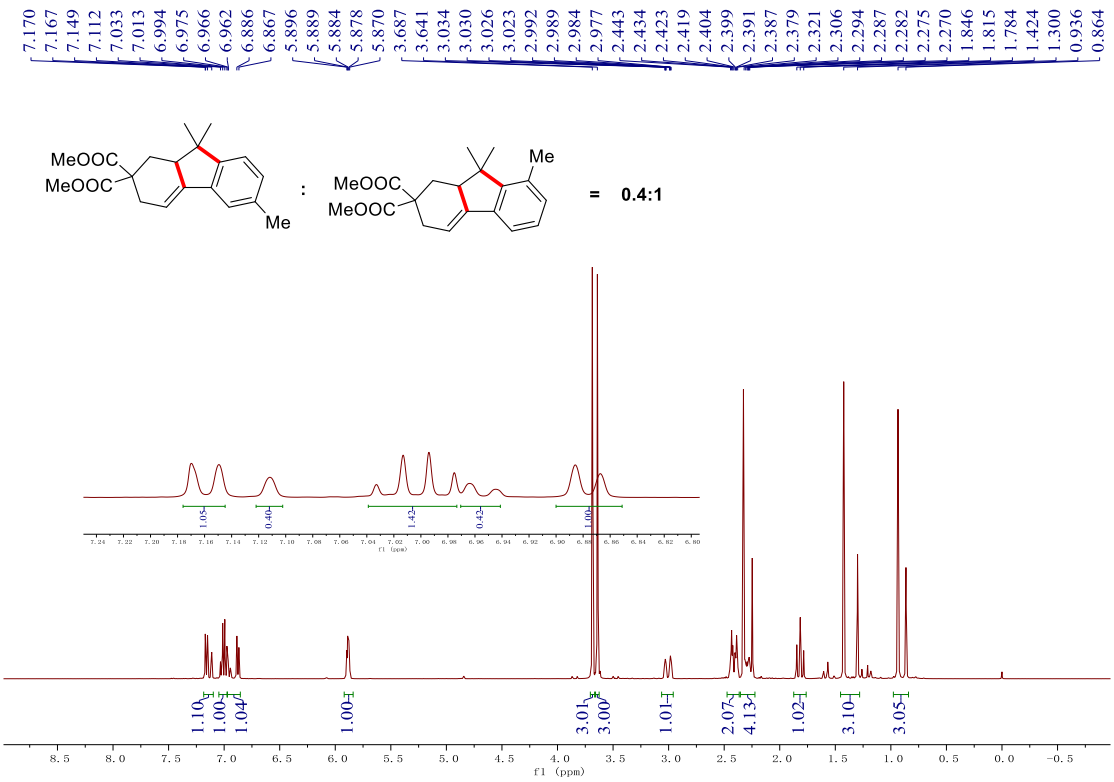
^{1}H NMR Spectrum of 42 ($CDCl_3$ as solvent, 400 MHz)



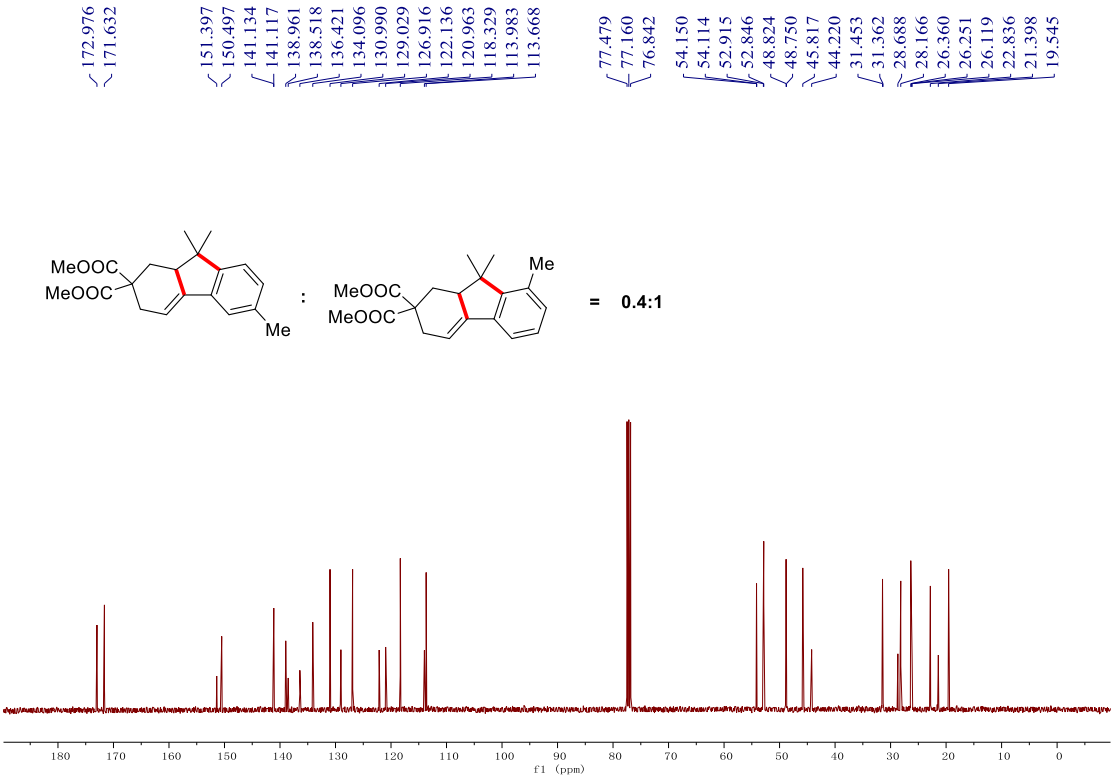
^{13}C {^{1}H} NMR Spectrum of 42 ($CDCl_3$ as solvent, 101 MHz)



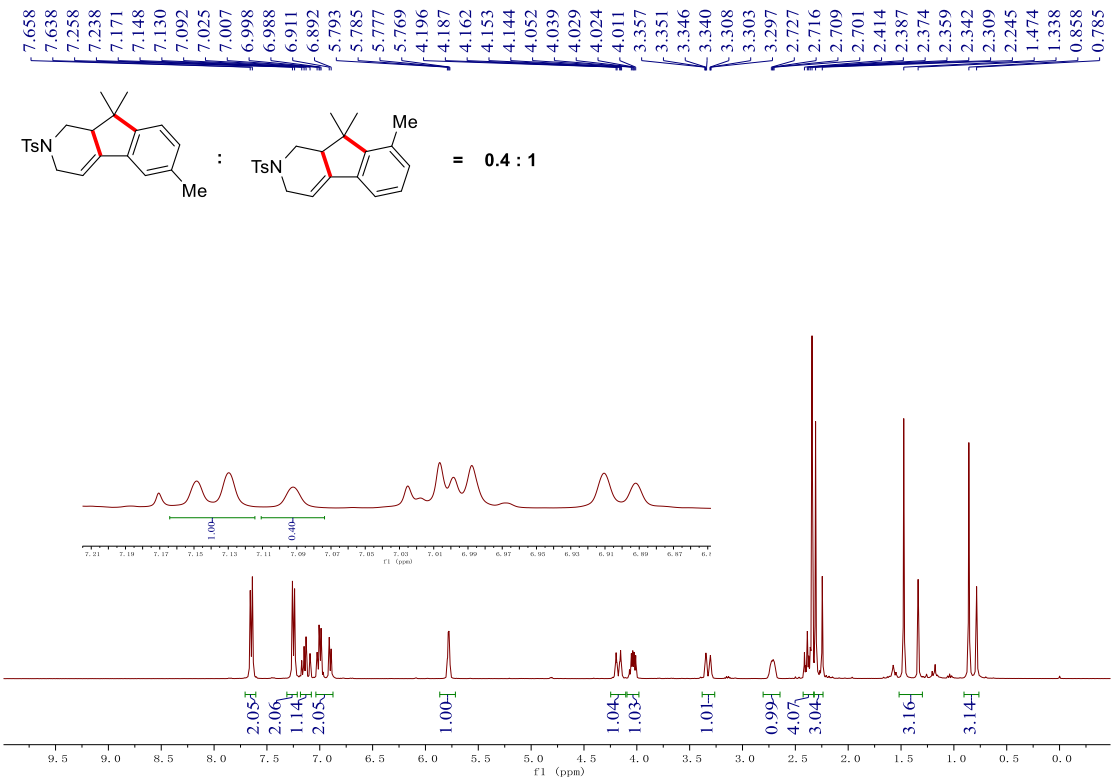
^{1}H NMR Spectrum of 43 ($CDCl_3$ as solvent, 400 MHz)



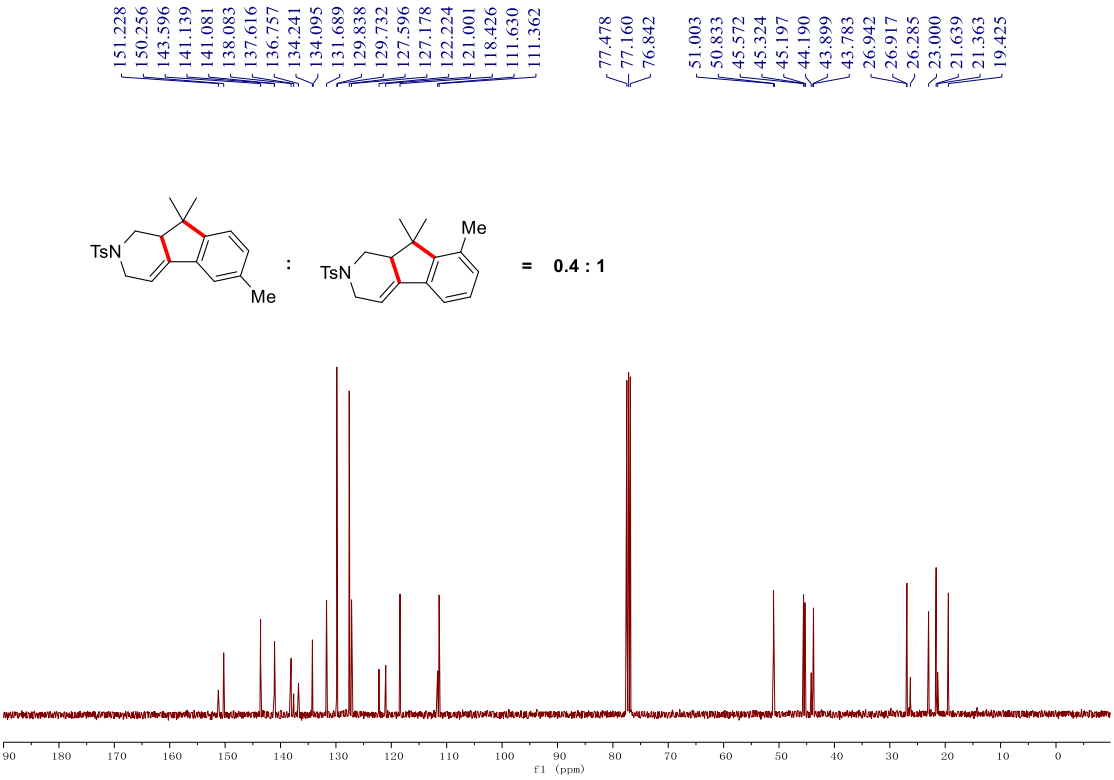
^{13}C {^{1}H} NMR Spectrum of 43 ($CDCl_3$ as solvent, 101 MHz)



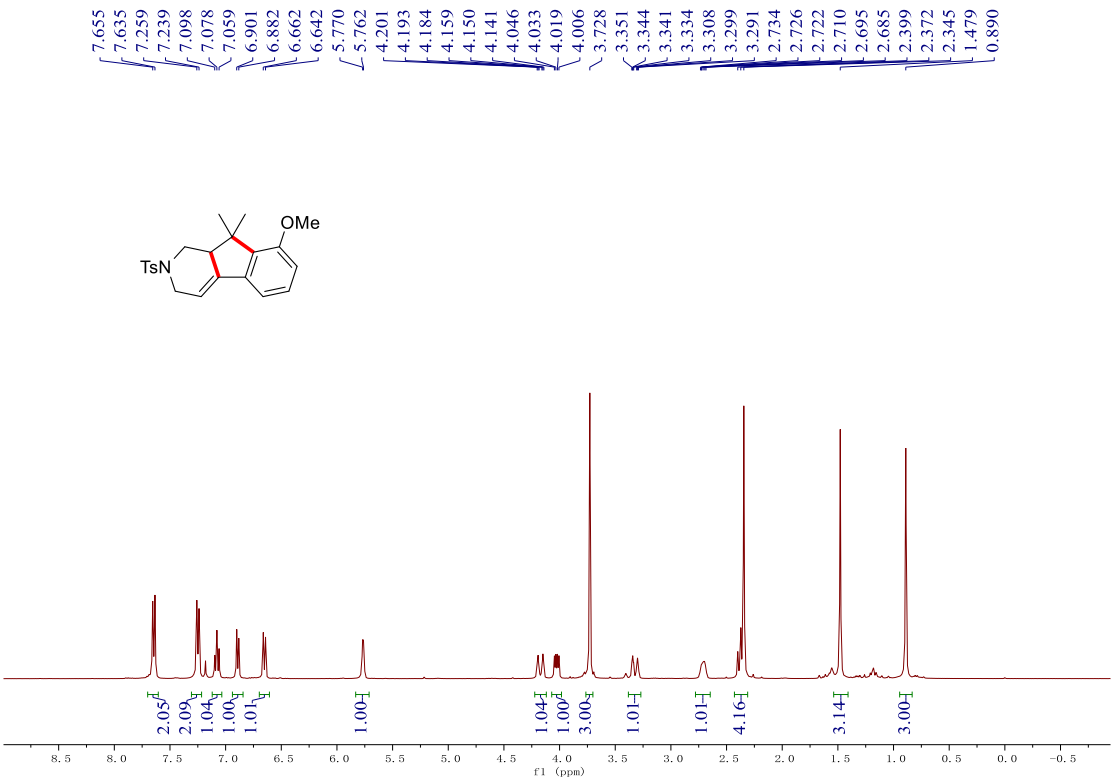
^{1}H NMR Spectrum of 44 ($CDCl_3$ as solvent, 400 MHz)



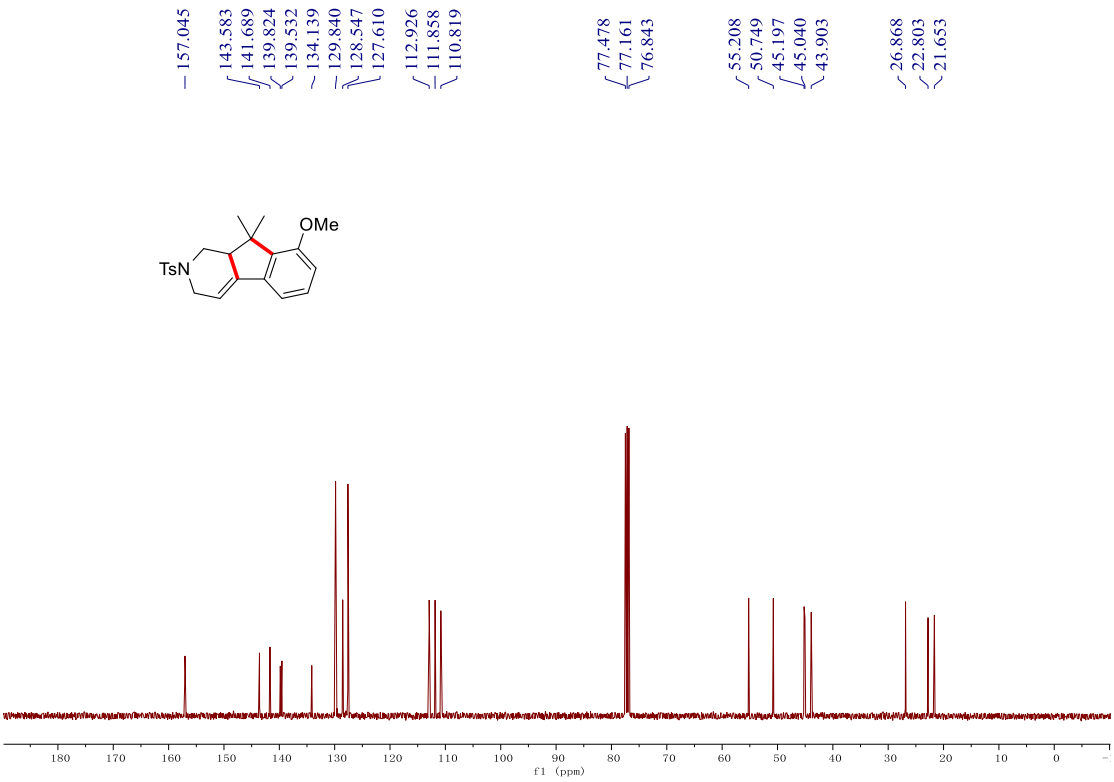
^{13}C {^{1}H} NMR Spectrum of 44 ($CDCl_3$ as solvent, 101 MHz)



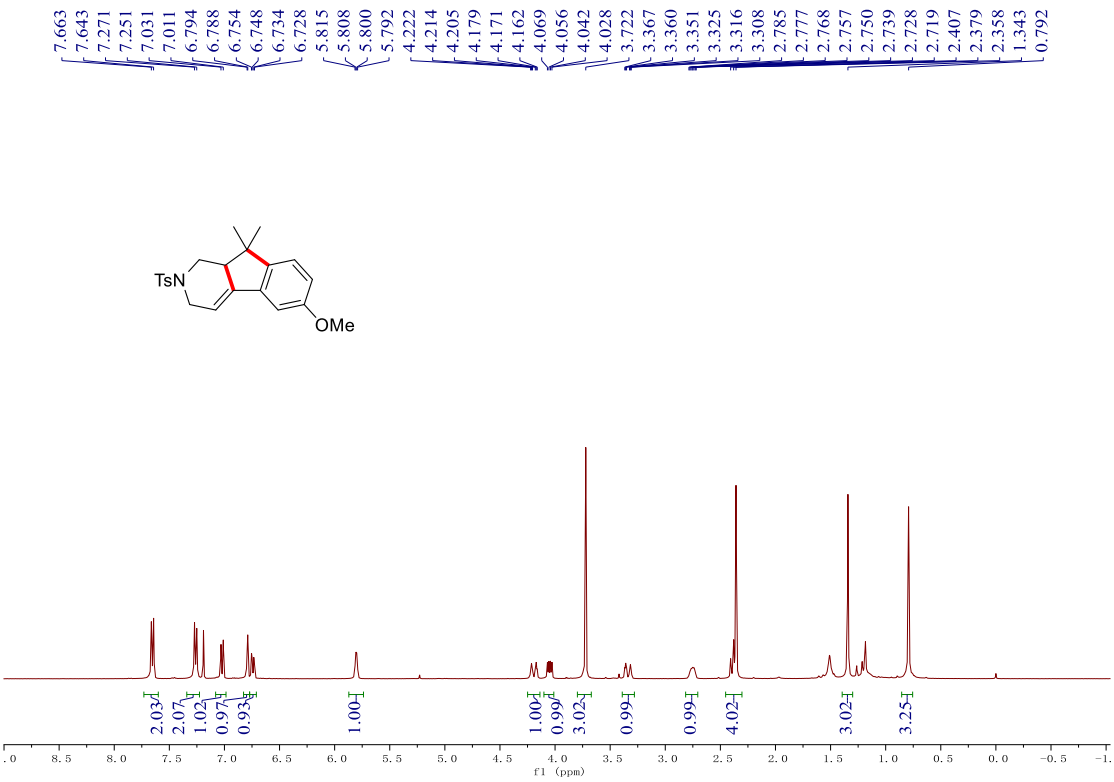
^{1}H NMR Spectrum of 45 ($CDCl_3$ as solvent, 400 MHz)



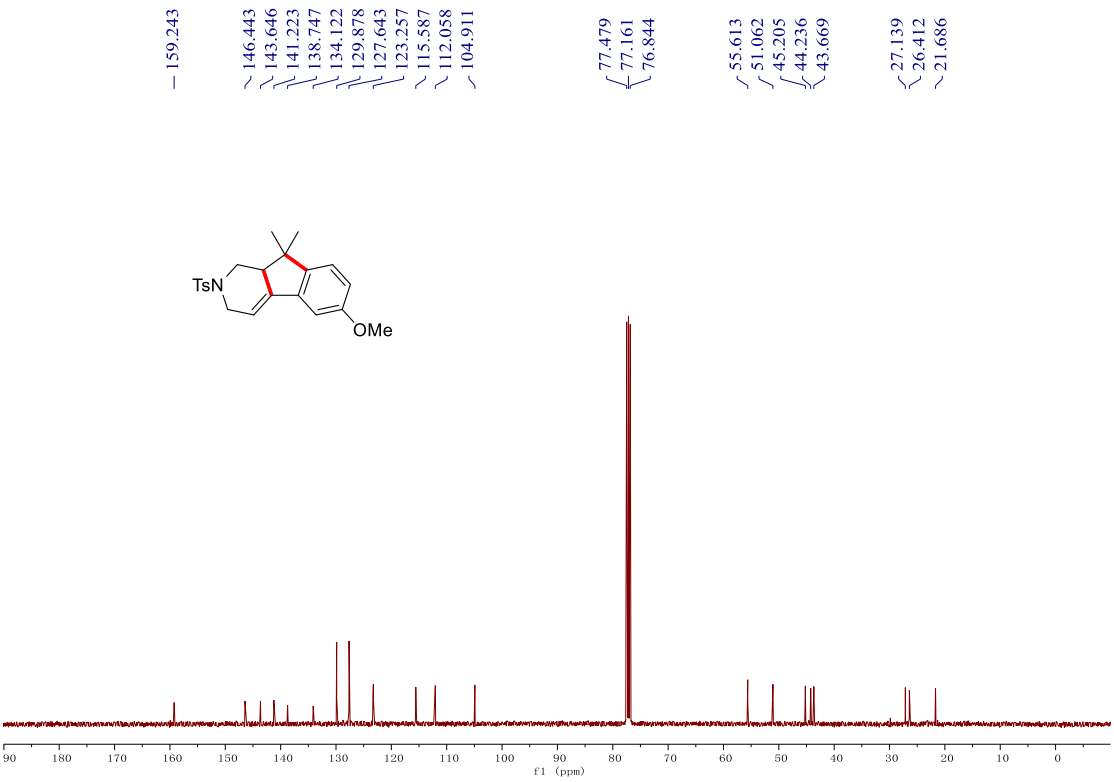
^{13}C {^{1}H} NMR Spectrum of 45 ($CDCl_3$ as solvent, 101 MHz)



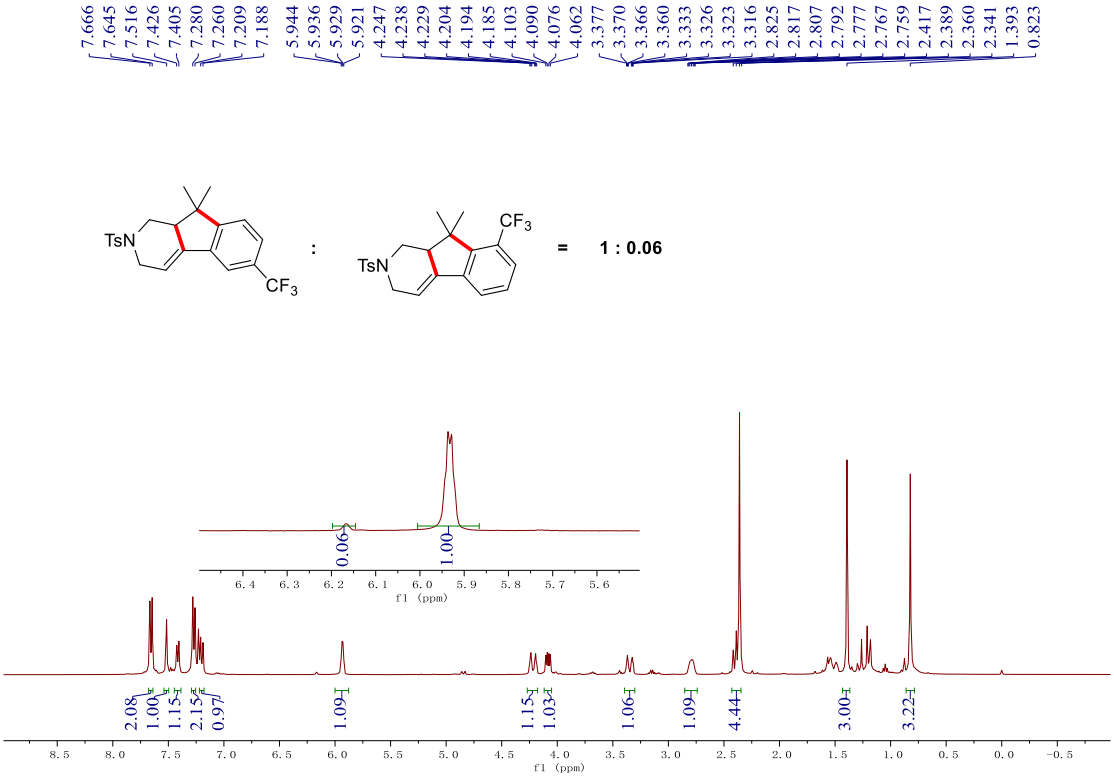
^{1}H NMR Spectrum of 45’ (CDCl$_3$ as solvent, 400 MHz)



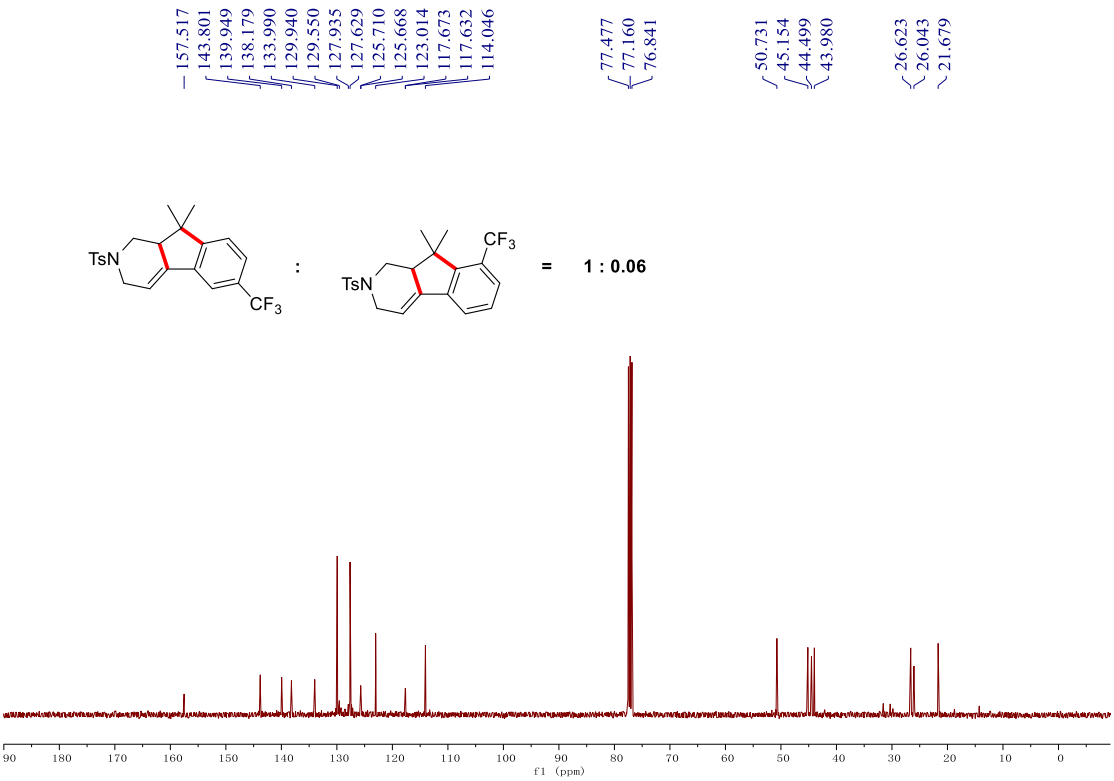
^{13}C {^{1}H} NMR Spectrum of 45’ (CDCl$_3$ as solvent, 101 MHz)



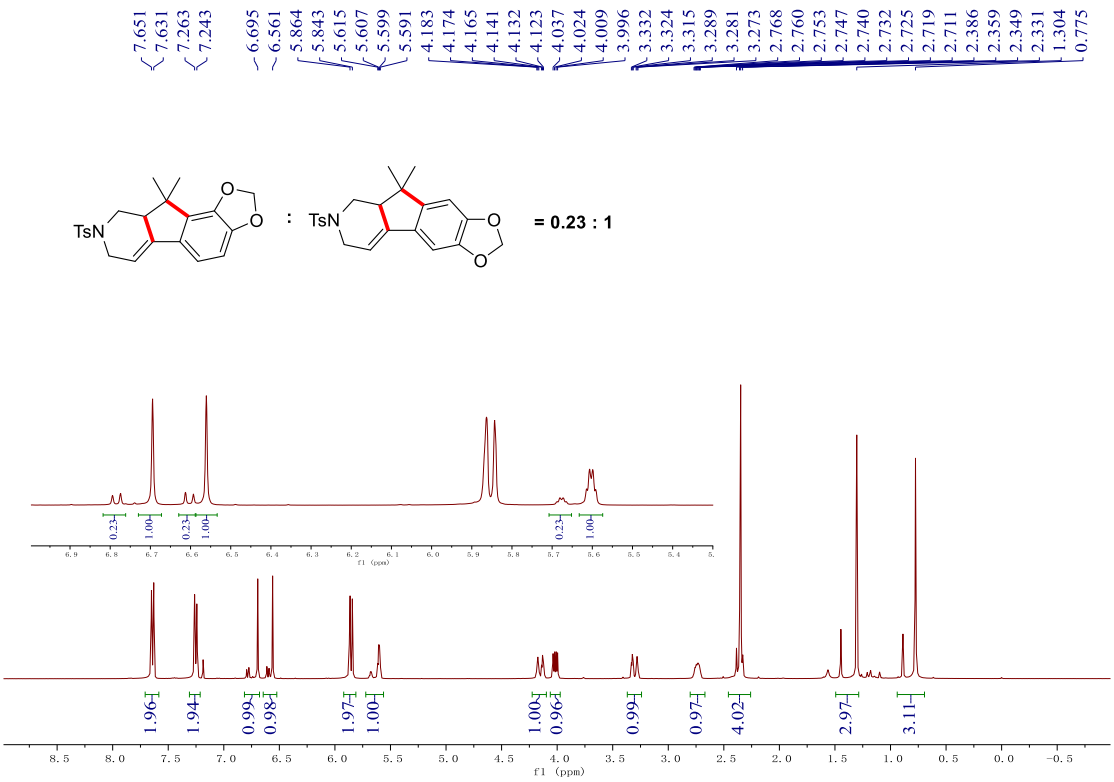
^{1}H NMR Spectrum of 46 ($CDCl_3$ as solvent, 400 MHz)



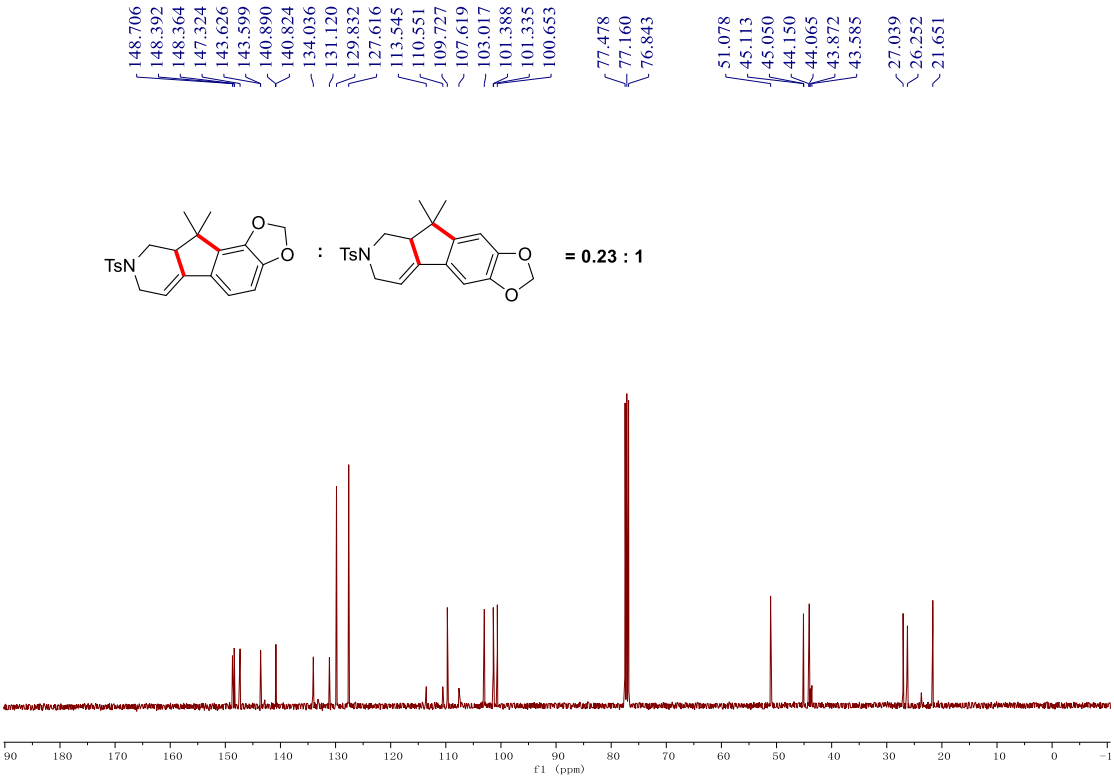
^{13}C {^{1}H} NMR Spectrum of 46 ($CDCl_3$ as solvent, 101 MHz)



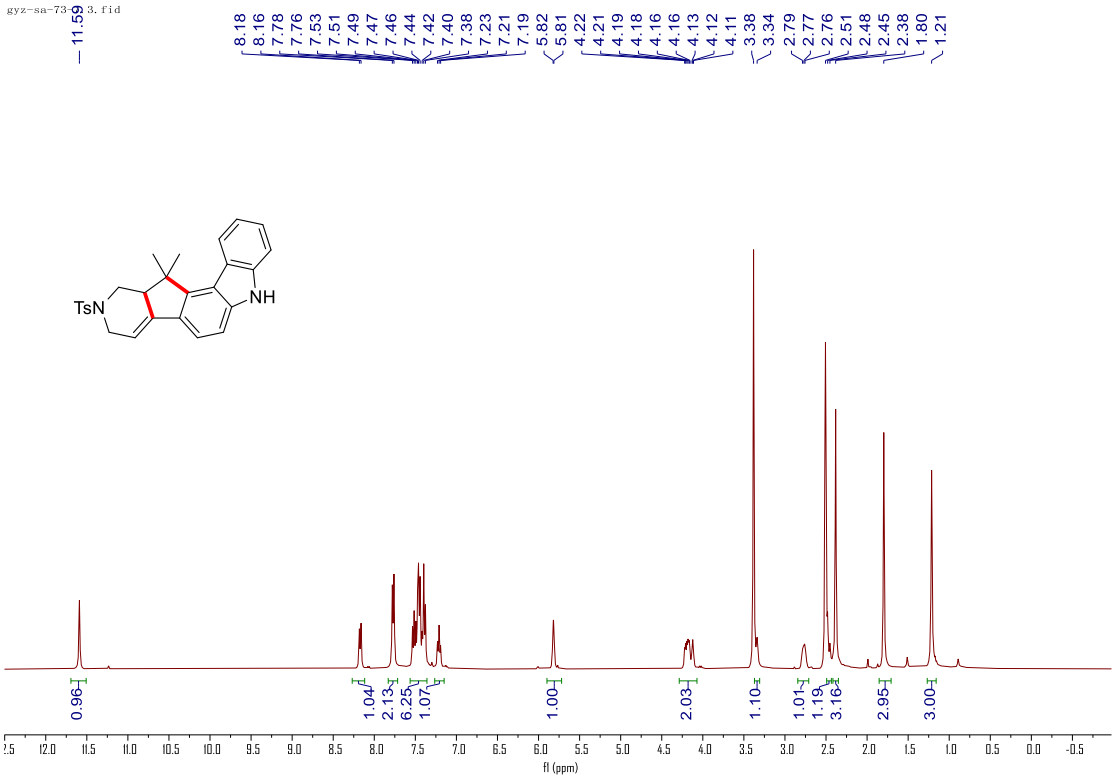
^{1}H NMR Spectrum of 47 ($CDCl_3$ as solvent, 400 MHz)



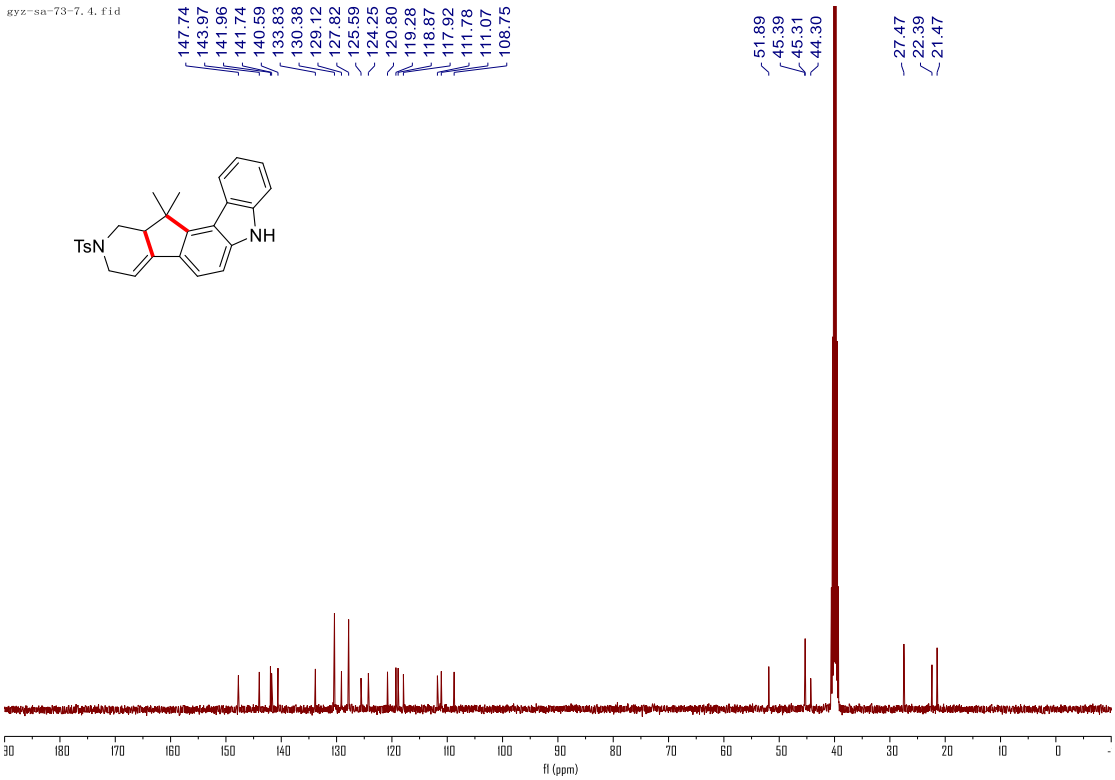
^{13}C {^{1}H} NMR Spectrum of 47 ($CDCl_3$ as solvent, 101 MHz)



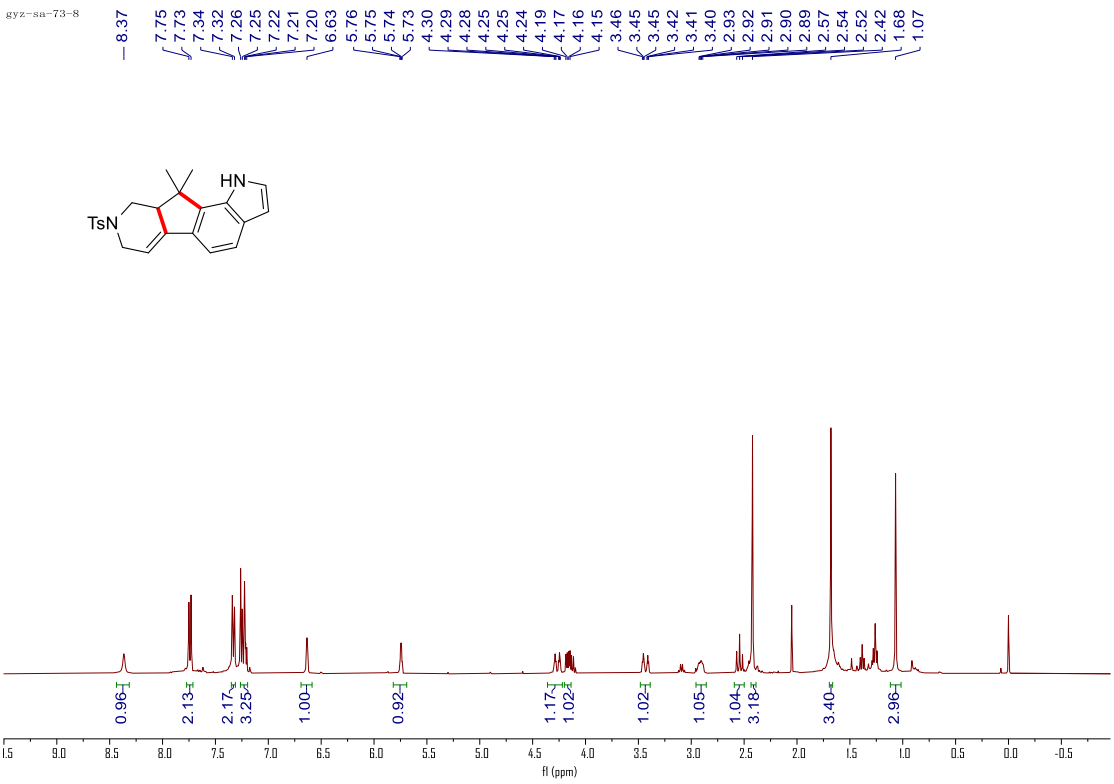
^{1}H NMR Spectrum of 48 (DMSO-d_6 as solvent, 400 MHz)



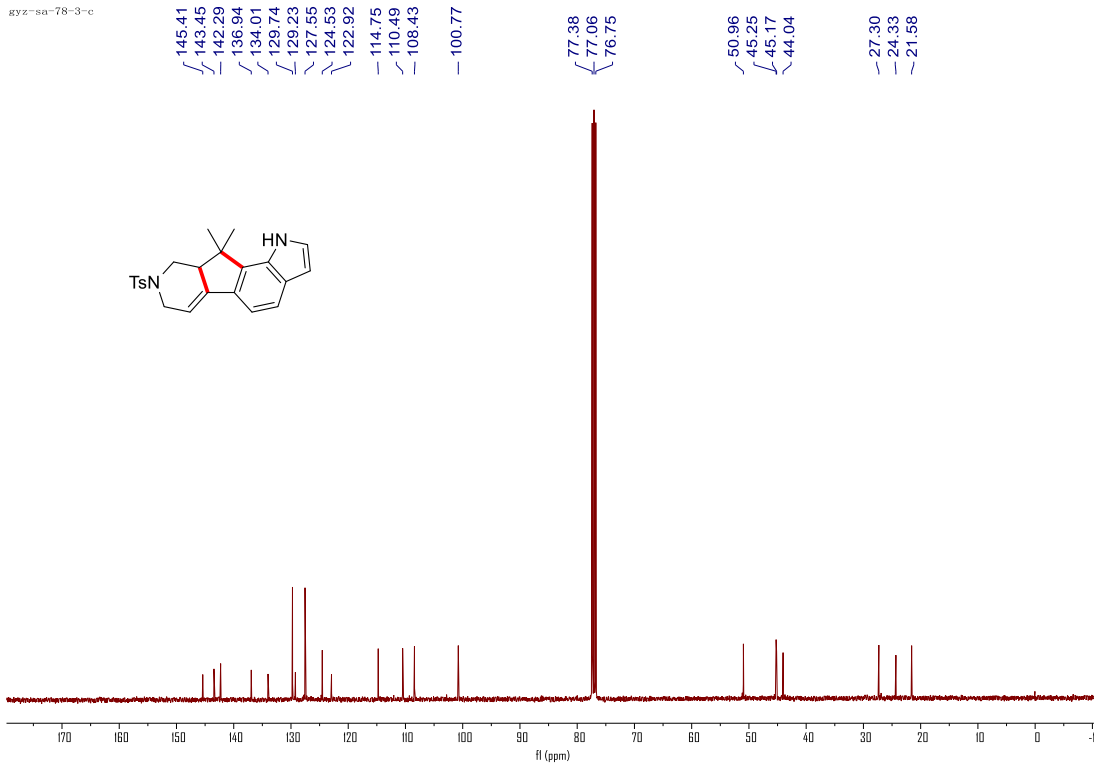
^{13}C {^{1}H} NMR Spectrum of 48 (DMSO-d_6 as solvent, 101 MHz)



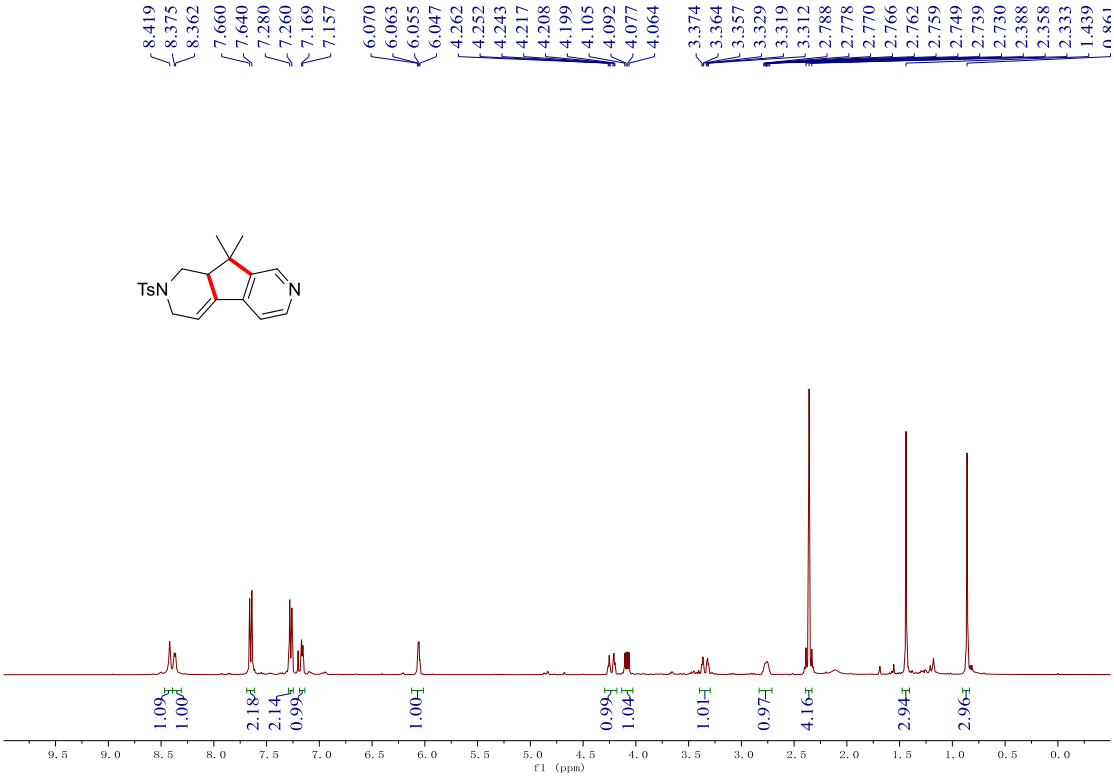
^{1}H NMR Spectrum of 49 ($CDCl_3$ as solvent, 400 MHz)



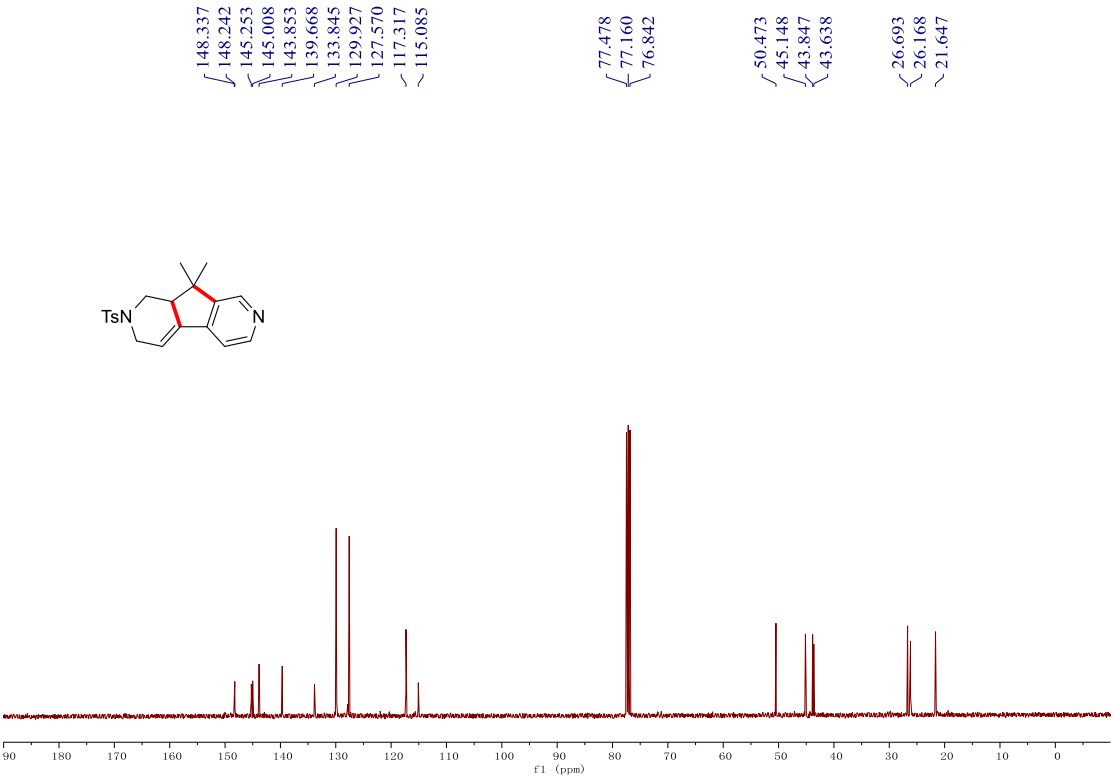
^{13}C {^{1}H} NMR Spectrum of 49 ($CDCl_3$ as solvent, 101 MHz)



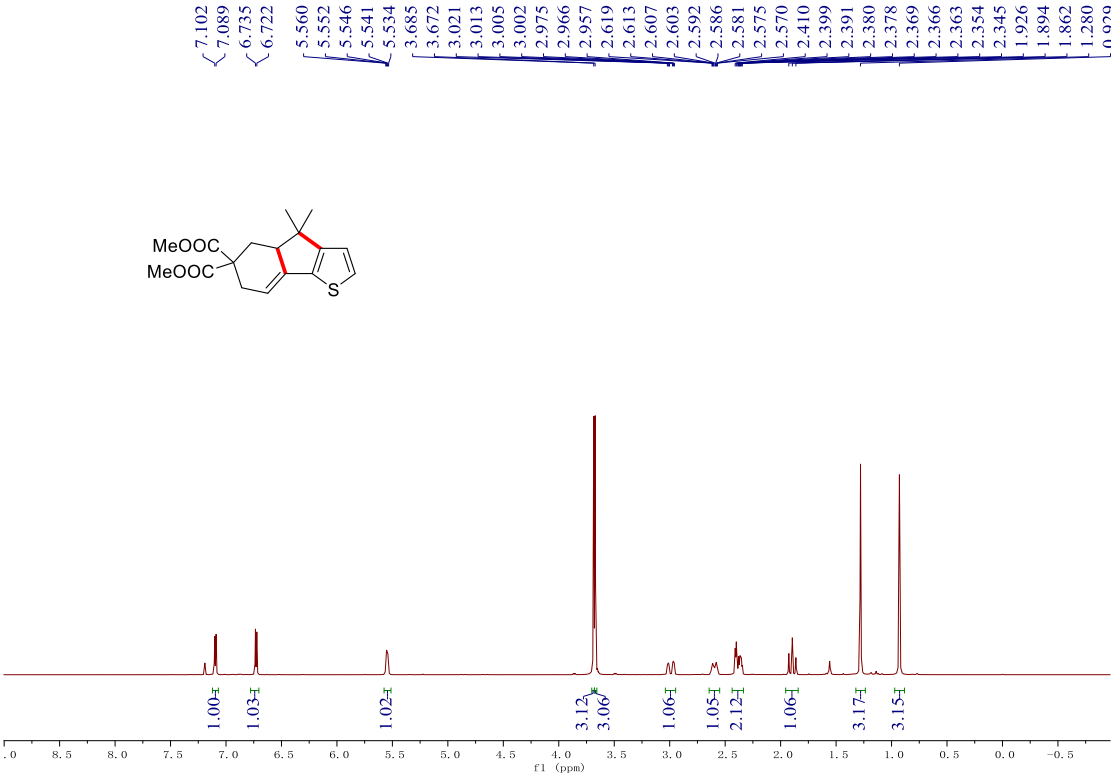
^{1}H NMR Spectrum of 50 ($CDCl_3$ as solvent, 400 MHz)



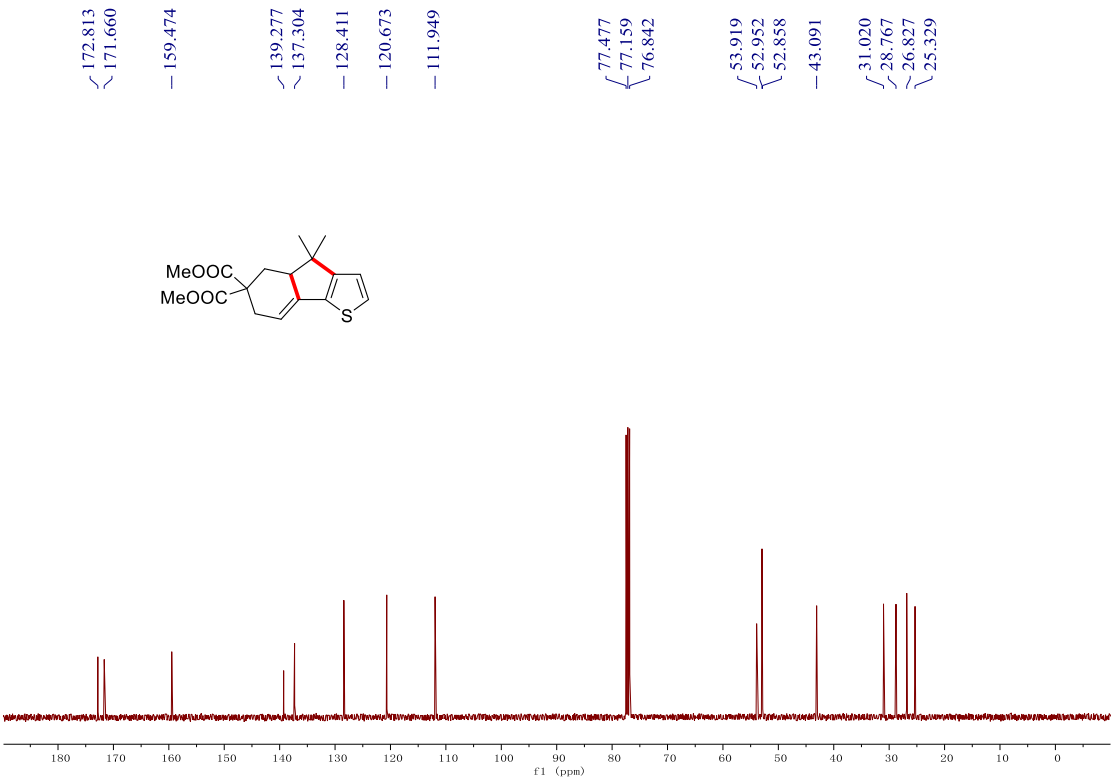
^{13}C {^{1}H} NMR Spectrum of 50 ($CDCl_3$ as solvent, 101 MHz)



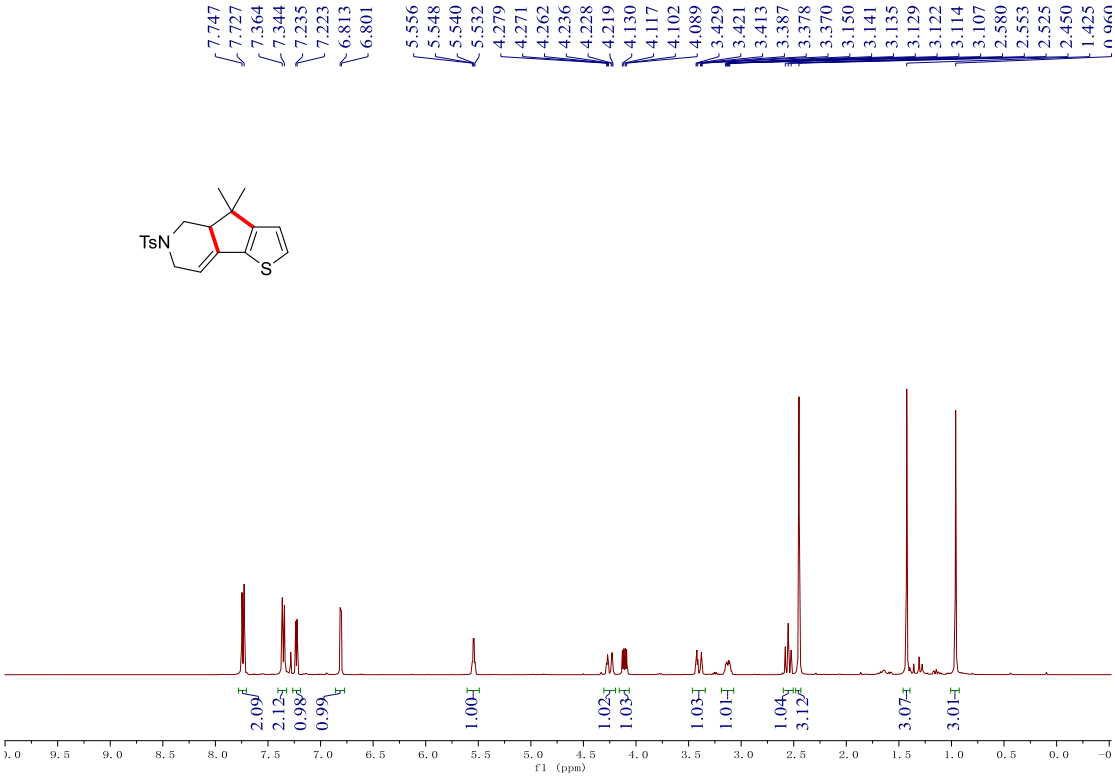
^{1}H NMR Spectrum of 51 ($CDCl_3$ as solvent, 400 MHz)



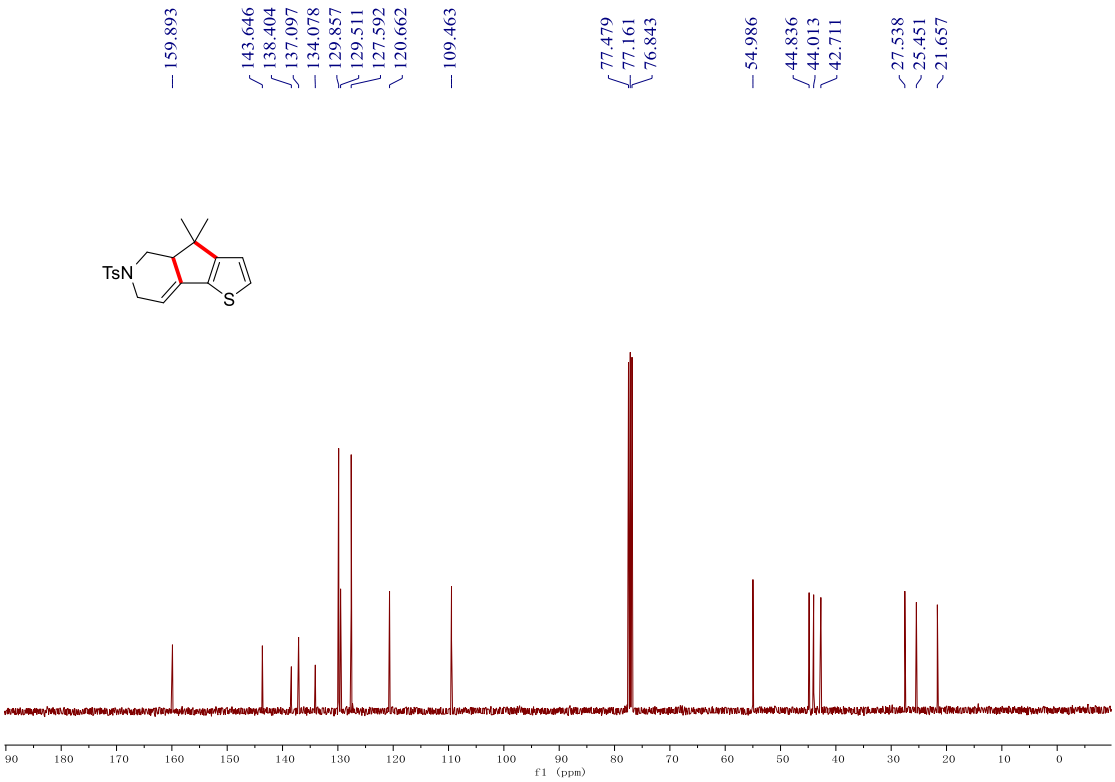
^{13}C {^{1}H} NMR Spectrum of 51 ($CDCl_3$ as solvent, 101 MHz)



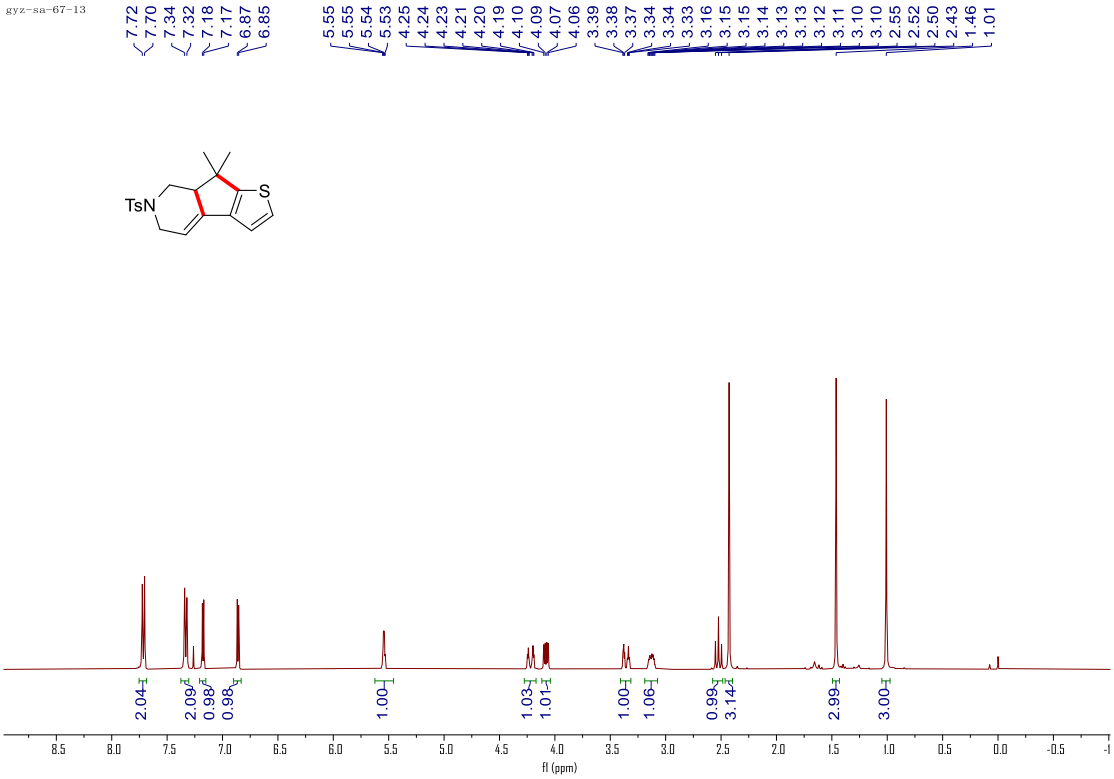
^{1}H NMR Spectrum of 52 ($CDCl_3$ as solvent, 400 MHz)



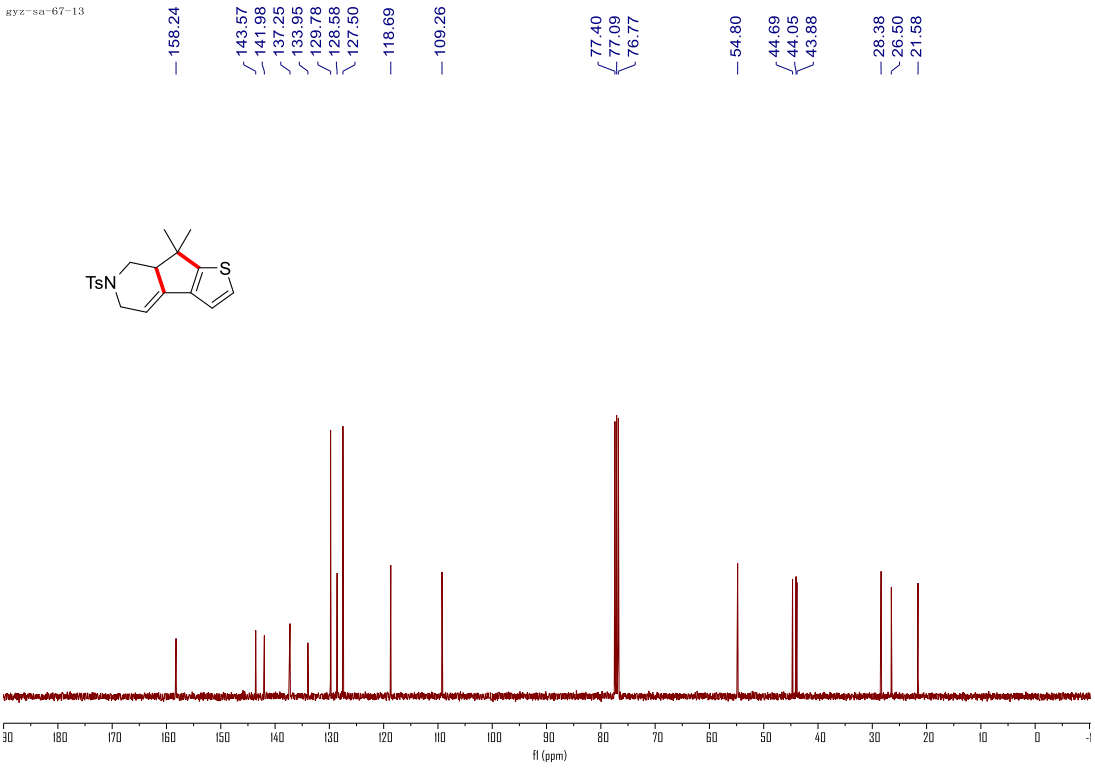
^{13}C {^{1}H} NMR Spectrum of 52 ($CDCl_3$ as solvent, 101 MHz)



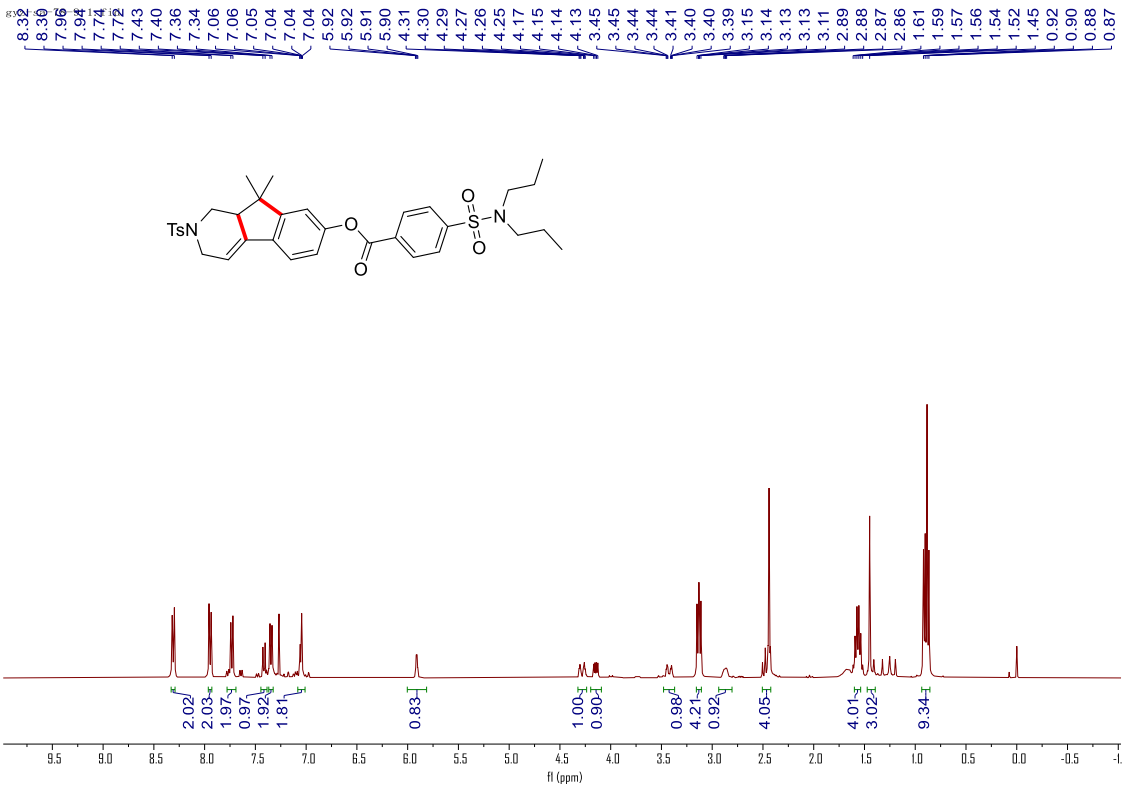
^{1}H NMR Spectrum of 53 ($CDCl_3$ as solvent, 400 MHz)



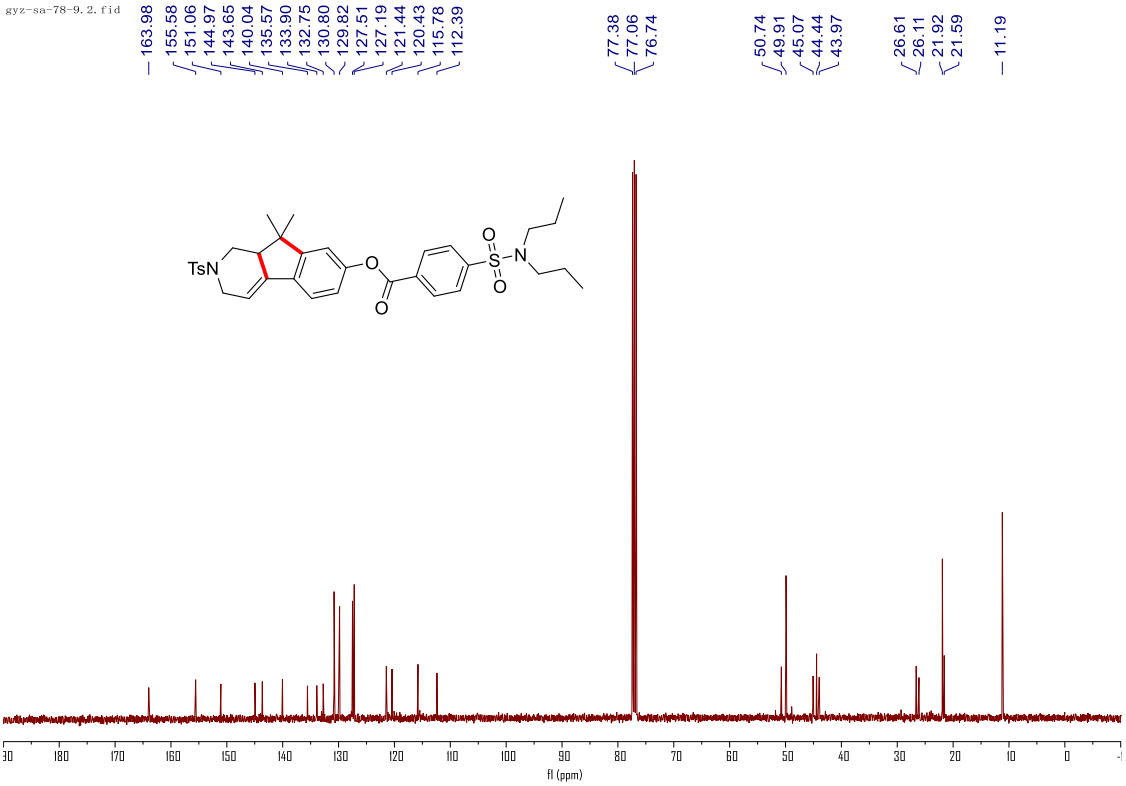
^{13}C {^{1}H} NMR Spectrum of 53 ($CDCl_3$ as solvent, 101 MHz)



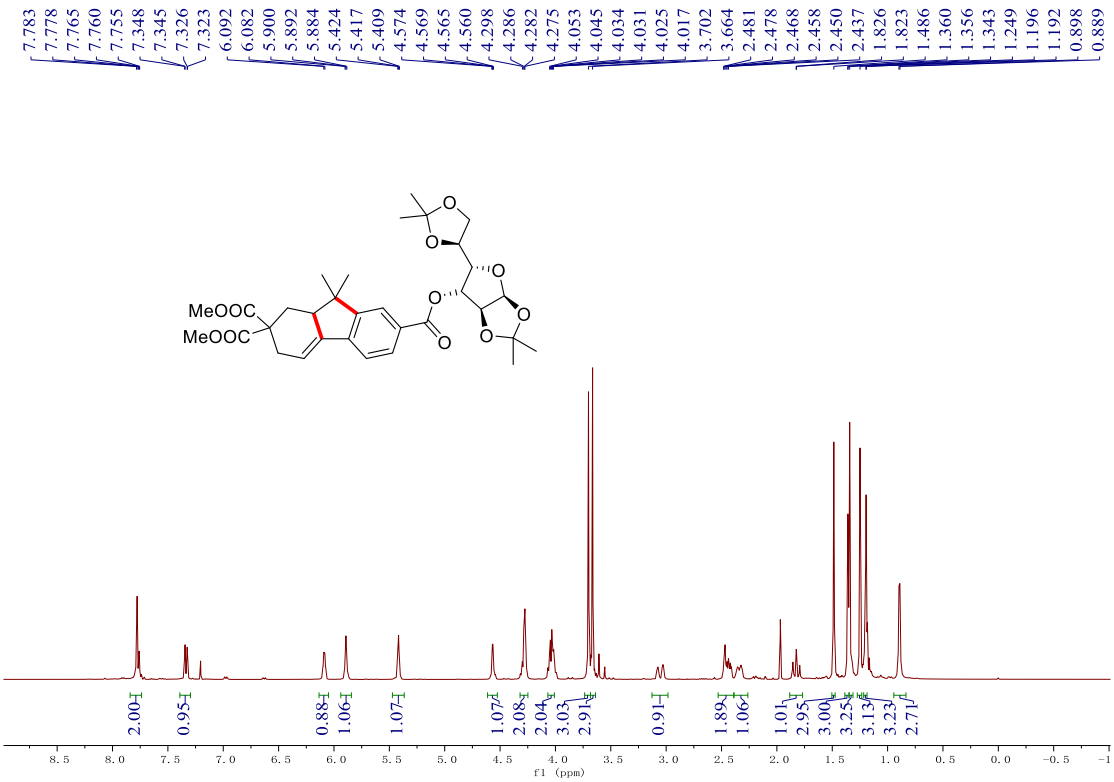
^{1}H NMR Spectrum of 55 ($CDCl_3$ as solvent, 400 MHz)



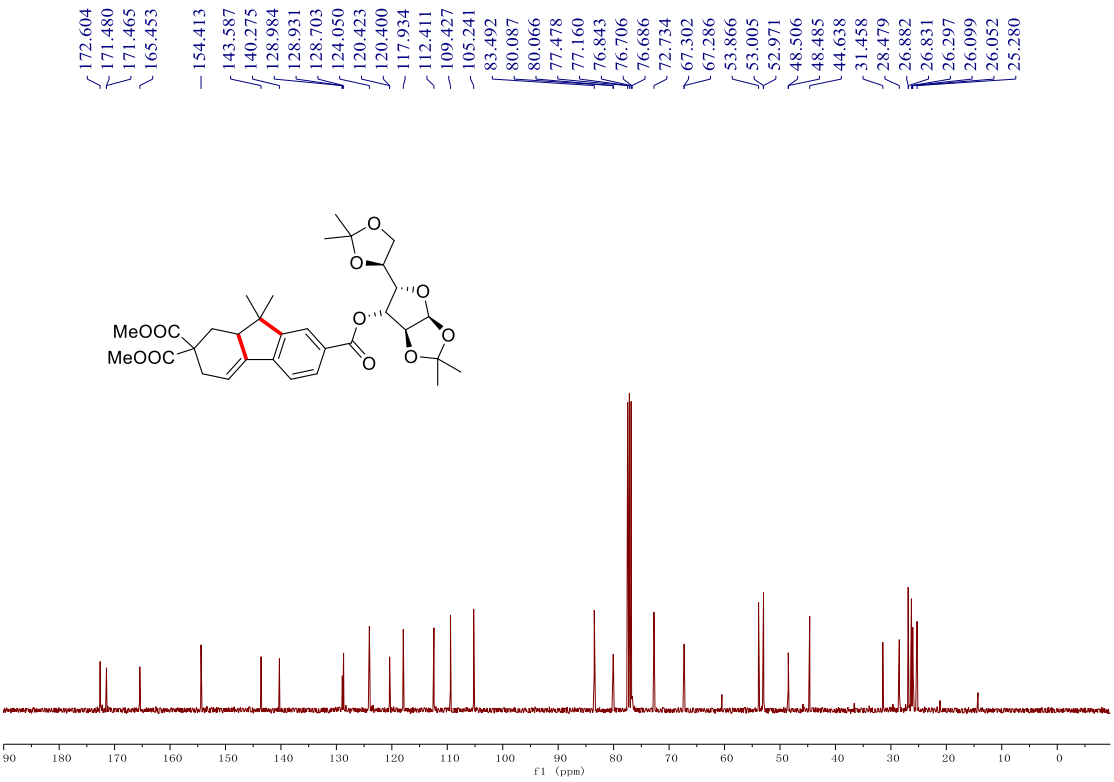
^{13}C {^{1}H} NMR Spectrum of 55 ($CDCl_3$ as solvent, 101 MHz)



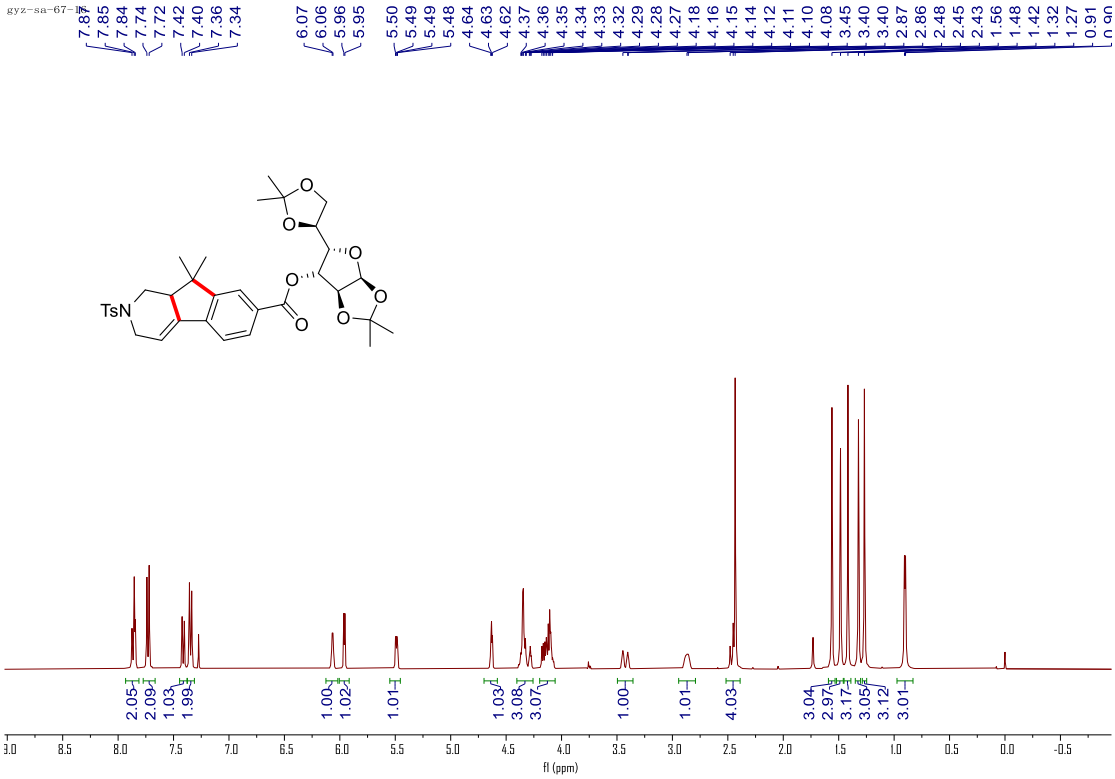
^{1}H NMR Spectrum of 56 ($CDCl_3$ as solvent, 400 MHz)



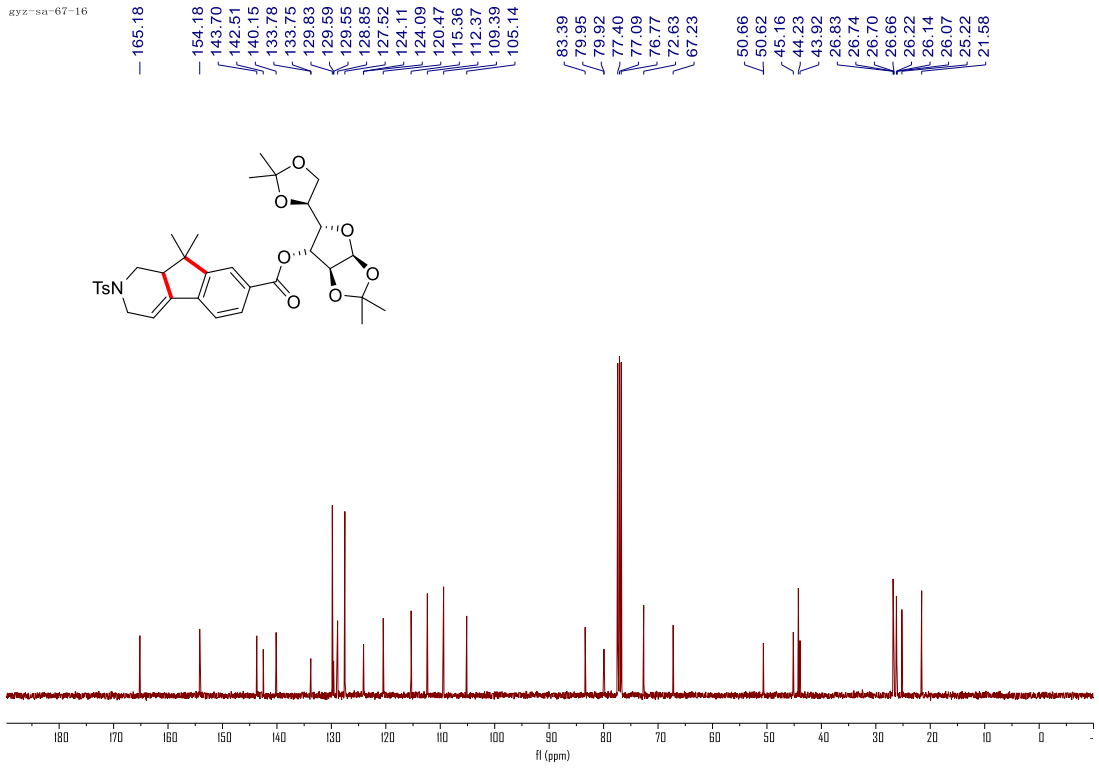
^{13}C {^{1}H} NMR Spectrum of 56 ($CDCl_3$ as solvent, 101 MHz)



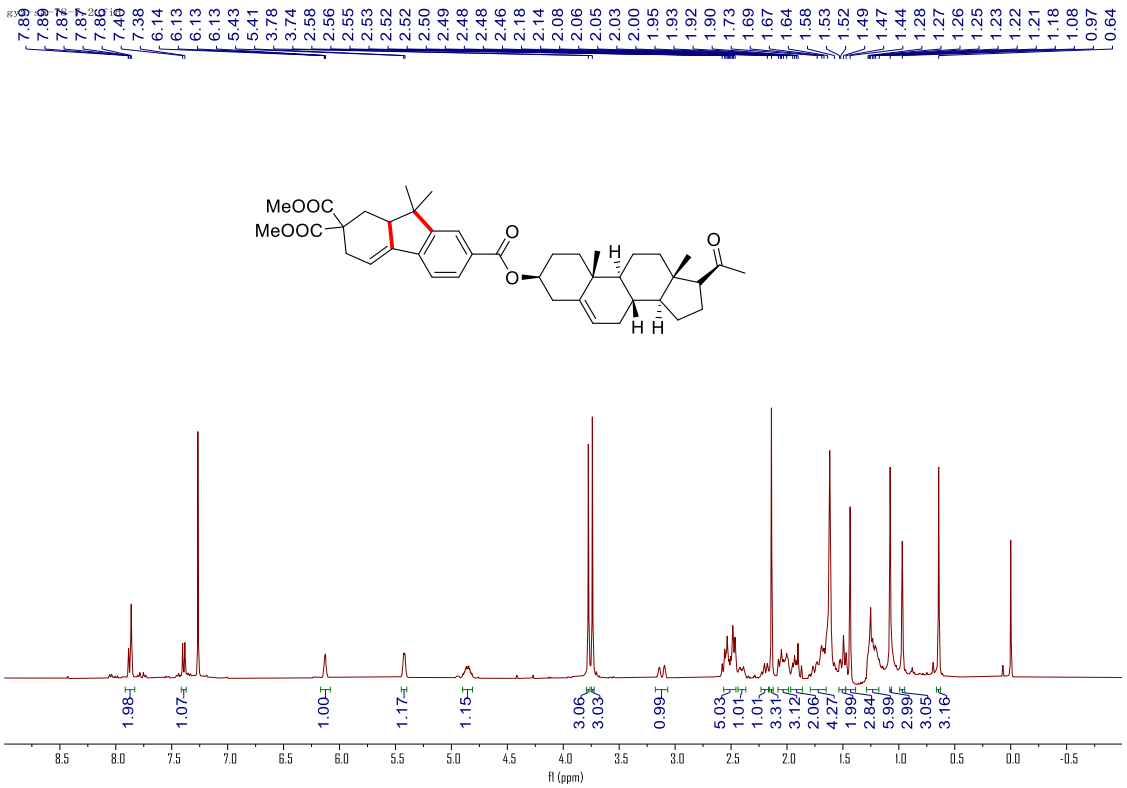
^{1}H NMR Spectrum of 57 ($CDCl_3$ as solvent, 400 MHz)



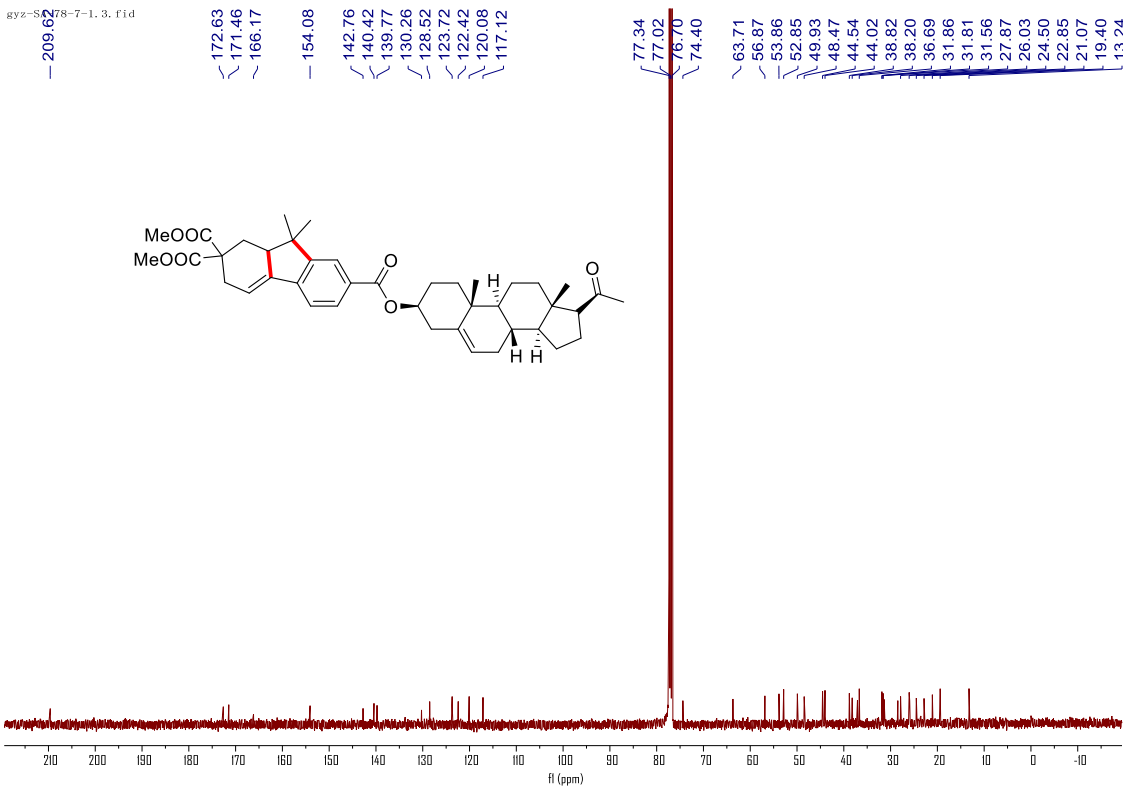
^{13}C {^{1}H} NMR Spectrum of 57 ($CDCl_3$ as solvent, 101 MHz)



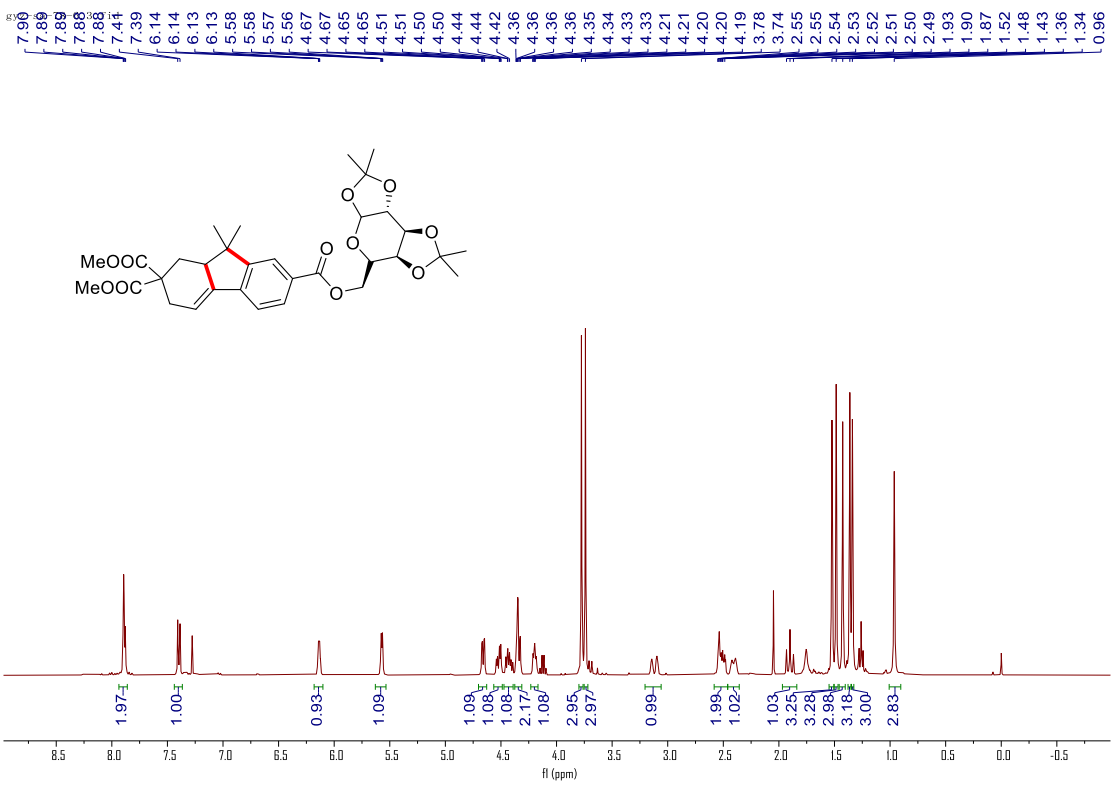
^{1}H NMR Spectrum of 58 ($CDCl_3$ as solvent, 400 MHz)



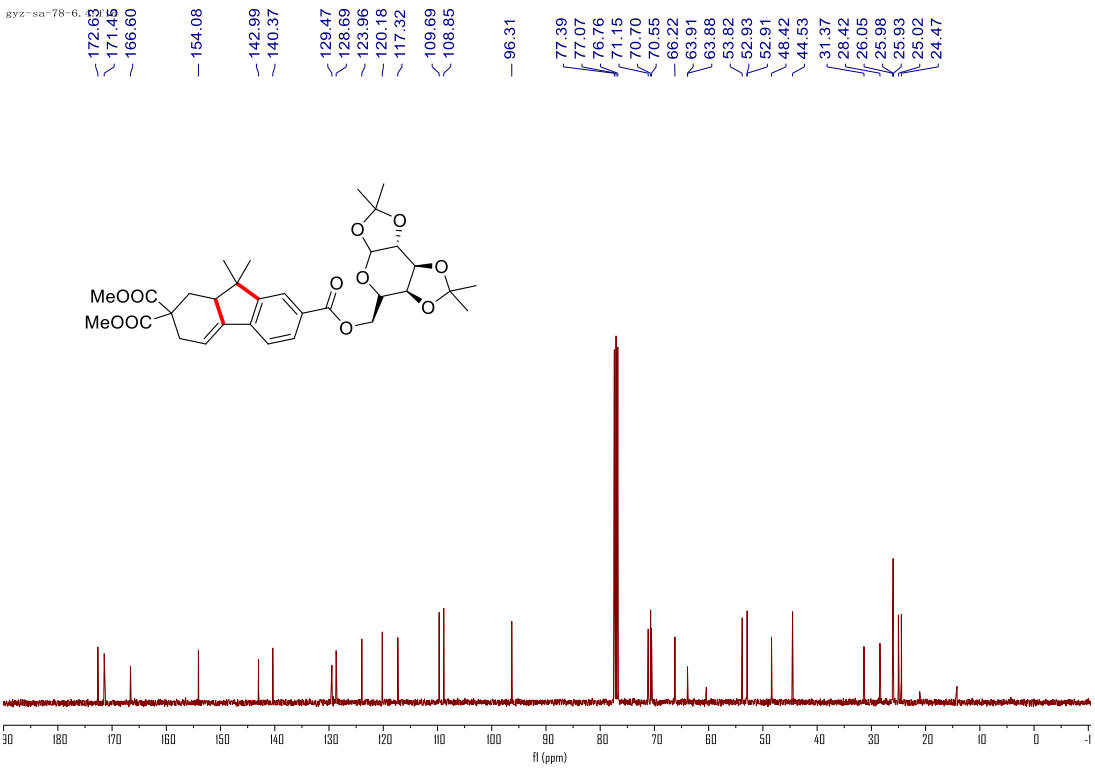
^{13}C {^{1}H} NMR Spectrum of 58 ($CDCl_3$ as solvent, 101 MHz)



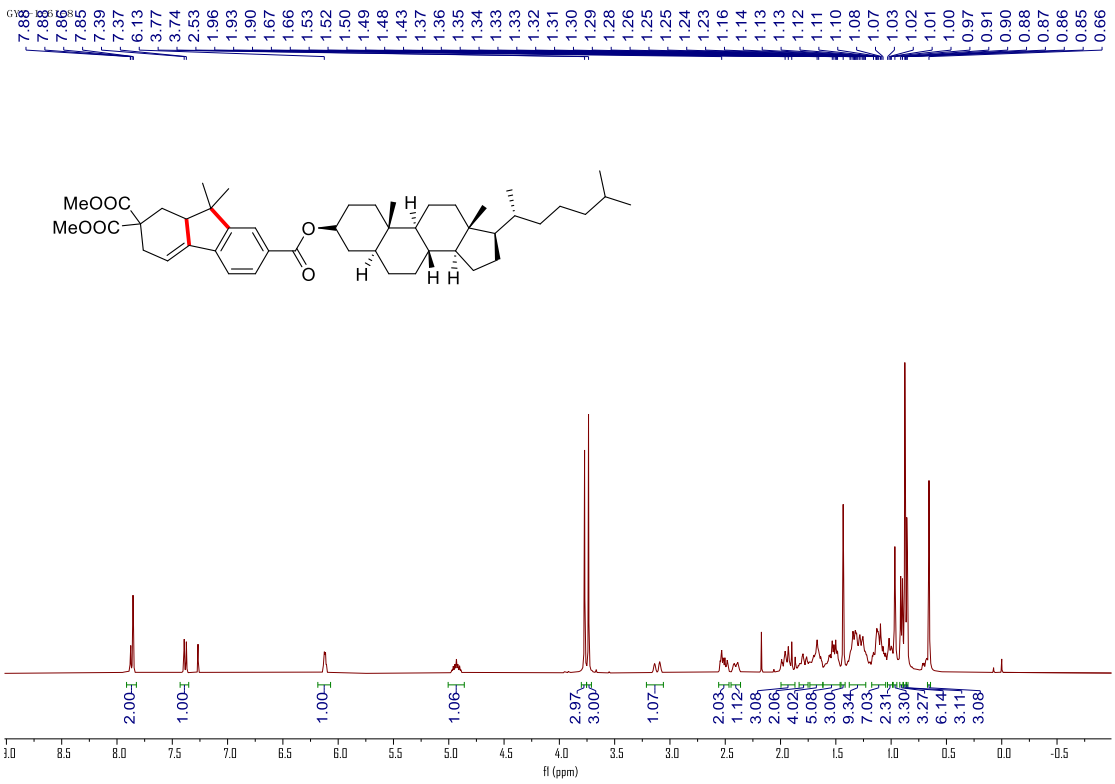
^{1}H NMR Spectrum of 59 ($CDCl_3$ as solvent, 400 MHz)



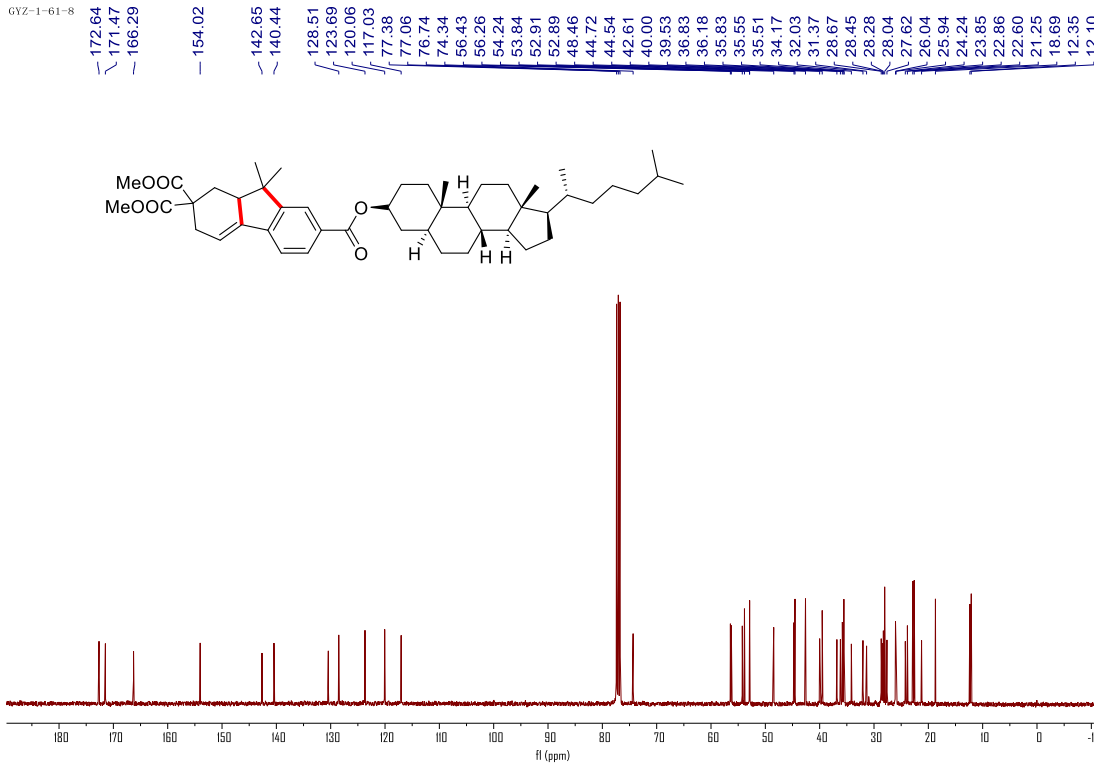
^{13}C {^{1}H} NMR Spectrum of 59 ($CDCl_3$ as solvent, 101 MHz)



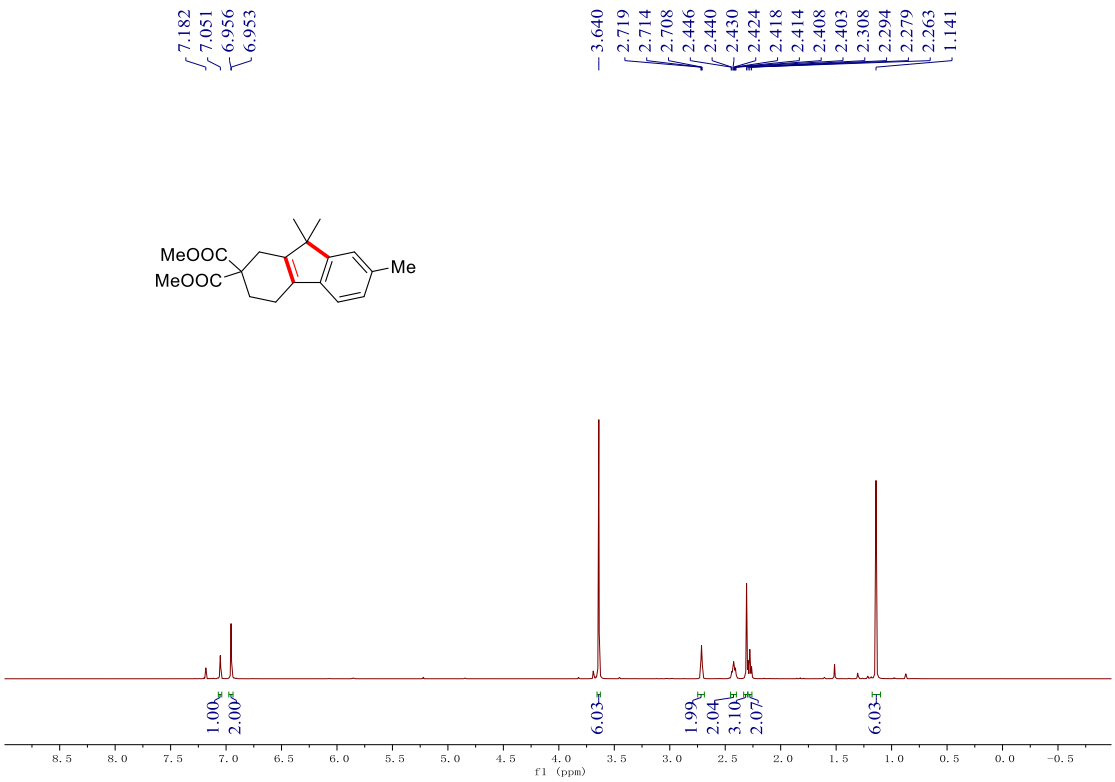
^{1}H NMR Spectrum of 60 ($CDCl_3$ as solvent, 400 MHz)



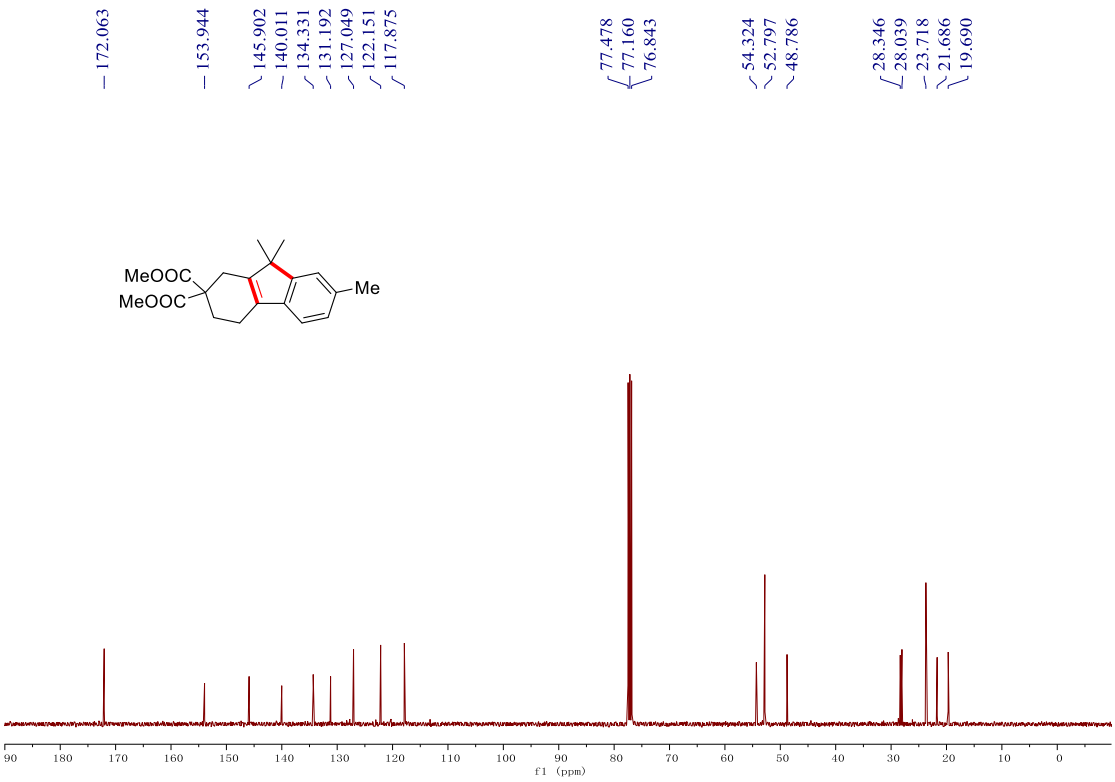
^{13}C {^{1}H} NMR Spectrum of 60 ($CDCl_3$ as solvent, 101 MHz)



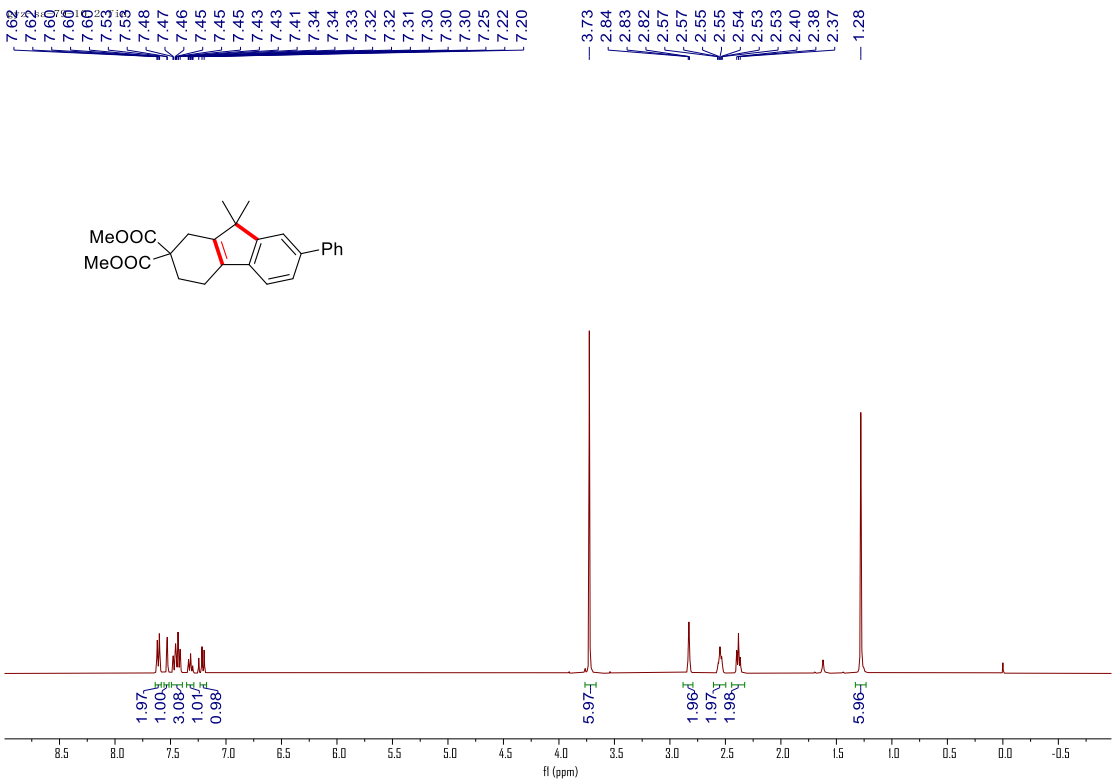
^{1}H NMR Spectrum of 61 ($CDCl_3$ as solvent, 400 MHz)



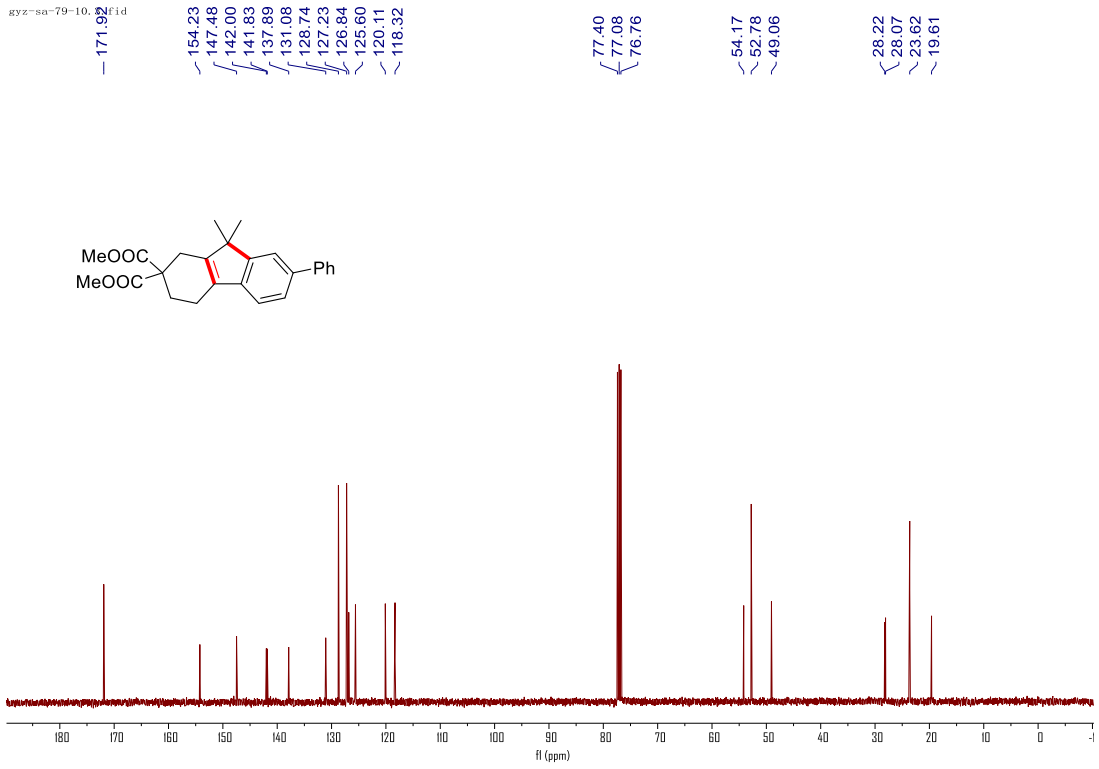
^{13}C {^{1}H} NMR Spectrum of 61 ($CDCl_3$ as solvent, 101 MHz)



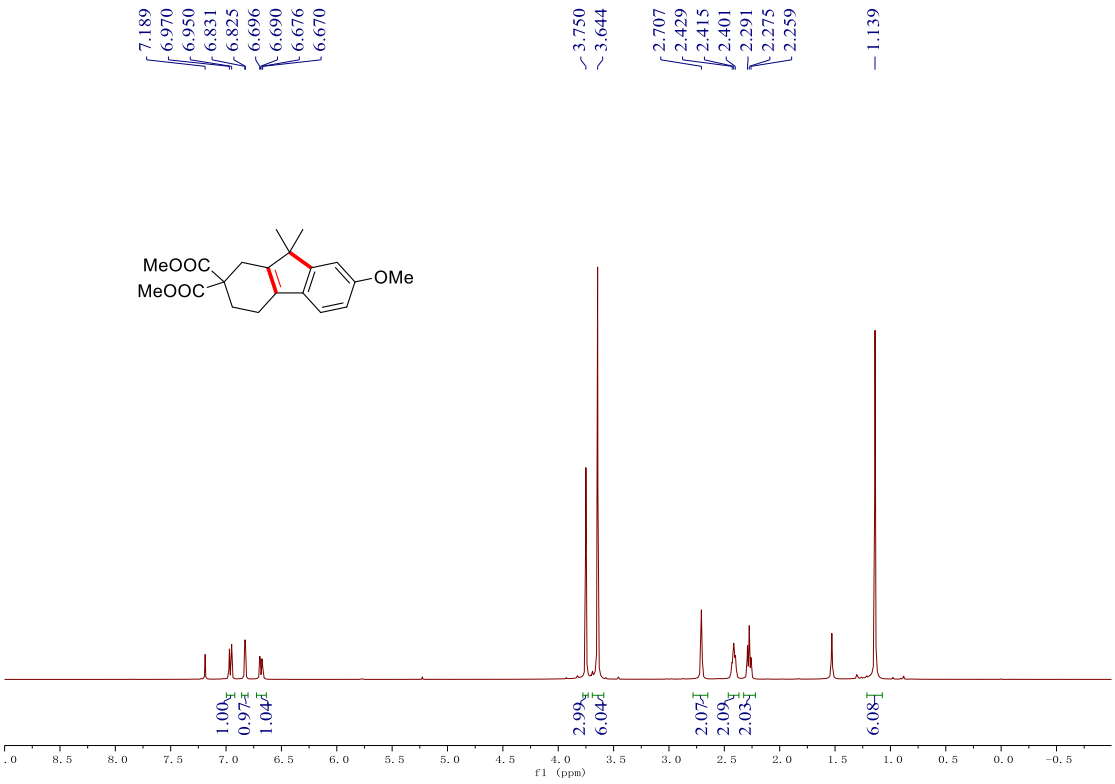
^{1}H NMR Spectrum of 62 ($CDCl_3$ as solvent, 400 MHz)



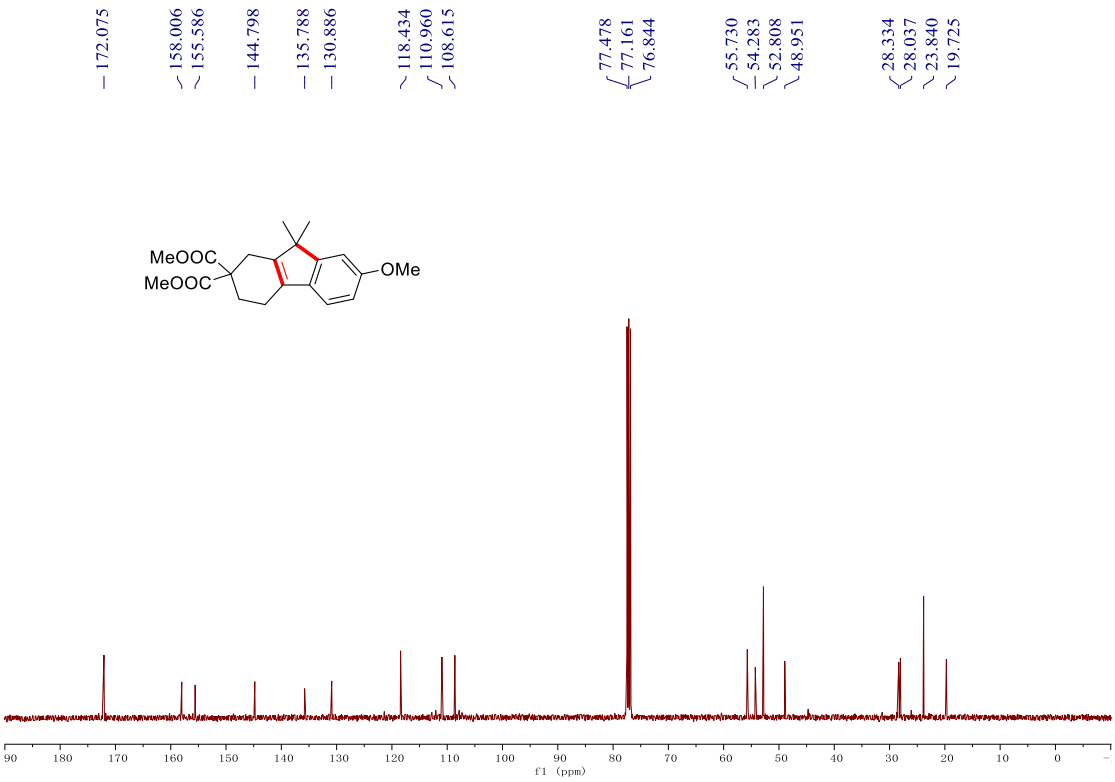
^{13}C {^{1}H} NMR Spectrum of 62 ($CDCl_3$ as solvent, 101 MHz)



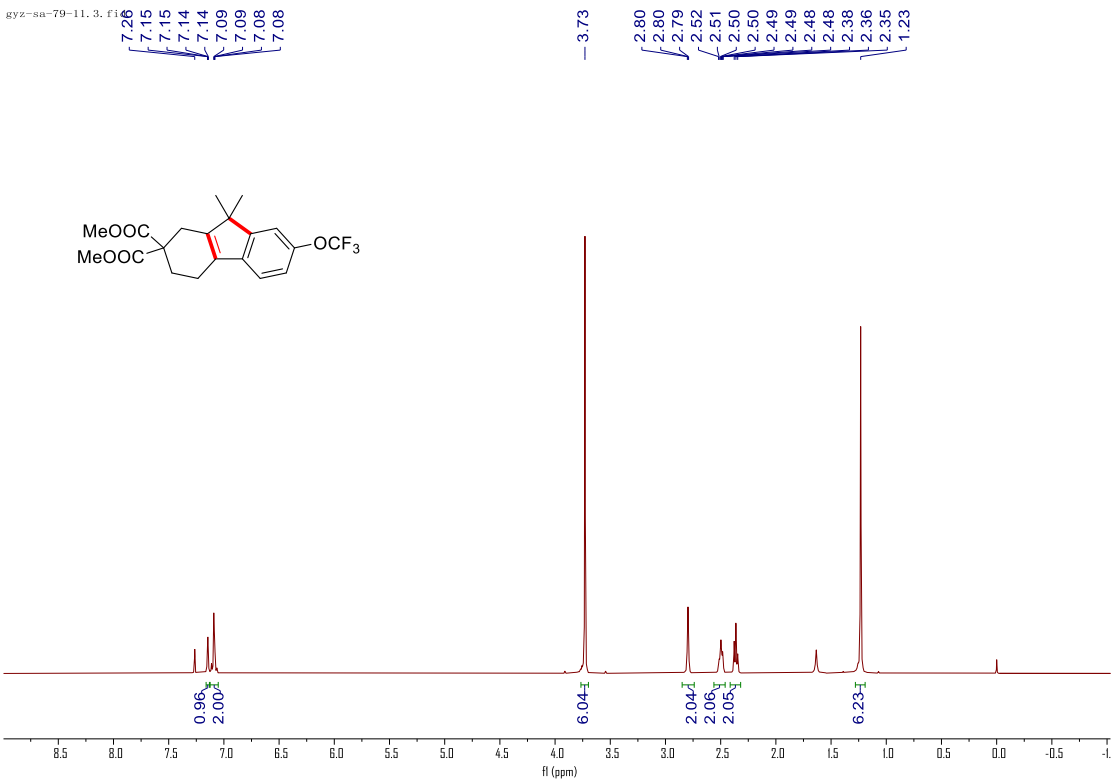
^{1}H NMR Spectrum of 63 ($CDCl_3$ as solvent, 400 MHz)



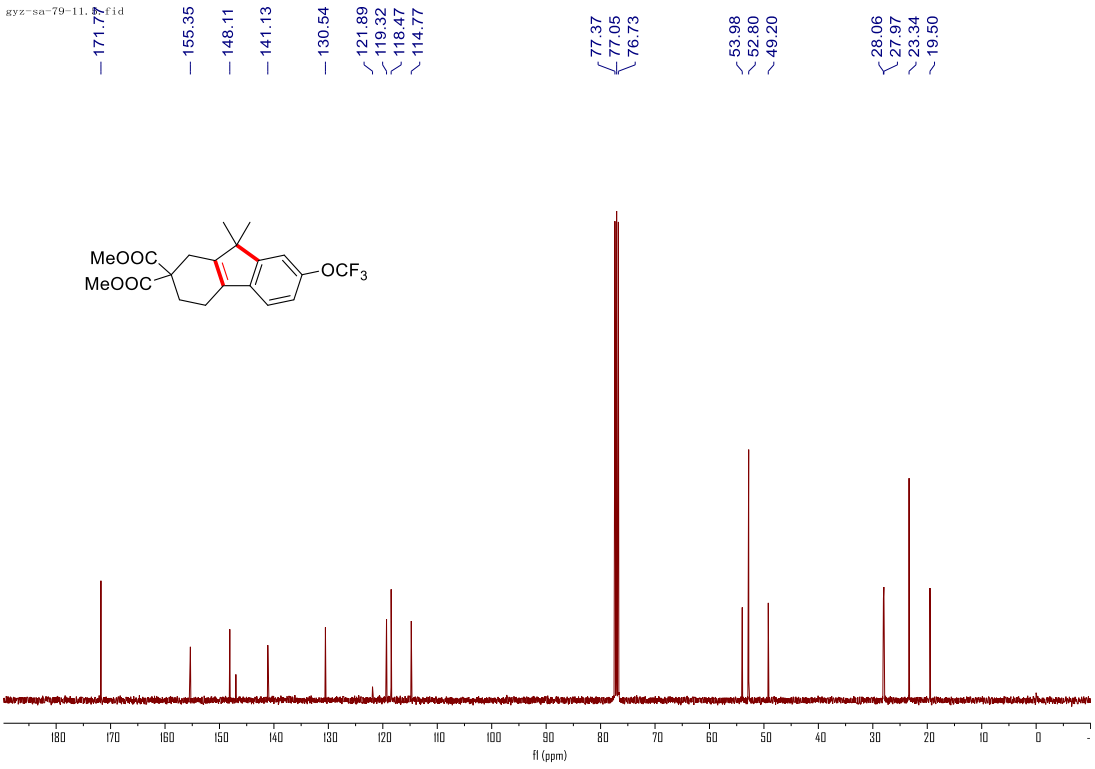
^{13}C {^{1}H} NMR Spectrum of 63 ($CDCl_3$ as solvent, 101 MHz)



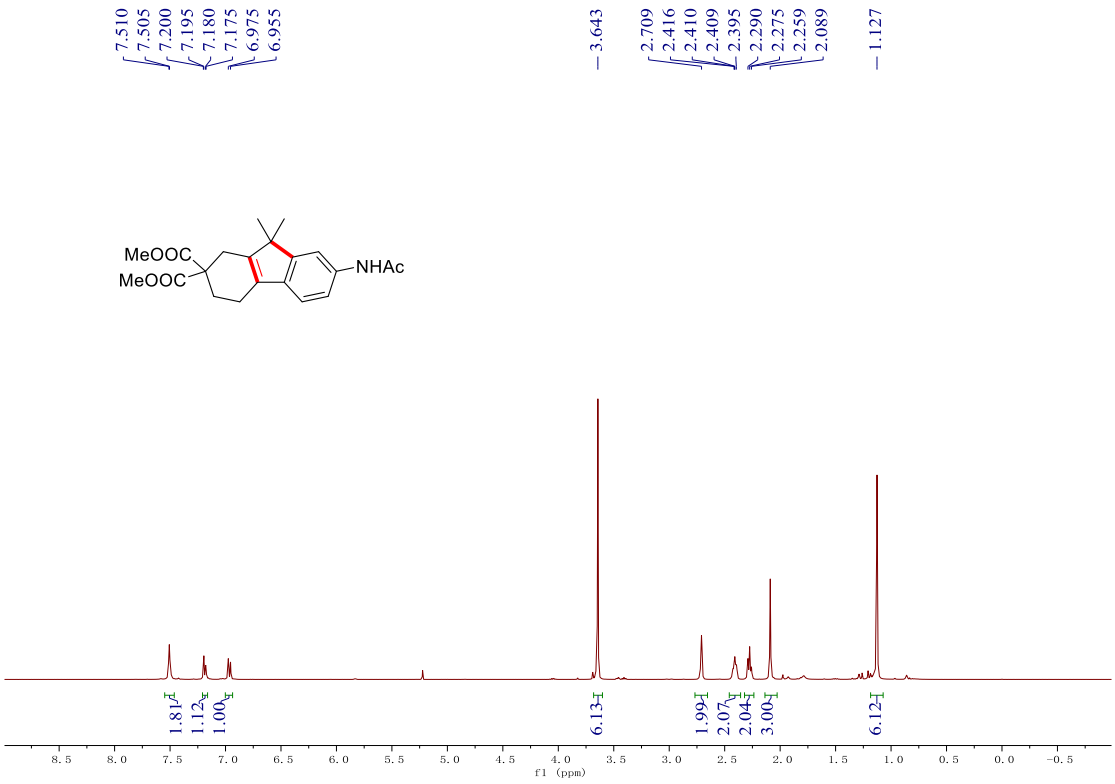
^{1}H NMR Spectrum of 64 ($CDCl_3$ as solvent, 400 MHz)



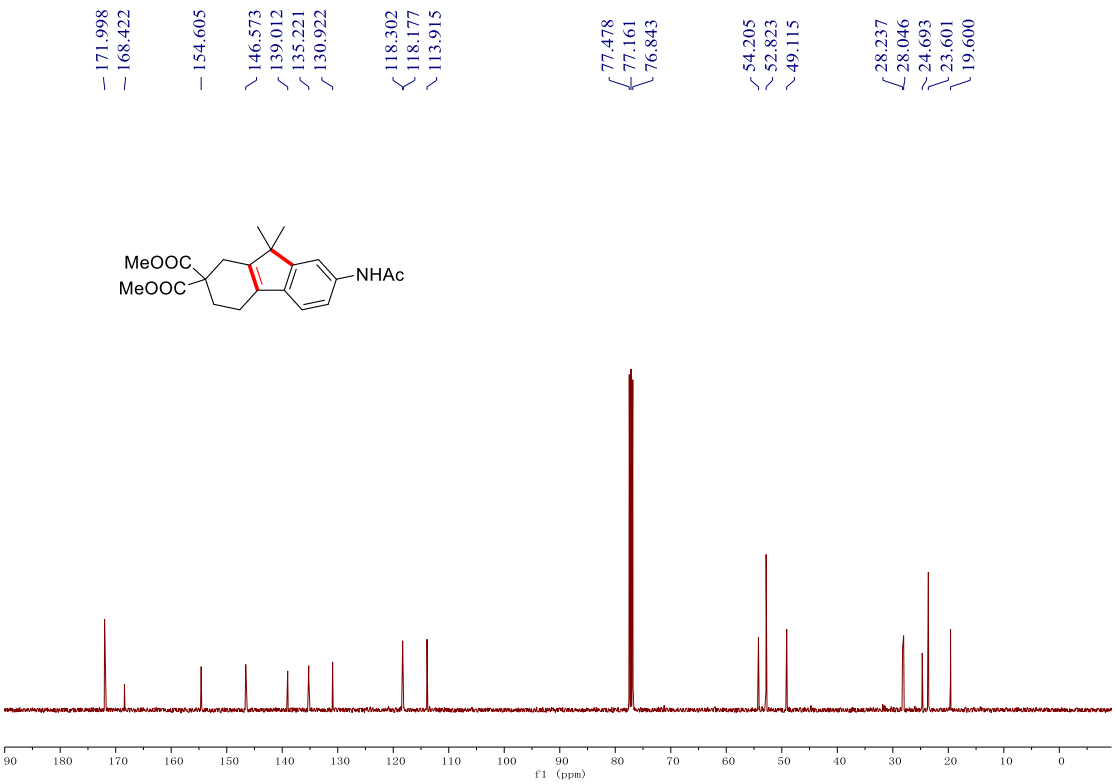
^{13}C {^{1}H} NMR Spectrum of 64 ($CDCl_3$ as solvent, 101 MHz)



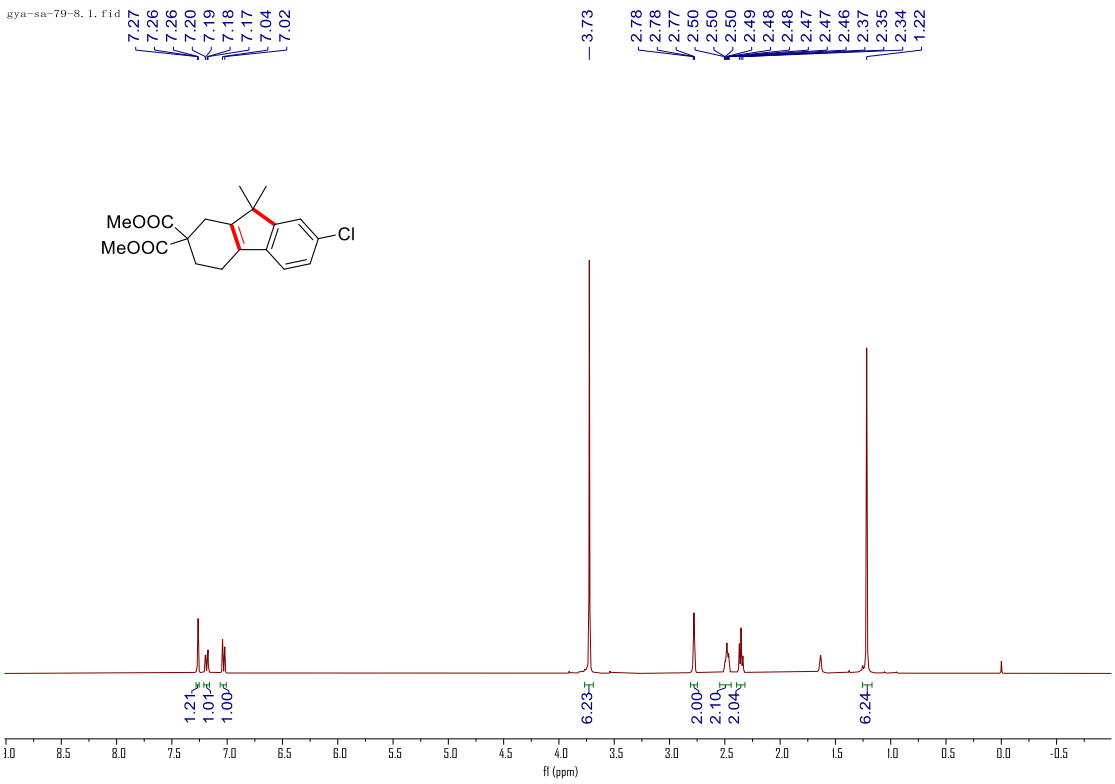
^{1}H NMR Spectrum of 65 ($CDCl_3$ as solvent, 400 MHz)



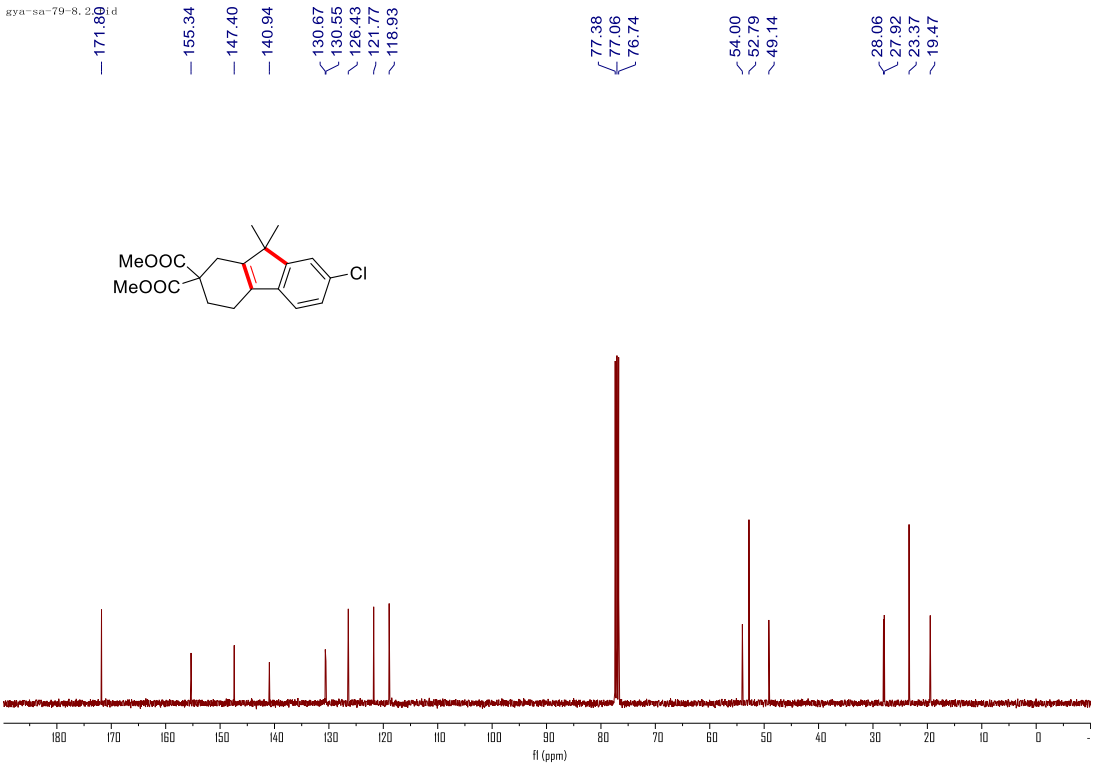
^{13}C {^{1}H} NMR Spectrum of 65 ($CDCl_3$ as solvent, 101 MHz)



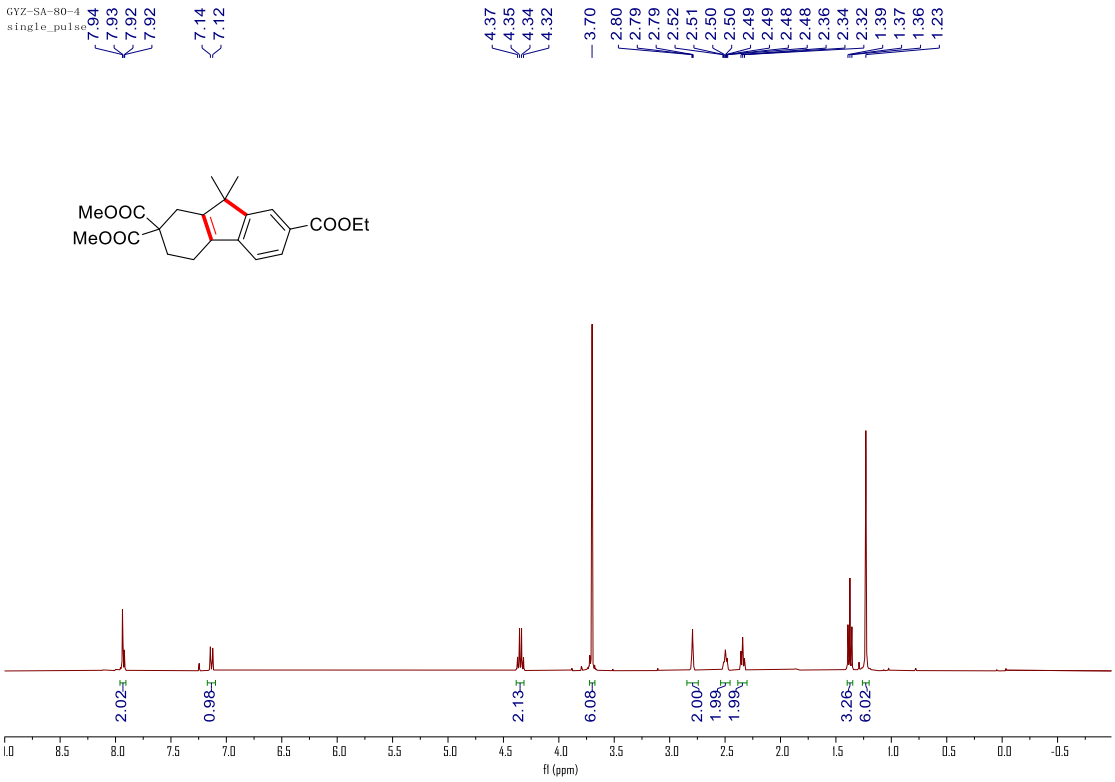
^{1}H NMR Spectrum of 66 ($CDCl_3$ as solvent, 400 MHz)



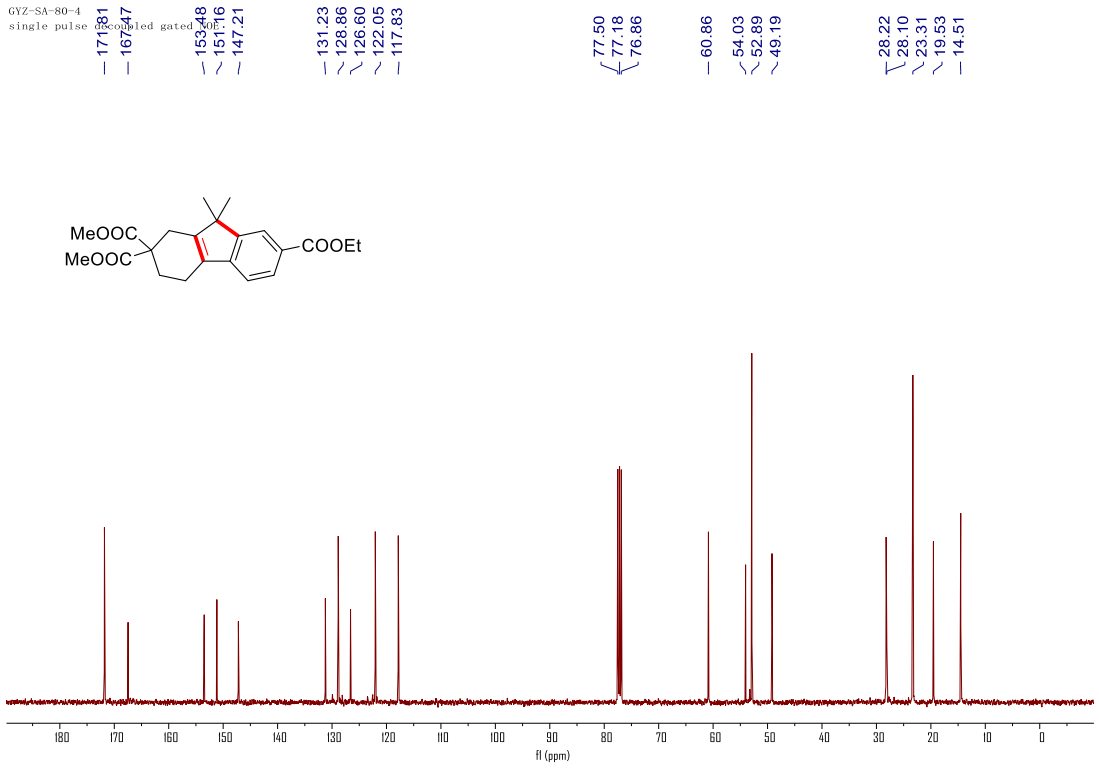
^{13}C {^{1}H} NMR Spectrum of 66 ($CDCl_3$ as solvent, 101 MHz)



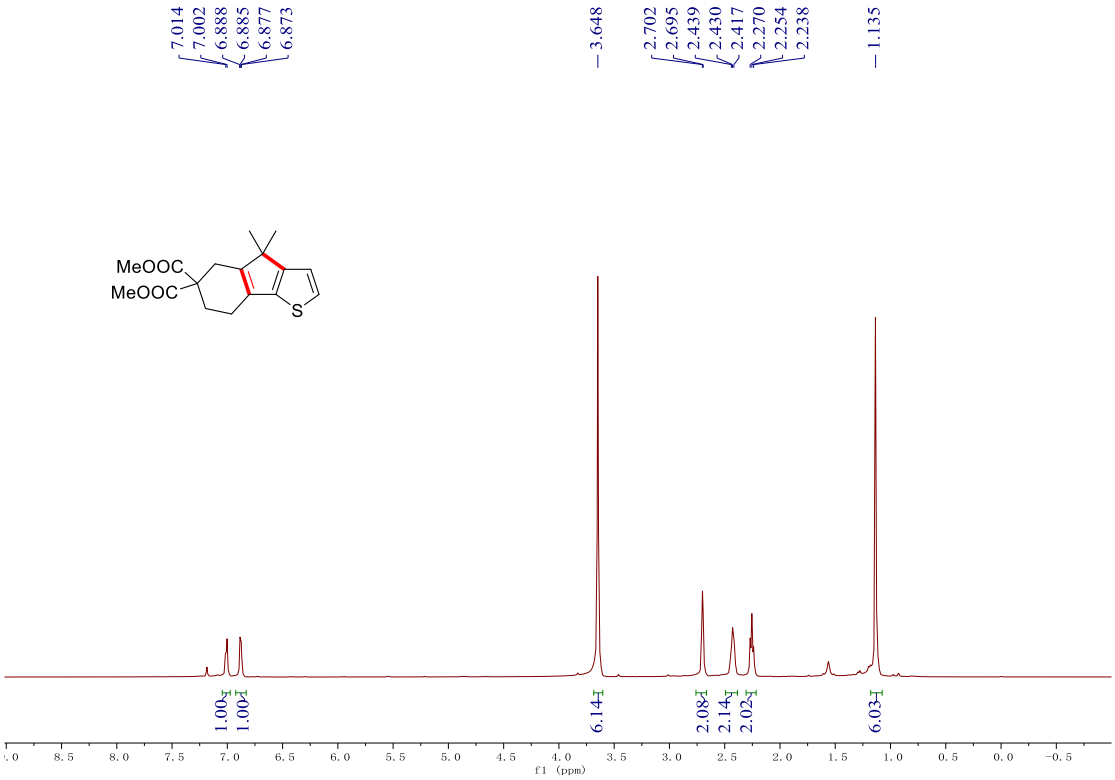
^{1}H NMR Spectrum of 67 ($CDCl_3$ as solvent, 400 MHz)



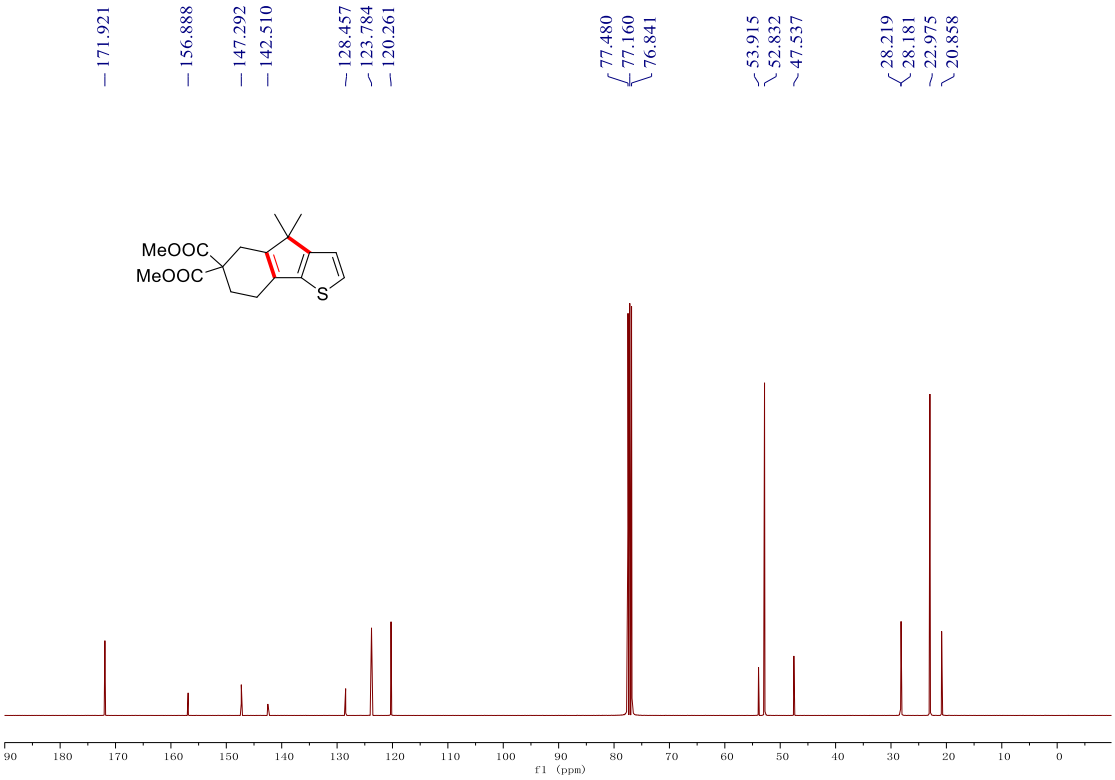
^{13}C {^{1}H} NMR Spectrum of 67 ($CDCl_3$ as solvent, 101 MHz)



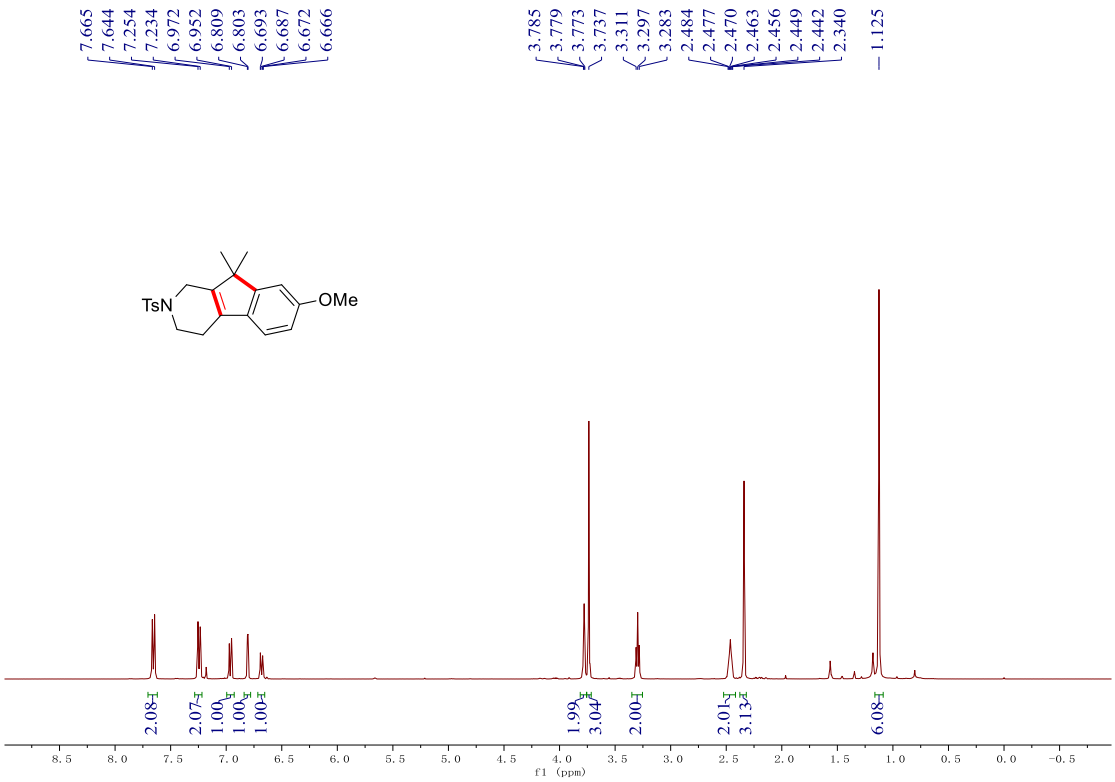
^{1}H NMR Spectrum of 68 ($CDCl_3$ as solvent, 400 MHz)



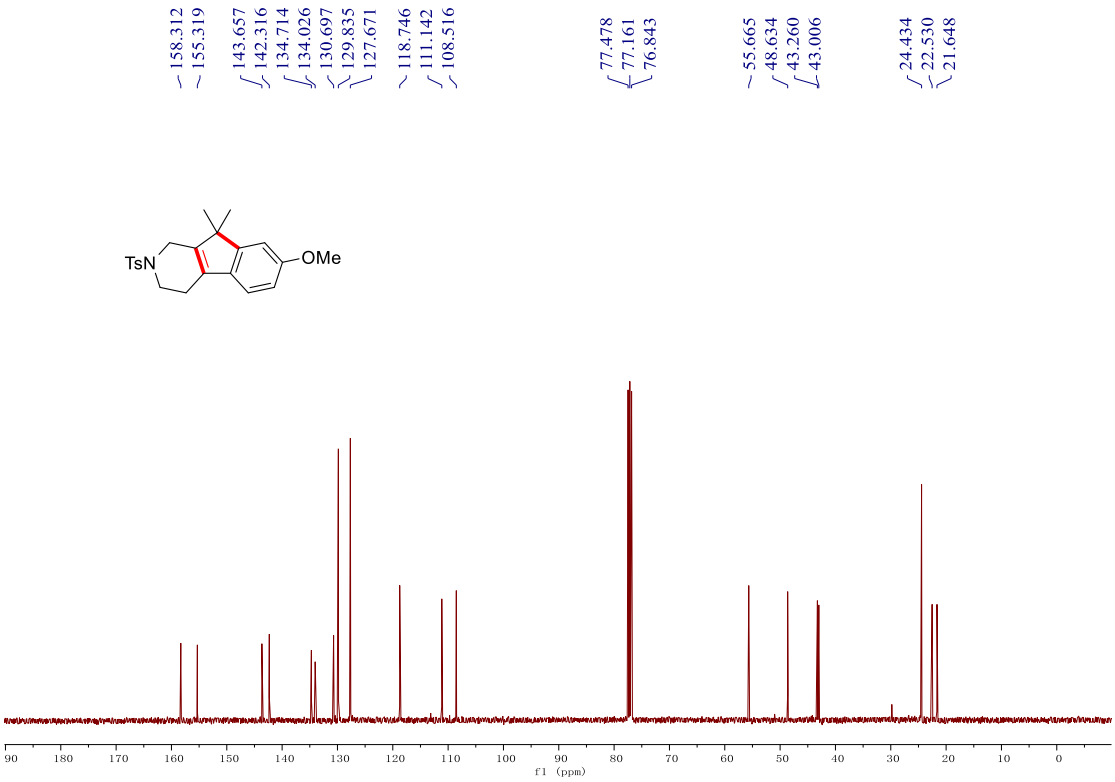
^{13}C {^{1}H} NMR Spectrum of 68 ($CDCl_3$ as solvent, 101 MHz)



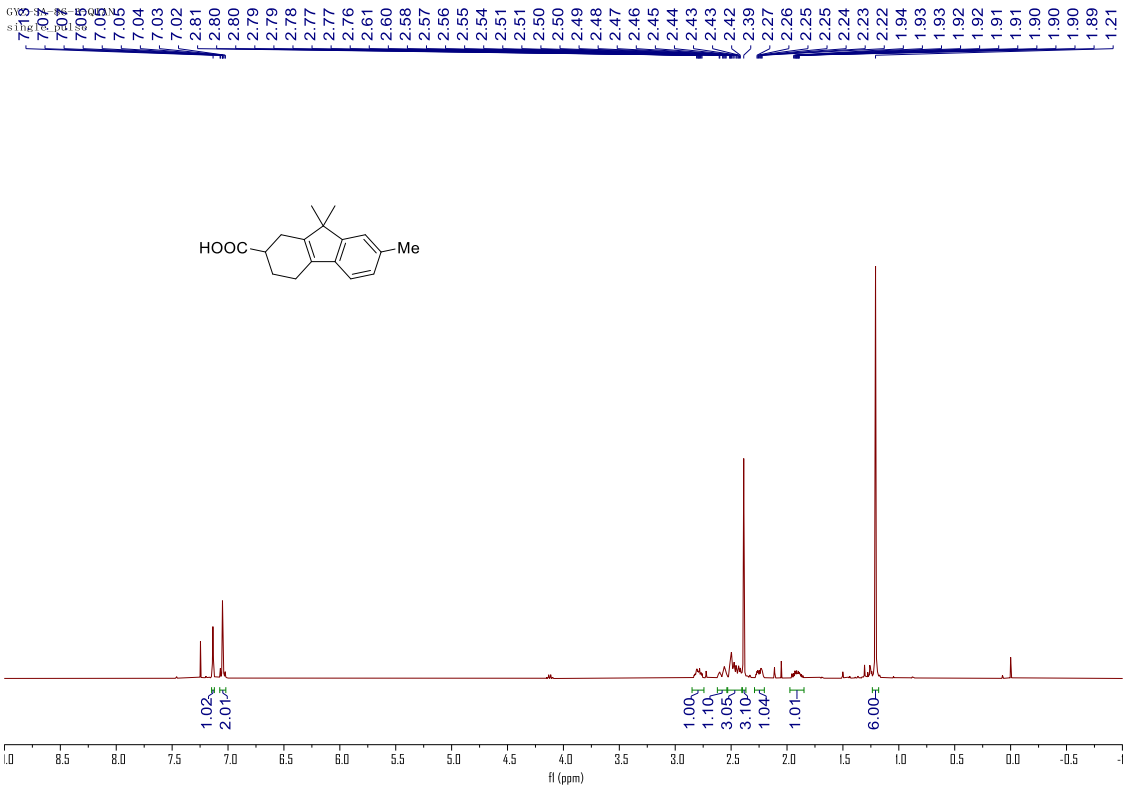
^{1}H NMR Spectrum of 69 ($CDCl_3$ as solvent, 400 MHz)



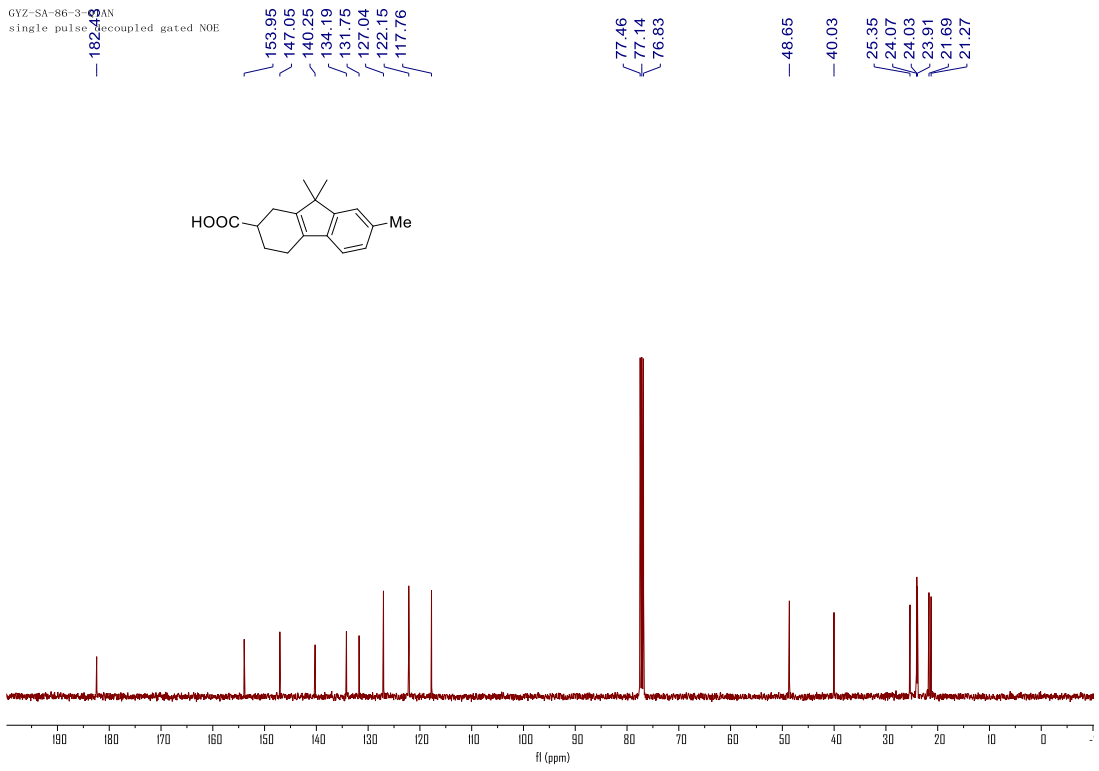
^{13}C {^{1}H} NMR Spectrum of 69 ($CDCl_3$ as solvent, 101 MHz)



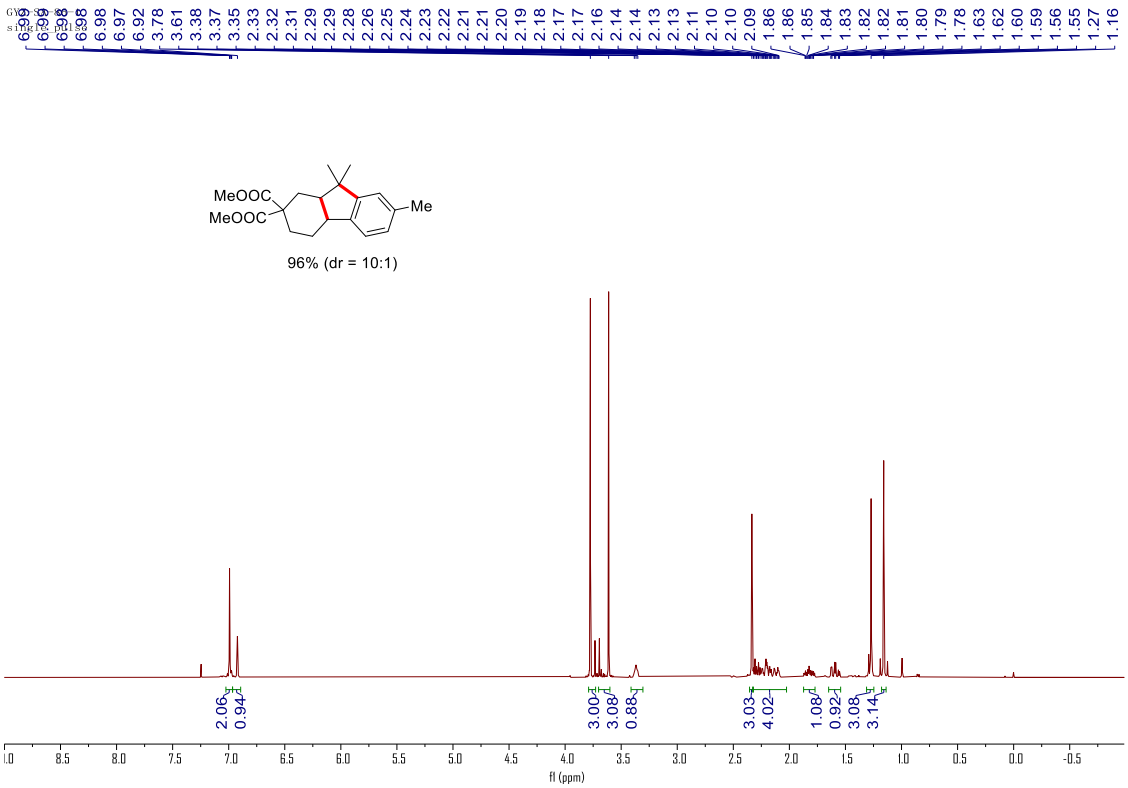
^{1}H NMR Spectrum of 70 ($CDCl_3$ as solvent, 400 MHz)



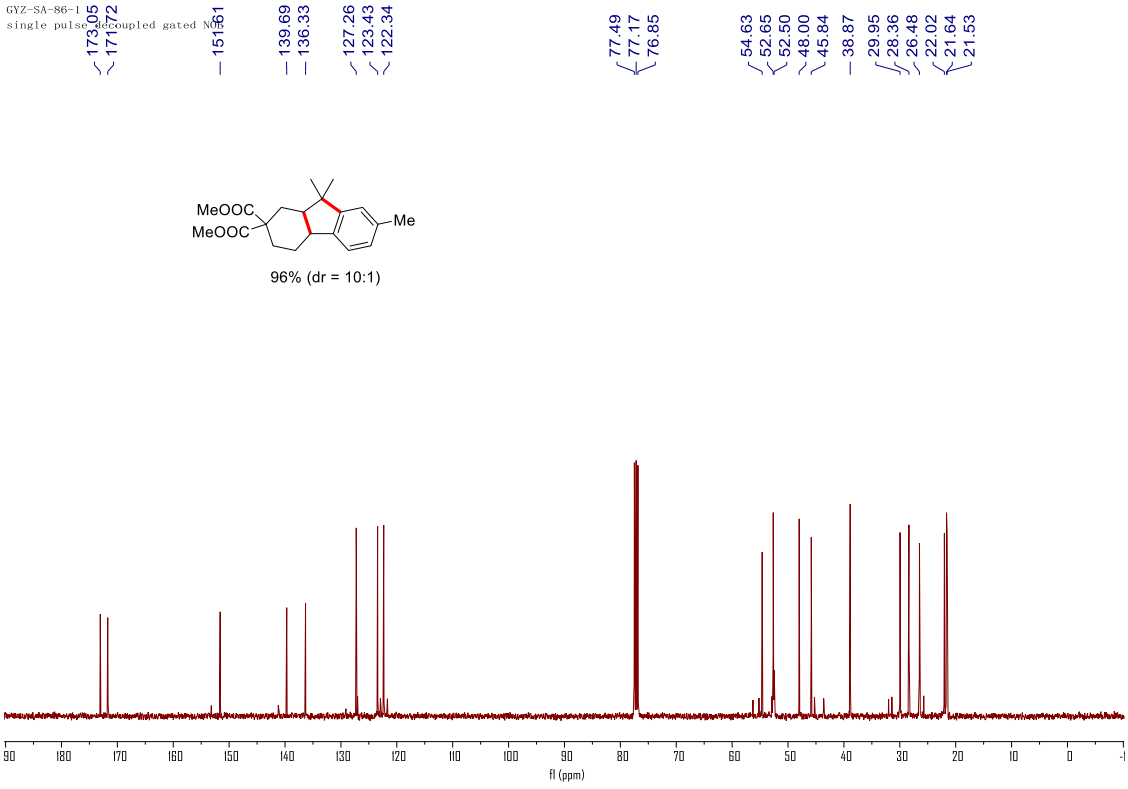
^{13}C {^{1}H} NMR Spectrum of 70 ($CDCl_3$ as solvent, 101 MHz)



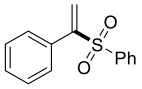
^{1}H NMR Spectrum of 71 ($CDCl_3$ as solvent, 400 MHz)

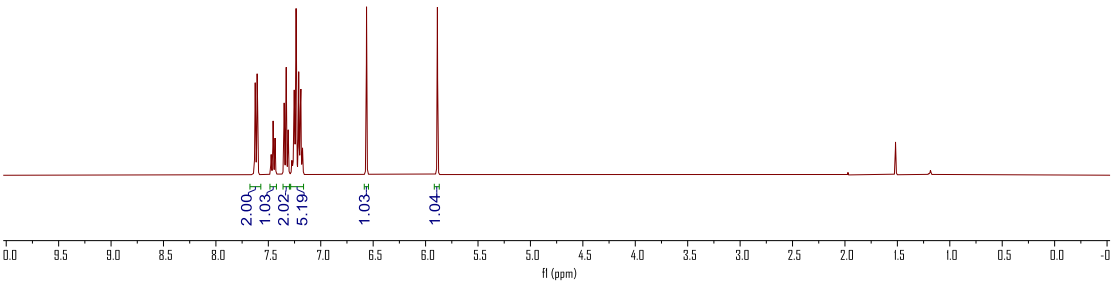


^{13}C {^{1}H} NMR Spectrum of 71 ($CDCl_3$ as solvent, 101 MHz)

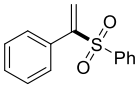


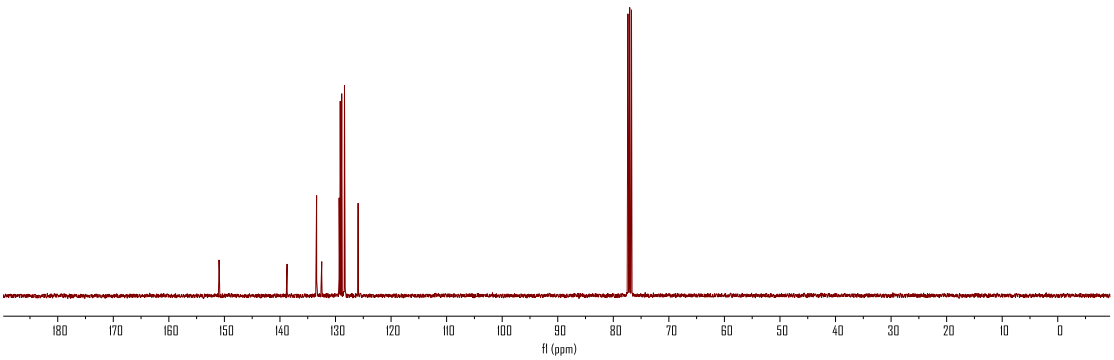
^{1}H NMR Spectrum of 72 ($CDCl_3$ as solvent, 400 MHz)



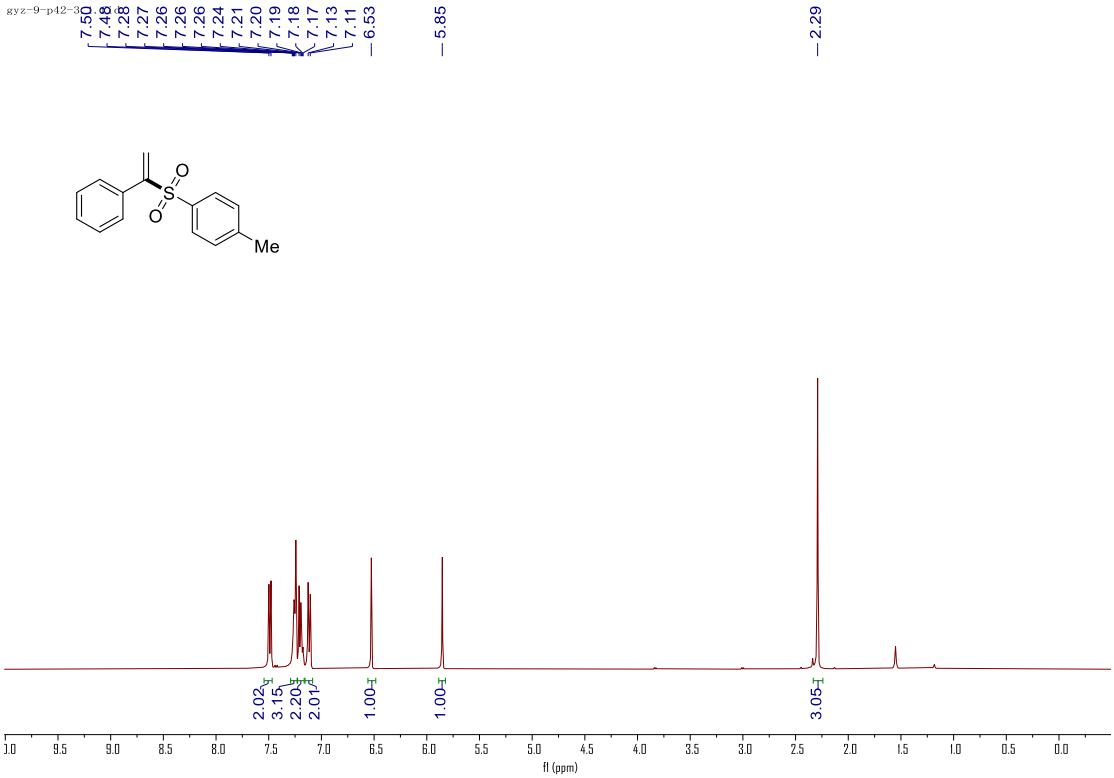


^{13}C {^{1}H} NMR Spectrum of 72 ($CDCl_3$ as solvent, 101 MHz)

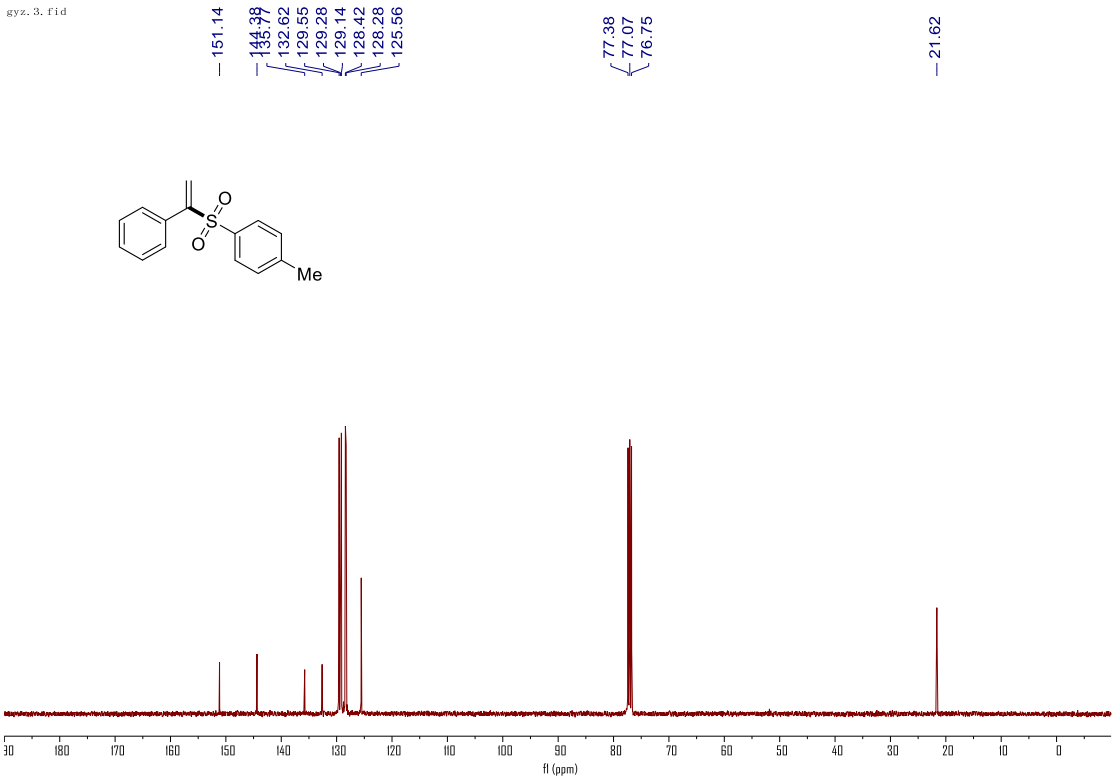




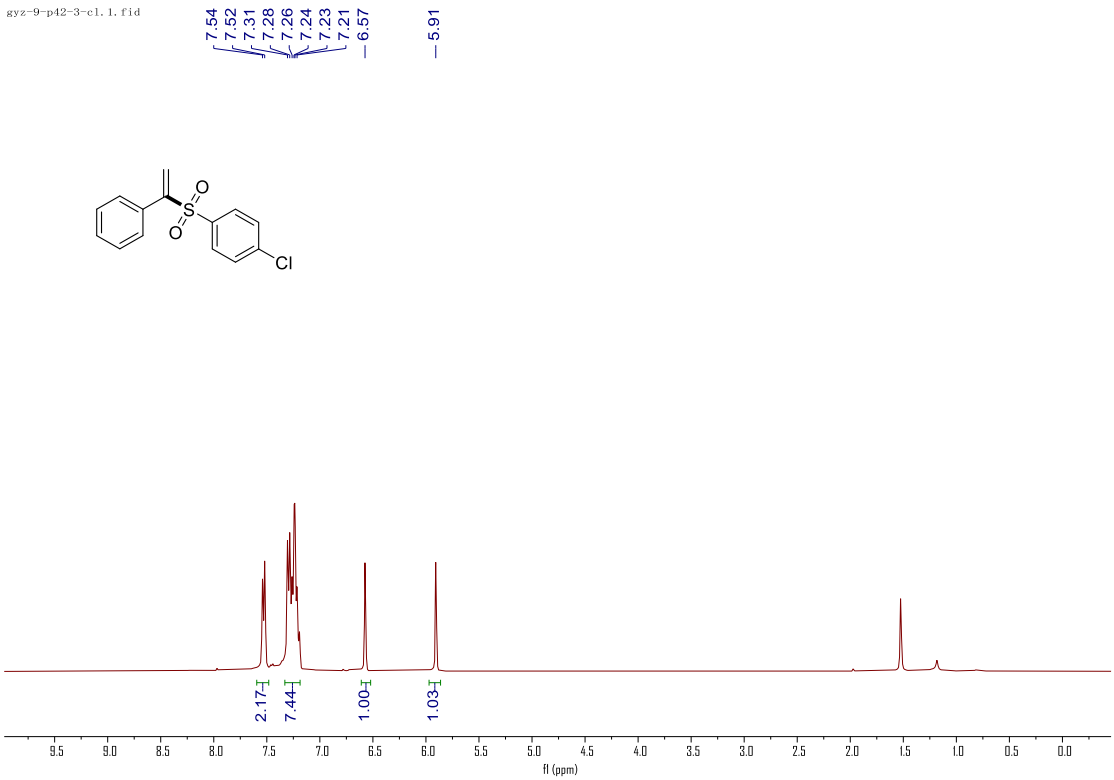
^{1}H NMR Spectrum of 73 ($CDCl_3$ as solvent, 400 MHz)



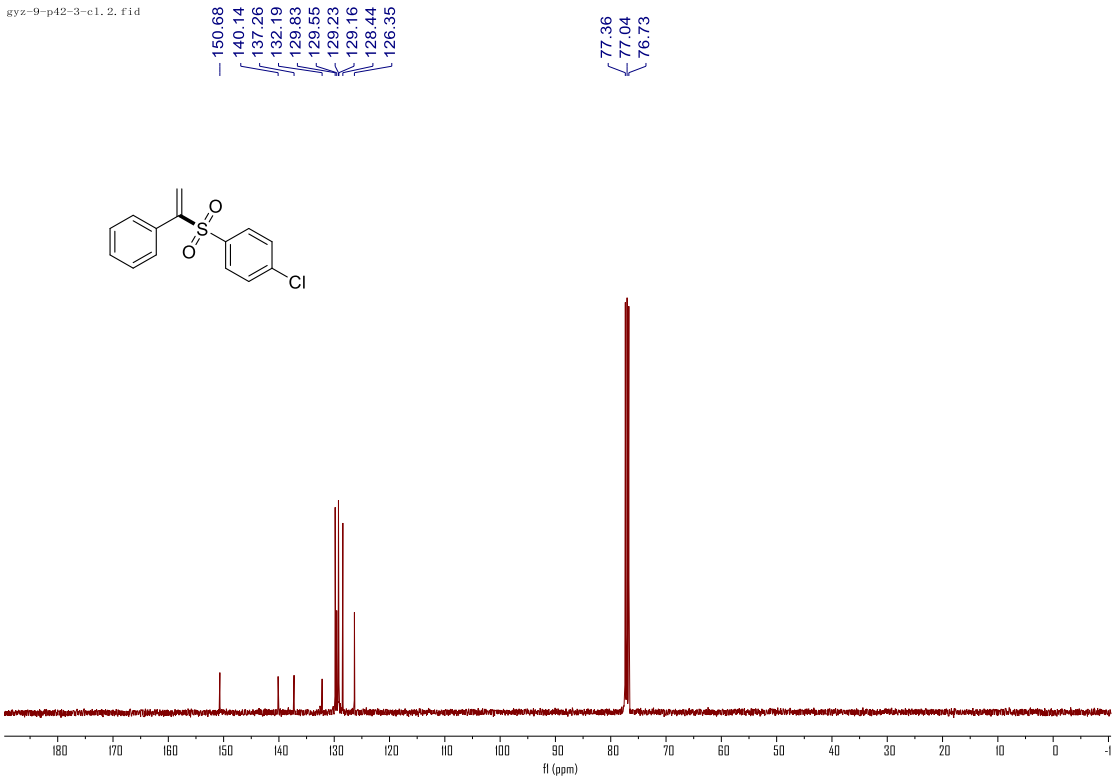
^{13}C {^{1}H} NMR Spectrum of 73 ($CDCl_3$ as solvent, 101 MHz)



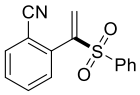
^{1}H NMR Spectrum of 74 ($CDCl_3$ as solvent, 400 MHz)

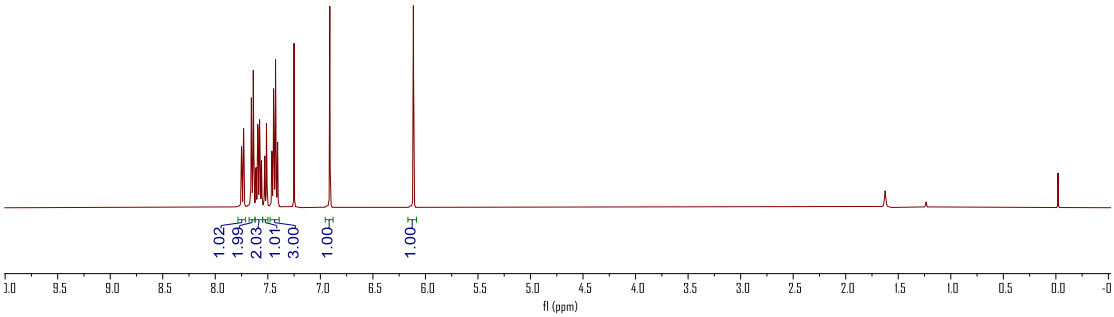


^{13}C {^{1}H} NMR Spectrum of 74 ($CDCl_3$ as solvent, 101 MHz)

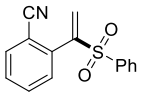


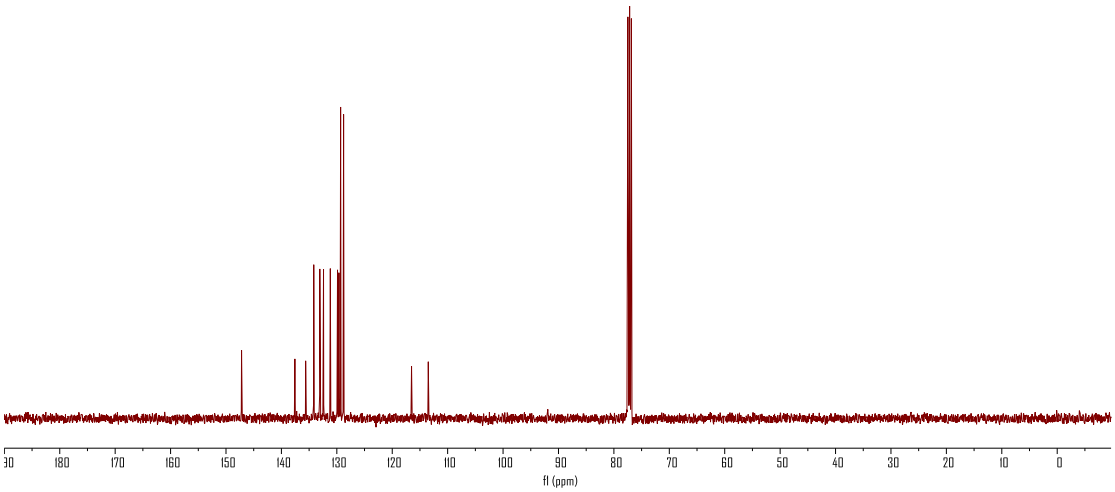
^{1}H NMR Spectrum of 75 ($CDCl_3$ as solvent, 400 MHz)



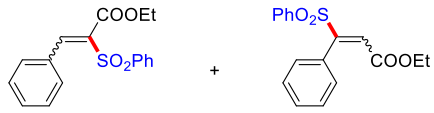


^{13}C {^{1}H} NMR Spectrum of 75 ($CDCl_3$ as solvent, 101 MHz)

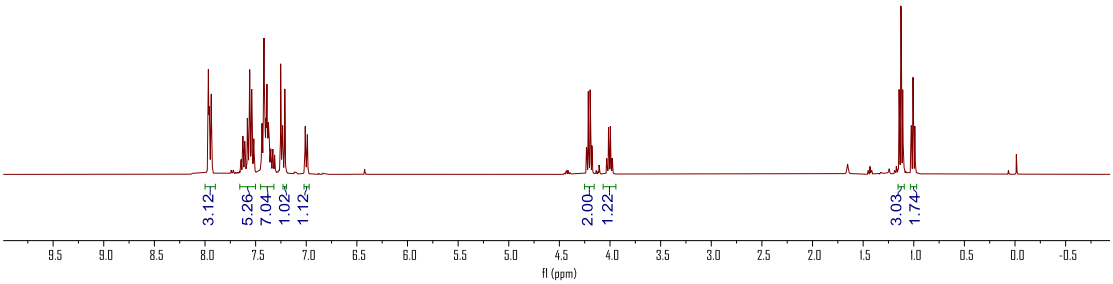




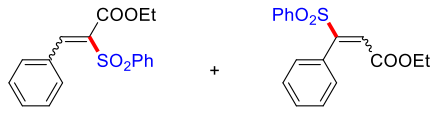
^{1}H NMR Spectrum of 76 and 77 ($CDCl_3$ as solvent, 400 MHz)



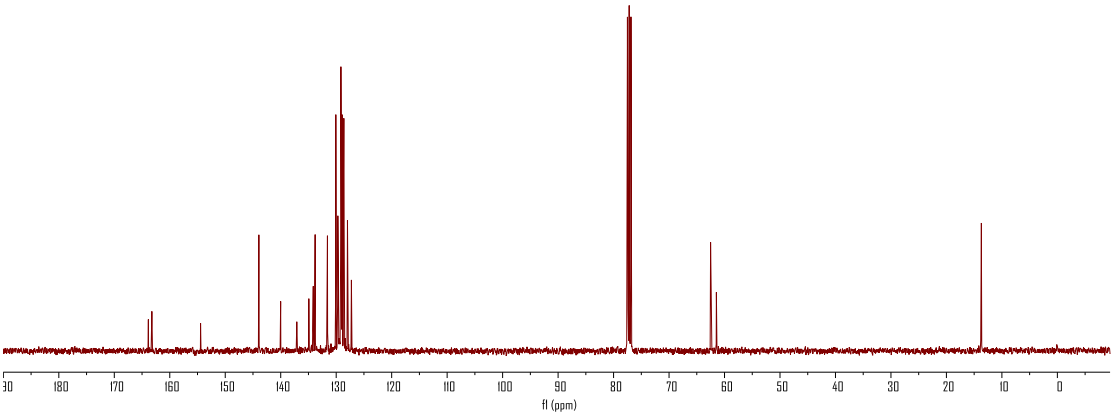
76, 55% **77**, 33%



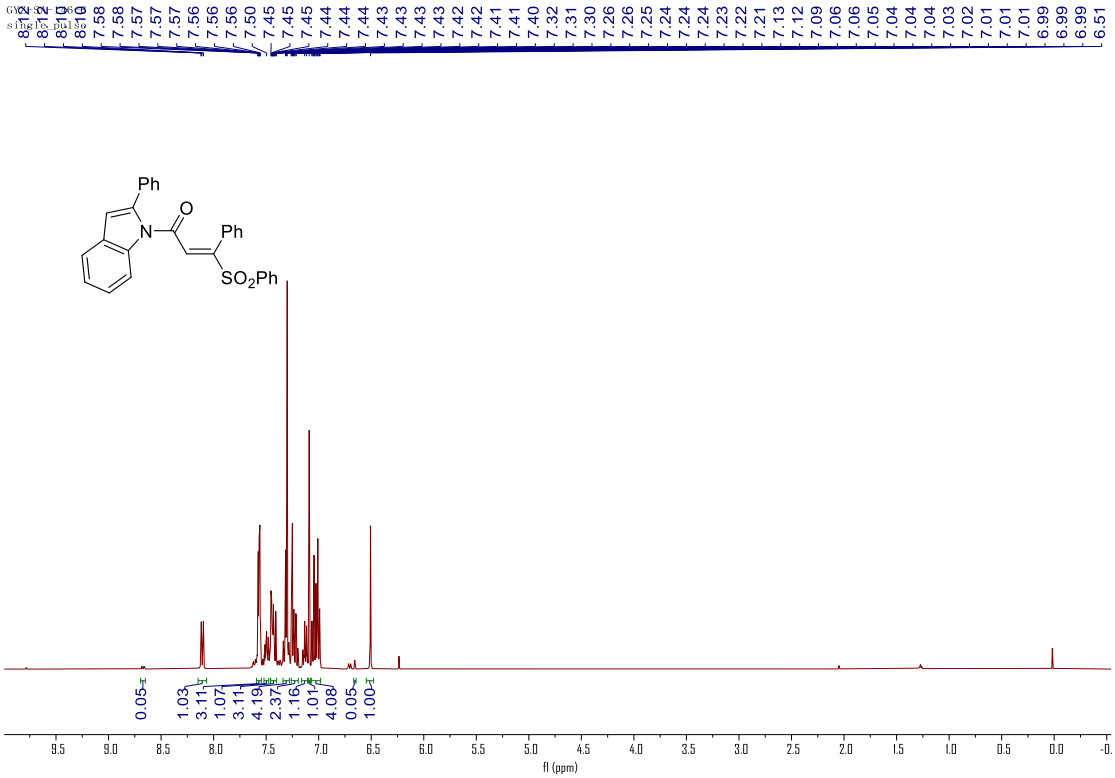
^{13}C {^{1}H} NMR Spectrum of 76 and 77 ($CDCl_3$ as solvent, 101 MHz)



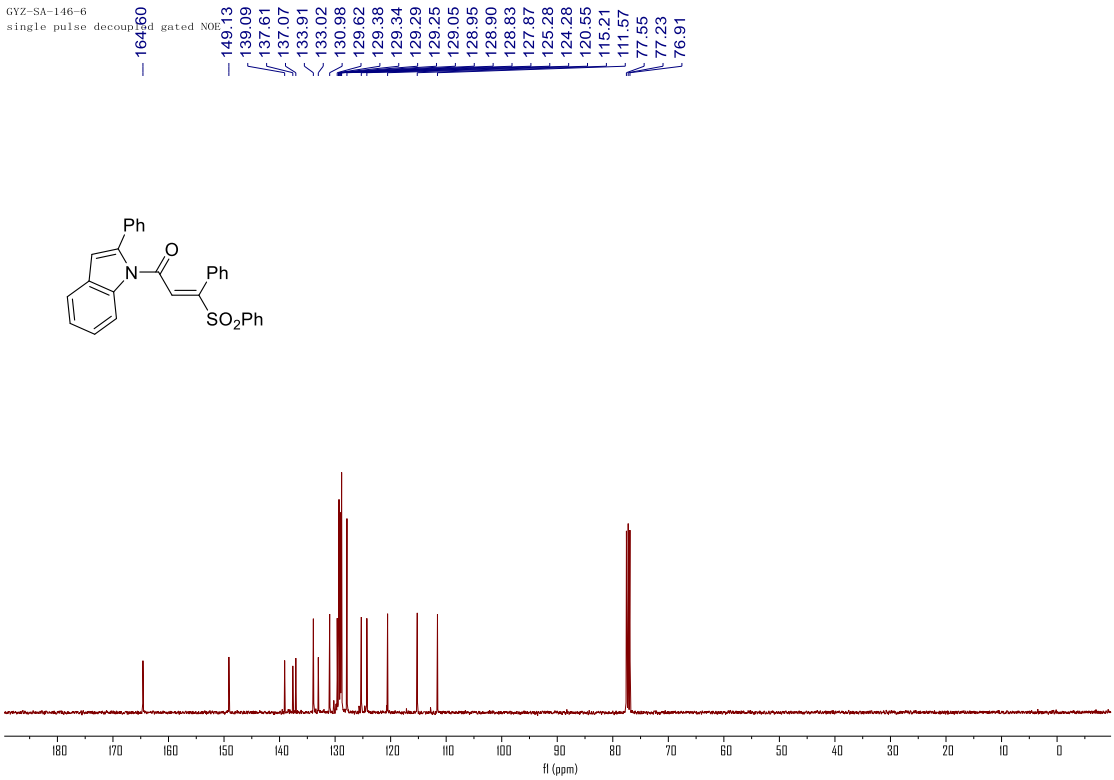
76, 55% **77**, 33%



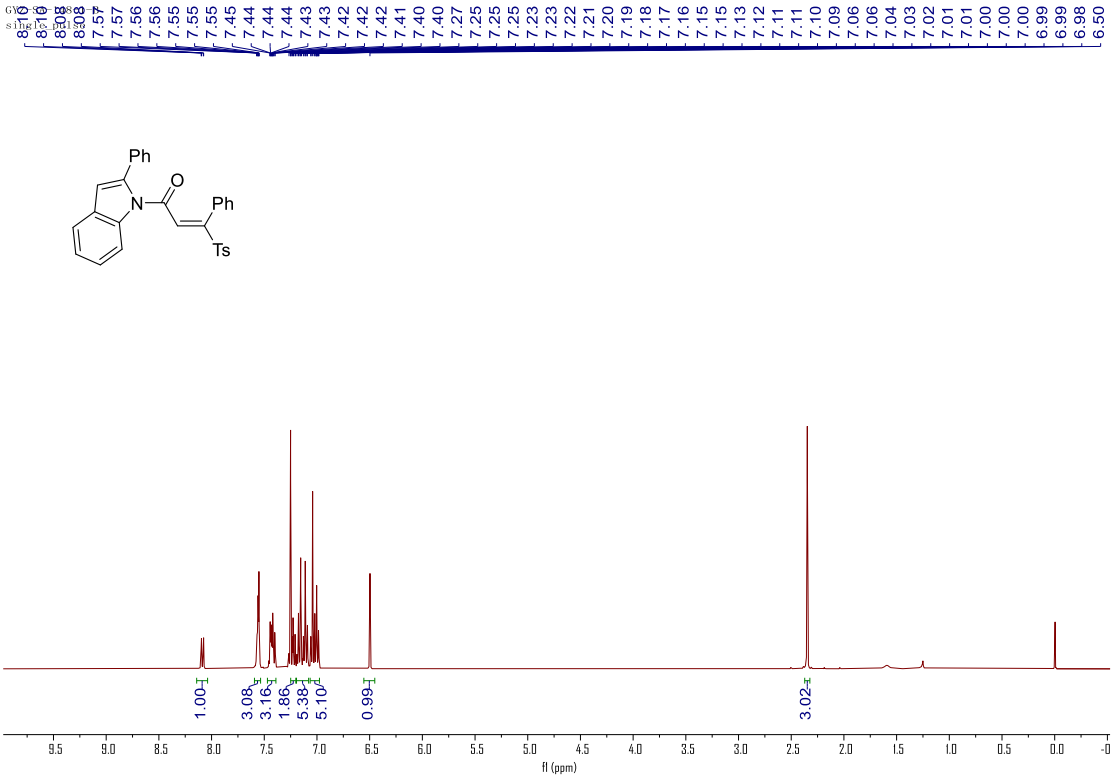
^{1}H NMR Spectrum of 78 ($CDCl_3$ as solvent, 400 MHz)



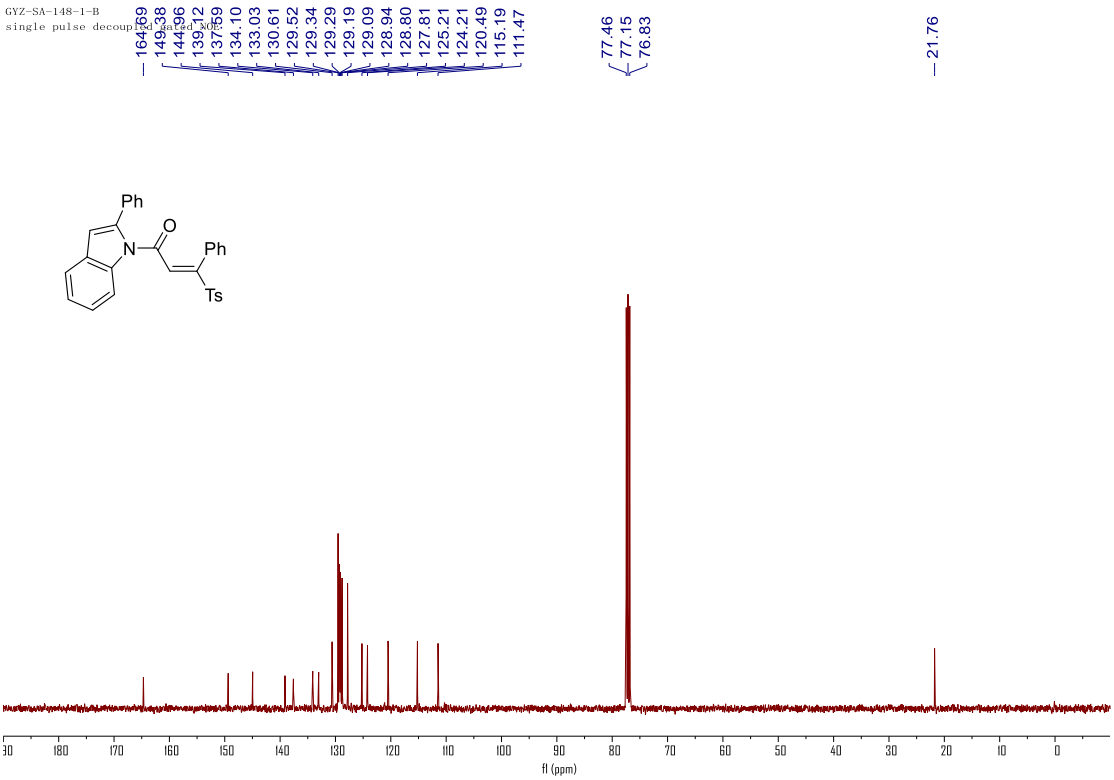
^{13}C {^{1}H} NMR Spectrum of 78 ($CDCl_3$ as solvent, 101 MHz)



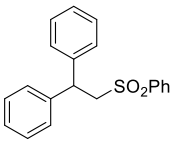
^{1}H NMR Spectrum of 79 ($CDCl_3$ as solvent, 400 MHz)

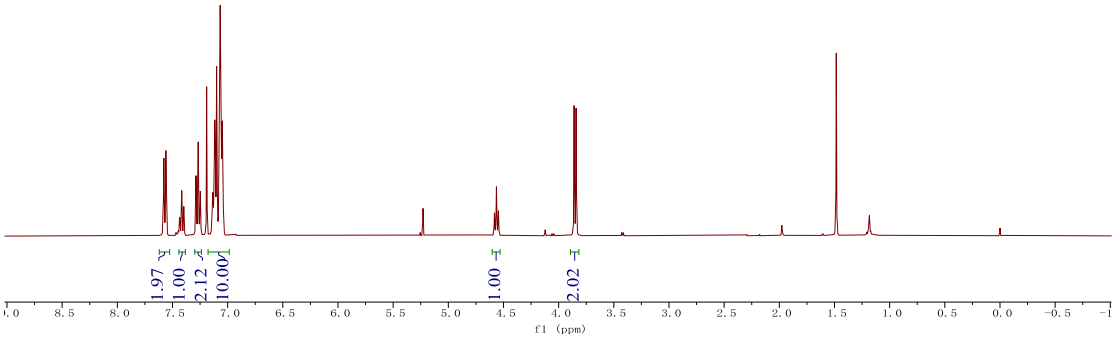


^{13}C {^{1}H} NMR Spectrum of 79 ($CDCl_3$ as solvent, 101 MHz)

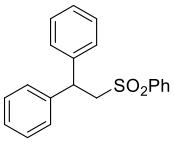


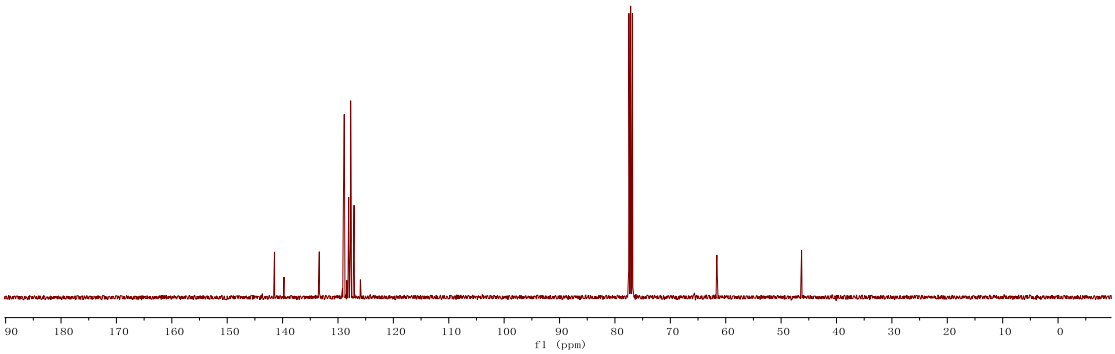
^{1}H NMR Spectrum of 80 ($CDCl_3$ as solvent, 400 MHz)



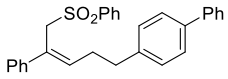


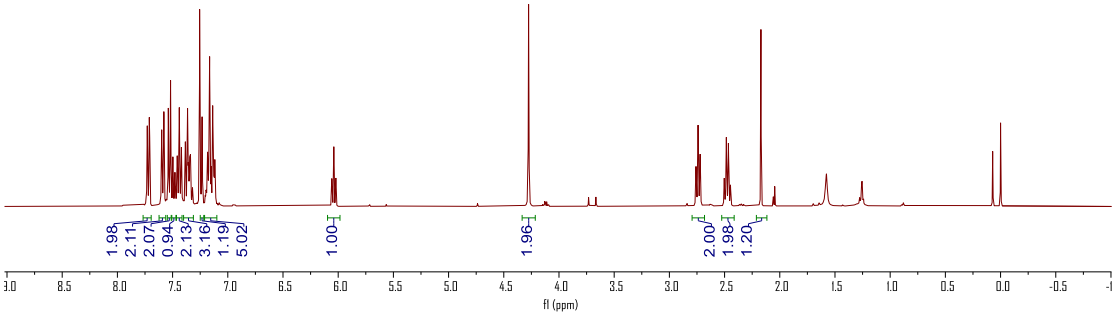
^{13}C {^{1}H} NMR Spectrum of 80 ($CDCl_3$ as solvent, 101 MHz)



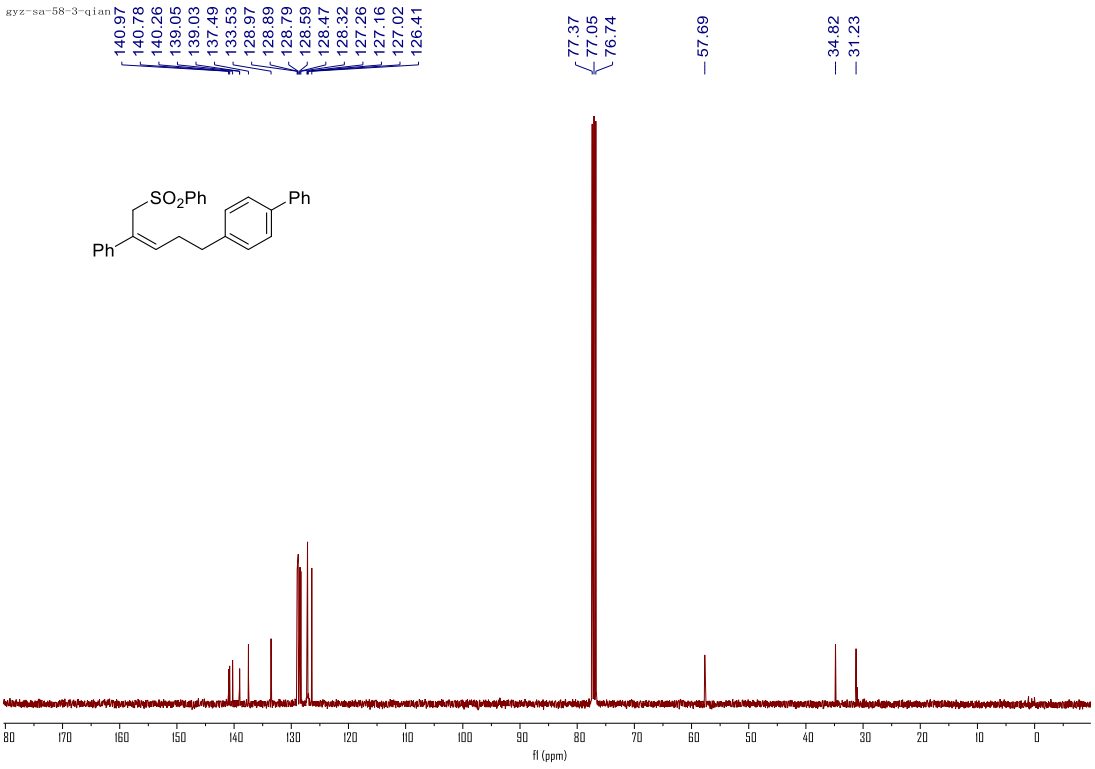


^{1}H NMR Spectrum of 82 ($CDCl_3$ as solvent, 400 MHz)



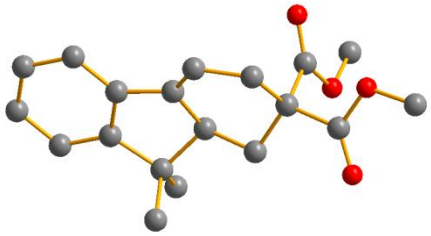


^{13}C {^{1}H} NMR Spectrum of 82 ($CDCl_3$ as solvent, 101 MHz)



5. X-Ray Crystallographic Spectrum of 8, 31 and 79

Crystallographic spectrum of product 8 (CCDC number: 2203604)



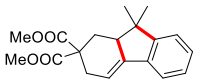
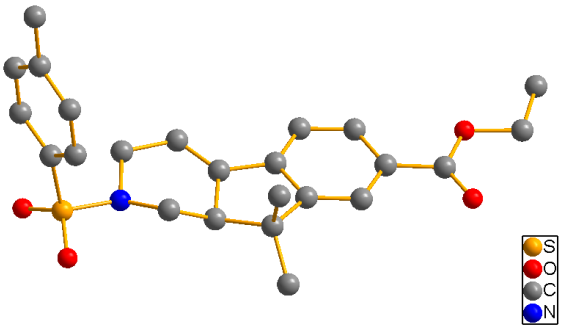


Table S1. Crystal data and structure refinement for GYZ2.

Identification code	gyz2	
Empirical formula	C19H22O4	
Formula weight	314.37	
Temperature	153(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 23.0076(2) Å	= 90 °.
	b = 7.76760(10) Å	= 99.8830(10) °.
	c = 18.0741(2) Å	= 90 °.
Volume	3182.16(6) $Å^3$	
Z	8	
Density (calculated)	1.312 Mg/m^3	
Absorption coefficient	0.739 mm^{-1}	
F(000)	1344	
Crystal size	0.1 x 0.1 x 0.1 mm^3	
Theta range for data collection	3.90 to 66.58 °.	
Index ranges	-27<=h<=27, -9<=k<=3, -21<=l<=20	
Reflections collected	8524	
Independent reflections	2777 [R(int) = 0.0230]	
Completeness to theta = 66.58 °	98.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1 and 0.50432	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2777 / 0 / 208	
Goodness-of-fit on F^2	1.104	
Final R indices [I>2sigma(I)]	R1 = 0.0421, wR2 = 0.1104	
R indices (all data)	R1 = 0.0446, wR2 = 0.1145	
Largest diff. peak and hole	0.287 and -0.286 $e.Å^{-3}$	

Crystallographic spectrum of product 31 (CCDC number: 2203603)



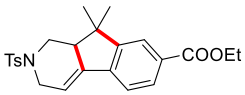
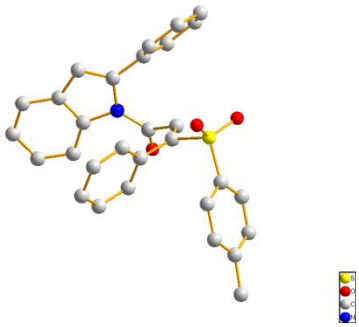


Table S2. Crystal data and structure refinement for GYZ1.

Identification code	gyz1	
Empirical formula	C24H27NO4S	
Formula weight	425.53	
Temperature	153(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 5.42480(10) Å	= 90°.
	b = 30.6105(6) Å	= 94.7720(10)°.
	c = 12.8838(2) Å	= 90°.
Volume	2132.01(7) $Å^3$	
Z	4	
Density (calculated)	1.326 Mg/m^3	
Absorption coefficient	1.601 mm^{-1}	
F(000)	904	
Crystal size	0.2 x 0.1 x 0.1 mm^3	
Theta range for data collection	2.89 to 66.60 °.	
Index ranges	-6<=h<=6, -35<=k<=35, -11<=l<=15	
Reflections collected	10342	
Independent reflections	3654 [R(int) = 0.0445]	
Completeness to theta = 66.60 °	96.7 %	
Max. and min. transmission	1 and 0.03312	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3654 / 0 / 271	
Goodness-of-fit on F^2	1.120	
Final R indices [I>2sigma(I)]	R1 = 0.0583, wR2 = 0.1855	
R indices (all data)	R1 = 0.0689, wR2 = 0.2147	
Largest diff. peak and hole	0.704 and -0.941 e.$Å^{-3}$	

Crystallographic spectrum of product 79 (CCDC number: 2249062)



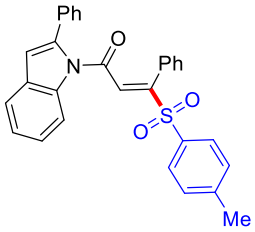


Table S3. Crystal data and structure refinement for Gao.

Identification code	gao	
Empirical formula	C30 H23 N O3 S	
Formula weight	477.55	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.3269(8) Å	α= 69.743(4) °.
	b = 11.8421(12) Å	β= 74.537(4) °.
	c = 13.6257(14) Å	γ = 81.231(4) °.
Volume	1212.2(2) $Å^3$	
Z	2	
Density (calculated)	1.308 Mg/m^3	
Absorption coefficient	0.166 mm^{-1}	
F(000)	500	
Crystal size	0.2 x 0.1 x 0.1 mm^3	
Theta range for data collection	2.54 to 28.29 °.	
Index ranges	-11<=h<=11, -15<=k<=15, -18<=l<=18	
Reflections collected	49873	
Independent reflections	6013 [R(int) = 0.1690]	
Completeness to theta = 28.29 °	99.8 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6013 / 0 / 316	
Goodness-of-fit on F^2	1.257	
Final R indices [I>2sigma(I)]	R1 = 0.0687, wR2 = 0.1731	
R indices (all data)	R1 = 0.1450, wR2 = 0.2314	
Largest diff. peak and hole	0.369 and -0.581 e.$Å^{-3}$	

6. References

[S1] (a) Qiu, Y.-F.; Zhu, X.-Y.; Li, Y.-X.; He, Y.-T.; Yang, F.; Wang, J.; Hua, H.-L.; Zheng, L.; Wang, L.-C.; Liu, X.-Y.; Liang, Y.-M. $AgSCF_3$-Mediated Trifluoromethylthiolation/Radical Cascade Cyclization of 1,6-Enynes. *Org. Lett.* **2015**, *17*, 3694-3697. (b) Franchino, A.; Martí, À.; Echavarren, A. M. H-Bonded Counterion-Directed Enantioselective Au(I) Catalysis. *J. Am. Chem. Soc.* **2022**, *144*, 3497-3509.

[S2] Wang, H.; Lu, Q.; Chiang, C.-W.; Luo, Y.; Zhou, J.; Wang, G.; Lei, A. Markovnikov-Selective Radical Addition of S-Nucleophiles to Terminal Alkynes through a Photoredox Process. *Angew. Chem., Int. Ed.* **2017**, *56*, 595-599.

[S3] Xiao, F.; Hu, Y.; Huang, H.; Xu, F.; Deng, G.-J. Base-Controlled Divergent Synthesis of Vinyl Sulfones from (Benzylsulfonyl)benzenes and Paraformaldehyde. *Org. Biomol. Chem.* **2020**, *18*, 3527-3535.

[S4] (a) Liu, L.; Sun, K.; Su, L.; Dong, J.; Cheng, L.; Zhu, X.; Au, C.-T.; Zhou, Y.; Yin, S.-F. Palladium-Catalyzed Regio- and Stereoselective Coupling−Addition of Propiolates with Arylsulfonyl Hydrazides: A Pattern for Difunctionalization of Alkynes. *Org. Lett.* **2018**, *20*, 4023−4027. (b) Sitte, N. A.; Köring, L.; Roesky, P. W.; Paradies, J. FLP-Catalysis Meets Hydrogen-Bond Activation. *Org. Biomol. Chem.* **2020**, *18*, 7321-7325.