Supporting Information

Photoinduced Tunable Fluoroalkylation or Sulfonylation/Cyclization of Methindolylstyrenes via Electron Donor-Acceptor Complexes

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Contents

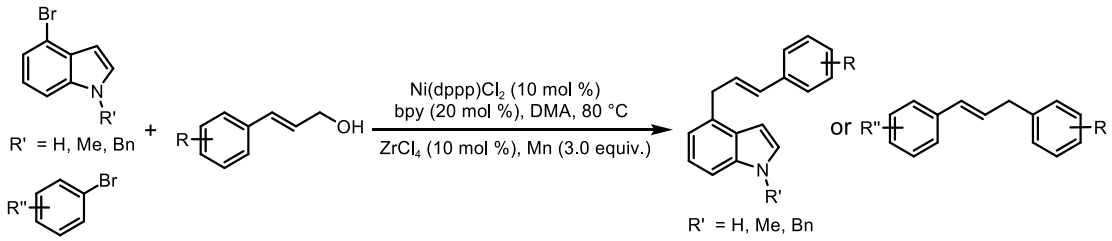
1. General information

Unless otherwise specified, all reagents were purchased from commercial suppliers, including Adamas, Alfa, J&K, Bide Pharm, and Energy Chemical, and were utilized without any further purification. All photo-induced reactions were conducted in a 25 mL Schlenk tube (from CHONGQING SYNTHWARE GLASS INC.) with dry solvents under an argon atmosphere. The Kessil LEDs (40 W, λmax = 390 nm) were used as the irradiation light. ^{1}H NMR (400 MHz), ^{13}C NMR (101 MHz), and ^{19}F (376 MHz) were recorded on an Agilent 400 or Bruker AVANCE NEO 400 instrument spectrometer in $CDCl_3$, CD_3OD, or DMSO-*d*6 using tetramethylsilane (TMS) or residual solvent peaks as internal reference and reported in parts per million (ppm). NMR data were reported as follows: chemical shift (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (*J* are given in Hertz, Hz), and integration. High-resolution mass spectra (HRMS) were obtained using a Q-TOF Analyzer with an ESI ionization source. The melting point was measured utilizing an SGW-X4B melting point apparatus. X-ray crystallographic data were collected employing a Rigaku Oxford Diffraction Supernova Dual Source diffractometer.

2. Preparation of substrates

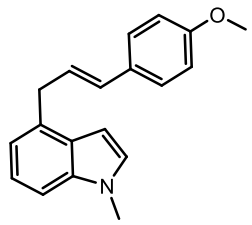
Except for B39 and B41, the remaining sulfonyl chlorides and fluoroalkylation reagent were commercially available and are not further

purified when used. Sulfonyl chlorides B39 and B41 were known compounds synthesized based on literature reports[1]. 1,3-diphenylpropene substrates A30-A35, A37 were known compounds and prepared according to the reported literature[2]. Other methindolylstyrene derivatives A1, A24-A29, and 1,3-diphenylpropene substrates A36 was new compounds and obtained depending on the following procedures[3].



Scheme **S1**

To a reaction tube charged with Ni(dppp)Cl_2 (542.05 mg, 1.0 mmol), bpy (312.36 mg, 2.0 mmol), $ZrCl_4$ (466.08 mg, 1.0 mmol) and Mn (1.65 g, 30.0 mmol) was added a solution of allylic alcohol (10.0 mmol) and aryl bromide (15.0 mmol) in DMA (50 mL, 0.2 M). The reaction tube was vacuumed and backfilled with argon (repeated three times). Then, the solution was warmed to 80 °C and continuously stirred. Upon completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature, quenched with water and extracted with EA. The combined organic layer was repeated washed with water and saturated brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column to give the following cross-coupling products.



A1

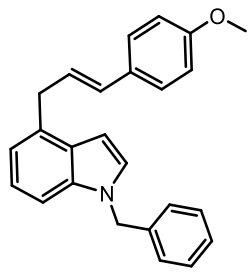
(*E*)-4-(3-(4-methoxyphenyl)allyl)-1-methyl-1*H*-indole (**A1)** was prepared following the above procedure in 68% yield (1.89 g) as a light yellow solid.

mp:78.9 - 80.2 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.6 Hz, 2H), 7.14 – 7.08 (m, 2H), 6.95 (d, *J* = 3.0 Hz, 1H), 6.90 (d, *J* = 5.7 Hz, 1H), 6.72 (d, *J* = 8.7 Hz, 2H), 6.48 (d, *J* = 3.0 Hz, 1H), 6.39 (d, *J* = 15.8 Hz, 1H), 6.30 – 6.18 (m, 1H), 3.72 (d, *J* = 6.5 Hz, 2H), 3.69 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 136.8, 132.8, 130.7, 130.2, 128.5, 128.0, 127.3, 127.2, 121.9, 119.0, 113.9, 107.6, 99.5, 55.4, 37.1, 33.1.

HRMS (ESI, Q-TOF) m/z: [M+H$^+$] Calcd for $C_{19}H_{20}ON$, 278.1539. Found: 278.1536.



A24

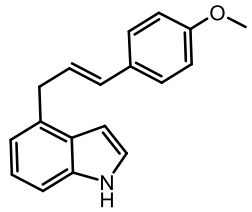
(*E*)-1-benzyl-4-(3-(4-methoxyphenyl)allyl)-1*H*-indole (**A24)** was prepared following the above procedure in 65% yield (2.30 g) as a white solid.

mp:95.8 - 96.8 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 5H), 7.20 – 7.11 (m, 5H), 7.00 (d, *J* = 6.8 Hz, 1H), 6.83 (d, *J* = 8.2 Hz, 2H), 6.65 (d, *J* = 2.3 Hz, 1H), 6.51 (d, *J* = 15.8 Hz, 1H), 6.40 – 6.31 (m, 1H), 5.33 (s, 2H), 3.83 (d, *J* = 6.6 Hz, 2H), 3.80 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 137.7, 136.4, 132.9, 130.7, 130.3, 128.9, 128.2, 128.0, 127.7, 127.3, 127.1, 126.9, 122.1, 119.3, 114.0, 108.1, 100.3, 55.4, 50.3, 37.1.

HRMS (ESI, Q-TOF) m/z: [M+H$^+$] Calcd for $C_{25}H_{24}NO$, 354.1852. Found: 354.1851.



A25

(*E*)-4-(3-(4-methoxyphenyl)allyl)-1*H*-indole (**A25)** was prepared following the above procedure in 61% yield (1.61 g) as a light yellow solid.

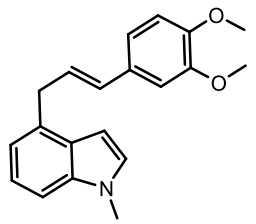
mp:92.9 - 93.9 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.38 – 7.27 (m, 3H), 7.22 – 7.15 (m, 2H), 7.03 (d, *J* = 7.0 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 2H), 6.67 (m, 1H), 6.52 (d, *J* = 15.7 Hz, 1H), 6.42 – 6.32 (m, 1H), 3.85 (d, *J* = 6.5 Hz, 2H), 3.81 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 135.9, 132.7, 130.7, 130.2, 127.4, 127.3, 127.1, 123.9, 122.3, 119.5, 114.0, 109.4, 101.2, 55.4, 37.2.

HRMS (ESI, Q-TOF) m/z: [M+H$^+$] Calcd for $C_{18}H_{18}NO$, 264.1383.

Found: 264.1385.



A26

(*E*)-4-(3-(3,4-dimethoxyphenyl)allyl)-1-methyl-1*H*-indole (**A26)** was prepared following the above procedure in 55% yield (1.69 g) as a white solid.

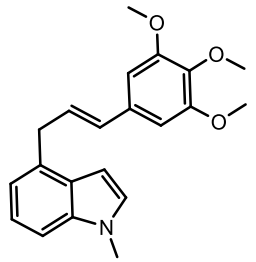
mp:128.7 - 129.8 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.20 (m, 2H), 7.08 (s, 1H), 7.03 (d, *J* = 5.8 Hz, 1H), 6.95 – 6.88 (m, 2H), 6.80 (d, *J* = 7.8 Hz, 1H), 6.60 (s, 1H), 6.50 (d, *J* = 15.8 Hz, 1H), 6.40 – 6.31 (m, 1H), 3.88 (s, 6H), 3.84 (d, *J* = 6.7 Hz, 2H), 3.81 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.0, 148.3, 136.8, 132.6, 130.9, 130.4, 128.6, 128.0, 127.5, 121.9, 119.2, 119.1, 111.1, 108.5, 107.6, 99.5, 56.0, 55.9, 37.1, 33.1.

HRMS (ESI, Q-TOF) m/z: [M+H$^+$] Calcd for $C_{20}H_{22}NO_2$, 308.1645.

Found: 308.1645.



A27

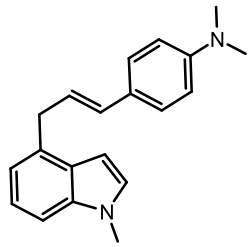
(*E*)-1-methyl-4-(3-(3,4,5-trimethoxyphenyl)allyl)-1*H*-indole (**A27)** was prepared

following the above procedure in 63% yield (2.12 g) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.07 (m, 3H), 6.99 (d, *J* = 1.8 Hz, 1H), 6.92 (d, *J* = 6.0 Hz, 1H), 6.50 (s, 2H), 6.41 – 6.27 (m, 2H), 3.76 (s, 6H), 3.75 (s, 3H), 3.73 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.3, 137.3, 136.8, 133.6, 132.4, 130.6, 129.0, 128.6, 128.0, 121.9, 119.2, 107.7, 103.1, 99.5, 61.0, 56.1, 37.0, 33.1.

HRMS (ESI, Q-TOF) m/z: [M+H$^+$] Calcd for $C_{21}H_{24}NO_3$, 338.1751. Found: 338.1755.



A28

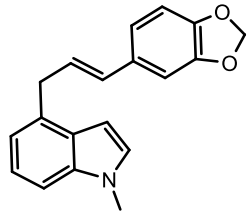
(*E*)-*N*,*N*-dimethyl-4-(3-(1-methyl-1*H*-indol-4-yl)prop-1-en-1-yl)aniline (**A28)** was prepared following the above procedure in 59% yield (1.71 g) as a yellow solid.

mp:74.9 - 76.4 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.2 Hz, 2H), 7.23 – 7.14 (m, 2H), 7.05 (s, 1H), 7.01 (d, *J* = 5.2 Hz, 1H), 6.67 (d, *J* = 7.7 Hz, 2H), 6.59 (s, 1H), 6.48 (d, *J* = 15.6 Hz, 1H), 6.33 – 6.23 (m, 1H), 3.87 – 3.73 (m, 5H), 2.94 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.8, 136.8, 133.2, 130.6, 128.4, 128.0, 127.1, 126.6, 125.1, 121.8, 119.0, 112.7, 107.5, 99.6, 40.8, 37.2, 33.1.

HRMS (ESI, Q-TOF) m/z: [M+H$^+$] Calcd for $C_{20}H_{23}N_2$, 291.1856. Found: 291.1859.



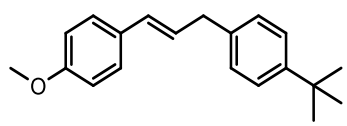
A29

(*E*)-4-(3-(benzo[*d*][1,3]dioxol-5-yl)allyl)-1-methyl-1*H*-indole (**A29)** was prepared following the above procedure in 71% yield (2.07 g) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.16 – 7.12 (m, 1H), 7.07 (d, *J* = 6.5 Hz, 1H), 6.99 (s, 1H), 6.84 (dd, *J* = 21.2, 8.0 Hz, 2H), 6.68 – 6.63 (m, 1H), 6.53 (d, *J* = 15.7 Hz, 1H), 6.45 – 6.35 (m, 1H), 6.00 (s, 2H), 3.92 – 3.85 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.0, 146.7, 136.8, 132.6 132.4, 130.4, 128.5, 128.0, 127.6, 121.9, 120.6, 119.0, 108.3, 107.6, 105.7, 101.0, 99.5, 37.0, 33.1.

HRMS (ESI, Q-TOF) m/z: [M+H$^+$] Calcd for $C_{19}H_{18}NO_2$, 292.1332. Found: 292.1330.



A36

(*E*)-1-(*tert*-butyl)-4-(3-(4-methoxyphenyl)allyl)benzene (A36) was prepared following the above procedure in 74% yield (2.1 g) as a colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.5 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 7.8 Hz, 2H), 6.85 (d, *J* = 8.0 Hz, 2H), 6.43 (d, *J* = 15.7 Hz, 1H), 6.28 – 6.19 (m, 1H), 3.81 (s, 3H), 3.52 (d, *J* = 6.8 Hz, 2H), 1.33 (s, 9H).

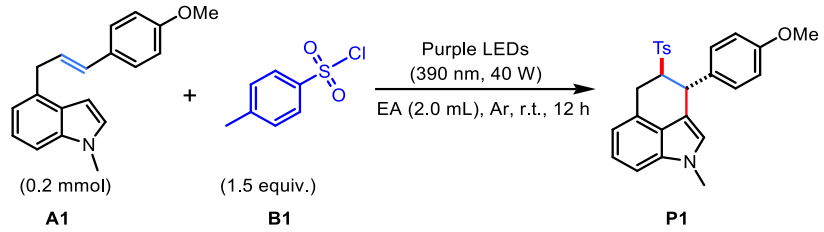
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 149.1, 137.6, 130.5, 130.4, 128.4, 127.4, 127.3, 125.5, 114.0, 55.4, 39.0, 34.5, 31.5.

HRMS (ESI, Q-TOF) m/z: [M+H$^+$] Calcd for $C_{20}H_{25}O$, 281.1900. Found: 281.1907.

3. Optimization of the reaction conditions

To a 25 mL Schlenk tube was added *β*-4'-methindolylstyrene (A1) (55.5 mg, 0.2 mmol, 1.0 equiv.), *p*-Toluenesulfonyl chloride (B1) (57.2 mg, 0.3 mmol, 1.5 equiv.). The Schlenk tube was evacuated and re-filled with argon (three times). After that, dry EA (2.0 mL, 0.1 M) was added into the Schlenk tube under argon counter flow. The reaction mixture was tightly sealed, stirred and irradiated with 40 W Kessil LEDs (λmax = 390 nm) at room temperature under continuous cooling via fan. Upon completion, the solvent was removed under reduced pressure. The residue was dissolved in 0.5 mL of $CDCl_3$ and used for ^{1}H NMR analysis using 2-Phenylethanol (40 μL) as the internal standard.

Table **S1** Data of optimization of the reaction conditions.



entry	Variation from the standard conditions	yield [b] (%)
1	none	73
2	DCM instead of EA	77
3	THF instead of EA	43
4	MeCN instead of EA	45
5	acetone instead of EA	25
6	DCE instead of EA	64
7	toluene instead of EA	34
8	DMF instead of EA	13
9	DMSO instead of EA	trace
10	1,4-dioxane instead of EA	33
11	1.0 equiv. of **B1** instead of 1.5 equiv. of **B1**	62
12	2.0 equiv. of **B1** instead of 1.5 equiv. of **B1**	58
13	3.0 equiv. of **B1** instead of 1.5 equiv. of **B1**	55
14	6 h instead of 12 h	48
15	24 h instead of 12 h	64
16	Blue LEDs instead of Purple LEDs	44
17	the addition of $NaHCO_3$ (2.0 equiv.)	50
18	the addition of Et_3N (2.0 equiv.)	59
19	the addition of K_2CO_3 (2.0 equiv.)	43
20	the addition of Cs_2CO_3 (2.0 equiv.)	49
21	Air instead of Ar	42
22	O_2 instead of Ar	trace
23	In dark	N.D.

[a] Reaction conditions: Unless mentioned otherwise, all reactions were performed with *β*-4'-methindolylstyrene (A1) (55.5 mg, 0.2 mmol, 1.0 equiv.), *p*-Toluenesulfonyl chloride (B1) (57.2 mg, 0.3 mmol, 1.5 equiv.) in 2.0 mL of solvent by 40 W Kessil LEDs (λmax = 390 nm) irradiation under argon atmosphere at room temperature.

[b] ^{1}H NMR analysis of the reaction mixture determined yields using 2-Phenylethanol as an internal standard.

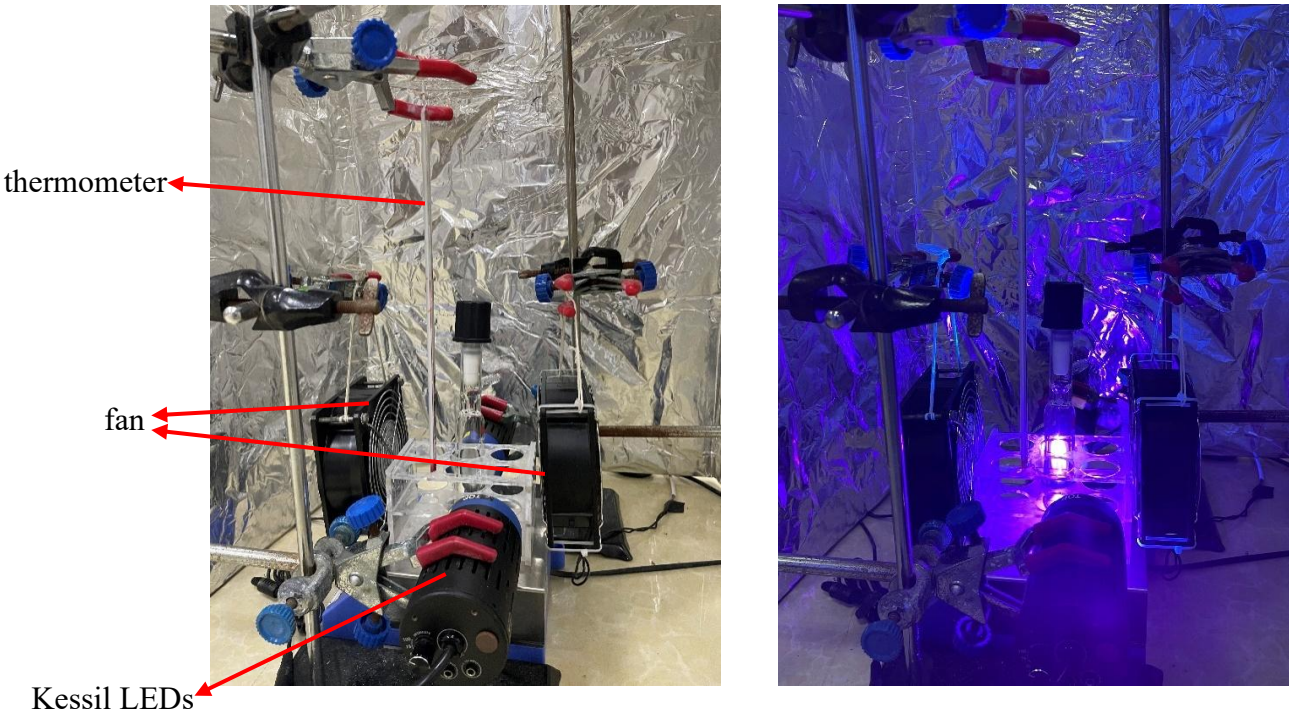
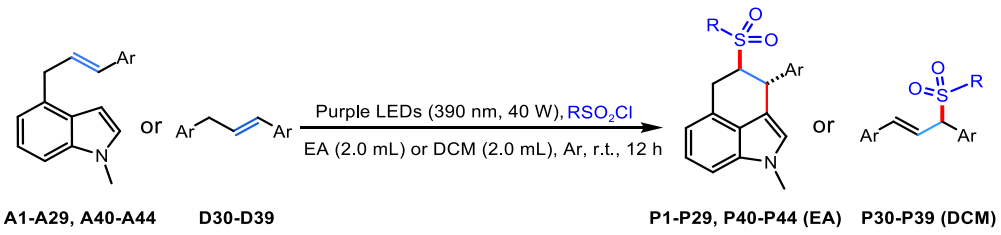


Figure **S1**. light setups

4. General procedure and characterization of products

4.1 General procedure A

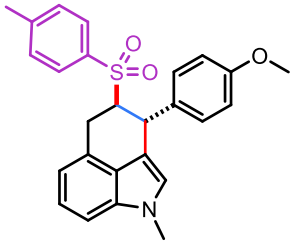


Scheme **S2**

To a 25 mL Schlenk tube were added *β*-4'-methindolylstyrene derivatives (A) (0.2 mmol, 1.0 equiv.) or 1,3-diphenylpropene derivatives

(D) (0.2 mmol, 1.0 equiv.), sulfonyl chlorides (B) (0.3 mmol, 1.5 equiv.). The Schlenk tube was evacuated and re-filled with argon (repeated three times). Subsequently, dry EA (2.0 mL, 0.1 M)/DCM (2.0 mL, 0.1 M) was introduced into the Schlenk tube under a counter flow of argon. The reaction mixture was sealed tightly, stirred, and irradiated with 40 W Kessil LEDs (λmax = 390 nm) for 12 h at room temperature under continuous cooling via the fan. Afterwards, the solvent was removed under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel using a gradient of petroleum ether and ethyl acetate (PE/EA = 15:1 to 5:1) to obtain the desired product **P1-P44**.

4.2 Characterization of products P1-P44



P1

3-(4-methoxyphenyl)-1-methyl-4-tosyl-1,3,4,5-tetrahydrobenzo[*cd*]indole (P1) (mixture of >20:1 inseparable isomers) was prepared according to general procedure **A**.

Yield: 61% (in EA, 52.6 mg, dark green solid)

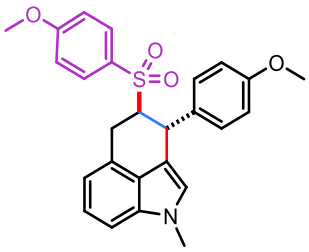
mp:82.5 - 83.8 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 7.9 Hz, 2H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.99 – 6.93 (m, 3H), 6.81 (d, *J* = 7.3 Hz, 1H), 6.78 (d, *J* = 7.8 Hz, 2H),

6.71 (d, J = 8.1 Hz, 2H), 6.48 (s, 1H), 4.97 (d, J = 2.6 Hz, 1H), 3.74 (s, 4H), 3.62 (s, 3H), 3.52 – 3.45 (m, 1H), 3.38 – 3.30 (m, 1H), 2.23 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 143.2, 135.3, 134.7, 134.2, 129.1, 128.1, 127.9, 126.6, 126.2, 124.4, 122.6, 116.1, 113.8, 111.4, 106.8, 68.8, 55.2, 38.6, 32.7, 25.0, 21.4.

HRMS (ESI, Q-TOF) m/z: [M+Na$^+$] Calcd for $NaC_{26}H_{25}O_3NS$, 454.1447. Found: 454.1445.



P2

3-(4-methoxyphenyl)-4-((4-methoxyphenyl)sulfonyl)-1-methyl-1,3,4,5-tetrahydrobenzo[*cd*]indole (P2) (mixture of >20:1 inseparable isomers) was prepared according to general procedure **A**.

Yield: 57% (in EA, 51.0 mg, dark green solid)

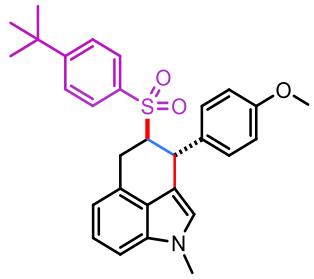
mp:84.0 - 85.6 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 8.8 Hz, 2H), 7.10 (t, J = 7.6 Hz, 1H), 7.00 – 6.92 (m, 3H), 6.81 (d, J = 7.0 Hz, 1H), 6.72 (d, J = 8.6 Hz, 2H), 6.50 (s, 1H), 6.41 (d, J = 8.8 Hz, 2H), 4.97 (d, J = 3.3 Hz, 1H), 3.75 (s, 3H), 3.73 (s, 3H), 3.71 – 3.68 (m, 1H), 3.63 (s, 3H), 3.52 – 3.46 (m, 1H), 3.36 – 3.29 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6, 158.3, 135.3, 134.2, 130.1, 129.1,

129.0, 126.5, 126.1, 124.4, 122.6, 116.1, 113.8, 112.4, 111.2, 106.9, 68.9, 55.4, 55.2, 38.6, 32.6, 24.9.

HRMS (ESI, Q-TOF) m/z: [M+Na$^+$] Calcd for $NaC_{25}H_{22}O_4NS$, 470.1397. Found: 470.1396.



P3

4-((4-(*tert*-butyl)phenyl)sulfonyl)-3-(4-methoxyphenyl)-1-methyl-1,3,4,5-tetrahydrobenzo[*cd*]indole (P3) (mixture of >20:1 inseparable isomers) was prepared according to general procedure **A**.

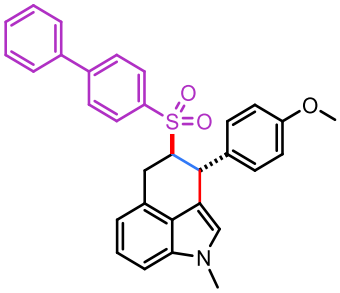
Yield: 64% (in EA, 60.6 mg, dark green solid)

mp:94.2 - 94.8 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 8.4 Hz, 2H), 7.09 – 7.04 (m, 1H), 6.97 (d, J = 8.4 Hz, 4H)), 6.91 (d, J = 8.1 Hz, 1H), 6.81 (d, J = 7.0 Hz, 1H), 6.70 (d, J = 8.6 Hz, 2H), 6.51 (s, 1H), 5.03 (d, J = 3.6 Hz, 1H), 3.75 (s, 4H), 3.63 (s, 3H), 3.56 – 3.50 (m, 1H), 3.41 – 3.33 (m, 1H), 1.21 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 156.0, 135.4, 134.8, 134.1, 129.1, 128.0, 126.5, 126.2, 124.3, 124.2, 122.5, 116.1, 113.8, 111.5, 107.1, 68.9, 55.2, 38.7, 34.9, 32.8, 31.0, 24.9.

HRMS (ESI, Q-TOF) m/z: [M+Na$^+$] Calcd for $NaC_{29}H_{31}O_3NS$, 496.1917. Found: 496.1917.



P4

4-([1,1'-biphenyl]-4-ylsulfonyl)-3-(4-methoxyphenyl)-1-methyl-1,3,4,5-tetrahydrobenzo[*cd*]indole (P4) (mixture of >20:1 inseparable isomers) was prepared according to general procedure **A**.

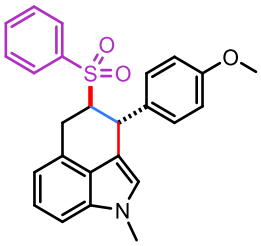
Yield: 52% (in EA, 51.3 mg, dark green solid)

mp:104.2 - 105.6 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.44 (m, 4H), 7.40 (d, *J* = 8.4 Hz, 3H), 7.14 – 7.09 (m, 3H), 6.98 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.2 Hz, 1H), 6.85 (d, *J* = 7.0 Hz, 1H), 6.72 (d, *J* = 8.7 Hz, 2H), 6.49 (s, 1H), 5.03 (d, *J* = 3.4 Hz, 1H), 3.79 – 3.77 (m, 1H), 3.73 (s, 3H), 3.60 – 3.53 (m, 1H), 3.51 (s, 3H), 3.42 – 3.35 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 145.1, 139.5, 136.3, 135.3, 134.3, 129.2, 129.1, 128.6, 128.5, 127.3, 126.8, 126.3, 125.7, 124.5, 122.7, 116.4, 113.9, 111.4, 107.1, 69.3, 55.3, 38.9, 32.9, 25.0.

HRMS (ESI, Q-TOF) m/z: [M+Na^+] Calcd for $NaC_{31}H_{27}O_3NS$, 516.1604. Found: 516.1605.



P5

3-(4-methoxyphenyl)-1-methyl-4-(phenylsulfonyl)-1,3,4,5-tetrahydrobenzo[*cd*]indole (P5) (mixture of >20:1 inseparable isomers) was prepared according to general procedure **A**.

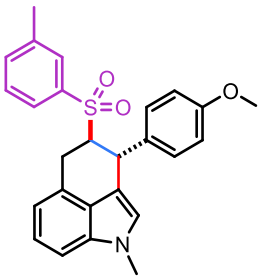
Yield: 59% (in EA, 49.3 mg, dark green solid)

mp:140.3 - 141.2 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 7.5 Hz, 2H), 7.25 – 7.20 (m, 1H), 7.13 – 7.07 (m, 1H), 7.03 – 6.93 (m, 5H), 6.83 (d, J = 6.8 Hz, 1H), 6.71 (d, J = 8.1 Hz, 2H), 6.48 (s, 1H), 4.99 (d, J = 1.4 Hz, 1H), 3.75 (s, 4H), 3.62 (s, 3H), 3.55 – 3.48 (m, 1H), 3.40 – 3.33 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 138.1, 135.2, 134.3, 132.4, 129.2, 128.2, 127.4, 126.7, 126.2, 124.4, 122.7, 116.3, 113.9, 111.5, 107.3, 69.1, 55.3, 38.8, 32.8, 25.1.

HRMS (ESI, Q-TOF) m/z: [M+Na^+] Calcd for $NaC_{25}H_{23}O_3NS$, 440.1291. Found: 440.1293.



P6

3-(4-methoxyphenyl)-1-methyl-4-(*m*-tolylsulfonyl)-1,3,4,5-tetrahydrobenzo[*cd*]indole (P6) (mixture of >20:1 inseparable isomers) was prepared according to general procedure **A**.

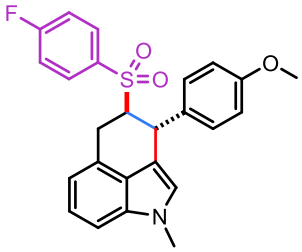
Yield: 63% (in EA, 54.4 mg, dark green solid)

mp:86.6 - 87.2 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (s, 1H), 7.11 – 7.06 (m, 2H), 7.01 (d, J = 7.6 Hz, 1H), 6.99 – 6.93 (m, 3H), 6.91 (t, J = 7.8 Hz, 1H), 6.83 (d, J = 7.0 Hz, 1H), 6.71 (d, J = 8.7 Hz, 2H), 6.47 (s, 1H), 4.98 (d, J = 3.8 Hz, 1H), 3.80 – 3.76 (m, 1H), 3.75 (s, 3H), 3.62 (s, 3H), 3.55 – 3.48 (m, 1H), 3.41 – 3.34 (m, 1H), 2.12 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 137.9, 137.6, 135.2, 134.3, 133.3, 129.3, 128.8, 127.3, 126.7, 126.4, 125.5, 124.3, 122.7, 116.2, 113.8, 111.8, 107.1, 69.0, 55.3, 39.0, 32.8, 25.2, 21.0.

HRMS (ESI, Q-TOF) m/z: [M+Na^+] Calcd for $NaC_{26}H_{25}O_3NS$, 454.1447. Found: 454.1448.



P7

4-((4-fluorophenyl)sulfonyl)-3-(4-methoxyphenyl)-1-methyl-1,3,4,5-tetrahydrobenzo[*cd*]indole (P7) (mixture of >20:1 inseparable isomers) was

prepared according to general procedure **A**.

Yield: 55% (in EA, 47.9 mg, dark green solid)

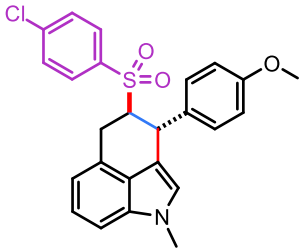
mp:149.4 - 150.5 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 2H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.99 – 6.93 (m, 3H), 6.81 (d, *J* = 7.0 Hz, 1H), 6.73 (d, *J* = 8.4 Hz, 2H), 6.56 (d, *J* = 8.5 Hz, 2H), 6.52 (s, 1H), 5.01 (d, *J* = 2.3 Hz, 1H), 3.75 (s, 3H), 3.73 – 3.69 (m, 1H), 3.63 (s, 3H), 3.55 – 3.47 (m, 1H), 3.37 – 3.30 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.9 (d, *J* = 254.8 Hz), 158.6, 135.2, 134.3, 133.6 (d, *J* = 3.1 Hz), 130.8 (d, *J* = 9.7 Hz), 129.1, 126.6, 126.0, 124.5, 122.9, 116.5, 114.1 (d, *J* = 22.6 Hz), 114.0, 110.9, 107.2, 69.4, 55.4, 38.7, 32.8, 24.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -105.50.

HRMS (ESI, Q-TOF) m/z: [M+Na^+] Calcd for $NaC_{25}H_{22}O_3FNS$, 458.1197. Found: 458.1196.



P8

4-((4-chlorophenyl)sulfonyl)-3-(4-methoxyphenyl)-1-methyl-1,3,4,5-tetrahydrobenzo[*cd*]indole (P8) (mixture of >20:1 inseparable isomers) was prepared according to general procedure **A**.

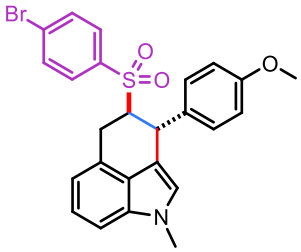
Yield: 51% (in EA, 46.1 mg, dark green solid)

mp:105.6 - 107.5 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.3 Hz, 2H), 7.12 (t, *J* = 7.7 Hz, 1H), 7.00 – 6.93 (m, 3H), 6.85 – 6.78 (m, 3H), 6.73 (d, *J* = 8.4 Hz, 2H), 6.51 (s, 1H), 5.00 (d, *J* = 1.7 Hz, 1H), 3.75 (s, 3H), 3.74 – 3.70 (m, 1H), 3.64 (s, 3H), 3.55 – 3.48 (m, 1H), 3.38 – 3.29 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 138.8, 135.7, 135.1, 134.2, 129.2, 129.0, 126.8, 126.6, 125.9, 124.5, 122.8, 116.5, 113.9, 110.6, 107.1, 69.4, 55.3, 38.6, 32.8, 24.7.

HRMS (ESI, Q-TOF) m/z: [M+Na^+] Calcd for $NaC_{25}H_{22}O_3ClNS$, 474.0901. Found: 474.0901.



P9

4-((4-bromophenyl)sulfonyl)-3-(4-methoxyphenyl)-1-methyl-1,3,4,5-tetrahydrobenzo[*cd*]indole (P9) (mixture of >20:1 inseparable isomers) was prepared according to general procedure **A**.

Yield: 40% (in EA, 39.7 mg, dark green solid)

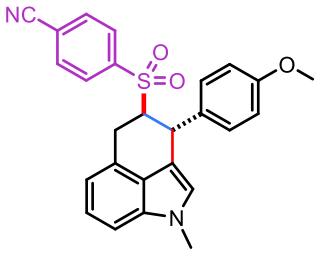
mp:160.2 - 162.2 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 – 7.10 (m, 3H), 7.00 – 6.93 (m, 5H), 6.82 (d, *J* = 6.9 Hz, 1H), 6.73 (d, *J* = 8.4 Hz, 2H), 6.51 (s, 1H), 4.99 (d, *J* = 1.4 Hz, 1H), 3.75 (s, 3H), 3.72 – 3.68 (m, 1H), 3.66 (s, 3H), 3.55 – 3.48

(m, 1H), 3.36 – 3.28 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 136.2, 135.1, 134.2, 129.8, 129.2, 129.1, 127.6, 126.7, 125.9, 124.6, 122.8, 116.6, 113.9, 110.6, 107.2, 69.5, 55.4, 38.6, 32.9, 24.7.

HRMS (ESI, Q-TOF) m/z: [M+Na^+] Calcd for $NaC_{25}H_{22}O_3BrNS$, 518.0396. Found: 518.0394.



P10

3-(4-methoxyphenyl)-1-methyl-1,3,4,5-tetrahydrobenzo[*cd*]indol-4-yl)sulfonyl)benzonitrile (P10) (mixture of >20:1 inseparable isomers) was prepared according to general procedure **A**.

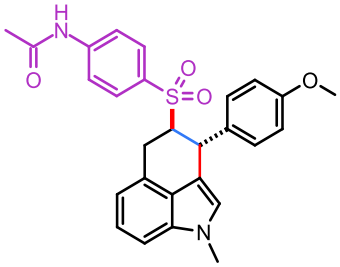
Yield: 59% (in EA, 52.2 mg, dark green solid)

mp:194.5 - 194.7 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 8.3 Hz, 2H), 7.14 – 7.06 (m, 3H), 6.99 – 6.90 (m, 3H), 6.81 (d, J = 7.0 Hz, 1H), 6.72 (d, J = 8.6 Hz, 2H), 6.55 (s, 1H), 5.03 (d, J = 2.1 Hz, 1H), 3.74 (s, 4H), 3.64 (s, 3H), 3.57 – 3.48 (m, 1H), 3.37 – 3.28 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 141.5, 134.7, 134.1, 129.9, 129.0, 128.2, 126.5, 125.6, 124.6, 122.9, 117.3, 116.7, 115.3, 113.9, 110.3, 107.31, 69.7, 55.3, 38.5, 32.8, 24.4.

HRMS (ESI, Q-TOF) m/z: [M+Na$^+$] Calcd for $NaC_{26}H_{22}O_3N_2S$, 465.1243. Found: 465.1245.



P11

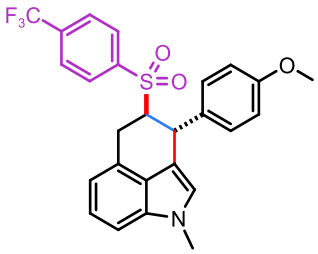
***N*-(4-((3-(4-methoxyphenyl)-1-methyl-1,3,4,5-tetrahydrobenzo[*cd*]indol-4-yl)sulfonyl)phenyl)acetamide (P11)** (mixture of >20:1 inseparable isomers) was prepared according to general procedure **A**.

Yield: 62% (in EA, 58.8 mg, dark green oil)

^{1}H NMR (400 MHz, DMSO-*d*6) δ 10.14 (s, 1H), 7.31 (d, *J* = 8.8 Hz, 2H), 7.24 (d, *J* = 8.8 Hz, 2H), 7.00 – 6.93 (m, 2H), 6.78 (d, *J* = 8.6 Hz, 2H), 6.71 (d, *J* = 6.3 Hz, 1H), 6.65 (d, *J* = 8.7 Hz, 2H), 6.62 (s, 1H), 4.65 (d, *J* = 3.9 Hz, 1H), 3.79 – 3.74 (m, 1H), 3.59 (s, 3H), 3.54 (s, 3H), 3.27 – 3.20 (m, 1H), 3.14 – 3.06 (m, 1H), 2.01 (s, 3H).

^{13}C NMR (101 MHz, DMSO-*d*6) δ 169.0, 158.0, 143.3, 135.0, 134.0, 131.1, 129.0, 128.9, 126.2, 125.8, 124.9, 122.1, 117.1, 115.7, 113.8, 111.2, 107.4, 67.0, 55.0, 38.2, 32.4, 24.7, 24.3.

HRMS (ESI, Q-TOF) m/z: [M+Na$^+$] Calcd for $NaC_{27}H_{26}O_4N_2S$, 497.1505. Found: 497.1505.



P12

3-(4-methoxyphenyl)-1-methyl-4-((4-(trifluoromethyl)phenyl)sulfonyl)-1,3,4,5-tetrahydrobenzo[*cd*]indole (P12) (mixture of >20:1 inseparable isomers) was prepared according to general procedure **A**.

Yield: 50% (in EA, 48.6 mg, dark green solid)

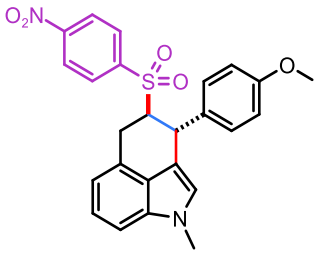
mp:174.2 - 175.0 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.1 Hz, 2H), 7.11 – 7.04 (m, 3H), 6.96 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.2 Hz, 1H), 6.82 (d, *J* = 7.0 Hz, 1H), 6.73 (d, *J* = 8.6 Hz, 2H), 6.53 (s, 1H), 5.06 (d, *J* = 2.3 Hz, 1H), 3.75 (s, 4H), 3.58 (s, 3H), 3.57 – 3.51 (m, 1H), 3.37 – 3.29 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 140.8, 134.9, 134.1, 133.3 (q, *J* = 32.7 Hz), 129.0, 128.2, 126.5, 125.6, 124.5, 123.2 (q, *J* = 3.7 Hz), 122.7, 121.8, 116.6, 113.9, 110.3, 107.4, 69.6, 55.2, 38.5, 32.5, 24.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -63.20.

HRMS (ESI, Q-TOF) m/z: [M+Na^+] Calcd for $NaC_{26}H_{22}O_3F_3NS$, 508.1165. Found: 508.1165.



P13

3-(4-methoxyphenyl)-1-methyl-4-((4-nitrophenyl)sulfonyl)-1,3,4,5-tetrahydrobenzo[*cd*]indole (P13) (mixture of >20:1 inseparable isomers) was prepared according to general procedure **A**.

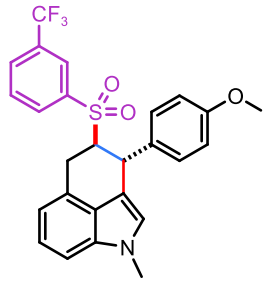
Yield: 48% (in EA, 44.4 mg, dark green solid)

mp:147.5 - 148.6 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.0 Hz, 2H), 7.45 (d, J = 8.1 Hz, 2H), 7.07 (t, J = 7.6 Hz, 1H), 6.95 (d, J = 8.1 Hz, 2H), 6.83 – 6.77 (m, 2H), 6.73 (d, J = 8.0 Hz, 2H), 6.60 (s, 1H), 5.09 – 5.05 (m, 1H), 3.74 (s, 4H), 3.60 (s, 3H), 3.55 – 3.49 (m, 1H), 3.37 – 3.28 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 149.4, 142.6, 134.8, 134.1, 129.1, 128.8, 126.6, 125.7, 124.7, 123.0, 121.0, 116.9, 114.0, 110.3, 107.2, 69.9, 55.3, 38.5, 32.8, 24.4.

HRMS (ESI, Q-TOF) m/z: [M+Na^+] Calcd for $NaC_{25}H_{22}O_5N_2S$, 485.1142. Found: 485.1142.



P14

3-(4-methoxyphenyl)-1-methyl-4-((3-(trifluoromethyl)phenyl)sulfonyl)-1,3,4,5-tetrahydrobenzo[*cd*]indole (P14) (mixture of >20:1 inseparable isomers) was prepared according to general procedure **A**.

Yield: 52% (in EA, 50.5 mg, dark green solid)

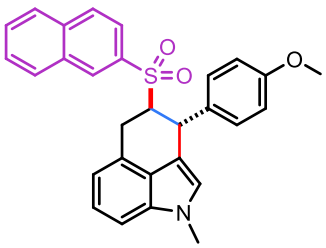
mp:75.4 - 75.7 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.50 (d, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.04 (t, *J* = 7.6 Hz, 1H), 7.00 – 6.94 (m, 3H), 6.84 (d, *J* = 8.2 Hz, 1H), 6.80 (d, *J* = 7.0 Hz, 1H), 6.73 (d, *J* = 8.6 Hz, 2H), 6.58 (s, 1H), 5.13 (d, *J* = 2.0 Hz, 1H), 3.79 – 3.76 (m, 1H), 3.75 (s, 3H), 3.58 (s, 3H), 3.57 – 3.51 (m, 1H), 3.38 – 3.30 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 138.7, 135.1, 134.1, 131.1, 129.3, 129.0, 128.8 (q, *J* = 3.4 Hz), 127.4 126.3, 125.4, 124.8 (q, *J* = 3.4 Hz), 124.5, 122.8, 121.7, 116.5, 113.9, 110.1, 107.3, 69.6, 55.2, 38.4, 32.6, 24.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.69.

HRMS (ESI, Q-TOF) m/z: [M+Na^+] Calcd for $NaC_{26}H_{22}O_3F_3NS$, 508.1165. Found: 508.1164.



P15

3-(4-methoxyphenyl)-1-methyl-4-(naphthalen-2-ylsulfonyl)-1,3,4,5-

tetrahydrobenzo[*cd*]indole (P15) (mixture of >20:1 inseparable isomers) was prepared according to general procedure **A**.

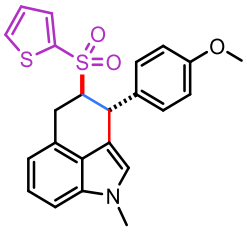
Yield: 61% (in EA, 57.0 mg, dark green solid)

mp:204.4 - 205.2 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.69 (d, *J* = 7.9 Hz, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.57 – 7.47 (m, 2H), 7.39 – 7.31 (m, 2H), 7.01 – 6.94 (m, 3H), 6.84 (d, *J* = 7.0 Hz, 1H), 6.64 (d, *J* = 8.5 Hz, 3H), 6.35 (s, 1H), 5.04 (d, *J* = 2.8 Hz, 1H), 3.86 – 3.81 (m, 1H), 3.63 (s, 3H), 3.62 – 3.56 (m, 1H), 3.44 – 3.36 (m, 1H), 3.22 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 135.1, 134.7, 134.5, 134.0, 131.0, 130.1, 129.3, 129.2, 128.6, 127.5, 127.0, 126.7, 126.6, 126.1, 124.2, 122.9, 122.7, 116.3, 113.8, 111.3, 107.0, 69.3, 55.2, 39.0, 32.3, 25.1.

HRMS (ESI, Q-TOF) m/z: [M+Na$^+$] Calcd for $NaC_{29}H_{25}O_3NS$, 490.1447. Found: 490.1446.



P16

3-(4-methoxyphenyl)-1-methyl-4-(thiophen-2-ylsulfonyl)-1,3,4,5-tetrahydrobenzo[*cd*]indole (P16) (mixture of >20:1 inseparable isomers) was prepared according to general procedure **A**.

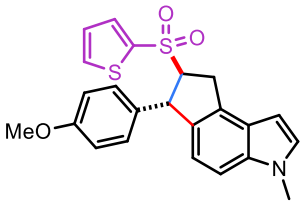
Yield: 56% (in EA, 47.4 mg, dark green solid)

mp:144.3 – 145.7 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 4.9 Hz, 1H), 7.17 – 7.12 (m, 1H), 7.07 – 6.98 (m, 4H), 6.85 (d, *J* = 7.0 Hz, 1H), 6.76 (d, *J* = 8.6 Hz, 2H), 6.69 – 6.63 (m, 1H), 6.54 (s, 1H), 5.01 (d, *J* = 3.9 Hz, 1H), 3.87 – 3.82 (m, 1H), 3.77 (s, 3H), 3.68 (s, 3H), 3.59 – 3.52 (m, 1H), 3.45 – 3.38 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 139.0, 135.4, 134.52, 134.47, 133.5, 129.2, 126.8, 126.1, 124.6, 122.8, 116.3, 112.0, 111.6, 107.3, 69.9, 55.4, 39.0, 32.9, 25.5.

HRMS (ESI, Q-TOF) m/z: [M+Na^+] Calcd for $NaC_{23}H_{21}O_3NS_2$, 446.0855. Found: 446.0854.



P16'

6-(4-methoxyphenyl)-3-methyl-7-(thiophen-2-ylsulfonyl)-3,6,7,8-tetrahydrocyclopenta[e]indole (**P16'**) (mixture of >20:1 inseparable isomers) was prepared according to general procedure **A**.

Yield: 28% (in EA, 23.7 mg, dark green solid)

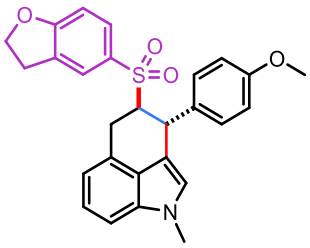
mp:218.0 - 218.9 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.65 (m, 1H), 7.64 – 7.59 (m, 1H), 7.13 (d, *J* = 8.3 Hz, 1H), 7.09 (d, *J* = 3.0 Hz, 1H), 7.07 – 7.03 (m, 1H), 6.93 (d, *J* = 8.6 Hz, 2H), 6.75 (d, *J* = 8.7 Hz, 2H), 6.70 (d, *J* = 8.4 Hz, 1H), 6.41 (d, *J* = 2.6 Hz, 1H), 5.00 (d, *J* = 5.9 Hz, 1H), 4.19 – 4.12 (m, 1H), 3.83 –

3.77 (m, 3H), 3.77 – 3.72 (m, 4H), 3.69 – 3.62 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 139.1, 136.5, 136.1, 134.8, 134.5, 134.3, 130.8, 129.5, 129.1, 127.8, 124.5, 118.5, 114.0, 109.2, 99.0, 73.7, 55.3, 52.3, 33.3, 32.4.

HRMS (ESI, Q-TOF) m/z: [M+Na^+] Calcd for $NaC_{23}H_{21}O_3NS_2$, 446.0855. Found: 446.0851.



P17

4-((2,3-dihydrobenzofuran-5-yl)sulfonyl)-3-(4-methoxyphenyl)-1-methyl-1,3,4,5-tetrahydrobenzo[*cd*]indole (P17) (mixture of >20:1 inseparable isomers) was prepared according to general procedure **A**.

Yield: 59% (in EA, 54.2 mg, dark green solid)

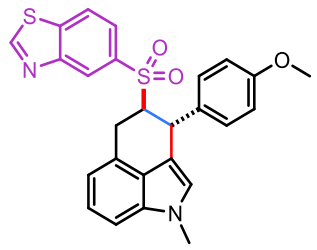
mp:163.4 - 164.5 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.4 Hz, 1H), 7.11 – 7.06 (m, 1H), 7.02 (s, 1H), 6.97 (d, *J* = 8.1 Hz, 3H), 6.82 (d, *J* = 7.0 Hz, 1H), 6.72 (d, *J* = 8.6 Hz, 2H), 6.49 (s, 1H), 6.30 (d, *J* = 8.4 Hz, 1H), 4.98 (d, *J* = 3.2 Hz, 1H), 4.51 (t, *J* = 8.8 Hz, 2H), 3.75 (s, 3H), 3.73 – 3.68 (m, 1H), 3.65 (s, 3H), 3.54 – 3.47 (m, 1H), 3.38 – 3.30 (m, 1H), 2.91 (t, *J* = 8.8 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.7, 158.4, 135.5, 134.3, 130.0, 129.1, 129.0, 126.6, 126.5, 126.4, 125.5, 124.4, 122.7, 116.2, 113.8, 111.5, 107.7,

106.8, 72.2, 69.1, 55.3, 38.8, 32. 8, 28.6, 25.0.

HRMS (ESI, Q-TOF) m/z: [M+Na$^+$] Calcd for $NaC_{27}H_{25}O_4NS$, 482.1397. Found: 482.1397.



P18

5-((3-(4-methoxyphenyl)-1-methyl-1,3,4,5-tetrahydrobenzo[*cd*]indol-4-yl)sulfonyl)benzo[*d*]thiazole (P18) (mixture of >20:1 inseparable isomers) was prepared according to general procedure **A**.

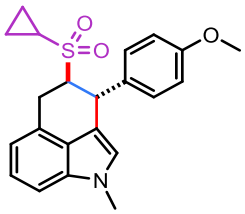
Yield: 41% (in EA, 38.9 mg, dark green solid)

mp:199.0 - 199.4 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.08 (s, 1H), 7.88 (d, *J* = 1.4 Hz, 1H), 7.61 (d, *J* = 8.6 Hz, 1H), 7.50 – 7.47 (m, 1H), 6.97 – 6.91 (m, 3H), 6.80 (d, *J* = 7.0 Hz, 1H), 6.69 – 6.64 (m, 3H), 6.45 (s, 1H), 5.05 (d, *J* = 3.1 Hz, 1H), 3.82 – 3.78 (m, 1H), 3.70 (s, 3H), 3.61 – 3.54 (m, 1H), 3.41 (s, 3H), 3.39 – 3.33 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 157.8, 155.3, 135.1, 134.9, 134.1, 132.2, 129.2, 126.5, 126.0, 125.8, 124.3, 123.4, 123.0, 121.9, 116.5, 113.9, 111.1, 107.3, 69. 8, 55.3, 38.9, 32.6, 24.9.

HRMS (ESI, Q-TOF) m/z: [M+Na$^+$] Calcd for $NaC_{26}H_{22}O_3N_2S_2$, 497.0964. Found: 497.0963.



P19

4-(cyclopropylsulfonyl)-3-(4-methoxyphenyl)-1-methyl-1,3,4,5-tetrahydrobenzo[*cd*]indole (P19) (mixture of >20:1 inseparable isomers) was prepared according to general procedure **A**.

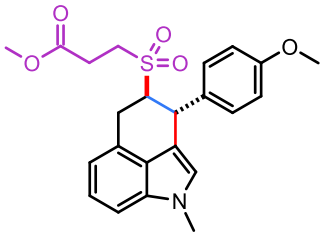
Yield: 41% (in EA, 31.3 mg, dark green solid)

mp:166.1 - 167.0 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.20 (m, 1H), 7.20 – 7.13 (m, 3H), 6.95 (d, *J* = 6.5 Hz, 1H), 6.83 (d, *J* = 8.7 Hz, 2H), 6.64 (s, 1H), 4.95 (d, *J* = 5.0 Hz, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 3.68 – 3.64 (m, 1H), 3.52 – 3.44 (m, 2H), 1.27 – 1.18 (m, 1H), 0.98 – 0.92 (m, 1H), 0.84 (m, 1H), 0.33 – 0.21 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 135.4, 134.6, 129.6, 127.3, 127.2, 124.5, 123.0, 116.3, 114.1, 112.7, 107.4, 68.4, 55.4, 39.6, 33.1, 29.5, 25.4, 5.0.

HRMS (ESI, Q-TOF) m/z: [M+Na^+] Calcd for $NaC_{22}H_{23}O_3NS$, 404.1291. Found: 404.1295.



P20

methyl 3-((3-(4-methoxyphenyl)-1-methyl-1,3,4,5-tetrahydrobenzo[*cd*]indol-4-yl)sulfonyl)propanoate (P20) (mixture of >20:1 inseparable isomers) was prepared according to general procedure **A**.

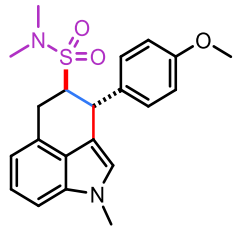
Yield: 46% (in EA, 39.3 mg, dark green solid)

mp:136.9 - 137.5 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.18 (m, 2H), 7.16 (d, *J* = 8.7 Hz, 2H), 6.97 (d, *J* = 6.4 Hz, 1H), 6.84 (d, *J* = 8.7 Hz, 2H), 6.65 (s, 1H), 4.89 (d, *J* = 5.4 Hz, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 3.68 – 3.62 (m, 1H), 3.60 (s, 3H), 3.53 – 3.47 (m, 2H), 2.54 – 2.36 (m, 3H), 2.34 – 2.25 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 159.0, 134.7, 134.6, 129.5, 126.7, 126.5, 124.7, 123.1, 116.4, 114.2, 112.3, 107.7, 68.1, 55.4, 52.2, 47.7, 39.6, 33.1, 26.0, 25.1.

HRMS (ESI, Q-TOF) m/z: [M+Na$^+$] Calcd for $NaC_{23}H_{25}O_5NS$, 450.1346. Found: 450.1346.



P21

3-(4-methoxyphenyl)-*N*,*N*,1-trimethyl-1,3,4,5-tetrahydrobenzo[*cd*]indole-4-sulfonamide (P21) (mixture of >20:1 inseparable isomers) was prepared according to general procedure **A**.

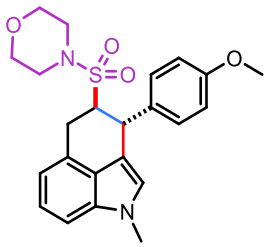
Yield: 29% (in EA, 22.3 mg, dark green solid)

mp:102.4 - 104.2 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 6.1 Hz, 2H), 7.05 (d, *J* = 8.6 Hz, 2H), 6.93 (d, *J* = 5.8 Hz, 1H), 6.80 (d, *J* = 8.7 Hz, 2H), 6.65 (s, 1H), 4.91 (d, *J* = 3.8 Hz, 1H), 3.84 – 3.81 (m, 1H), 3.78 (s, 3H), 3.78 (s, 3H), 3.49 – 3.42 (m, 1H), 3.37 – 3.30 (m, 1H), 2.15 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 136.2, 134.6, 129.1, 127.3, 126.7, 124.4, 123.0, 116.2, 114.0, 112.4, 107.4, 67.5, 55.4, 39.3, 36.9, 33.1, 25.9.

HRMS (ESI, Q-TOF) m/z: [M+Na$^+$] Calcd for $NaC_{21}H_{24}O_3N_2S$, 407.1400. Found: 407.1403.



P22

4-((3-(4-methoxyphenyl)-1-methyl-1,3,4,5-tetrahydrobenzo[*cd*]indol-4-yl)sulfonyl)morpholine (P22) (mixture of >20:1 inseparable isomers) was prepared according to general procedure **A**.

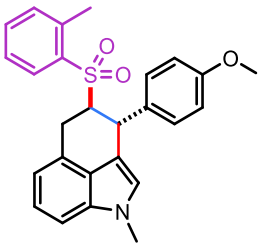
Yield: 23% (in EA, 19.6 mg, dark green solid)

mp:172.1 - 173.4 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 3.5 Hz, 2H), 7.01 (d, *J* = 8.6 Hz, 2H), 6.94 – 6.90 (m, 1H), 6.79 (d, *J* = 8.6 Hz, 2H), 6.71 (s, 1H), 4.94 (d, *J* = 2.6 Hz, 1H), 3.80 (s, 3H), 3.77 (s, 4H), 3.48 – 3.41 (m, 1H), 3.34 – 3.27 (m, 1H), 3.11 – 3.02 (m, 4H), 2.63 – 2.48 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 136.3, 134.6, 129.0, 126.9, 126.8, 124.2, 123.2, 116.2, 114.0, 111.6, 107.7, 67.8, 66.6, 55.4, 45.9, 38.8, 33.2, 25.3.

HRMS (ESI, Q-TOF) m/z: [M+Na^+] Calcd for $NaC_{23}H_{26}O_4N_2S$, 449.1505. Found: 449.1507.



P23

3-(4-methoxyphenyl)-1-methyl-4-(*o*-tolylsulfonyl)-1,3,4,5-tetrahydrobenzo[*cd*]indole (P23) (mixture of >20:1 inseparable isomers) was prepared according to general procedure **A**.

Yield: 41% (in EA, 35.4 mg, dark green solid)

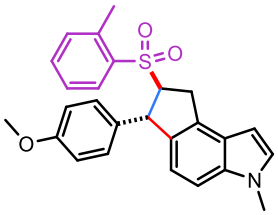
mp:189.1 - 189.7 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 7.3 Hz, 2H), 7.12 – 7.08 (m, 1H), 6.99 – 6.94 (m, 3H), 6.83 – 6.76 (m, 3H), 6.71 (d, *J* = 8.6 Hz, 2H), 6.49 (s, 1H), 4.97 (d, *J* = 3.2 Hz, 1H), 3.75 (s, 3H), 3.73 – 3.70 (m, 1H), 3.63 (s, 3H), 3.51 – 3.44 (m, 1H), 3.37 – 3.29 (m, 1H), 2.23 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 137.5, 137.3, 134.3, 134.2, 132.7, 132.0, 130.5, 129.3, 126.8, 126.6, 125.9, 124.4, 122.6, 115.9, 113.8, 113.6, 107.3, 67.1, 55.2, 39.8, 32.9, 25.9, 20.7.

HRMS (ESI, Q-TOF) m/z: [M+Na^+] Calcd for $NaC_{26}H_{25}O_3NS$, 454.1447.

Found: 454.1449.



P23'

6-(4-methoxyphenyl)-3-methyl-7-(*o*-tolylsulfonyl)-3,6,7,8-tetrahydrocyclopenta[*e*]indole (P23') (mixture of >20:1 inseparable isomers) was prepared according to general procedure **A**.

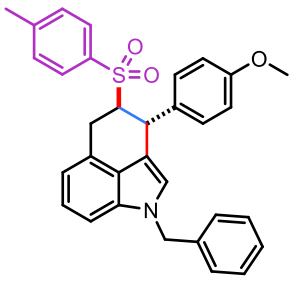
Yield: 25% (in EA, 21.6 mg, dark green solid)

mp:83.4 - 84.8 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.0 Hz, 2H), 7.13 – 7.08 (m, 1H), 7.00 – 6.94 (m, 3H), 6.83 – 6.76 (m, 3H), 6.72 (d, *J* = 8.3 Hz, 2H), 6.49 (s, 1H), 4.97 (d, *J* = 2.7 Hz, 1H), 3.75 (s, 3H), 3.73 – 3.70 (m, 1H), 3.63 (s, 3H), 3.52 – 3.45 (m, 1H), 3.37 – 3.29 (m, 1H), 2.24 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 143.2, 135.3, 134.8, 134.2, 129.7, 129.1, 128.7, 128.1, 127.9, 126.6, 126.2, 124.3, 122.6, 116.2, 113.8, 111.4, 106.8, 68.8, 55.3, 38.6, 32.7, 25.0, 21.5.

HRMS (ESI, Q-TOF) m/z: [M+Na$^+$] Calcd for $NaC_{26}H_{25}O_3NS$, 454.1447. Found: 454.1448.



P24

1-benzyl-3-(4-methoxyphenyl)-4-tosyl-1,3,4,5-tetrahydrobenzo[*cd*]indole (P24) (mixture of >20:1 inseparable isomers) was prepared according to general procedure **A**.

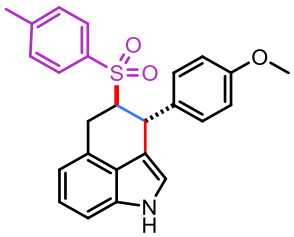
Yield: 53% (in EA, 53.8 mg, dark green solid)

mp:76.6 - 77.6 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 5H), 7.14 (d, *J* = 6.8 Hz, 2H), 7.07 – 7.02 (m, 1H), 6.98 (d, *J* = 8.5 Hz, 2H), 6.95 (d, *J* = 8.3 Hz, 1H), 6.81 – 6.75 (m, 3H), 6.72 (d, *J* = 8.7 Hz, 2H), 6.62 (s, 1H), 5.14 (s, 2H), 5.00 (d, *J* = 4.0 Hz, 1H), 3.81 – 3.77 (m, 1H), 3.76 (s, 3H), 3.52 – 3.45 (m, 1H), 3.41 – 3.34 (m, 1H), 2.21 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 143.3, 137.5, 135.2, 134.9, 133.9, 129.1, 128.8, 128.21, 128.17, 127.7, 127.1, 126.8, 126.4, 123.7, 122.7, 116.5, 113.8, 112.4, 107.3, 68.7, 55.2, 50.3, 38.9, 25.2, 21.4.

HRMS (ESI, Q-TOF) m/z: [M+Na^+] Calcd for $NaC_{32}H_{29}O_3NS$, 530.1760. Found: 530.1760.



P25

3-(4-methoxyphenyl)-4-tosyl-1,3,4,5-tetrahydrobenzo[*cd*]indole (P25) (mixture of >20:1 inseparable isomers) was prepared according to general procedure

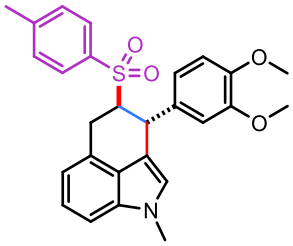
A.

Yield:39% (in EA, 32.6 mg, dark green oil)

^{1}H NMR (400 MHz, DMSO-*d*6) δ 10.68 (d, *J* = 1.2 Hz, 1H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.03 – 6.94 (m, 3H), 6.91 (t, *J* = 7.6 Hz, 1H), 6.77 (d, *J* = 8.6 Hz, 2H), 6.68 (d, *J* = 7.0 Hz, 1H), 6.64 (d, *J* = 8.8 Hz, 3H), 4.64 (d, *J* = 4.5 Hz, 1H), 3.87 – 3.81 (m, 1H), 3.60 (s, 3H), 3.26 – 3.19 (m, 1H), 3.17 – 3.10 (m, 1H), 2.19 (s, 3H).

^{13}C NMR (101 MHz, DMSO-*d*6) δ 157.9, 143.3, 135.2, 135.0, 133.2, 128.9, 128.6, 127.8 126.0, 125.6, 121.9, 120.4, 115.5, 113.7, 112.0, 109.0, 66.7, 55.0, 38.5, 24.9, 21.0.

HRMS (ESI, Q-TOF) m/z: [M+Na$^+$] Calcd for $NaC_{25}H_{23}O_3NS$, 440.1291. Found: 440.1293.



P26

3-(3,4-dimethoxyphenyl)-1-methyl-4-tosyl-1,3,4,5-tetrahydrobenzo[*cd*]indole (**P26**) (mixture of >20:1 inseparable isomers) was prepared according to general procedure **A**.

Yield: 54% (in EA, 49.9 mg, dark green solid)

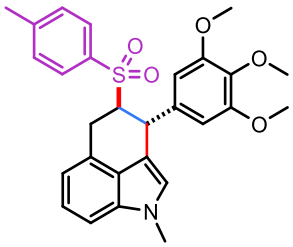
mp:78.9 - 81.2 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.23 (m, 2H), 7.11 (t, *J* = 7.5 Hz,

1H), 6.96 (d, J = 8.7 Hz, 1H), 6.82 (d, J = 7.1 Hz, 1H), 6.78 (d, J = 7.8 Hz, 2H), 6.65 – 6.59 (m, 2H), 6.51 (d, J = 8.2 Hz, 1H), 6.47 (s, 1H), 4.92 (d, J = 4.4 Hz, 1H), 3.88 – 3.86 (m, 1H), 3.82 (s, 3H), 3.72 (s, 3H), 3.64 (s, 3H), 3.53 – 3.46 (m, 1H), 3.45 – 3.38 (m, 1H), 2.23 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.0, 148.1, 143.3, 135.5, 135.2, 134.4, 128.2, 128.0, 126.8, 126.5, 124.5, 122.8, 120.7, 116.3, 112.0, 111.1, 110.9, 107.0, 68.8, 56.0, 55.9, 39.7, 32.9, 25.5, 21.5.

HRMS (ESI, Q-TOF) m/z: [M+Na$^+$] Calcd for $NaC_{27}H_{27}O_4NS$, 484.1553. Found: 484.1554.



P27

1-methyl-4-tosyl-3-(3,4,5-trimethoxyphenyl)-1,3,4,5-tetrahydrobenzo[*cd*]indole (**P27**) (mixture of >20:1 inseparable isomers) was prepared according to general procedure **A**.

Yield: 39% (in EA, 38.3 mg, dark green solid)

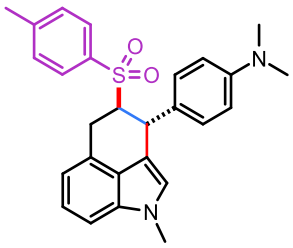
mp:178.4 - 179.5 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, J = 8.3 Hz, 2H), 7.14 – 7.09 (m, 1H), 6.97 (d, J = 8.2 Hz, 1H), 6.84 (d, J = 7.0 Hz, 1H), 6.80 (d, J = 8.0 Hz, 2H), 6.45 (s, 1H), 6.25 (s, 2H), 4.88 (d, J = 5.0 Hz, 1H), 3.85 – 3.82 (m, 1H), 3.80 (s, 3H), 3.66 (s, 6H), 3.63 (s, 3H), 3.54 – 3.47 (m, 2H), 2.23 (s,

3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.2, 143.4, 138.5, 136.8, 135.5, 134.4, 128.11, 128.09, 126.7, 126.4, 124.7, 122.8, 116.4, 112.1, 107.1, 105.4, 68.5, 60.9, 56.2, 40.7, 32.9, 29.8, 25.8, 21.5.

HRMS (ESI, Q-TOF) m/z: [M+Na^+] Calcd for $NaC_{27}H_{27}O_5NS$, 514.1659. Found: 514.1658.



P28

***N,N*-dimethyl-4-(1-methyl-4-tosyl-1,3,4,5-tetrahydrobenzo[*cd*]indol-3-yl)aniline** (**P28**) (mixture of >20:1 inseparable isomers) was prepared according to general procedure **A**.

Yield: 32% (in EA, 28.5 mg, dark green solid)

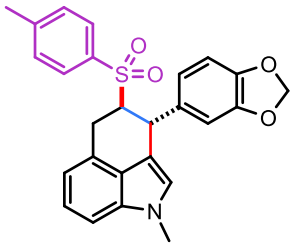
mp:184.5 - 185.5 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.2 Hz, 2H), 7.12 – 7.07 (m, 1H), 6.94 (d, *J* = 8.2 Hz, 1H), 6.91 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 7.0 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 2H), 6.56 (d, *J* = 8.5 Hz, 2H), 6.50 (s, 1H), 4.94 (d, *J* = 3.4 Hz, 1H), 3.75 – 3.70 (m, 1H), 3.63 (s, 3H), 3.51 – 3.43 (m, 1H), 3.39 – 3.31 (m, 1H), 2.89 (s, 6H), 2.22 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.5, 143.1, 135.0, 134.3, 128.8, 128.2, 127.9, 126.9, 126.5, 124.4, 122.6, 116.2, 112.7, 111.8, 106.8, 69.1, 40.8,

38.6, 32.8, 25.1, 21.5.

HRMS (ESI, Q-TOF) m/z: [M+Na$^+$] Calcd for $NaC_{27}H_{28}O_2N_2S$, 467.1764. Found: 467.1762.



P29

3-(benzo[*d*][1,3]dioxol-5-yl)-1-methyl-4-tosyl-1,3,4,5-tetrahydrobenzo[*cd*]indole (P29) (mixture of >20:1 inseparable isomers) was prepared according to general procedure **A**.

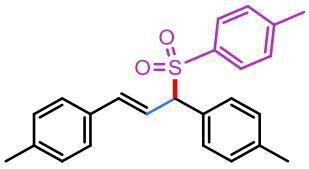
Yield: 62% (in EA, 55.2 mg, dark green solid)

mp:151.9 - 152.4 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 7.8 Hz, 2H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.95 (d, *J* = 8.1 Hz, 1H), 6.84 – 6.77 (m, 3H), 6.61 (dd, *J* = 21.0, 7.8 Hz, 2H), 6.49 (s, 1H), 6.43 (s, 1H), 5.86 (d, *J* = 7.3 Hz, 2H), 4.91 (d, *J* = 3.3 Hz, 1H), 3.73 – 3.68 (m, 1H), 3.63 (s, 3H), 3.51 – 3.44 (m, 1H), 3.40 – 3.32 (m, 1H), 2.24 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7, 146.4, 143.3, 137.1, 134.9, 134.3, 128.2, 128.0, 126.6, 126.2, 124.4, 122.7, 121.6, 116.3, 111.5, 108.4, 108.1, 106.9, 101.0, 68.8, 39.4, 32.8, 25.2, 21.5.

HRMS (ESI, Q-TOF) m/z: [M+Na$^+$] Calcd for $NaC_{26}H_{23}O_4NS$, 468.1240. Found: 468.1245.



P30

(*E*)-4,4'-(3-tosylprop-1-ene-1,3-diyl)bis(methylbenzene) (**P30**) was prepared according to general procedure **A**.

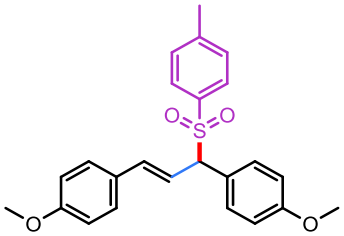
Yield: 47% (in DCM, 35.4 mg, white solid)

mp:91.2 - 92.0 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.8 Hz, 2H), 7.26 – 7.20 (m, 6H), 7.16 – 7.08 (m, 4H), 6.55 – 6.42 (m, 2H), 4.78 (d, *J* = 8.0 Hz, 1H), 2.40 (s, 3H), 2.35 (s, 3H), 2.34 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 138.8, 138.4, 137.6, 134.6, 133.3, 129.6, 129.4, 129.32, 129.28, 126.7, 119.4, 75.2, 21.7, 21.3, 21.2.

The spectra data are consistent with those reported in literature[4].



P31

(*E*)-4,4'-(3-tosylprop-1-ene-1,3-diyl)bis(methoxybenzene) (**P31**) was prepared according to general procedure **A**.

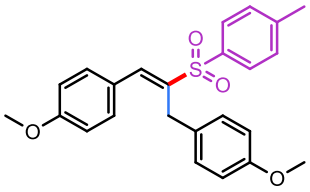
Yield: 50% (in MeCN, 40.9 mg, colorless oil)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.30 – 7.20 (m, 6H), 6.87 – 6.82 (m, 4H), 6.47 – 6.35 (m, 2H), 4.75 (d, *J* = 7.9 Hz, 1H),

3.80 (s, 6H), 2.40 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 159.9, 144.6, 137.3, 134.7, 131.0, 129.5, 129.4, 128.9, 128.2, 124.6, 118.1, 114.2, 114.1, 74.9, 55.4, 21.8.

HRMS（ESI, Q-TOF）m/z: [M+H$^+$] Calcd for $C_{24}H_{25}O_4S$, 409.1468. Found: 409.1463.



P31'

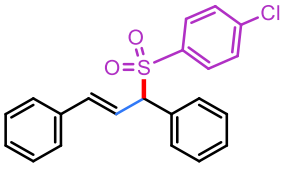
(*E*)-4,4'-(2-tosylprop-1-ene-1,3-diyl)bis(methoxybenzene) P31' was prepared according to general procedure **A** (DCM as solvent).

Yield: 33% (in DCM, 27.0 mg, colorless oil)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.62 (d, J = 7.9 Hz, 2H), 7.38 (d, J = 8.5 Hz, 2H), 7.14 (d, J = 7.6 Hz, 2H), 6.93 (d, J = 8.2 Hz, 2H), 6.84 (d, J = 8.5 Hz, 2H), 6.65 (d, J = 8.4 Hz, 2H), 3.94 (s, 2H), 3.78 (s, 3H), 3.73 (s, 3H), 2.34 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0, 158.2, 143.8, 139.5, 137.2, 137.0, 131.7, 129.5, 129.0, 128.3, 128.2, 125.8, 114.4, 113.9, 55.4, 55.3, 32.1, 21.6.

HRMS (ESI, Q-TOF) m/z: [M+H$^+$] Calcd for $C_{24}H_{25}O_4S$, 409.1468. Found: 409.1469.



P32

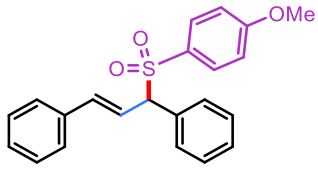
(*E*)-(3-((4-chlorophenyl)sulfonyl)prop-1-ene-1,3-diyl)dibenzene (P32) was prepared according to general procedure **A**.

Yield: 56% (in DCM, 41.3 mg, colorless oil)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.7 Hz, 2H), 7.39 – 7.33 (m, 12H), 6.58 (d, *J* = 1.8 Hz, 2H), 4.88 – 4.81 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.5, 138.6, 136.0, 135.8, 132.1, 130.8, 129.8, 129.2, 129.1, 128.9, 128.80, 128.75, 126.9, 119.6, 75.6.

The spectra data are consistent with those reported in literature[4].



P33

(*E*)-(3-((4-methoxyphenyl)sulfonyl)prop-1-ene-1,3-diyl)dibenzene (P33) was prepared according to general procedure **A**.

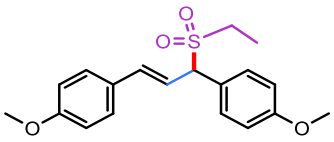
Yield: 40% (in DCM, 29.2 mg, colorless oil)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.5 Hz, 2H), 7.29 – 7.18 (m, 10H), 6.79 (d, *J* = 8.5 Hz, 2H), 6.55 – 6.45 (m, 2H), 4.74 (d, *J* = 7.2 Hz, 1H), 3.76 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.8, 138.0, 136.1, 132.8, 131.6, 129.8,

129.0, 128.9, 128.8, 128.7, 128.5, 126.9, 120.4, 114.0, 75.6, 55.7.

The spectra data are consistent with those reported in literature[4].



P34

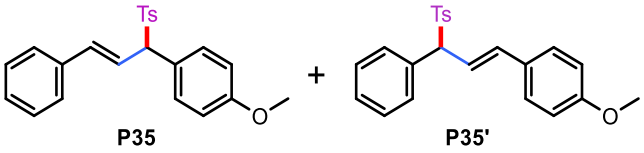
(*E*)-4,4'-(3-(ethylsulfonyl)prop-1-ene-1,3-diyl)bis(methoxybenzene) (P34) was prepared according to general procedure **A**.

Yield: 43% (in DCM, 29.8 mg, colorless oil)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 6.95 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.3 Hz, 2H), 6.68 (d, *J* = 15.8 Hz, 1H), 6.50 – 6.42 (m, 1H), 4.80 (d, *J* = 9.2 Hz, 1H), 3.82 (s, 3H), 3.81 (s, 3H), 2.92 (q, *J* = 7.4 Hz, 2H), 1.35 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 160.1, 137.0, 130.8, 128.6, 128.3, 124.2, 118.5, 114.6, 114.2, 71.1, 55.5, 45.0, 6.6.

HRMS (ESI, Q-TOF) m/z: [M+Na$^+$] Calcd for $NaC_{19}H_{22}O_4S$, 369.1131. Found: 369.1134.



P35 + P35'

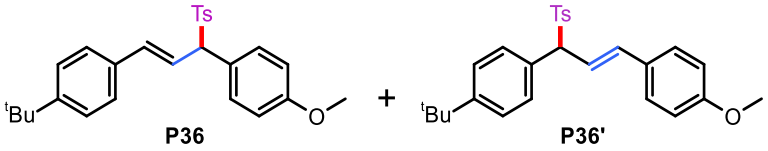
(*E*)-1-methoxy-4-(3-phenyl-1-tosylallyl)benzene (P35) + (*E*)-1-methoxy-4-(3-phenyl-3-tosylprop-1-en-1-yl)benzene (P35') (mixture of 1:1 inseparable mixture) was prepared according to general procedure **A**.

Yield: 47% (in DCM, 48.6 mg, colorless oil)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (t, *J* = 6.6 Hz, 2H), 7.34 – 7.19 (m, 9H), 6.88 – 6.82 (m, 2H), 6.56 – 6.39 (m, 2H), 4.79 (d, *J* = 6.8 Hz, 1H), 3.80 (s, 3H), 2.39 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 159.9, 144.6, 137.8, 137.6, 136.1, 134.6, 132.8, 131.0, 129.8, 129.43, 129.38, 128.9, 128.83, 128.75, 128.7, 128.5, 128.2, 126.8, 124.3, 120.5, 117.8, 114.2, 114.1, 75.6, 74.7, 55.4, 21.8.

HRMS (ESI, Q-TOF) m/z: [M+Na^+] Calcd for $NaC_{23}H_{22}O_3S$, 401.1182. Found: 401.1182.



P36 + P36'

(*E*)-1-(*tert*-butyl)-4-(3-(4-methoxyphenyl)-3-tosylprop-1-en-1-yl)benzene (P36) + (*E*)-1-(*tert*-butyl)-4-(3-(4-methoxyphenyl)-1-tosylallyl)benzene (P36') (mixture of 1:1 inseparable isomers) was prepared according to general procedure **A**.

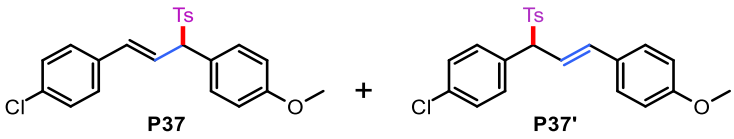
Yield: 51% (in DCM, 52.7 mg, colorless oil)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.2 Hz, 2H), 7.37 – 7.33 (m, 2H), 7.30 – 7.26 (m, 3H), 7.25 – 7.17 (m, 3H), 6.85 (t, *J* = 8.3 Hz, 2H), 6.49 (d, *J* = 7.0 Hz, 1H), 6.43 – 6.38 (m, 1H), 4.80 – 4.75 (m, 1H), 3.81 (s, 3H), 2.40 (d, *J* = 1.8 Hz, 3H), 1.31 (d, *J* = 1.4 Hz, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 159.9, 152.0, 151.7, 144.6, 144.5,

137.5, 137.3, 134.7, 134.6, 133.4, 131.0, 129.47, 129.45, 129.3, 128.9, 128.1, 126.6, 125.8, 125.7, 124.4, 119.7, 118.2, 114.2, 114.1, 75.3, 74.8, 55.4, 34.8, 34.7, 31.38, 31.35, 21.8.

HRMS (ESI, Q-TOF) m/z: [M+Na$^+$] Calcd for $NaC_{23}H_{21}O_3S$, 400.1104. Found: 400.1101.



P37 + P37'

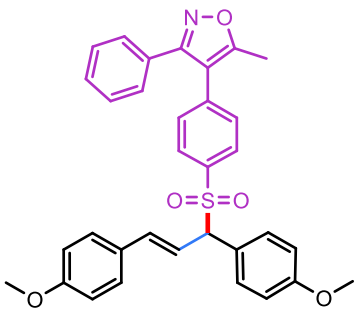
(*E*)-1-chloro-4-(3-(4-methoxyphenyl)-3-tosylprop-1-en-1-yl)benzene (P37) + (*E*)-1-chloro-4-(3-(4-methoxyphenyl)-1-tosylallyl)benzene (P37') (mixture of 1:1 inseparable isomers) was prepared according to general procedure **A**.

Yield: 38% (in DCM, 31.4 mg, colorless oil)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.49 (m, 2H), 7.28 – 7.25 (m, 4H), 7.23 – 7.14 (m, 4H), 6.86 – 6.81 (m, 2H), 6.52 – 6.34 (m, 2H), 4.75 (d, *J* = 8.3 Hz, 1H), 3.78 (s, 3H), 2.38 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.2, 160.0, 144.9, 144.7, 137.9, 136.6, 135.0, 134.5, 134.4, 134.2, 131.3, 131.1, 131.0, 129.53, 129.46, 129.42, 129.39, 129.0, 128.9, 128.6, 128.2, 128.1, 124.1, 121.1, 117.2, 114.3, 114.2, 74.8, 74.7, 55.4, 21.8.

HRMS (ESI, Q-TOF) m/z: [M+Na$^+$] Calcd for $NaC_{23}H_{21}ClO_3S$, 435.0792. Found: 435.0796.



P38

4-(4-((1,3-bis(4-methoxyphenyl)allyl)sulfonyl)phenyl)-5-methyl-3-phenylisoxazole (P38) was prepared according to general procedure **A**.

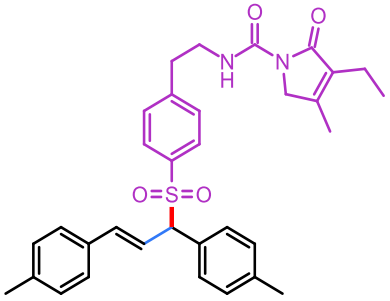
Yield: 41% (in DCM, 45.2 mg, white solid)

mp:77.2 - 78.1 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.1 Hz, 2H), 7.42 – 7.37 (m, 1H), 7.35 – 7.26 (m, 8H), 7.21 (d, *J* = 8.1 Hz, 2H), 6.88 – 6.82 (m, 4H), 6.50 – 6.37 (m, 2H), 4.80 (d, *J* = 8.6 Hz, 1H), 3.81 (s, 3H), 3.80 (s, 3H), 2.43 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 160.3, 160.1, 137.8, 136.9, 136.2, 131.0, 130.0, 129.9, 129.8, 128.81, 128.75, 128.6, 128.2, 124.2, 117.5, 114.6, 114.3, 114.2, 75.1, 55.5, 11.8.

HRMS (ESI, Q-TOF) m/z: [M+Na^+] Calcd for $NaC_{33}H_{29}O_5NS$, 574.1659. Found: 574.1653.



P39

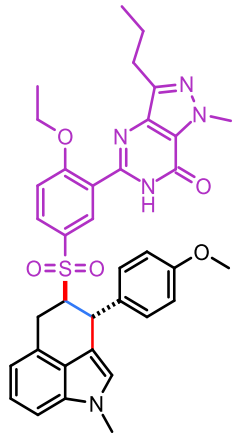
***N*-(4-((1,3-di-*p*-tolylallyl)sulfonyl)phenethyl)-3-ethyl-4-methyl-2-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxamide (P39)** was prepared according to general procedure **A**.

Yield: 51% (in DCM, 56.8 mg, colorless oil)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 – 8.43 (m, 1H), 7.58 (d, *J* = 7.9 Hz, 2H), 7.26 (d, *J* = 9.8 Hz, 2H), 7.23 – 7.16 (m, 4H), 7.13 – 7.07 (m, 4H), 6.51 – 6.41 (m, 2H), 4.76 (d, *J* = 7.3 Hz, 1H), 4.16 (s, 2H), 3.59 – 3.53 (m, 2H), 2.92 (t, *J* = 7.0 Hz, 2H), 2.32 (s, 6H), 2.27 – 2.23 (m, 2H), 2.03 (s, 3H), 1.04 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 152.7, 150.5, 145.4, 138.9, 138.5, 137.9, 135.6, 133.9, 133.3, 129.8, 129.7, 129.5, 129.4, 129.1, 126.8, 119.3, 75.3, 52.3, 40.6, 36.1, 21.4, 21.3, 16.7, 13.3, 12.9.

HRMS (ESI, Q-TOF) m/z: [M+Na^+] Calcd for $NaC_{33}H_{36}O_4N_2S$, 579.2288. Found: 579.2293.



P40

5-(2-ethoxy-5-((3-(4-methoxyphenyl)-1-methyl-1,3,4,5-tetrahydrobenzo[*cd*]indol-

4-yl)sulfonyl)phenyl)-1-methyl-3-propyl-1,6-dihydro-7*H*-pyrazolo[4,3-*d*]pyrimidin-7-one (P40) (mixture of >20:1 inseparable isomers) was prepared according to general procedure **A**.

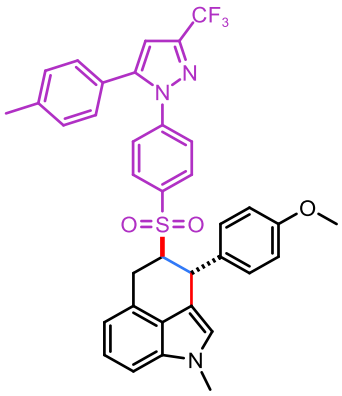
Yield: 43% (in EA, 56.1 mg, dark green solid)

mp:128.3 - 130.2 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.69 (s, 1H), 8.31 (d, *J* = 2.3 Hz, 1H), 7.28 (d, *J* = 2.1 Hz, 1H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 7.2 Hz, 1H), 6.78 (d, *J* = 8.2 Hz, 1H), 6.73 – 6.67 (m, 3H), 6.54 (s, 1H), 6.37 (d, *J* = 8.8 Hz, 1H), 5.09 (d, *J* = 2.2 Hz, 1H), 4.26 (s, 3H), 4.19 – 4.11 (m, 2H), 3.70 (s, 3H), 3.68 – 3.64 (m, 1H), 3.52 – 3.46 (m, 1H), 3.35 (s, 3H), 3.33 – 3.26 (m, 1H), 2.97 (t, *J* = 7.5 Hz, 2H), 1.96 – 1.87 (m, 2H), 1.57 (t, *J* = 6.9 Hz, 3H), 1.07 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 158.4, 153.6, 146.8, 146.4, 138.4, 135.5, 134.1, 131.9, 131.3, 130.1, 128.9, 126.4, 126.0, 124.7, 124.2, 122.6, 118.3, 116.6, 113.9, 110.74, 110.71, 106.6, 69.1, 65.8, 55.2, 38.5, 38.3, 32.6, 27.7, 24.5, 22.4, 14.6, 14.1.

HRMS (ESI, Q-TOF) m/z: [M+Na^+] Calcd for $NaC_{36}H_{37}O_5N_5S$, 674.2408. Found: 674.2408.



P41

3-(4-methoxyphenyl)-1-methyl-4-((4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)phenyl)sulfonyl)-1,3,4,5-tetrahydrobenzo[*cd*]indole (P41) (mixture of >20:1 inseparable isomers) was prepared according to general procedure **A**.

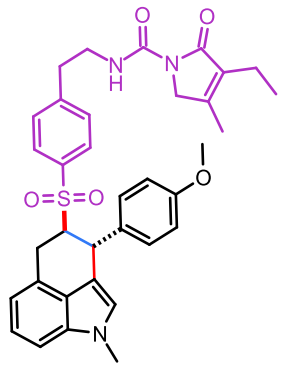
Yield: 38% (in EA, 48.8 mg, dark green oil)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.9 Hz, 2H), 7.09 (d, *J* = 7.6 Hz, 2H), 7.02 – 6.94 (m, 5H), 6.87 (d, *J* = 8.3 Hz, 1H), 6.79 – 6.68 (m, 6H), 6.53 (s, 1H), 5.01 (d, *J* = 1.8 Hz, 1H), 3.74 (s, 3H), 3.70 (s, 4H), 3.52 – 3.46 (m, 1H), 3.34 – 3.27 (m, 1H), 2.33 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 145.0, 143.7, 142.3, 139.7, 136.9, 135.2, 134.4, 129.9, 129.7, 129.2, 128.8, 128.7, 126.7, 125.69, 125.65, 124.7, 123.2, 122.6, 116.4, 114.0, 110.5, 107.8, 106.0, 69.6, 55.4, 38.7, 32.9, 24.8, 21.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.37.

HRMS (ESI, Q-TOF) m/z: [M+Na^+] Calcd for $NaC_{36}H_{30}O_3F_3N_3S$, 664.1852. Found: 664.1854.



P42

3-ethyl-*N*-(4-((3-(4-methoxyphenyl)-1-methyl-1,3,4,5-tetrahydrobenzo[*cd*]indol-4-yl)sulfonyl)phenethyl)-4-methyl-2-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxamide (**P42**) (mixture of >20:1 inseparable isomers) was prepared according to general procedure **A**.

Yield: 34% (in EA, 41.6 mg, dark green solid)

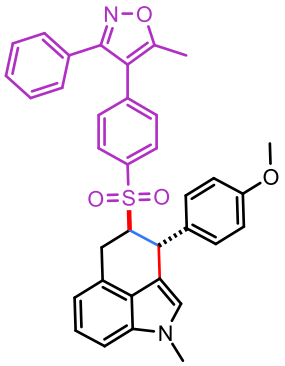
mp:85.0 - 86.3 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (t, *J* = 5.5 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.09 – 7.05 (m, 1H), 7.00 – 6.91 (m, 3H), 6.84 (d, *J* = 8.1 Hz, 2H), 6.80 (d, *J* = 7.0 Hz, 1H), 6.71 (d, *J* = 8.6 Hz, 2H), 6.51 (s, 1H), 4.99 (d, *J* = 3.5 Hz, 1H), 4.19 (s, 2H), 3.76 – 3.71 (m, 4H), 3.63 (s, 3H), 3.52 – 3.41 (m, 3H), 3.37 – 3.30 (m, 1H), 2.74 (t, *J* = 7.6 Hz, 2H), 2.31 – 2.24 (m, 2H), 2.06 – 2.01 (m, 3H), 1.06 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 158.5, 152.6, 150.5, 144.1, 136.0, 135.4, 134.3, 134.0, 129.2, 128.5, 127.7, 126.7, 126.2, 124.4, 122.7, 116.3, 113.9, 111.5, 107.1, 69.0, 55.3, 52.3, 40.8, 38.7, 36.1, 32.9, 25.0, 16.7, 13.3, 12.9.

HRMS (ESI, Q-TOF) m/z: [M+Na^+] Calcd for $NaC_{35}H_{37}O_5N_3S$, 634.2346.

Found: 634.2345.



P43

4-(4-((3-(4-methoxyphenyl)-1-methyl-1,3,4,5-tetrahydrobenzo[*cd*]indol-4-yl)sulfonyl)phenyl)-5-methyl-3-phenylisoxazole (P43) (mixture of >20:1 inseparable isomers) was prepared according to general procedure **A**.

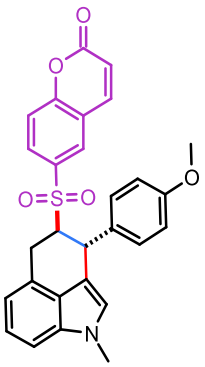
Yield: 52% (in EA, 59.8 mg, dark green solid)

mp:156.3 - 157.2 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 3H), 7.34 – 7.28 (m, 4H), 7.09 (t, *J* = 7.5 Hz, 1H), 7.00 – 6.94 (m, 3H), 6.86 (d, *J* = 7.7 Hz, 2H), 6.82 (d, *J* = 6.9 Hz, 1H), 6.72 (d, *J* = 8.1 Hz, 2H), 6.54 (s, 1H), 5.03 (d, *J* = 2.9 Hz, 1H), 3.85 – 3.80 (m, 1H), 3.73 (s, 3H), 3.62 (s, 3H), 3.55 – 3.48 (m, 1H), 3.44 – 3.37 (m, 1H), 2.48 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 161.1, 158.6, 137.6, 135.2, 135.1, 134.3, 129.8, 129.3, 128.8, 128.5, 128.4, 126.8, 126.2, 124.4, 122.8, 116.2, 114.5, 113.9, 111.8, 107.2, 69.1, 55.3, 38.9, 33.0, 25.2, 11.9.

HRMS (ESI, Q-TOF) m/z: [M+Na^+] Calcd for $NaC_{35}H_{30}O_4N_2S$, 597.1818. Found: 597.1819.



P44

6-((3-(4-methoxyphenyl)-1-methyl-1,3,4,5-tetrahydrobenzo[*cd*]indol-4-yl)sulfonyl)-2*H*-chromen-2-one (P44) (mixture of >20:1 inseparable isomers) was prepared according to general procedure **A**.

Yield: 40% (in EA, 38.8 mg, dark green solid)

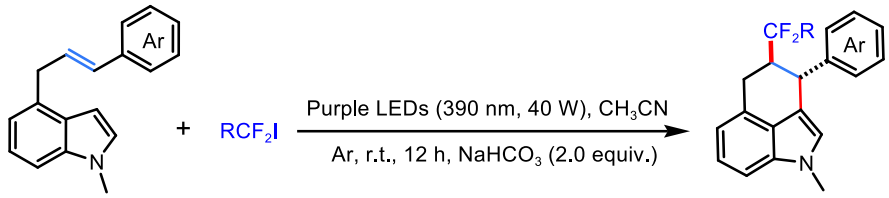
mp:176.7 - 177.4 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.6 Hz, 1H), 7.38 – 7.32 (m, 2H), 6.99 (d, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 6.9 Hz, 1H), 6.77 – 6.70 (m, 4H), 6.54 (s, 1H), 6.38 (d, *J* = 9.6 Hz, 1H), 5.05 (s, 1H), 3.72 (s, 4H), 3.57 – 3.50 (m, 4H), 3.34 – 3.27 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 158.7, 156.1, 142.8, 135.1, 134.3, 133.4, 130.9, 129.1, 128.6, 126. 6, 125.9, 124.5, 123. 1, 116.9, 116.7, 115.1, 114.1, 110.7, 107.2, 69.6, 55.4, 38.6, 32.8, 24.5.

HRMS (ESI, Q-TOF) m/z: [M+Na$^+$] Calcd for $NaC_{28}H_{23}O_5NS$, 508.1189. Found: 508.1190.

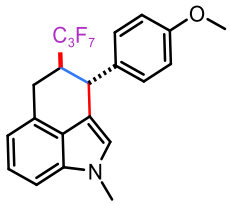
4.3 General procedure B



Scheme **S3**

β-4'-methindolylstyrene derivatives (0.2 mmol, 1.0 equiv.), fluoroalkylation reagent (0.3 mmol, 1.5 equiv.), $NaHCO_3$ (0.4 mmol, 2.0 equiv.) was sequentially added to a 25 mL Schlenk tube containing a magnetic stirring bar. The Schlenk tube was evacuated and purged with argon three times. Subsequently, dry MeCN (2.0 mL, 0.1 M) was introduced into the Schlenk tube under a counter flow of argon. The reaction mixture was tightly sealed, stirred, and irradiated with 40 W Kessil LEDs (λmax = 390 nm) at room temperature while continuously cooled with a fan. After the reaction was complete, the solvent was evaporated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (PE/EA = 30:1) to obtain the desired product **P45-P48**.

4.4 Characterization of products **P45-P48**



P45

3-(4-methoxyphenyl)-1-methyl-4-(perfluoropropyl)-1,3,4,5-tetrahydrobenzo[*cd*]indole (P45) (mixture of >20:1 inseparable isomers) was

prepared according to general procedure **B**.

Yield: 47% (41.9 mg, dark green solid)

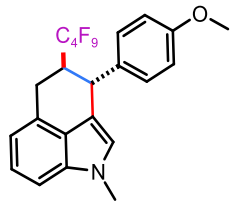
mp:72.4 - 73.5 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.16 (m, 2H), 7.02 (d, *J* = 8.3 Hz, 2H), 6.90 (d, *J* = 6.2 Hz, 1H), 6.81 (d, *J* = 8.4 Hz, 2H), 6.61 (s, 1H), 4.68 (d, *J* = 4.1 Hz, 1H), 3.78 (s, 3H), 3.77 (s, 3H), 3.21 – 3.16 (m, 2H), 3.09 – 2.98 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 136.7, 134.5, 129.1, 127.7, 126.9, 124.2, 122.7, 115.6, 113.9, 113.1, 107.3, 55.4, 45.0 (t, *J* = 18.9 Hz), 37.5 (d, *J* = 3.3 Hz), 33.1, 24.4 (d, *J* = 3.7 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.50 (t, *J* = 11.0 Hz, 3F), -109.83 – -110.77 (m, 1F), -114.66 – -115.62 (m, 1F), -123.31 – -124.18 (m, 1F), -125.32 – -126.17 (m,1F).

HRMS (ESI, Q-TOF) m/z: [M+Na$^+$] Calcd for $NaC_{22}H_{18}OF_7N$, 468.1169. Found: 468.1168.



P46

3-(4-methoxyphenyl)-1-methyl-4-(perfluorobutyl)-1,3,4,5-tetrahydrobenzo[*cd*]indole (P46) (mixture of >20:1 inseparable isomers) was prepared according to general procedure **B**.

Yield: 58% (57.5 mg, dark green solid)

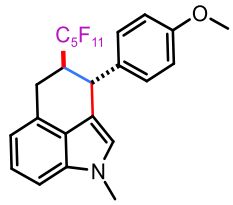
mp:86.5 - 87.2 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.17 (m, 2H), 7.02 (d, *J* = 8.5 Hz, 2H), 6.91 (d, *J* = 6.1 Hz, 1H), 6.81 (d, *J* = 8.5 Hz, 2H), 6.62 (s, 1H), 4.70 (d, *J* = 3.6 Hz, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 3.22 – 3.16 (m, 2H), 3.13 – 2.97 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 136.7, 134.5, 129.2, 127.7, 127.0, 124.1, 122.7, 115.6, 113.9, 112.9, 107.3, 55.4, 45.2 (t, *J* = 19.1 Hz), 37.5, 33.1, 24.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.90 (t, *J* = 9.5 Hz, 3F), -109.64 – -110.58 (m, 1F), -113.82 – -114.74 (m, 1F), -120.85 – -121.44 (m, 1F), -121.55 – -122.12 (m, 1F), -124.69 – -125.72 (m, 1F), -126.21 – -127.12 (m, 1F).

HRMS (ESI, Q-TOF) m/z: [M+H$^+$] Calcd for $C_{23}H_{19}OF_9N$, 496.1317. Found: 496.1311.



P47

3-(4-methoxyphenyl)-1-methyl-4-(perfluoropentyl)-1,3,4,5-tetrahydrobenzo[*cd*]indole (P47) (mixture of >20:1 inseparable isomers) was prepared according to general procedure **B**.

Yield: 51% (55.6 mg, dark green solid)

mp:93.5 - 94.3 °C

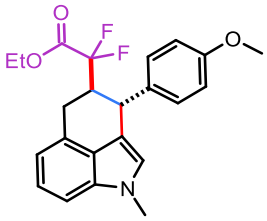
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.19 (m, 1H), 7.18 (d, *J* = 8.3 Hz,

1H), 7.01 (d, J = 8.4 Hz, 2H), 6.90 (d, J = 6.1 Hz, 1H), 6.80 (d, J = 8.5 Hz, 2H), 6.62 (s, 1H), 4.69 (d, J = 3.8 Hz, 1H), 3.78 (s, 3H), 3.76 (s, 3H), 3.21 – 3.15 (m, 2H), 3.08 – 3.00 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 136.7, 134.5, 129.1, 127.7, 127.0, 124.1, 122.7, 115.6, 113.9, 112.9, 107.3, 55.4, 45.2 (t, J = 19.2 Hz), 37.5, 33.1, 24.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.79 (t, J = 9.9 Hz, 3F), -109.48 – -110.52 (m, 1F), -113.62 – -114.74 (m, 1F), -119.70 – -120.98 (m, 2F), -122.22 – -123.80 (m, 2F), -125.02 – -127.36 (m, 2F).

HRMS (ESI, Q-TOF) m/z: [M+H$^+$] Calcd for $C_{24}H_{19}OF_{11}N$, 546.1286. Found: 546.1285.



P48

ethyl 2,2-difluoro-2-(3-(4-methoxyphenyl)-1-methyl-1,3,4,5-tetrahydrobenzo[*cd*]indol-4-yl)acetate (P48) (mixture of >20:1 inseparable isomers) was prepared according to general procedure **B**.

Yield: 62% (49.5 mg, dark green oil)

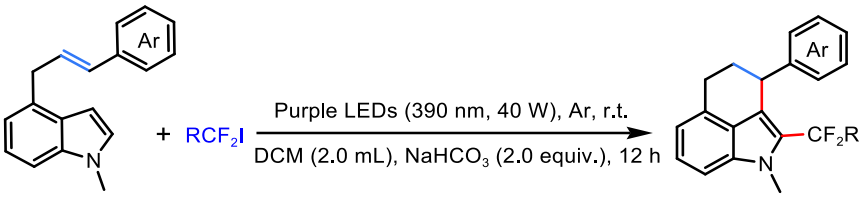
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.12 (m, 4H), 6.92 (d, J = 7.0 Hz, 1H), 6.82 (d, J = 7.9 Hz, 2H), 6.36 (s, 1H), 4.34 (d, J = 8.0 Hz, 1H), 3.80 (s, 4H), 3.74 – 3.65 (m, 5H), 3.31 – 3.17 (m, 2H), 1.13 (t, J = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 134.6, 134.5, 130.4, 129.7, 128.6, 126.9, 124.2, 122.7, 115.84, 115.77, 113.9, 113.6, 107.0, 62.6, 55.4, 46.9 (t, J = 20.0 Hz), 39.7, 33.0, 26.1, 13.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -102.95 – -103.85 (m, 1F), -112.77 – -113.69 (m, 1F).

HRMS (ESI, Q-TOF) m/z: [M+Na^+] Calcd for $NaC_{23}H_{23}O_3F_2N$, 422.1538. Found: 422.1539.

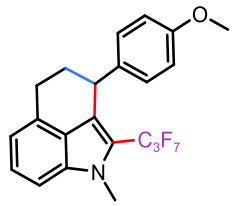
4.5 General procedure C



Scheme **S4**

A mixture of *β*-4'-methindolylstyrene derivatives (A) (0.2 mmol, 1.0 equiv.), fluoroalkylation reagent (0.3 mmol, 1.5 equiv.), $NaHCO_3$ (0.4 mmol, 2.0 equiv.) in DCM (2.0mL) was tightly sealed, stirred, and irradiated with 40 W Kessil LEDs (λmax = 390 nm) for 12 h at room temperature while continuously cooled with a fan. Upon completion of the reaction, the solvent was removed under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel using a gradient of petroleum ether and ethyl acetate gradient (PE/EA = 30:1) to obtain the desired product **P49-P52**.

4.6 Characterization of products **P49-P5**2



P49

3-(4-methoxyphenyl)-1-methyl-2-(perfluoropropyl)-1,3,4,5-tetrahydrobenzo[*cd*]indole (P49) was prepared according to general procedure **C**.

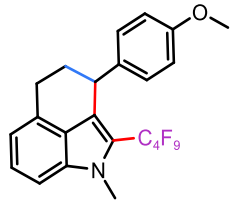
Yield: 49% (43.6 mg, dark green oil)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 1H), 6.94 (d, *J* = 6.8 Hz, 1H), 6.85 (d, *J* = 8.5 Hz, 2H), 6.74 (d, *J* = 8.7 Hz, 2H), 4.53 – 4.47 (m, 1H), 3.84 (s, 3H), 3.75 (s, 3H), 2.83 – 2.72 (m, 2H), 2.29 – 2.15 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8, 137.4, 137.3, 134.0, 128.6, 125.9, 125.5, 121.74, 121.71, 117.2, 113.5, 107.2, 55.3, 37.5, 37.4, 33.2, 22.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.13 (t, *J* = 9.9 Hz, 3F), -104.37 – -105.31 (m, 1F), -106.03 – -107.08 (m, 1F), -124.88 – -125.47 (m, 1F), -125.52 – -126.34 (m, 1F).

HRMS (ESI, Q-TOF) m/z: [M+H$^+$] Calcd for $C_{22}H_{19}OF_7N$, 446.1349. Found: 446.1350.



P50

3-(4-methoxyphenyl)-1-methyl-2-(perfluorobutyl)-1,3,4,5-

tetrahydrobenzo[*cd*]indole (P50) was prepared according to general procedure **C**.

Yield: 43% (42.6 mg, dark green solid)

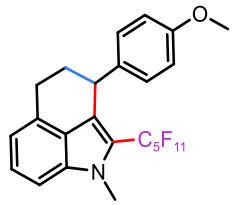
mp:72.7 - 73.6 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 1H), 6.94 (d, *J* = 6.8 Hz, 1H), 6.85 (d, *J* = 8.5 Hz, 2H), 6.74 (d, *J* = 8.7 Hz, 2H), 4.53 – 4.47 (m, 1H), 3.84 (s, 3H), 3.75 (s, 3H), 2.83 – 2.72 (m, 2H), 2.29 – 2.15 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 137.4, 134.0, 128.6, 125.9, 125.6, 121.93, 121.90, 121.88, 117.2, 113.5, 107.2, 55.3, 37.5, 33.2, 32.0, 22.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.13 – -80.18 (m, 3F), -104.86 (d, *J* = 292.9 Hz, 1F), -106.60 (d, *J* = 294.7 Hz, 1F), -125.47 – -125.53 (m, 2F), -125.61 – -125.66 (m, 2F).

HRMS (ESI, Q-TOF) m/z: [M+H$^+$] Calcd for $C_{23}H_{19}OF_9N$, 496.1317. Found: 496.1311.



P51

3-(4-methoxyphenyl)-1-methyl-2-(perfluoropentyl)-1,3,4,5-tetrahydrobenzo[*cd*]indole (P51) was prepared according to general procedure **C**.

Yield: 60% (65.4 mg, dark green solid)

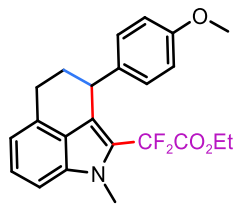
mp:93.4 - 94.6 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 1H), 7.22 (d, *J* = 8.1 Hz, 1H), 6.94 (d, *J* = 6.6 Hz, 1H), 6.85 (d, *J* = 7.9 Hz, 2H), 6.74 (d, *J* = 8.4 Hz, 2H), 4.53 – 4.46 (m, 1H), 3.84 (s, 3H), 3.75 (s, 3H), 2.82 – 2.71 (m, 2H), 2.29 – 2.15 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 137.41, 137.36, 134.1, 128.6, 125.9, 125.6, 117.2, 113.5, 107.2, 55.3, 37.5, 33.3, 32.0, 22.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.77 (t, *J* = 9.2 Hz, 3F), -103.29 – -104.35 (m, 1F), -105.24 – -106.21 (m, 1F), -121.23 (d, *J* = 14.8 Hz, 2F), -122.66 (s, 2F), -126.14 (s, 2F).

HRMS (ESI, Q-TOF) m/z: [M+H$^+$] Calcd for $C_{24}H_{19}OF_{11}N$, 546.1286. Found: 546.1289.



P52

ethyl -2,2-difluoro-2-(3-(4-methoxyphenyl)-1-methyl-1,3,4,5-tetrahydrobenzo[*cd*]indol-2-yl)acetate (P52) was prepared according to general procedure **C**.

Yield: 56% (44.7 mg, dark green oil)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 1H), 7.19 (d, *J* = 8.1 Hz, 1H), 6.90 (d, *J* = 6.9 Hz, 1H), 6.86 (d, *J* = 8.2 Hz, 2H), 6.73 (d, *J* = 8.3 Hz, 2H), 4.59 – 4.53 (m, 1H), 4.10 – 3.99 (m, 2H), 3.87 (s, 3H), 3.75 (s, 3H),

2.77 – 2.68 (m, 2H), 2.27 – 2.14 (m, 2H), 1.11 (t, J = 7.1 Hz, 3H).

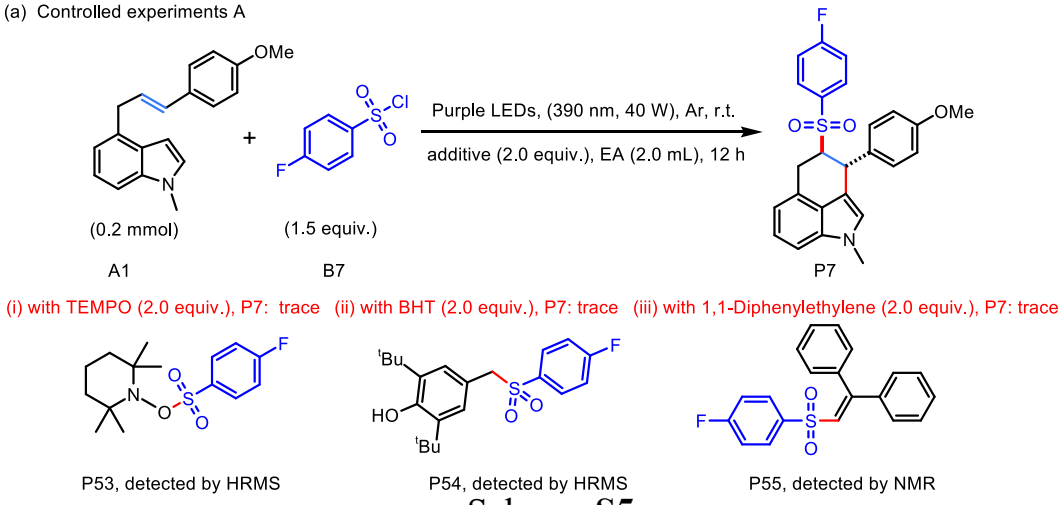
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6, 157.8, 137.3, 136.8, 133.8, 128.8, 126.0, 124.8, 118.3, 118.23, 118.16, 116.8, 113.4, 106.9, 63.3, 55.3, 37.1, 33.4, 31.8, 22.9, 13.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -97.94 (d, J = 272.4 Hz, 1F), -98.94 (d, J = 272.4 Hz, 1F).

HRMS (ESI, Q-TOF) m/z: [M+Na^+] Calcd for $NaC_{23}H_{23}O_3F_2N$, 422.1538. Found: 422.1537.

5. Mechanistic studies

5.1 Radical inhibition experiments and control experiments



Scheme **S5**

β-4'-methoxyindolylstyrene (A1) (0.2 mmol, 1.0 equiv.), *p*-Fluorobenzenesulfonyl chloride (B7) (0.3 mmol, 1.5 equiv.), and additive (0.4 mmol, 2.0 equiv.) were sequentially added to a 25 mL Schlenk tube containing a magnetic stirring bar. The tube was evacuated and purged with argon three times. After that, dry EA (2 mL, 0.1 M) was added under argon counterflow. The reaction mixture was tightly sealed, stirred, and irradiated

with 40 W Kessil LEDs (λmax = 390 nm) for 12 h at room temperature under continuous cooling via a fan. However, the reaction was found to be completely inhibited in the presence of additives, resulting in a significant decrease in the yield of P7 with only trace amounts of the target product obtained. Additionally, HRMS detected *p*-Fluorobenzenesulfonyl radical-TEMPO adduct and *p*-Fluorobenzenesulfonyl radical-BHT adduct, while NMR detected *p*-Fluorobenzenesulfonyl radical-1,1-Diphenylethylene adduct in the reactions.

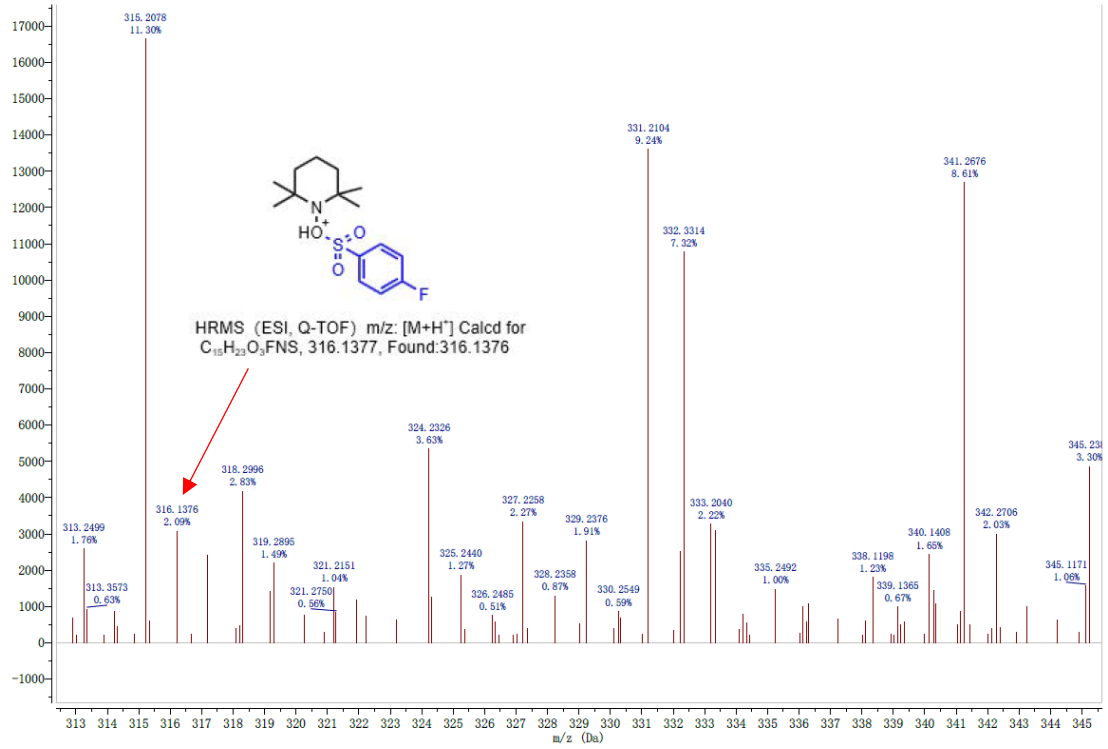


Figure **S2**. Analysis of reaction by HRMS

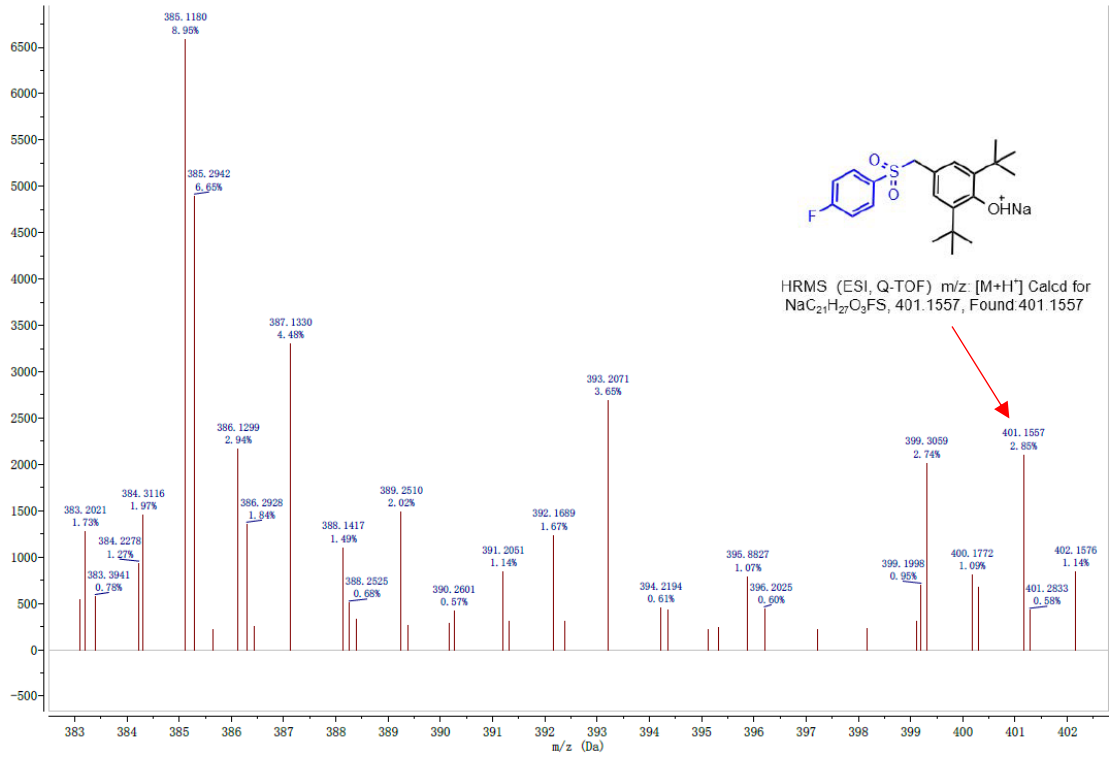
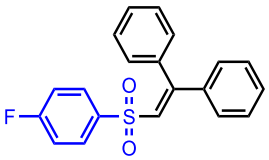


Figure **S3**. Analysis of reaction by HRMS

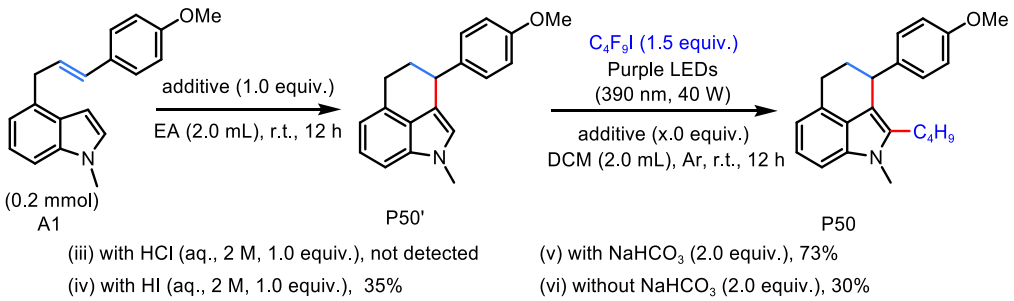


p-Fluorobenzenesulfonyl radical-1,1-Diphenylethylene adduct (P55)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.51 (m, 2H), 7.41 – 7.35 (m, 2H), 7.34 – 7.27 (m, 4H), 7.21 (d, *J* = 7.5 Hz, 2H), 7.09 – 7.03 (m, 3H), 6.99 (t, *J* = 8.6 Hz, 2H).

The spectra data are consistent with those reported in literature[5].

(b) Controlled experiments B



(iii) with HCl (aq., 2 M, 1.0 equiv.), not detected

(iv) with HI (aq., 2 M, 1.0 equiv.), 35%

(v) with $NaHCO_3$ (2.0 equiv.), 73%

(vi) without $NaHCO_3$ (2.0 equiv.), 30%

Scheme **S6**

To a 25 mL Schlenk tube were added *β*-4'-methindolylstyrene derivatives (A1) (0.2 mmol, 1.0 equiv.) HCl (aq. 2 M, 1.0 equiv.) or HI (aq. 2 M, 1.0 equiv.). The Schlenk tube was evacuated and re-filled with argon (repeated three times). Subsequently, dry EA (2.0 mL, 0.1 M) was introduced into the Schlenk tube under a counter flow of argon. The reaction mixture was sealed tightly, stirred, and irradiated with 40 W Kessil LEDs (λmax = 390 nm) for 12 h at room temperature under continuous cooling via the fan. Afterwards, the solvent was removed under reduced pressure. It was observed that the addition of HI (aq. 2 M, 1.0 equiv.) could lead to the formation of compound P50' in 35% yield, while HCl (aq. 2 M, 1.0 equiv.) was ineffective for this transformation. Then, the compound P50' (0.2 mmol, 1.0 equiv.), C_4F_9I (0.3 mmol, 1.5 equiv.), and additive (0.4 mmol, 2.0 equiv.) were sequentially added to a 25 mL Schlenk tube containing a magnetic stirring bar. The tube was evacuated and purged with argon three times. After that, dry DCM (2.0 mL, 0.1 M) was added under argon counterflow. The reaction mixture was tightly sealed, stirred, and irradiated with 40 W Kessil LEDs (λmax = 390 nm) for 12 h at room temperature under continuous cooling via a fan. Afterwards, the solvent was removed under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel using a gradient of petroleum ether and ethyl acetate gradient (PE/EA = 30:1) to obtain the desired product P50 in 73% and 30% yields, respectively.

5.2 Analysis of UV-Vis absorption spectra

UV-Vis absorption spectra were obtained using a UV-visible spectrophotometer (recorded in DCM in 1 mm path quartz cuvettes using a UV-5100H UV-Visible Spectrophotometer). The following samples were analyzed: a): A1 (0.01 M), TsCl (0.015 M), [A1 + TsCl] (0.01 M+0.015 M, A1: TsCl = 1:1.5); b): A1 (0.01 M), ICF_2COOEt (0.015 M), [A1 + ICF_2COOEt] (0.01 M+0.015 M, A1: ICF_2COOEt = 1:1.5); c): D2 (0.01 M), TsCl (0.015 M), [D2 + TsCl] (0.01 M+0.015 M, D2: TsCl = 1:1.5). Experimental results indicated that within the 300 nm-500/600 nm range, the mixed components [A1 + TsCl]/[A1 + ICF_2COOEt]/D2 + TsCl] exhibited a slight red-shift in absorbance compared to individual components, indicative of an EDA complex formation. The noticeable color change in the solution further supported the formation of the EDA complex. (In contrast, the color of DCM solution of 1,3-diphenylpropene and TsCl did not change immediately. However, after exposure to purple light for 1 hour, the stirring solution of 1,3-diphenylpropene D2 and tosyl chloride turned yellow). Absorption spectra of the individual reaction components and their mixtures were depicted in Figure S4/S5/S6.

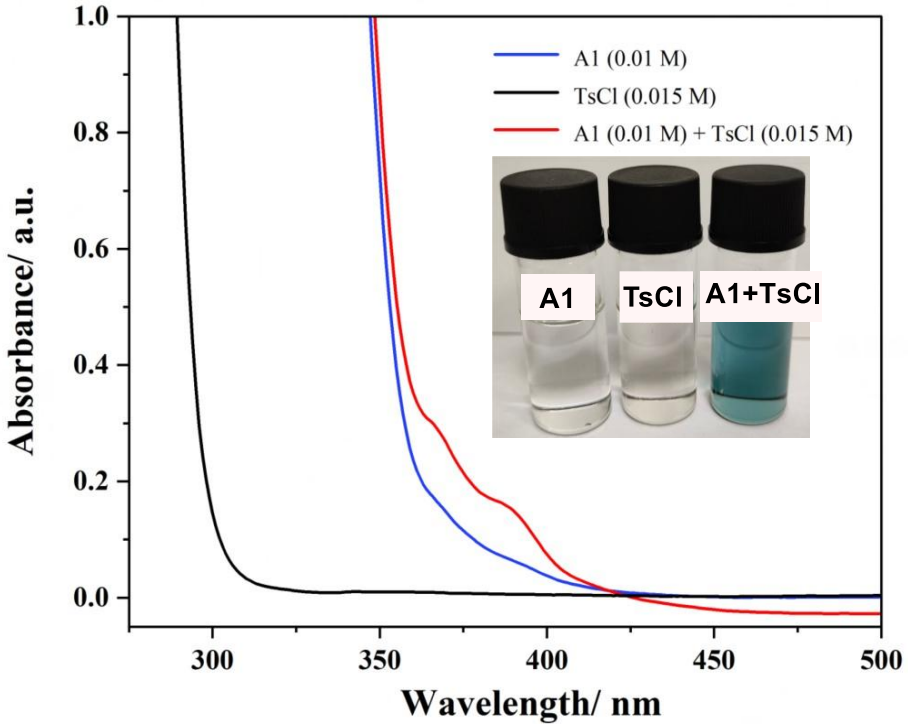


Figure **S4**. UV-vis spectrum of A1 and TsCl in DCM solution and their mixture

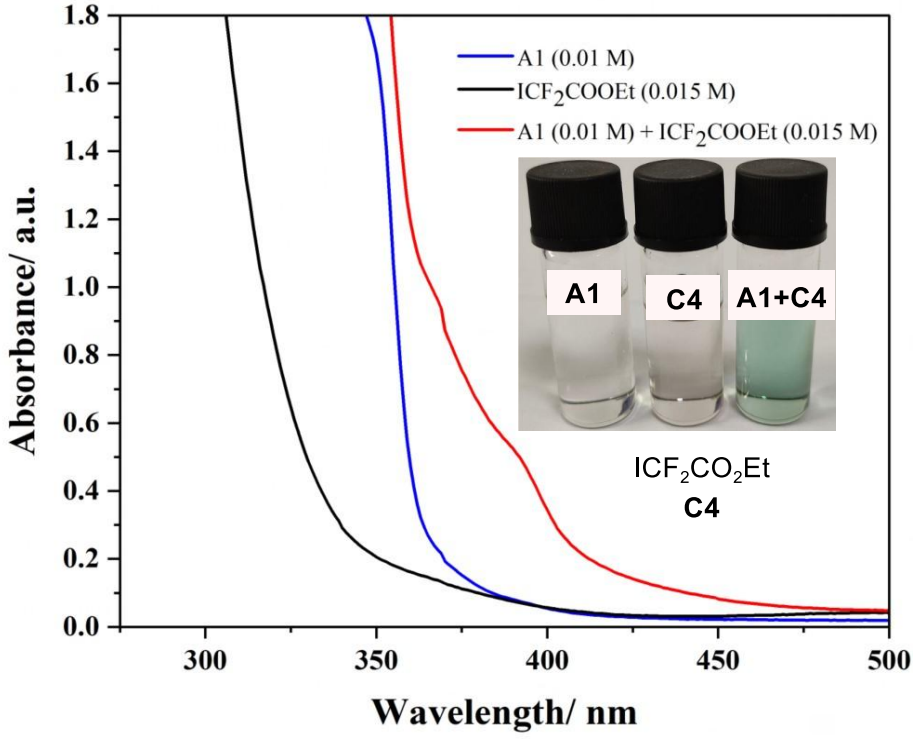


Figure **S5**. UV-vis spectrum of A1 and ICF_2COOEt in DCM solution and their mixture

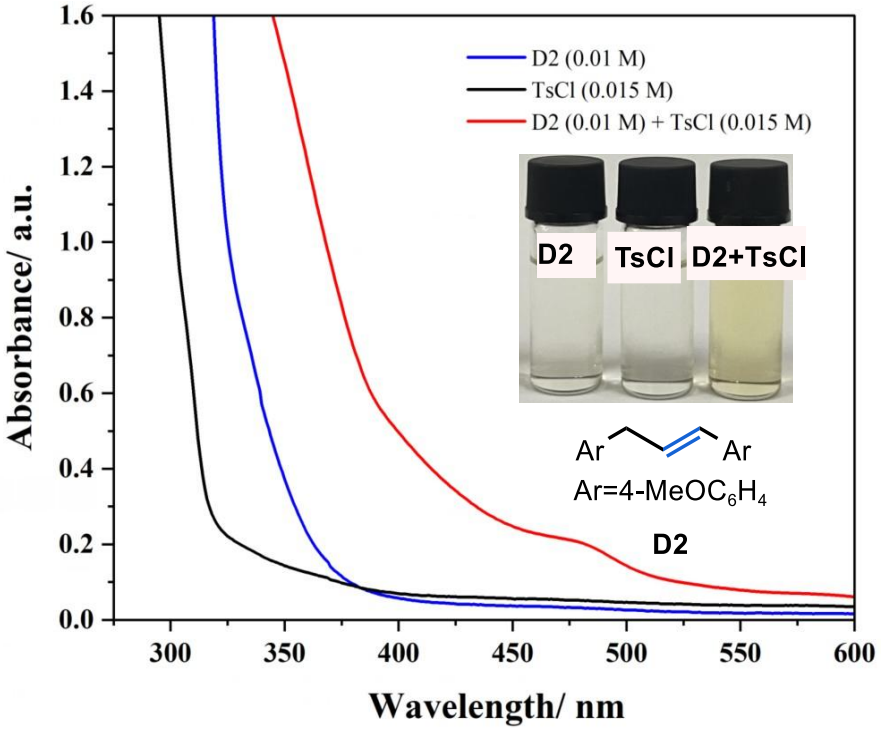


Figure **S6**. UV-vis spectrum of D2 and TsCl in DCM solution and their mixture

5.3 Stern-Volmer Fluorescence Quenching Experiments.

Fluorescence quenching experiments were conducted on *β*-4'-methoxyindolylstyrene (A1) with *p*-Toluenesulfonyl chloride (B1). The solution was irradiated at 330 nm, and fluorescence measurements were taken from 340 nm to 500 nm. Data was collected using an Agilent Cary Eclipse Fluorescence Spectrophotometer at 25 ℃. The experimental parameters were as follows: excitation wavelength: 330 nm, excitation bandwidth: 1.5 nm, emission bandwidth: 20.0 nm. The samples were analyzed in quartz cuvettes with a chamber volume of 10 mm (dimensions: H × W × D = 45 mm × 12.5 mm × 12.5 mm).

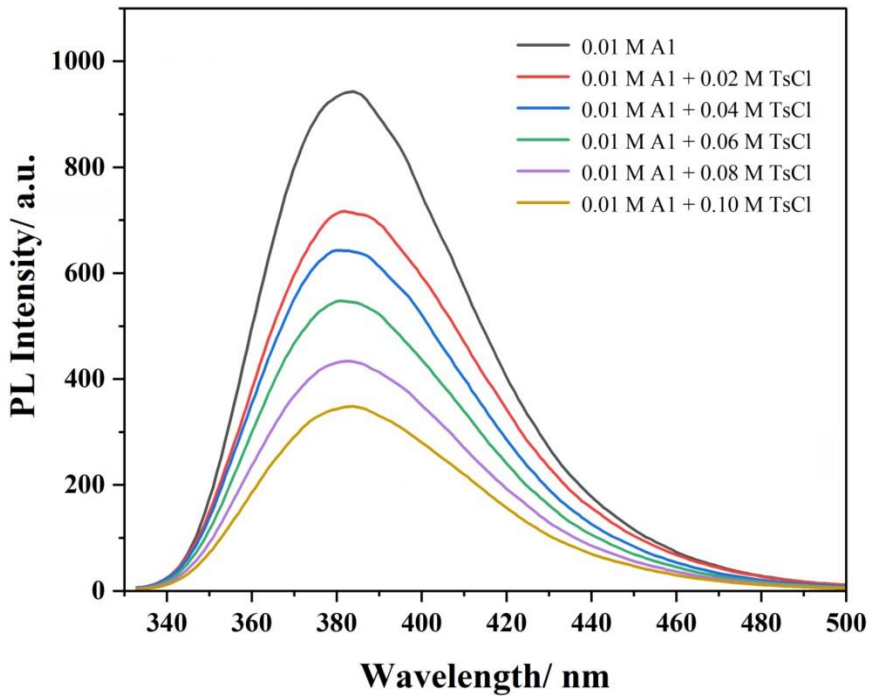


Figure **S7**. Fluorescence quenching of A1 (0.01 M) by increasing concentrations of TsCl

5.4 Job Plots

A Job's plot was drawn to evaluate the stoichiometry of the EDA complex involving *β*-4'-methoxyindolylstyrene (A1) and TsCl. Initially, the absorption spectrum of the EDA complex was recorded using a UV-5100H UV-Vis spectrophotometer in a 1 mm path quartz cuvette to identify its maximum absorption wavelength (refer to Figure S4). Subsequently, the absorption between 370-410 nm of an DCM solution with varying donor/acceptor ratios at a constant concentration (0.02 M) of both components was measured. The Job plot curve was generated using the mole fraction (%) of A1 on the x-axis and its corresponding absorbance on the y-axis. The findings indicated that at a mole fraction of 50% for A1, the

maximum absorbance value observed suggested a 1:1 stoichiometric ratio for the EDA complex formed by A1 and TsCl in the solution.

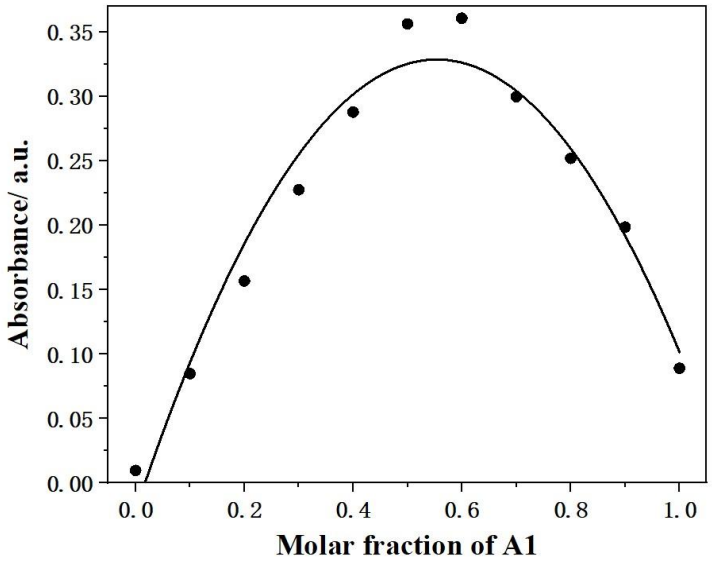
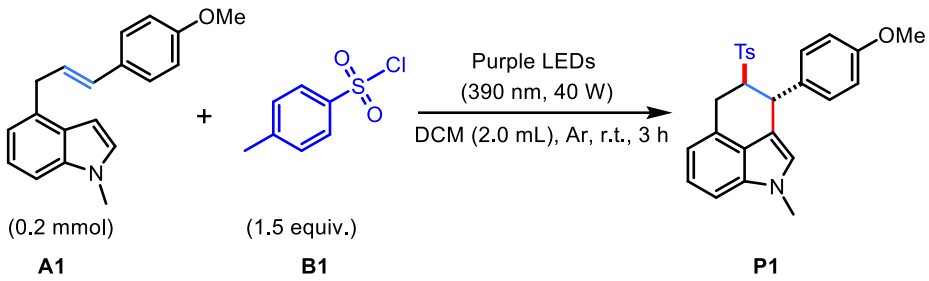


Figure **S8**. Job plot of A1 and TsCl

5.5 Light on-off experiment



Scheme **S7**

To a 25 mL Schlenk tube was added *β*-4'-methindolylstyrene (A1) (55.5 mg, 0.2 mmol, 1.0 equiv.), *p*-Toluenesulfonyl chloride (B1) (57.2 mg, 0.3 mmol, 1.5 equiv.). The Schlenk tube was evacuated and re-filled with argon three times. After that, dry DCM (2.0 mL, 0.1 M) was added into the Schlenk tube under argon counterflow. The reaction mixture was tightly sealed, stirred, and irradiated with 40 W Kessil LEDs (λmax = 390 nm) for 3 h at room temperature under continuous cooling via a fan. After

completion, the solvent was removed under reduced pressure. The residue was dissolved in 0.5 mL of $CDCl_3$ and utilized for ^1H NMR analysis, with 2-Phenylethanol (40 μL) serving as the internal standard.

Table **S2** Data of light on-off experiment.

Entry		yield of P1
1	Light On 0.5 h	12%
2	1 + Light Off 0.5 h	13%
3	2 + Light On 0.5 h	33%
4	3 + Light Off 0.5 h	32%
5	4 + Light On 0.5 h	55%
6	5 + Light Off 0.5 h	54%

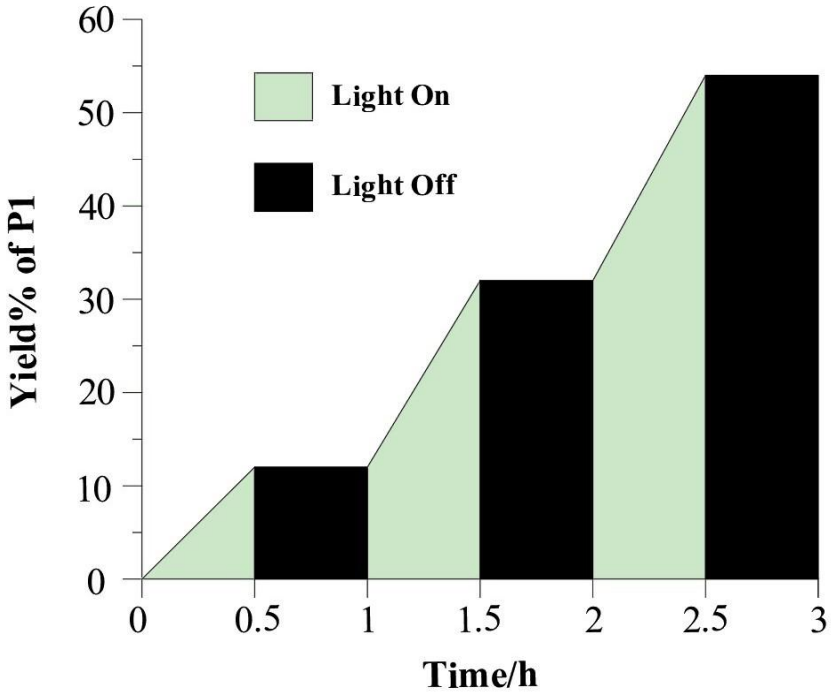


Figure **S9**. Light on-off experiment

5.6 Quantum yield measurements

Purple LED (λmax = 390 nm) was used for measurement of quantum yield.

Determination of the light intensity at 390 nm

According to the procedure of Xue[6], the photon flux of the LED (λmax = 390 nm) was determined by standard ferrioxalate actinometry. A 0.15 M solution of ferrioxalate was prepared by dissolving potassium ferrioxalate hydrate (0.737 g) in H_2SO_4 (10 mL of a 0.05 M solution). A buffered solution of 1,10-phenanthroline was prepared by dissolving 1,10-phenanthroline (10.0 mg) and sodium acetate (2.25 g) in H_2SO_4 (10.0 mL of a 0.5 M solution). Both solutions were stored in the dark. To determine the photon flux of the LED, the ferrioxalate solution (2.0 mL) was placed in a cuvette and irradiated for 30 seconds at λmax = 390 nm. After irradiation, the phenanthroline solution (0.35 mL) was added to the cuvette and the mixture was allowed to stir in the dark for 1 h to allow the ferrous ions to completely coordinate to the phenanthroline. The absorbance of the solution was measured at 510 nm. A non-irradiated sample was also prepared and the absorbance at 510 nm was measured. Conversion was calculated using eq 1.

$$\text{mol } Fe^{2+} = V \times \Delta A/1 \times \varepsilon = 0.00235 \times 1.6343/ 1 \text{ cm} \times 11100 \text{ L mol}^{-1}\text{cm}^{-1}$$

$$= 3.46 \times 10^{-7} \text{ mol} \quad (1)$$

V is the total volume (0.00235 L) of the solution after addition of phenanthroline, ΔA is the difference in absorbance at 510 nm between the

irradiated and non-irradiated solutions, l is the path length (1.00 cm), and ε is the molar absorptivity of the ferrioxalate actinometer at 510 nm (11,100 L $mol^{-1}cm^{-1}$). The photon flux can be calculated using eq 2.

Photon flux = mol $Fe^{2+}/\Phi*t*f$ = 3.46 x 10^{-7} mol /1.1 x 30 s x 0.999

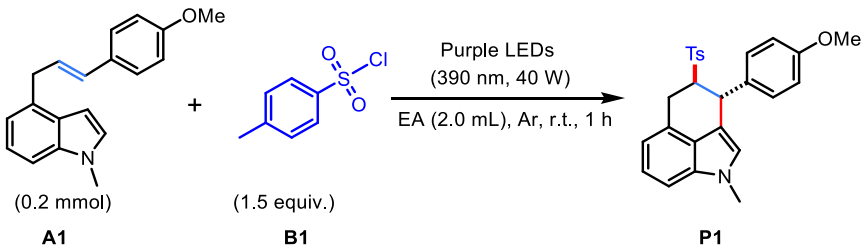
= 1.05 x 10^{-8} einsteins s^{-1}. (2)

Where Φ is the quantum yield for the ferrioxalate actinometer (1.1 at λ = 390 nm) is the irradiation time (30 s), and f is the fraction of light absorbed at 390 nm by the ferrioxalate actinometer. This value is calculated using eq 3 where $A_{390\ nm}$ is the absorbance of the ferrioxalate solution at 390 nm. An absorption spectrum gave an $A_{390\ nm}$ value of > 3, indicating that the fraction of absorbed light (f) is > 0.999.

$$f = 1 - 10^{-A} \quad (3)$$

According to the above formula, the photon flux was calculated to be 1.05 x 10^{-8} einsteins s^{-1}.

Determination of quantum yield:



Scheme **S8**

To a 25 mL Schlenk tube was added *β*-4'-methindolylstyrene (A1) (55.5 mg, 0.2 mmol, 1.0 equiv.), *p*-Toluenesulfonyl chloride (B1) (57.2 mg, 0.3 mmol, 1.5 equiv.). The Schlenk tube was evacuated and re-filled with argon (three times). After that, dry EA (2.0 mL, 0.1 M) was added into the

Schlenk tube under argon counter flow. The reaction mixture was tightly sealed, stirred and irradiated with 40 W Kessil LEDs (λmax = 390 nm) at room temperature under continuous cooling via fan. After irradiation, the solvent was removed under reduced pressure. The residue was dissolved in 0.5 mL of $CDCl_3$ and used for ^1H NMR analysis using 2-Phenylethanol (40 μL) as the internal standard, the yield of product to be 15%.

The quantum yield was determined using eq 4.

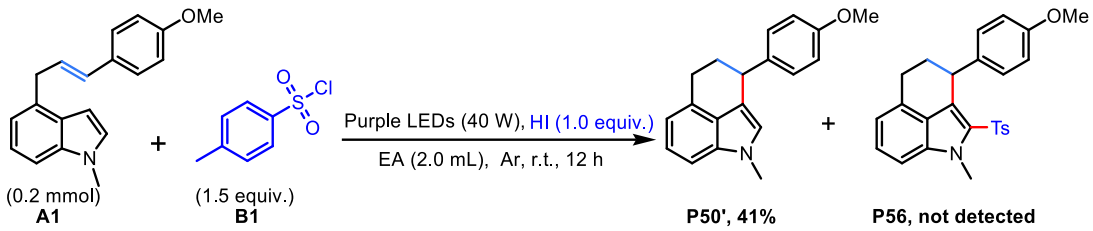
Φ = moles of product formed/ Photon flux x t x f (4)

$= 0.2 \times 0.15 \times 10^{-3} / 1.05 \times 10^{-8} \times 3600 \times 0.999$

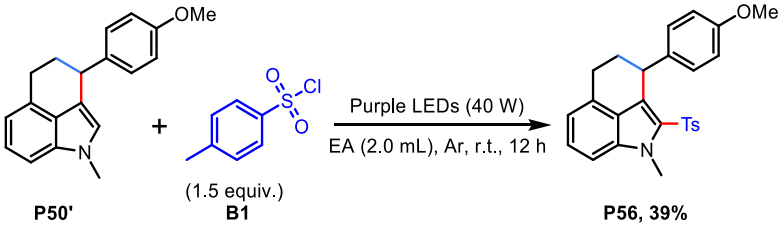
=0.8

The quantum yield Φ for the reaction was calculated to be 0.8.

6. Failed examples



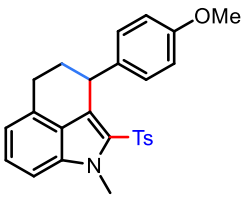
Scheme **S9**



Scheme **S10**

To a 25 mL Schlenk tube were added *β*-4'-methindolylstyrene derivatives (A1) (0.2 mmol, 1.0 equiv.), *p*-Toluenesulfonyl chloride (B1) (0.3 mmol, 1.5 equiv.), HI (aq. 2 M, 1.0 equiv.). The Schlenk tube was

evacuated and re-filled with argon (repeated three times). Subsequently, dry EA (2.0 mL, 0.1 M) was introduced into the Schlenk tube under a counter flow of argon. The reaction mixture was sealed tightly, stirred, and irradiated with 40 W Kessil LEDs (λmax = 390 nm) for 12 h at room temperature under continuous cooling via the fan. Afterwards, the solvent was removed under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel using a gradient of petroleum ether and ethyl acetate gradient (PE/EA = 30:1) to obtain the desired product P50'. Then, the compound P50' (0.2 mmol, 1.0 equiv.), *p*-Toluenesulfonyl chloride (B1) (0.3 mmol, 1.5 equiv.) were sequentially added to a 25 mL Schlenk tube containing a magnetic stirring bar. The tube was evacuated and purged with argon three times. After that, dry EA (2 mL, 0.1 M) was added under argon counterflow. The reaction mixture was tightly sealed, stirred, and irradiated with 40 W Kessil LEDs (λmax = 390 nm) for 12 h at room temperature under continuous cooling via a fan. Afterwards, the solvent was removed under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel using a gradient of petroleum ether and ethyl acetate gradient (PE/EA = 15:1 to 10:1) to obtain the desired product P56 in 39% yield.



P56

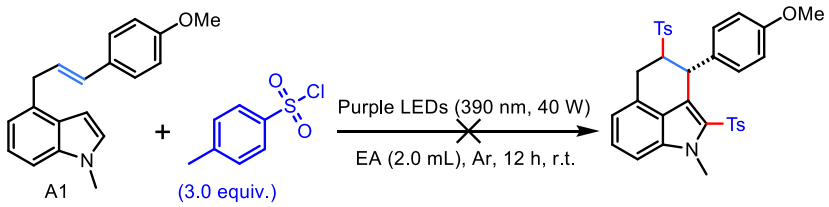
3-(4-methoxyphenyl)-1-methyl-2-tosyl-1,3,4,5-tetrahydrobenzo[cd]indole (P56) was prepared according to the above procedure.

Yield: 39% (33.7 mg, dark green oil)

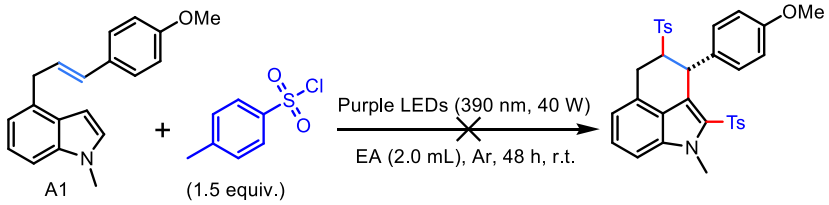
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.23 (m, 1H), 7.18 – 7.14 (m, 1H), 6.97 – 6.89 (m, 5H), 6.77 (d, *J* = 8.0 Hz, 2H), 6.71 (d, *J* = 8.4 Hz, 2H), 4.39 (t, *J* = 4.1 Hz, 1H), 3.87 – 3.76 (m, 2H), 3.75 (s, 3H), 3.68 (s, 3H), 2.92 – 2.83 (m, 2H), 2.24 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8, 137.6, 136.5, 135.4, 133.7, 132.7, 129.7, 129.0, 126.9, 126.7, 123.8, 123.6, 122.0, 116.1, 113.5, 107.0, 55.3, 38.0, 33.8, 30.1, 24.3, 21.0.

HRMS (ESI, Q-TOF) m/z: [M+Na$^+$] Calcd for $NaC_{26}H_{25}O_3NS$, 454.1453. Found: 454.1455.



Scheme **S11**

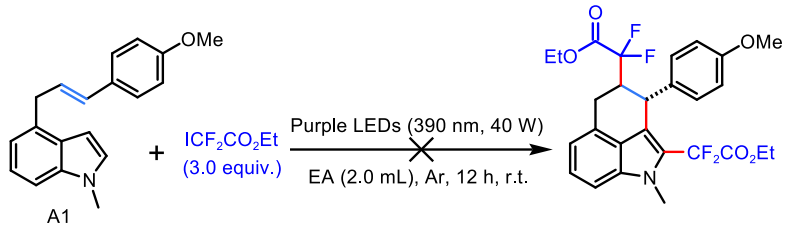


Scheme **S12**

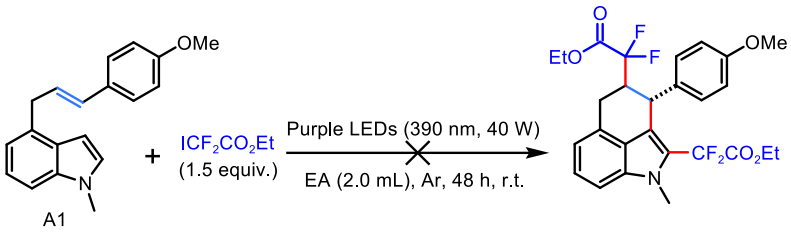
Condition A: To a 25 mL Schlenk tube were added *β*-4'-methindolylstyrene derivatives (A1) (0.2 mmol, 1.0 equiv.), *p*-Toluenesulfonyl chloride (B1) (0.6 mmol, 3.0 equiv.). The Schlenk tube was evacuated and re-filled with argon (repeated three times).

Subsequently, dry EA (2.0 mL, 0.1 M) was introduced into the Schlenk tube under a counter flow of argon. The reaction mixture was sealed tightly, stirred, and irradiated with 40 W Kessil LEDs (λmax = 390 nm) for 12 h at room temperature under continuous cooling via the fan. Afterwards, the solvent was removed under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel using a gradient of petroleum ether and ethyl acetate gradient (PE/EA = 15:1-5:1) to obtain the desired product A1.

Condition B: To a 25 mL Schlenk tube were added *β*-4'-methindolylstyrene derivatives (A1) (0.2 mmol, 1.0 equiv.), *p*-Toluenesulfonyl chloride (B1) (0.3 mmol, 1.5 equiv.). The Schlenk tube was evacuated and re-filled with argon (repeated three times). Subsequently, dry EA (2.0 mL, 0.1 M) was introduced into the Schlenk tube under a counter flow of argon. The reaction mixture was sealed tightly, stirred, and irradiated with 40 W Kessil LEDs (λmax = 390 nm) for 48 h at room temperature under continuous cooling via the fan. Afterwards, the solvent was removed under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel using a gradient of petroleum ether and ethyl acetate gradient (PE/EA = 15:1-5:1) to obtain the desired product A1.



Scheme **S13**

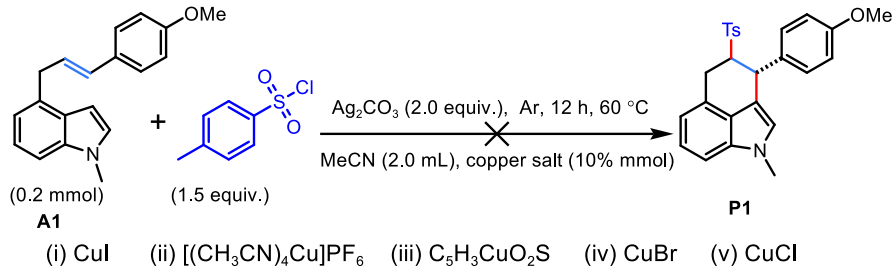


Scheme **S14**

Condition A: To a 25 mL Schlenk tube were added *β*-4'-methindolylstyrene derivatives (A1) (0.2 mmol, 1.0 equiv.), ICF_2CO_2Et (C4) (0.6 mmol, 3.0 equiv.). The Schlenk tube was evacuated and re-filled with argon (repeated three times). Subsequently, dry EA (2.0 mL, 0.1 M) was introduced into the Schlenk tube under a counter flow of argon. The reaction mixture was sealed tightly, stirred, and irradiated with 40 W Kessil LEDs (λmax = 390 nm) for 12 h at room temperature under continuous cooling via the fan. Afterwards, the solvent was removed under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel using a gradient of petroleum ether and ethyl acetate gradient (PE/EA = 15:1-5:1) to obtain the desired product A1.

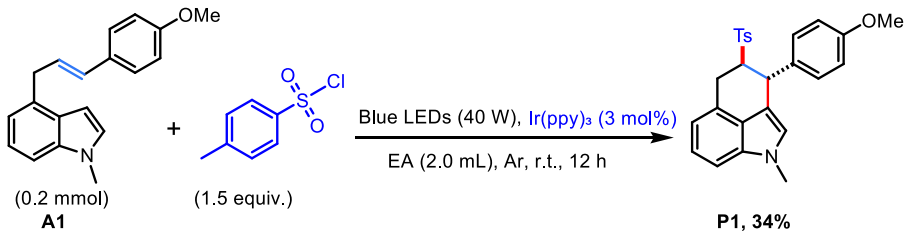
Condition B: To a 25 mL Schlenk tube were added *β*-4'-methindolylstyrene derivatives (A1) (0.2 mmol, 1.0 equiv.), ICF_2CO_2Et (C4) (0.3 mmol, 1.5 equiv.). The Schlenk tube was evacuated and re-filled with argon (repeated three times). Subsequently, dry EA (2.0 mL, 0.1 M)

was introduced into the Schlenk tube under a counter flow of argon. The reaction mixture was sealed tightly, stirred, and irradiated with 40 W Kessil LEDs (λmax = 390 nm) for 48 h at room temperature under continuous cooling via the fan. Afterwards, the solvent was removed under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel using a gradient of petroleum ether and ethyl acetate gradient (PE/EA = 15:1-5:1) to obtain the desired product A1.



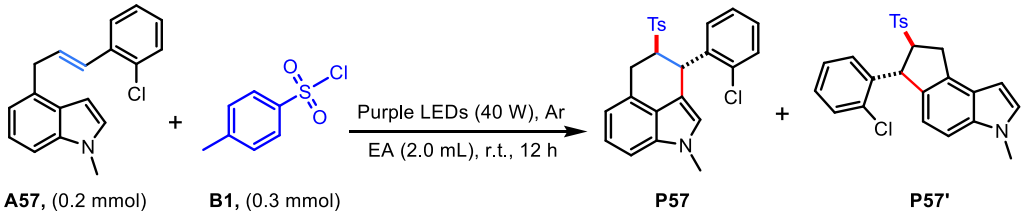
Scheme **S15**

To an oven-dried undivided 5 mL Reacti-Vial equipped with a stir bar was added (2.0 mL), *β*-4'-methindolylstyrene derivatives (A1) (0.2 mmol, 1.0 equiv.), *p*-Toluenesulfonyl chloride (B1) (0.3 mmol, 1.5 equiv.), Ag_2CO_3 (0.4 mmol, 2.0 equiv.), and copper salt (10% mmol). Then the reaction mixture was stirred under air atmosphere at 60 °C for 12 h. Afterwards, the mixture was concentrated under reduced pressure to afford the crude material. The pure product was isolated by flash column chromatography on silica gel using a gradient of petroleum ether and ethyl acetate gradient (PE/EA = 15:1 to 5:1) to obtain the desired product A1.



Scheme **S16**

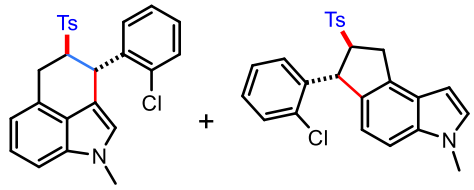
To a 25 mL Schlenk tube were added *β*-4'-methindolylstyrene derivatives (A1) (0.2 mmol, 1.0 equiv.), *p*-Toluenesulfonyl chloride (B1) (0.3 mmol, 1.5 equiv.), and $Ir(ppy)_3$ (3 mmol%). The Schlenk tube was evacuated and re-filled with argon (repeated three times). Subsequently, dry EA (2.0 mL, 0.1 M) was introduced into the Schlenk tube under a counter flow of argon. The reaction mixture was sealed tightly, stirred, and irradiated with 40 W Kessil LEDs (λmax = 456 nm) for 12 h at room temperature under continuous cooling via the fan. Afterwards, the solvent was removed under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel using a gradient of petroleum ether and ethyl acetate gradient (PE/EA = 15:1-5:1) to obtain the desired product P1.



Scheme **S17**

To a 25 mL Schlenk tube were added *β*-4'-methindolylstyrene derivatives (A57) (0.2 mmol, 1.0 equiv.), *p*-Toluenesulfonyl chloride (B1) (0.3 mmol, 1.5 equiv.). The Schlenk tube was evacuated and re-filled with

argon (repeated three times). Subsequently, dry EA (2.0 mL, 0.1 M) was introduced into the Schlenk tube under a counter flow of argon. The reaction mixture was sealed tightly, stirred, and irradiated with 40 W Kessil LEDs (λmax = 390 nm) for 12 h at room temperature under continuous cooling via the fan. Afterwards, the solvent was removed under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel using a gradient of petroleum ether and ethyl acetate gradient (PE/EA = 15:1-5:1) to obtain the desired product P57 and P57'.



P57+ P57'

3-(2-chlorophenyl)-1-methyl-4-tosyl-1,3,4,5-tetrahydrobenzo[cd]indole (P57) + 6-(2-chlorophenyl)-3-methyl-7-tosyl-3,6,7,8-tetrahydrocyclopenta[e]indole (P57') (mixture of 1:1.3 inseparable mixture) was prepared according to above procedure.

Yield: 27% (23.5 mg, dark green oil)

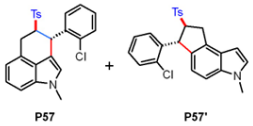
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.26 – 7.22 (m, 2H), 7.22 – 7.12 (m, 6H), 7.11 (t, *J* = 3.6 Hz, 1H), 7.09 – 7.01 (m, 3H), 6.95 (d, *J* = 8.3 Hz, 1H), 6.94 – 6.89 (m, 2H), 6.81 (d, *J* = 7.1 Hz, 1H), 6.77 (d, *J* = 8.2 Hz, 1H), 6.68 (d, *J* = 8.4 Hz, 1H), 6.51 (s, 1H), 6.40 (d, *J* = 3.0 Hz, 1H), 5.04 (d, *J* = 3.2 Hz, 1H), 4.96 (d, *J* = 6.2 Hz,

1H), 4.16 – 4.09 (m, 1H), 3.77 (s, 3H), 3.77 – 3.69 (m, 2H), 3.64 (s, 2H), 3.62 – 3.53 (m, 1H), 3.52 – 3.43 (m, 1H), 3.34 – 3.25 (m, 1H), 2.40 (s, 3H), 2.23 (s, 2H).

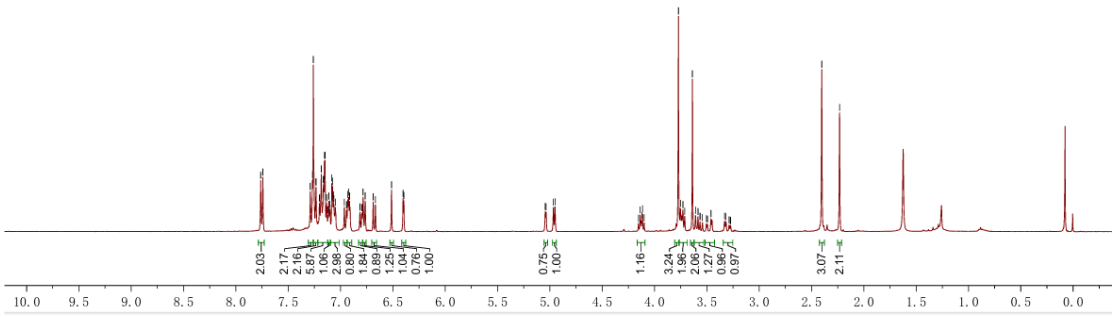
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.6, 144.1, 143.5, 143.4, 136.5, 135.6, 134.7, 134.5, 134.4, 131.1, 129.8, 129.4, 128.8, 128.6, 128.5, 128.3, 128.18, 128.15, 128.0, 126.9, 126.8, 126.7, 126.2, 124.5, 122.7, 118.5, 116.3, 111.0, 109.1, 106.9, 99.1, 72.3, 68.9, 52.6, 39.3, 33.3, 32.8, 32.1, 25.0, 21.7, 21.5.

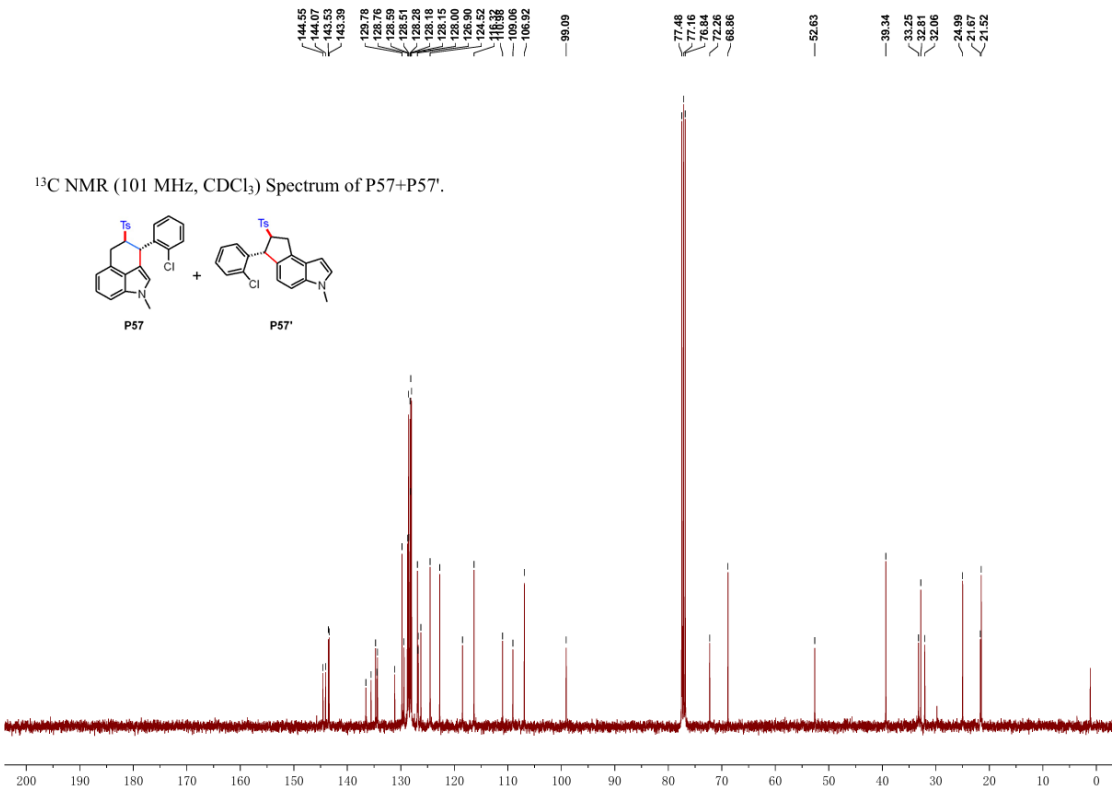
HRMS (ESI, Q-TOF) m/z: [M+Na$^+$] Calcd for $NaC_{25}H_{22}ClNO_2S$, 458.0952. Found: 458.0955.

^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P57+P57'.



P57 P57'



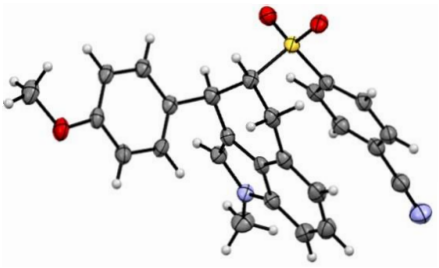


7. X-ray crystallographic data

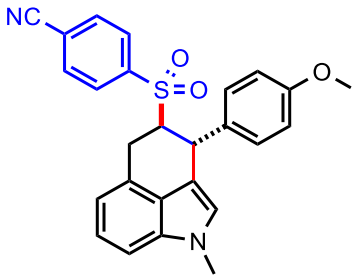
Preparation of the crystal: Single crystals for X-ray studies of compounds **P10 and P16'** were obtained by slow evaporation of a solution of the compound in the mixture of trichloromethane and *n*-heptane at room temperature.

Crystal measurement: Single crystals of compounds **P10 and P16'** were collected on a Rigaku Oxford Diffraction Supernova Dual Source, Cu at Zero, AtlasS2 diffractometer using Cu Kα radiation. The data were collected and processed using CrysAlisPro. Crystallographic data for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Center and allocated with the deposition numbers: CCDC 2286314 or compounds **P10**; CCDC 2286315 or compounds **P16'**

The ellipsoids are shown at 30% probability levels



X-ray of **P10**

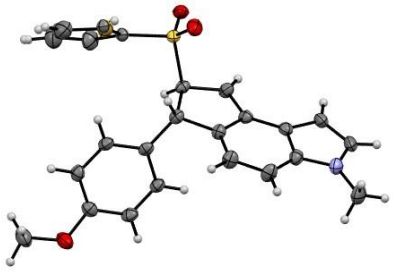


2286314

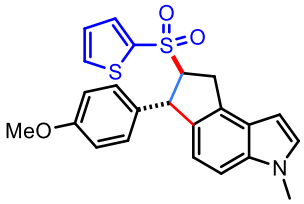
Identification code	**P10**
Empirical formula	$C_{26}H_{22}N_2O_3S$
Formula weight	442.51
Temperature/K	149.99(10)
Crystal system	triclinic
Space group	P-1
a/Å	8.8126(4)
b/Å	16.8927(7)
c/Å	19.2951(8)
α/°	65.104(4)
β/°	82.811(4)
γ/°	84.903(4)
Volume/Å^3	2582.9(2)
Z	4
ρ_{calc}g/cm^3	1.138
μ/mm^{-1}	1.329

F(000)	928.0
Crystal size/mm^3	0.16 × 0.14 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.074 to 133.186
Index ranges	$-10 \leq h \leq 10$, $-19 \leq k \leq 20$, $-11 \leq l \leq 22$
Reflections collected	16282
Independent reflections	9103 [R_{int} = 0.0820, R_{sigma} = 0.0904]
Data/restraints/parameters	9103/524/581
Goodness-of-fit on F^2	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.1100, wR_2 = 0.3322
Final R indexes [all data]	R_1 = 0.1368, wR_2 = 0.3525
Largest diff. peak/hole / e $Å^{-3}$	1.32/-0.86

The ellipsoids are shown at 30% probability levels



X-ray of **P16'**



2286315

Identification code	**P16'**
Empirical formula	$C_{23}H_{20}NO_3S_2$
Formula weight	422.52
Temperature/K	150.00(10)
Crystal system	orthorhombic
Space group	Pbca
a/Å	11.0229(2)
b/Å	16.8862(3)
c/Å	21.3037(3)
α/°	90
β/°	90
γ/°	90
Volume/Å3	3965.36(12)
Z	8
ρcalcg/cm3	1.415
μ/mm-1	2.644

F(000)	1768.0
Crystal size/mm3	0.16 × 0.14 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.3 to 147.244
Index ranges	-13 ≤ h ≤ 13, -10 ≤ k ≤ 20, -24 ≤ l ≤ 26
Reflections collected	10428
Independent reflections	3921 [Rint = 0.0450, Rsigma = 0.0454]
Data/restraints/parameters	3921/45/286
Goodness-of-fit on F2	1.037
Final R indexes [I>=2σ (I)]	R1 = 0.0590, wR2 = 0.1562
Final R indexes [all data]	R1 = 0.0694, wR2 = 0.1678
Largest diff. peak/hole / e Å-3	0.73/-0.71

8. References

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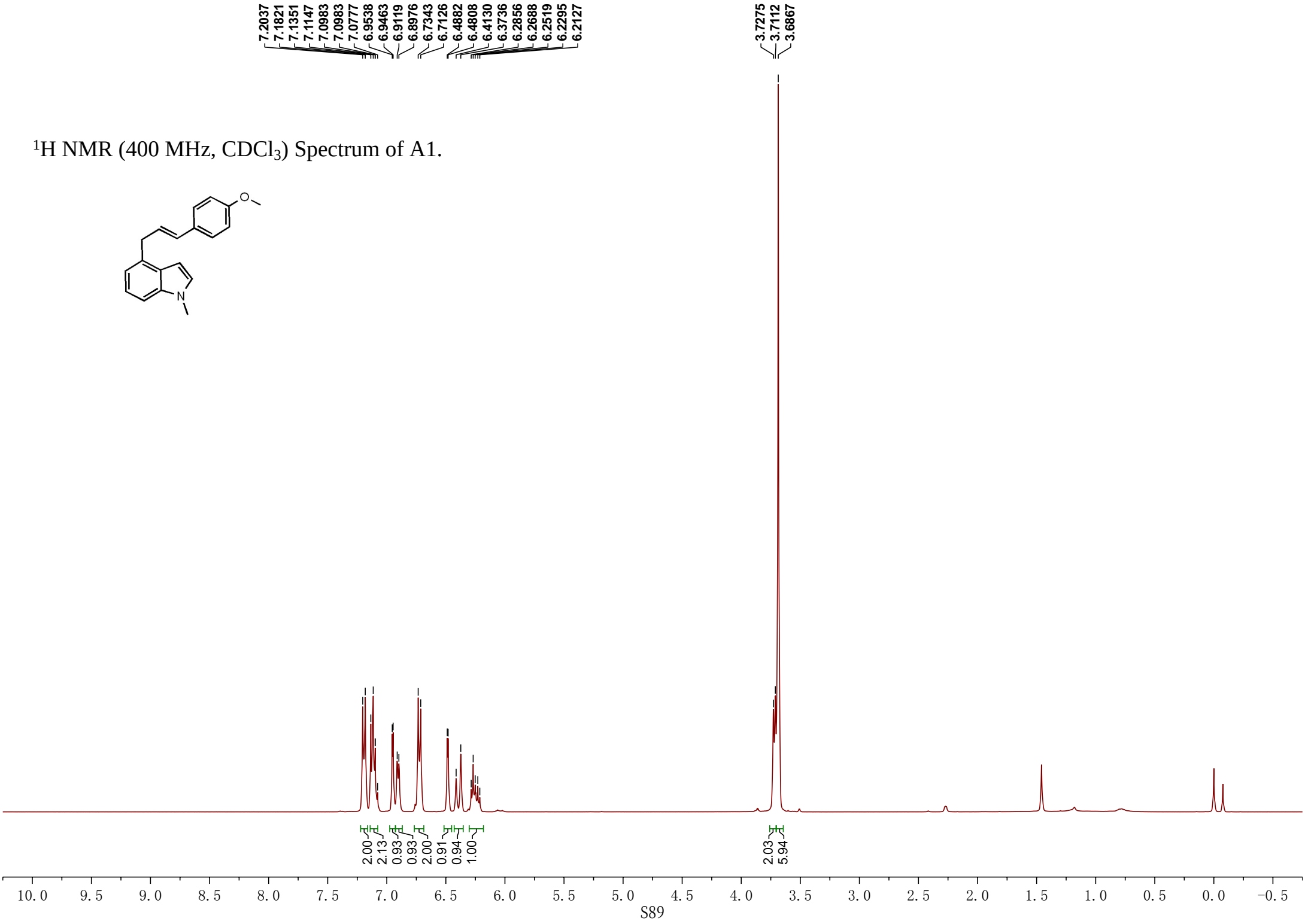
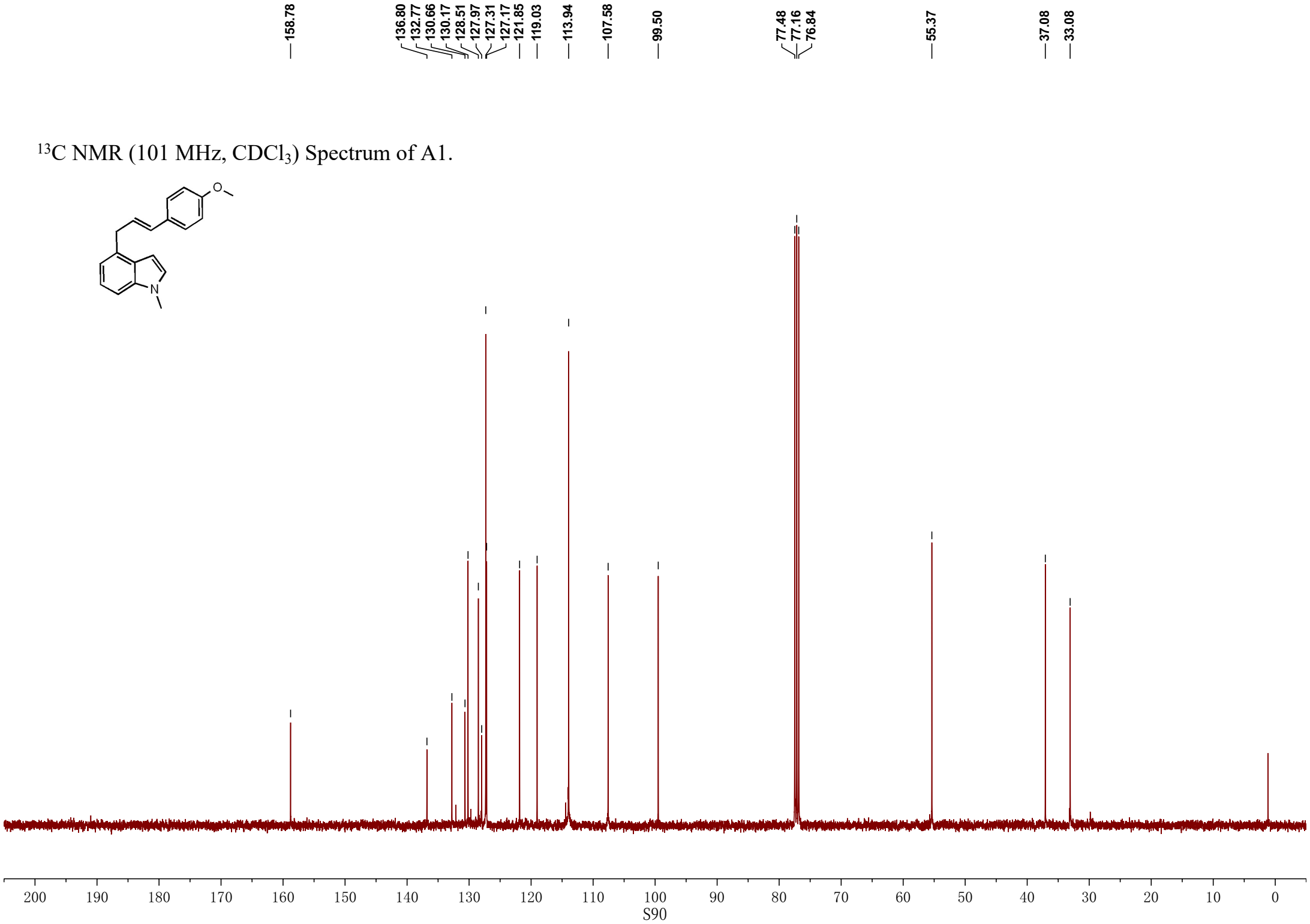
M. Liang, *Chem. Eur. J.*, 2014, **20**, 16093-16096.

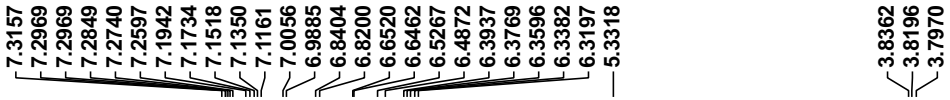
5. J. D. Lasso, D. J. Castillo-Pazos, J. M. Salgado, C. Ruchlin, L. Lefebvre, D. Farajat, D. F. Perepichka and C.-J. Li, *J. Am. Chem. Soc.*, 2024, **146**, 2583-2592.
6. Q. Jiang, J. Dong, C. Wang, F. Li, X. Zhou, Y. Wang, H. Liao, J. Dang, G. Li and D. Xue, *Org. Lett.,* 2024, **26**, 6230–6235.



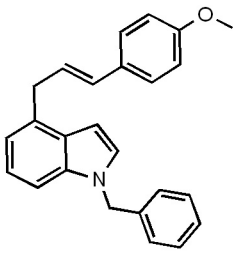
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of A1.

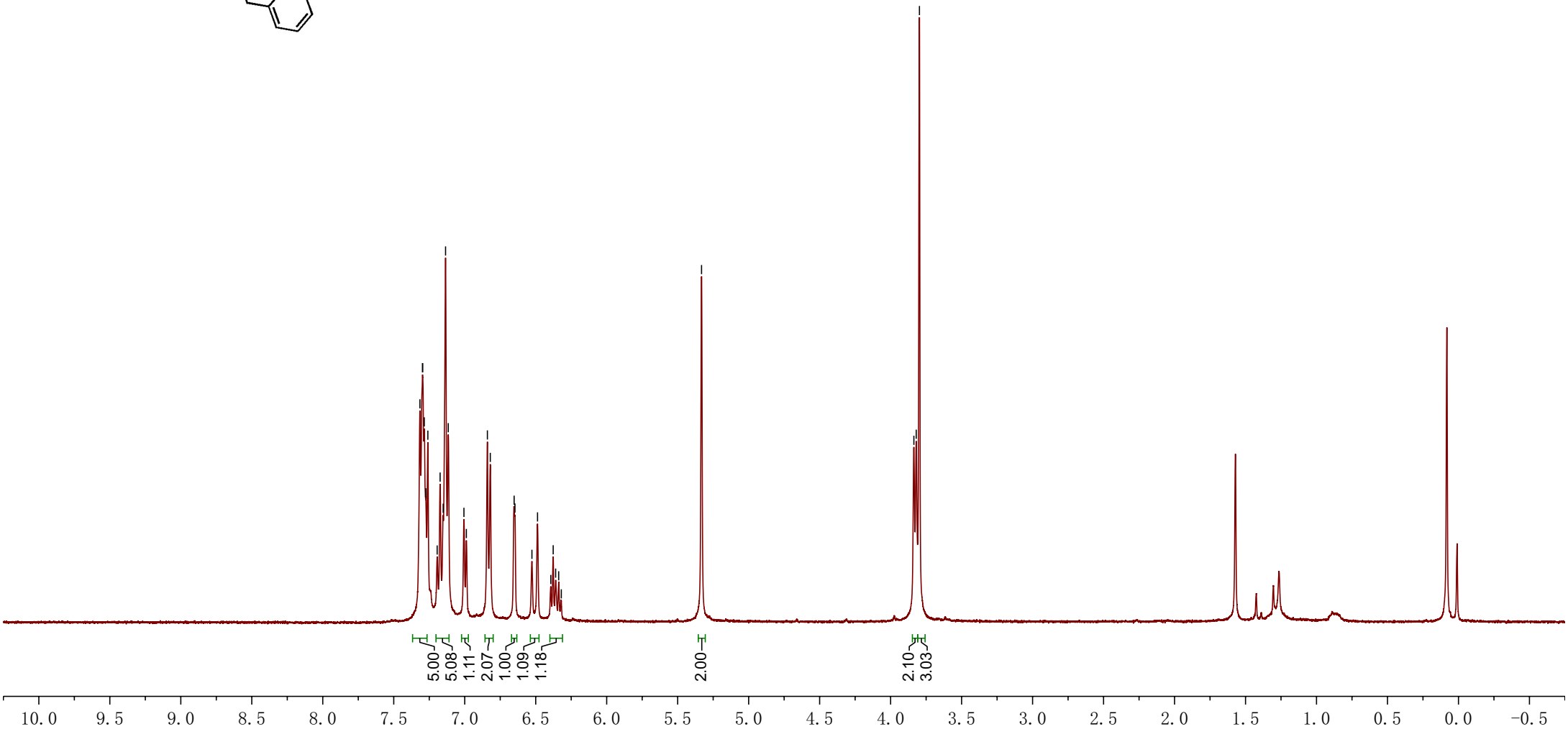


^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of A1.

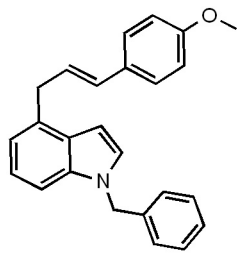


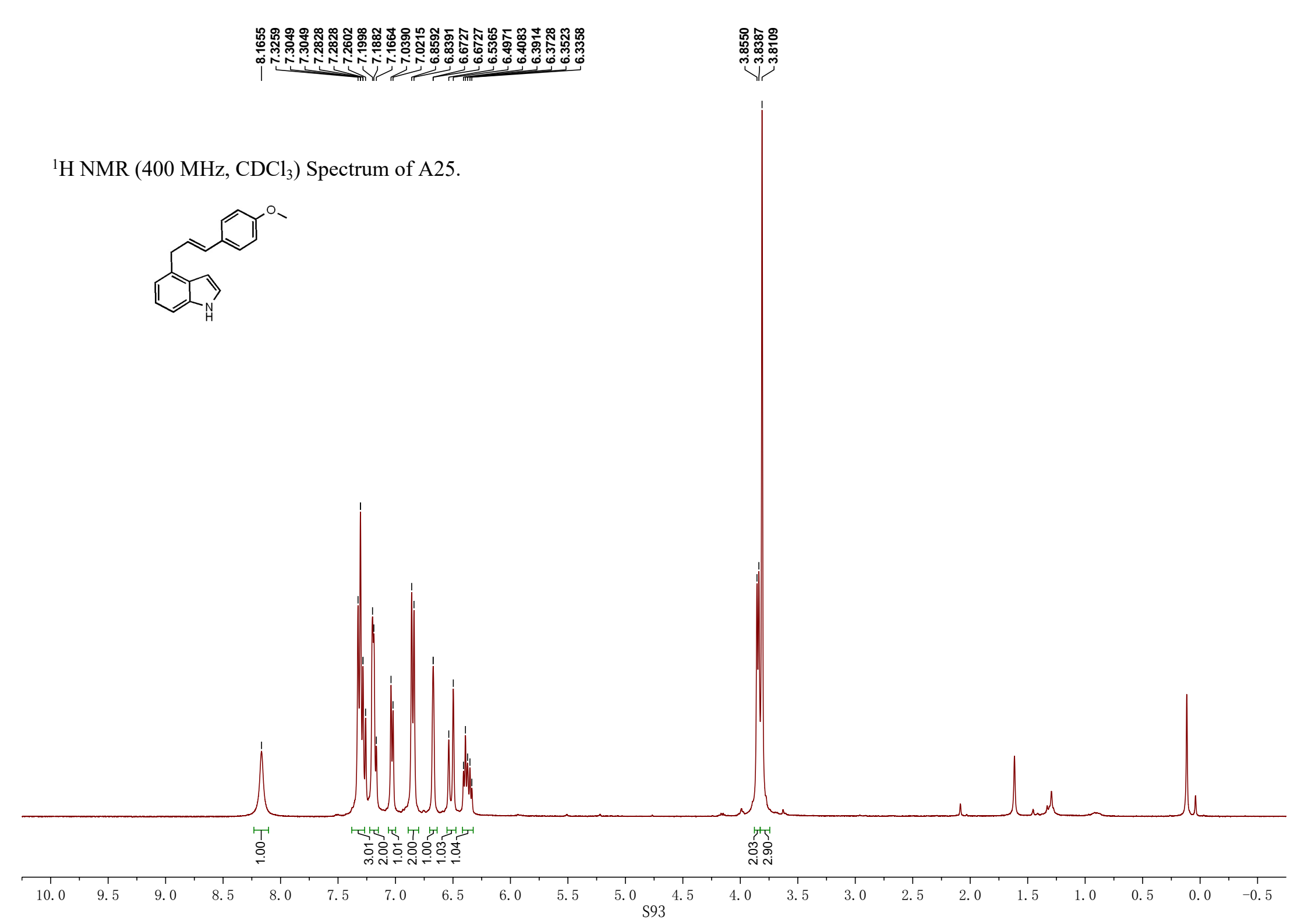
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of A24.



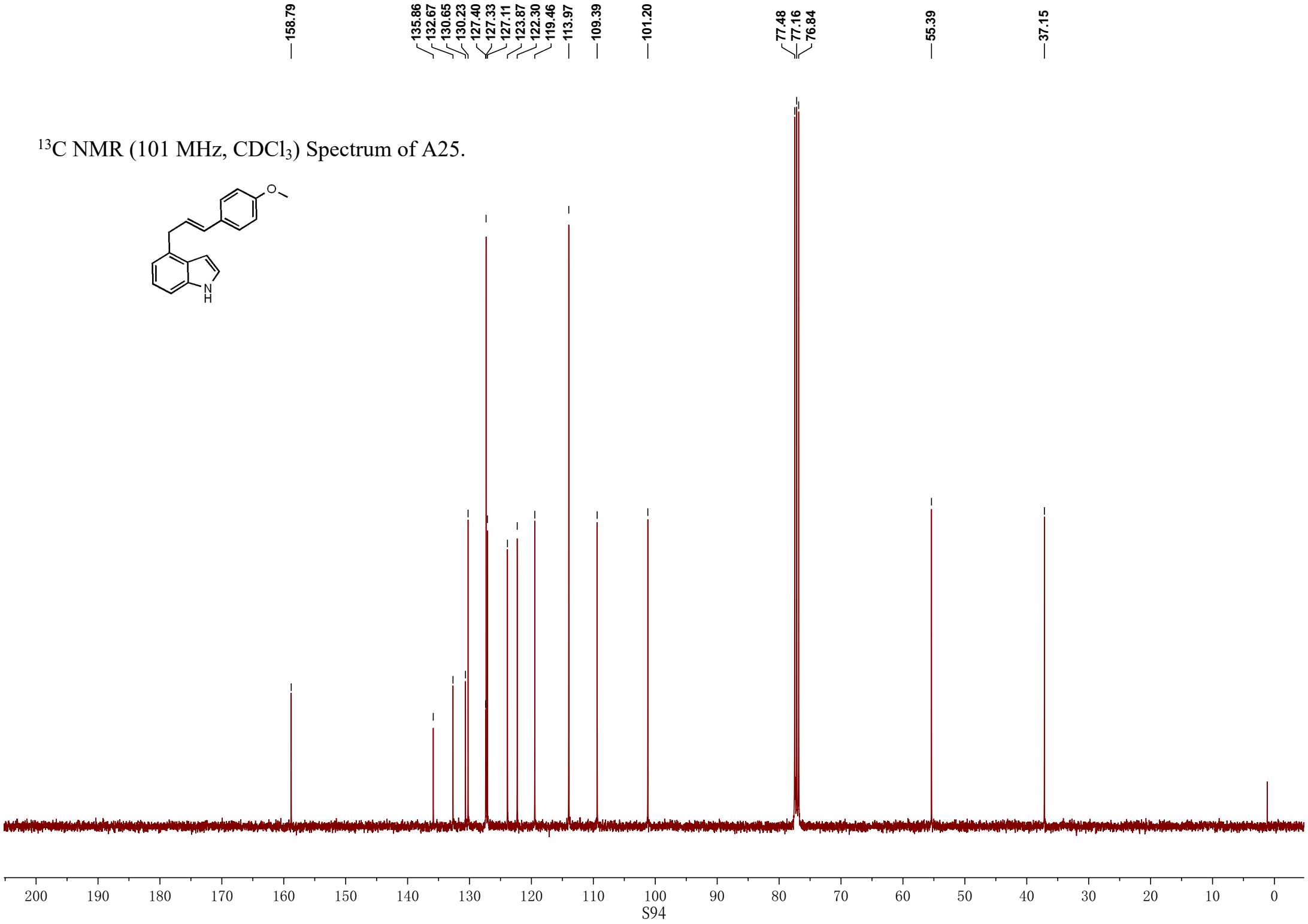


^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of A24.



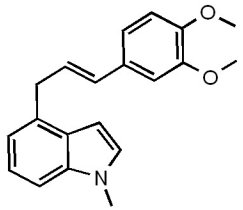


^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of A25.

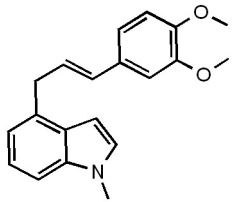


^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of A25.

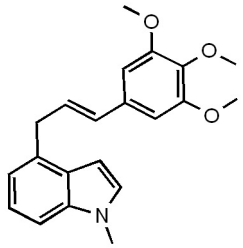
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of A26.



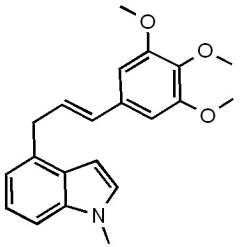
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of A26.



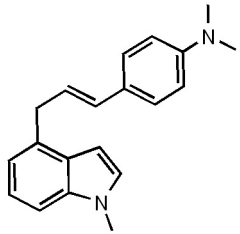
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of A27.



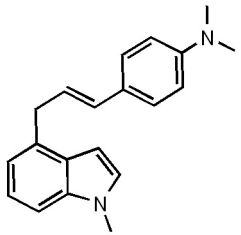
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of A27.

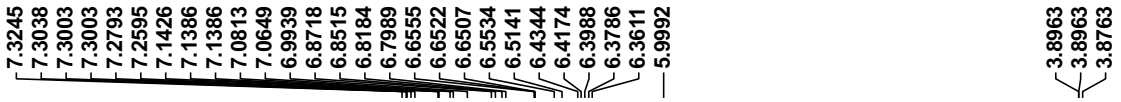


^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of A28.

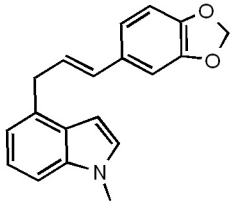


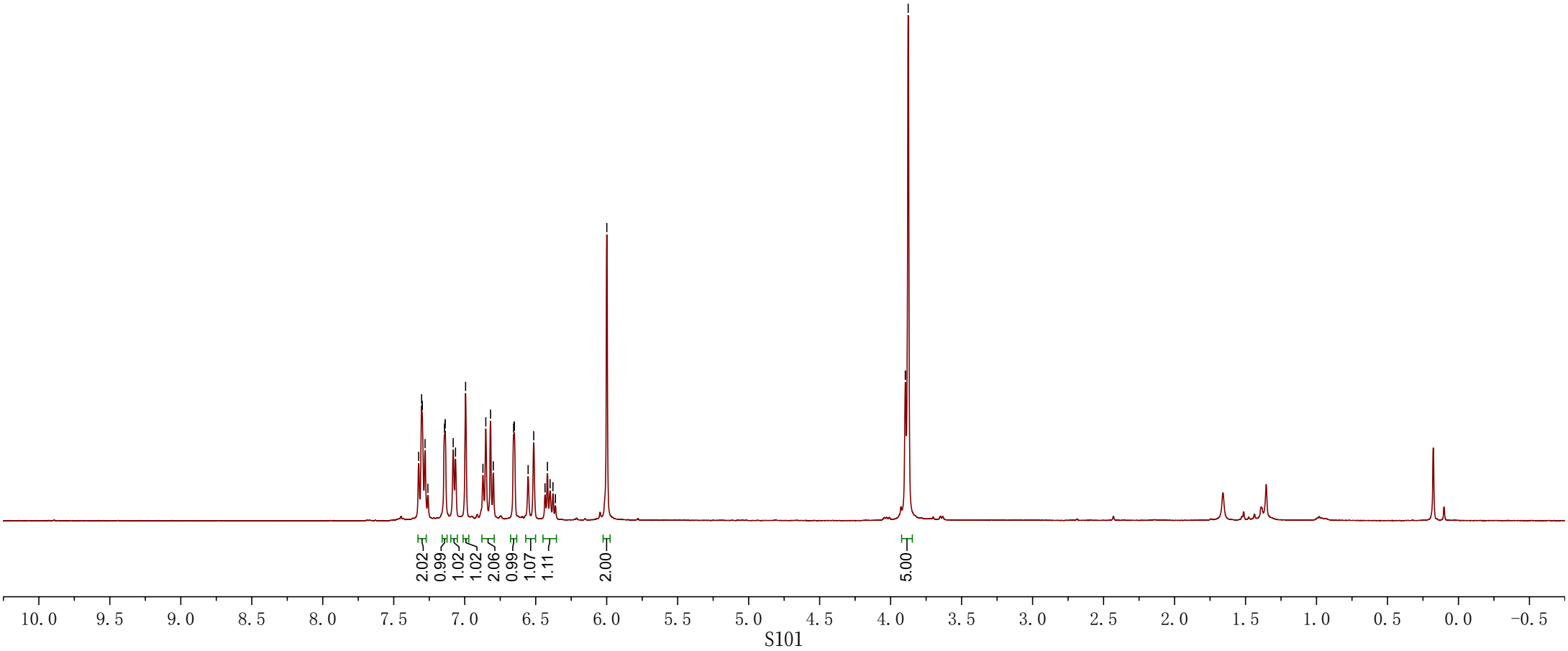
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of A28.



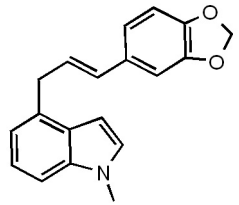


^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of A29.

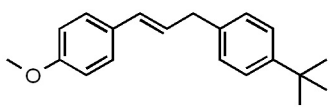




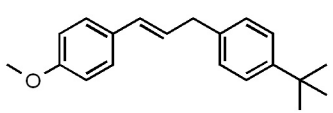
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of A29.



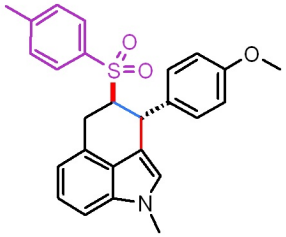
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of A36.



^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of A36.



^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P1.



158.38
143.21
135.27
134.70
134.20
129.05
128.05
127.87
126.16
124.35
122.56
116.13
113.76
111.35
106.83
77.48
77.16
76.84
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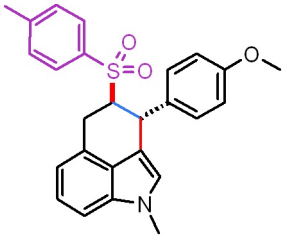
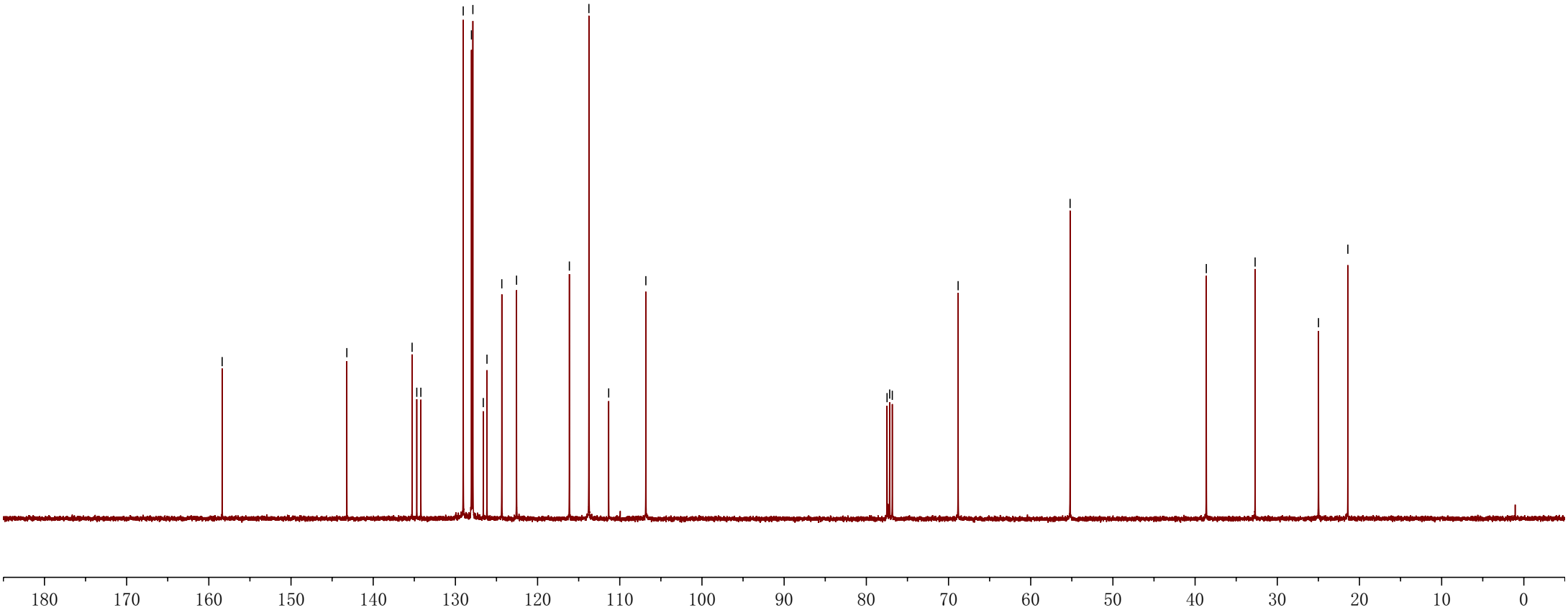
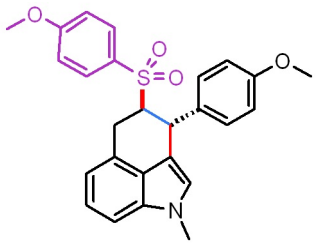
55.21
38.63
32.70
24.99
21.41

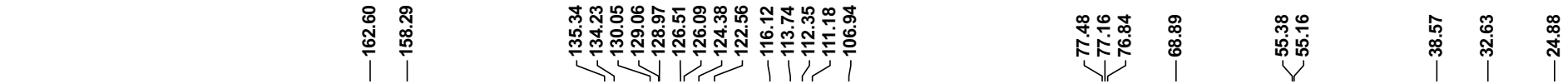
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P1.



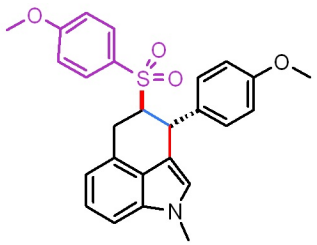


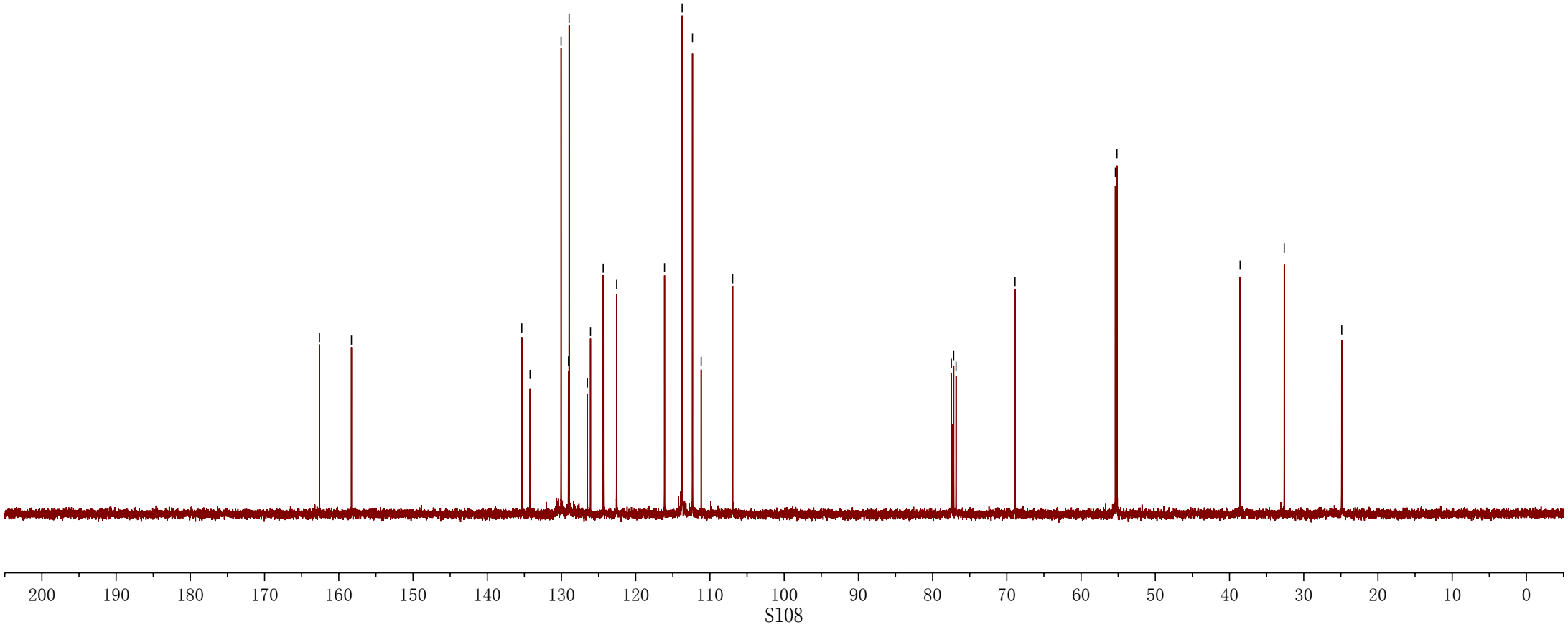
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P2.



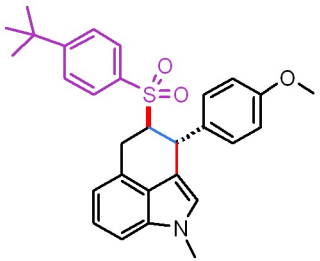


^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P2.



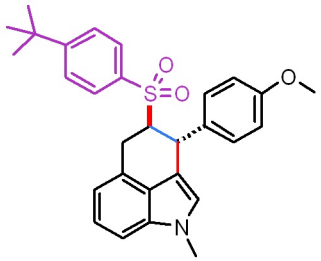


^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P3.

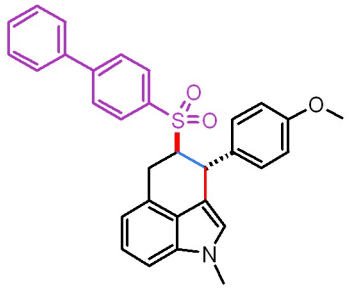


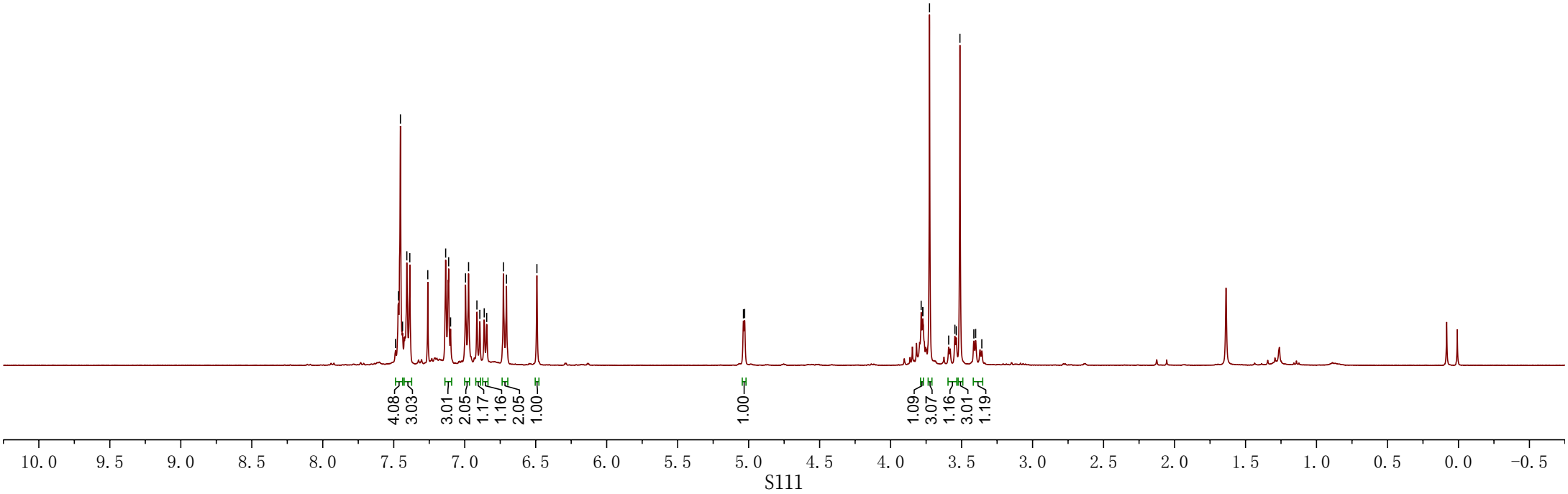
158.36
156.02
135.36
134.80
134.11
129.08
127.97
126.16
124.26
124.17
122.49
116.12
113.77
111.50
107.06
77.48
77.16
76.84
68.86
55.21
38.71
34.85
32.78
31.01
24.91

^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P3.

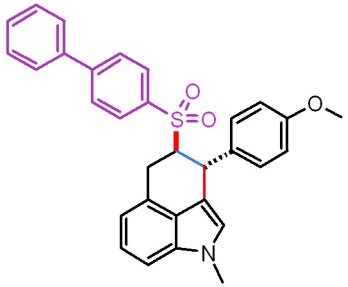


^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P4.

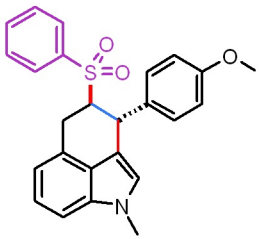


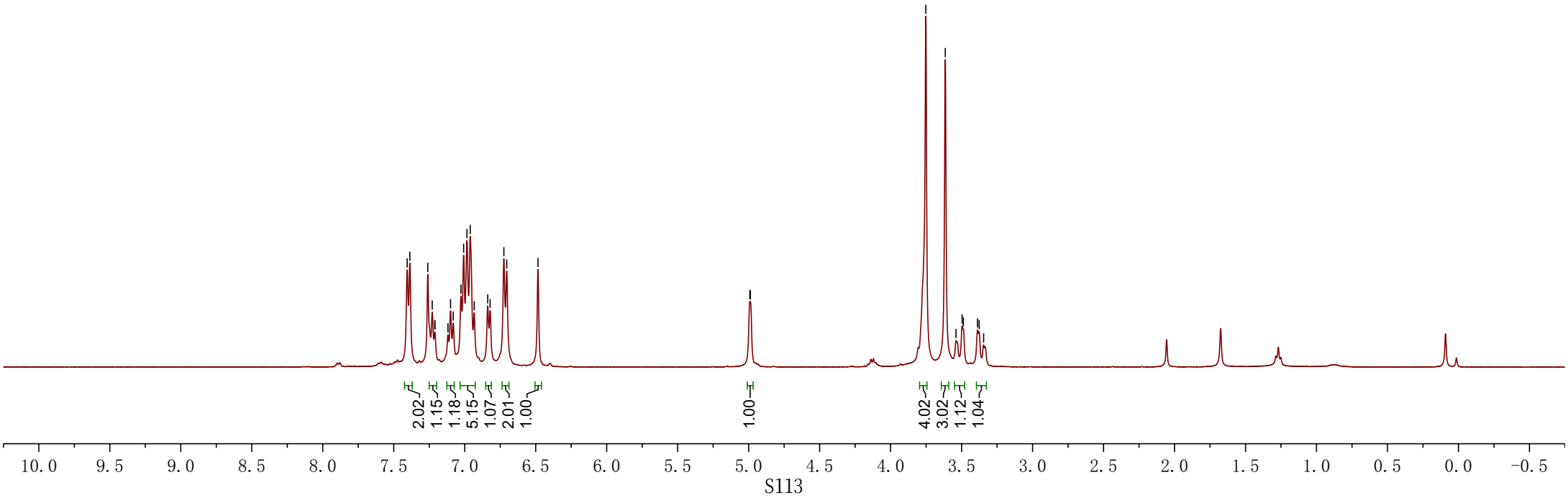


^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P4.



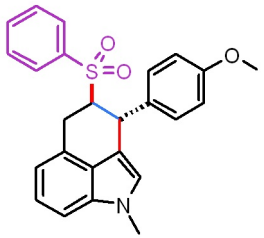
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P5.

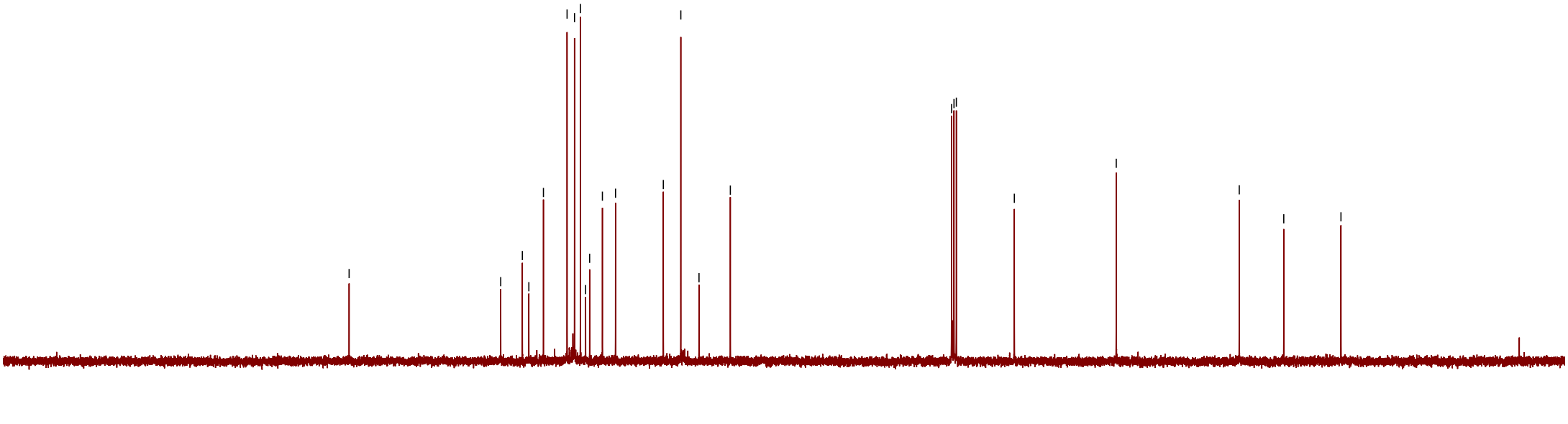


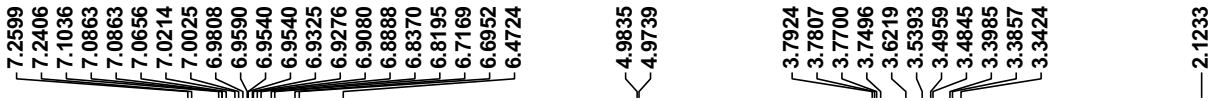


158.50
138.11
135.20
134.33
132.37
129.19
128.19
127.40
126.70
126.16
124.44
122.67
116.25
113.89
111.45
107.24
77.48
77.16
76.84
69.05
55.34
38.80
32.81
25.12

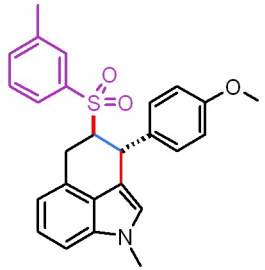
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P5.

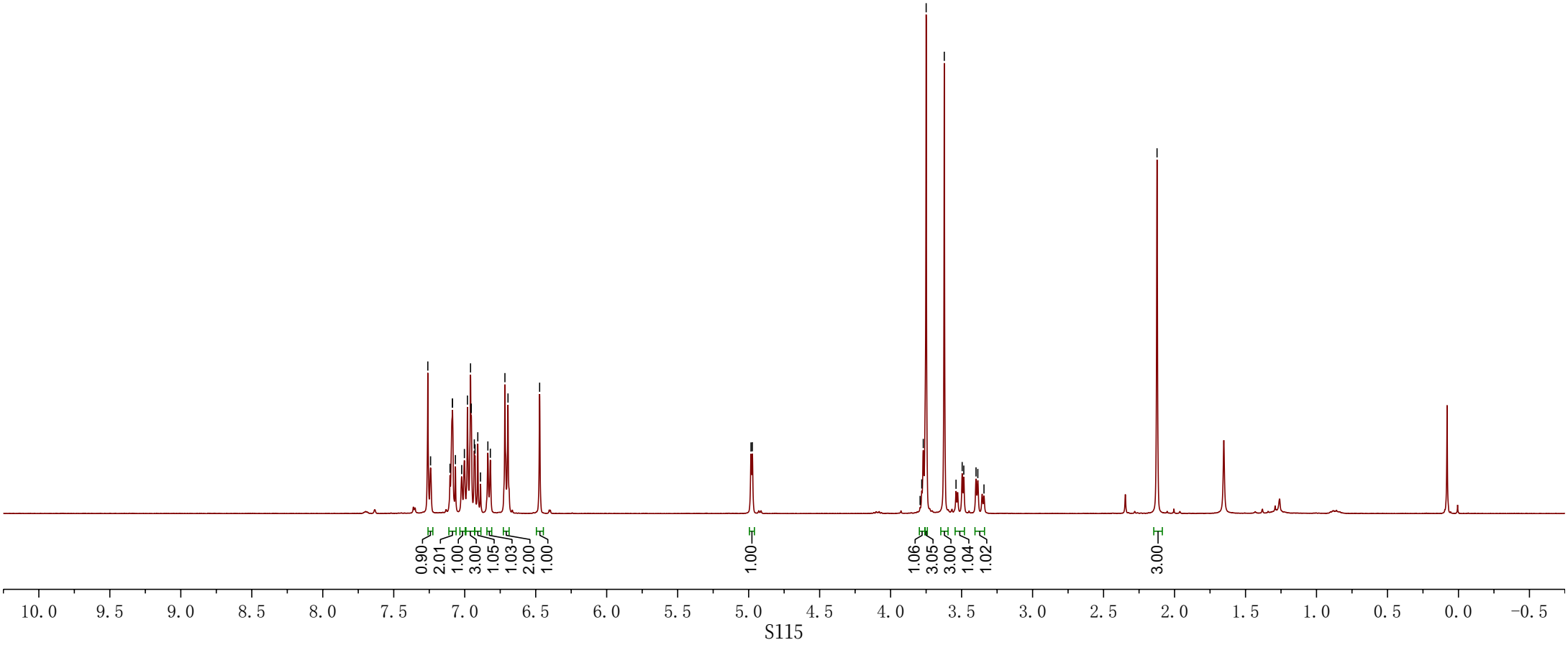






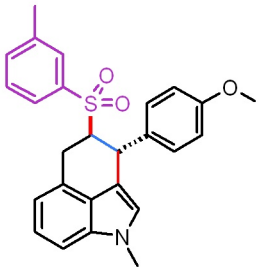
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P6.

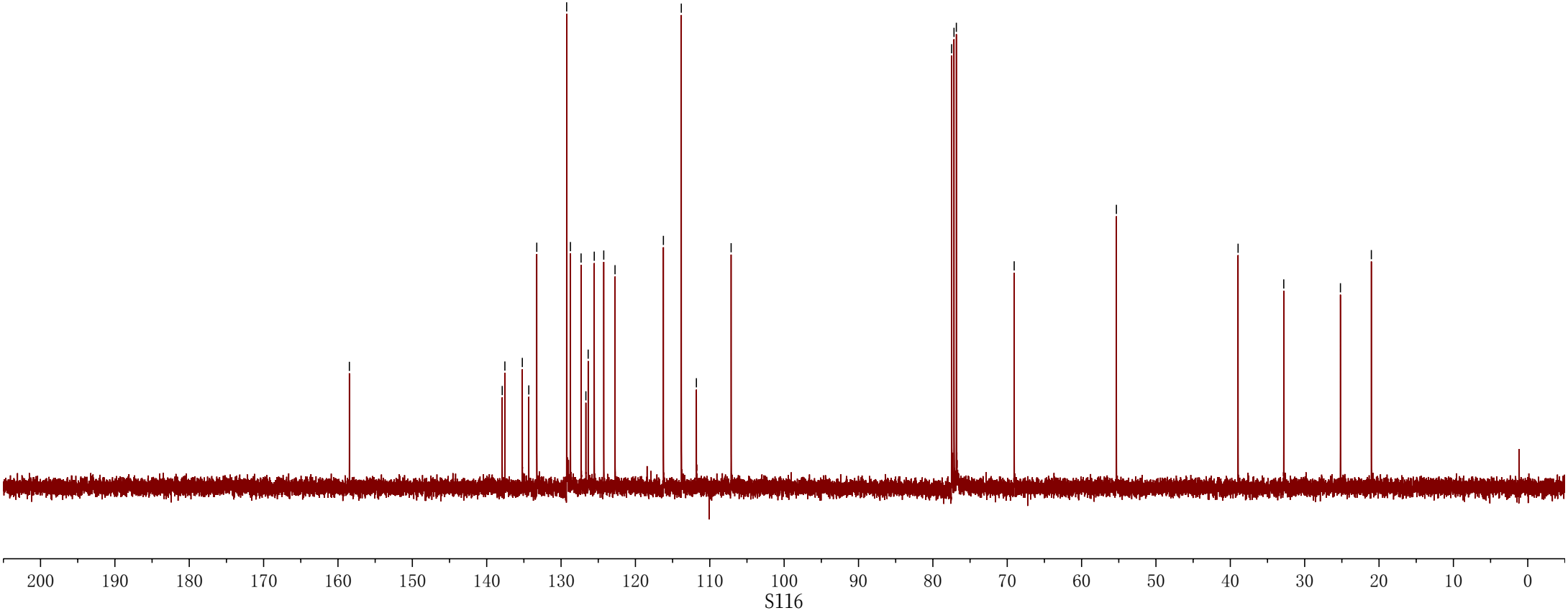




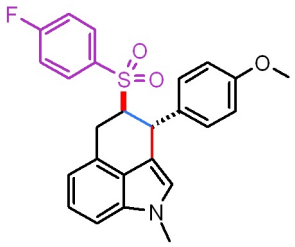
158.47
137.91
137.56
135.21
134.34
133.27
129.25
128.74
127.31
126.66
126.35
125.54
124.26
122.74
116.24
113.83
111.80
107.13
77.48
77.16
76.84
69.06
55.32
38.96
32.81
25.19
21.03

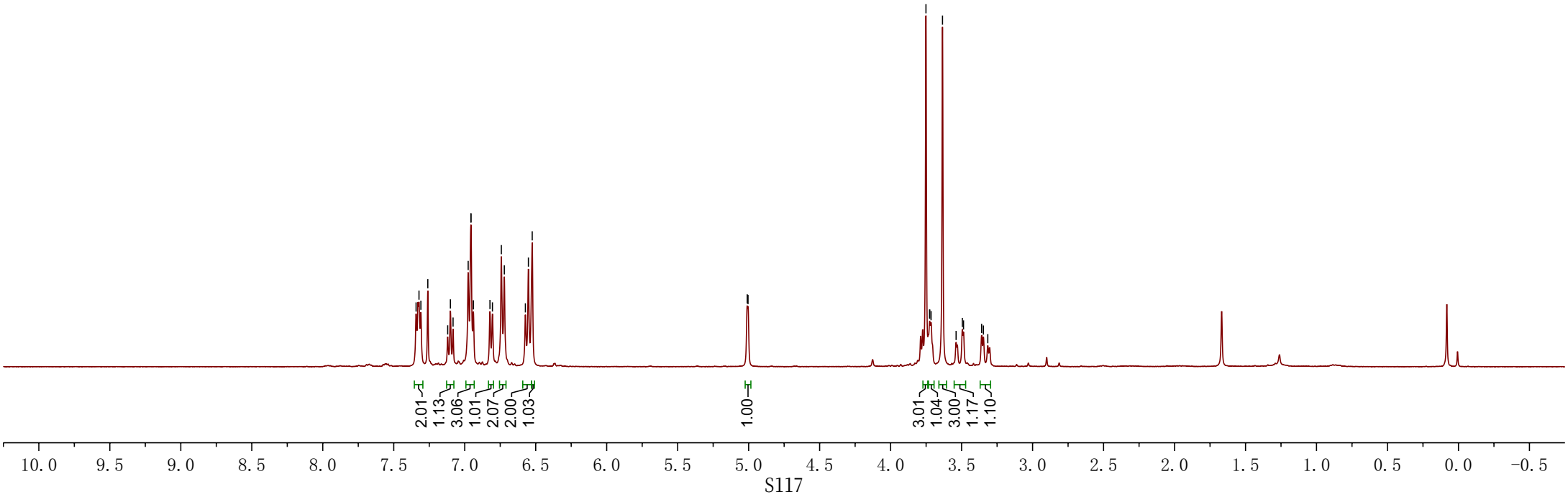
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P6.



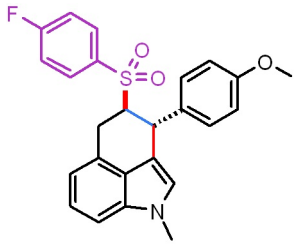


^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P7.



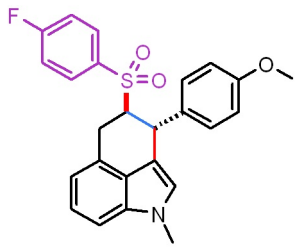


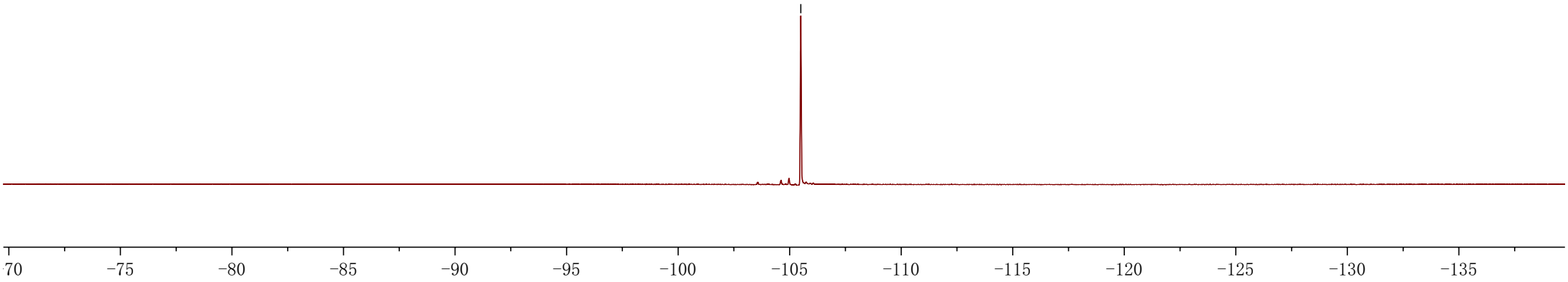
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P7.



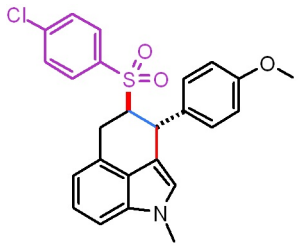
-105.50

^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of P7.

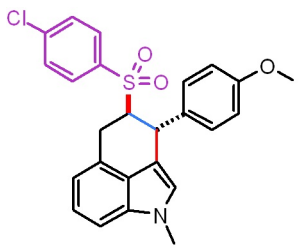




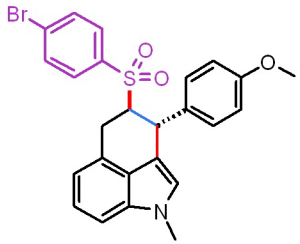
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P8.



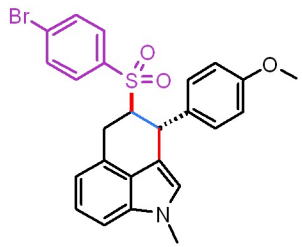
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P8.



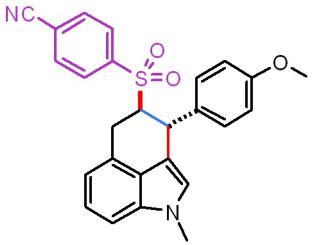
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P9.



^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P9.

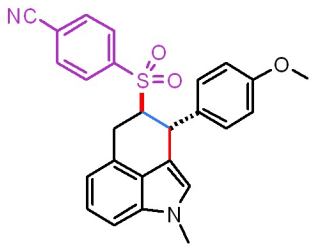


^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P10.

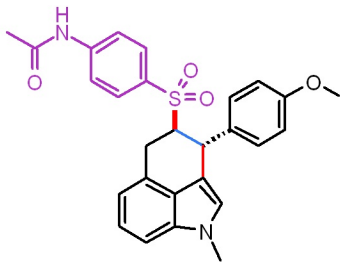


158.61
141.46
134.67
134.09
129.89
129.01
128.18
125.58
124.56
122.91
117.31
116.72
115.30
113.94
110.33
107.31
77.48
77.16
76.84
69.67
55.28
38.49
32.79
24.43

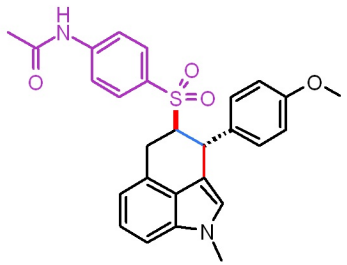
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P10.



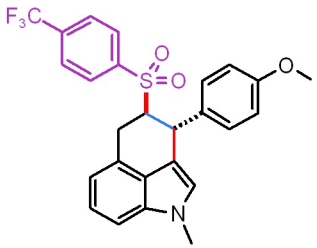
^{1}H NMR (400 MHz, DMSO-*d*6) Spectrum of P11.

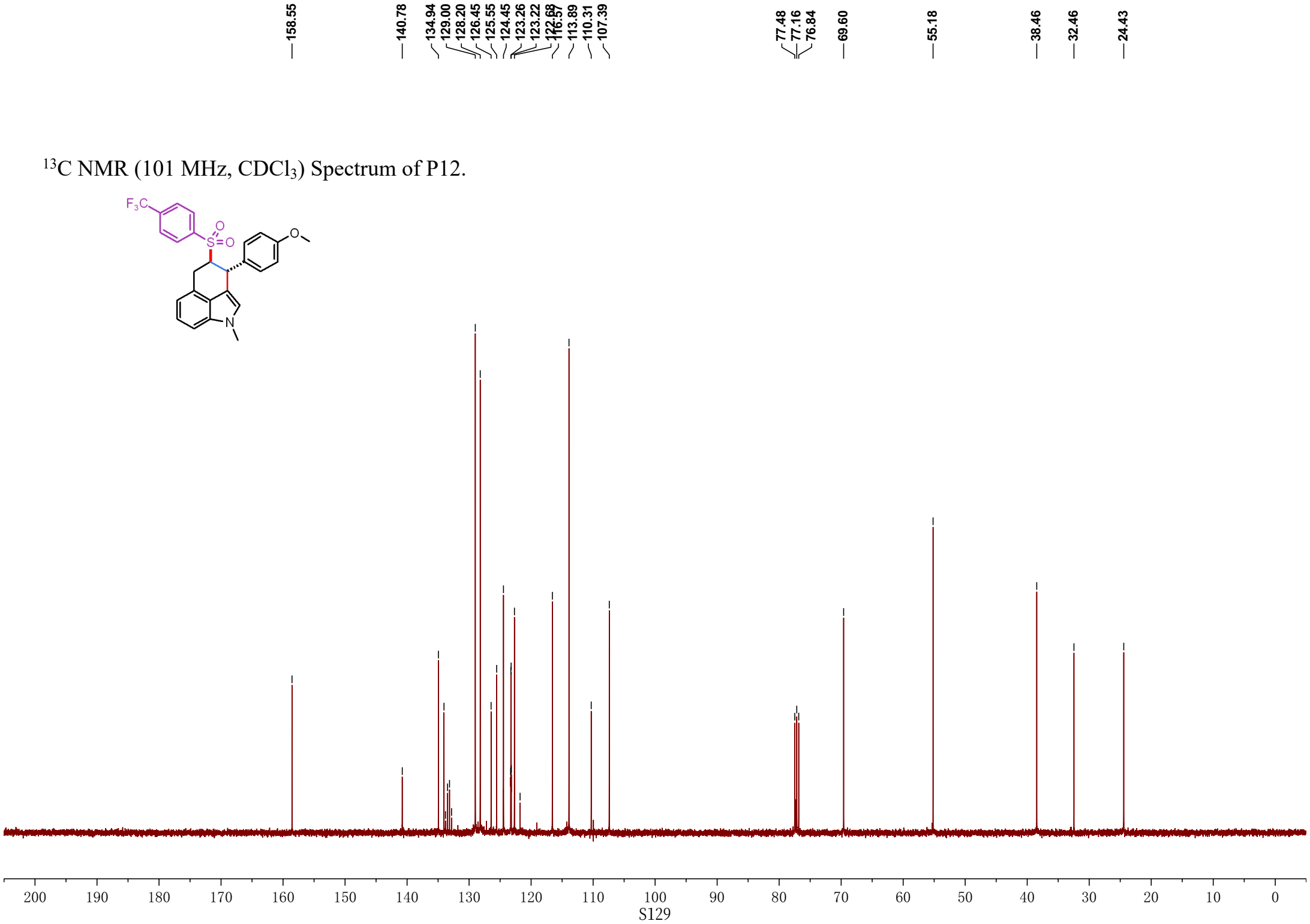


^{13}C NMR (101 MHz, DMSO-*d*6) Spectrum of P11.



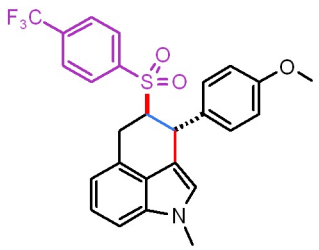
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P12.

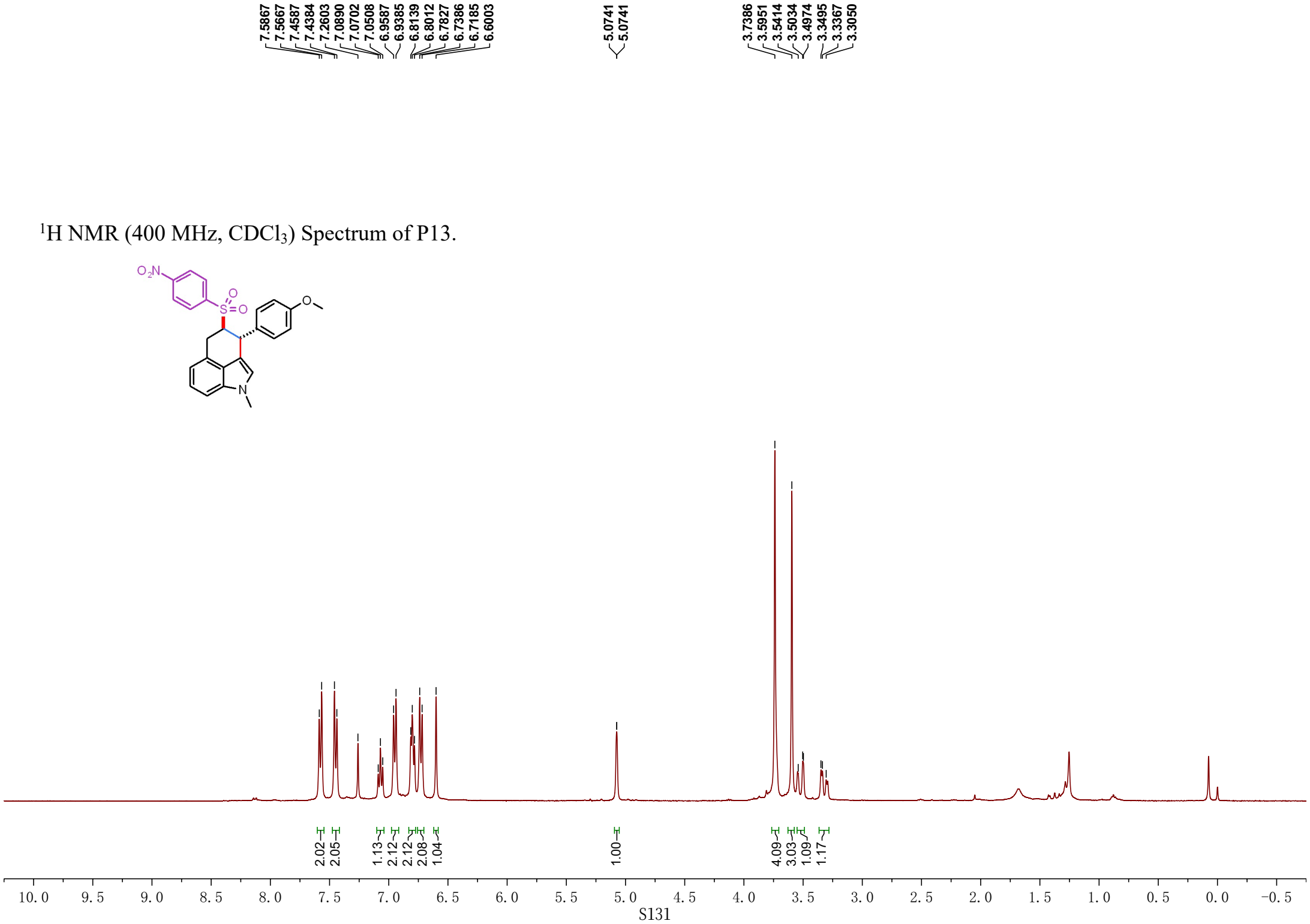




^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P12.

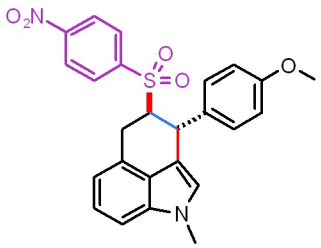
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of P12.



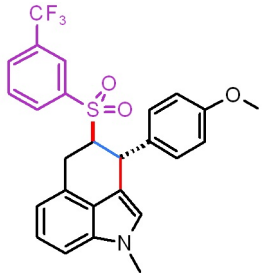


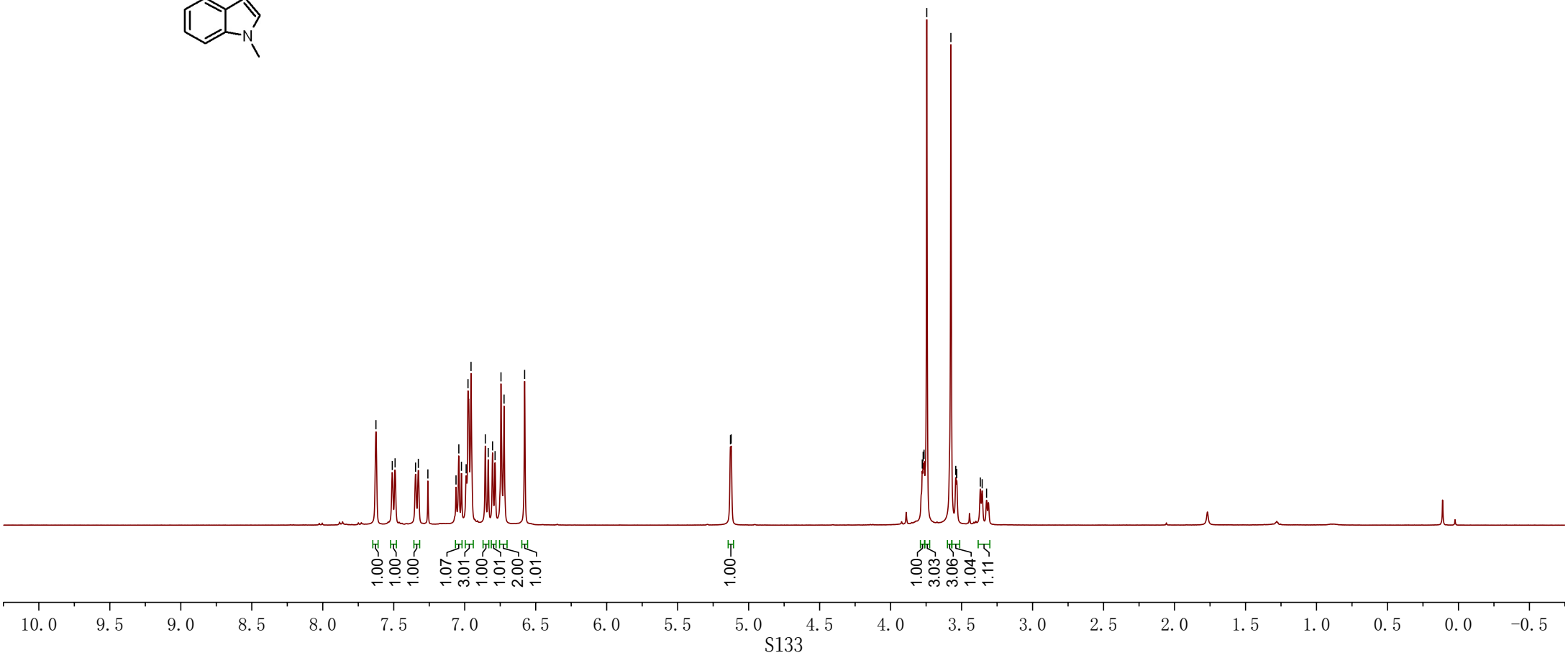
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P13.

^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P13.



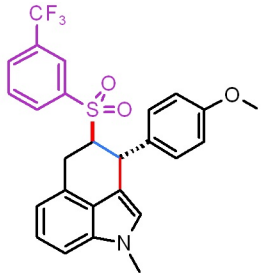
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P14.

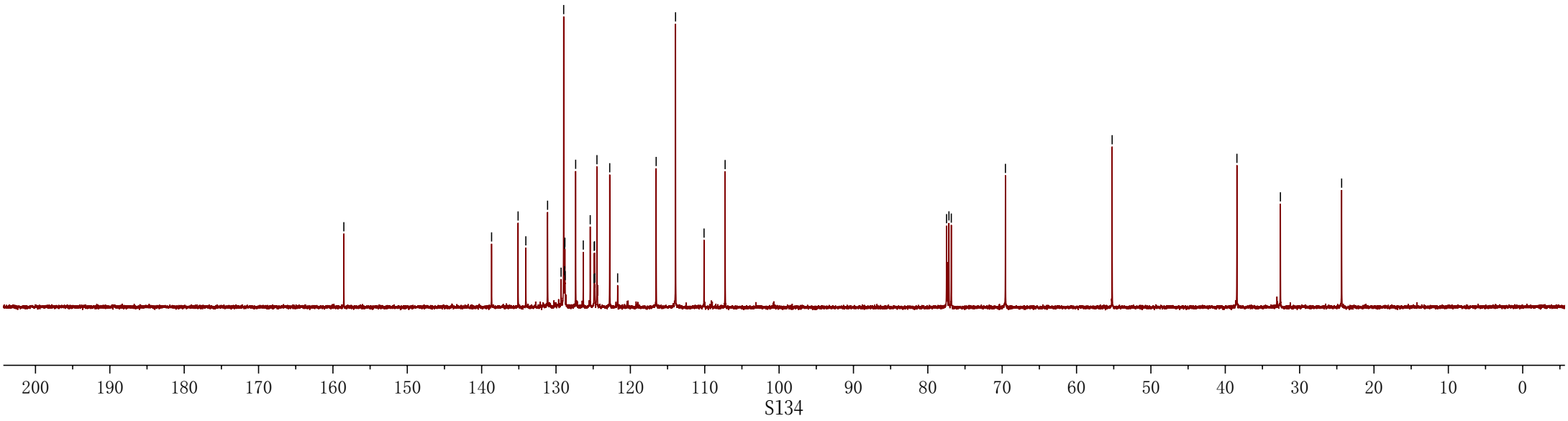




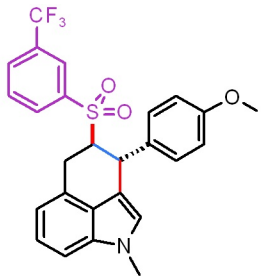
158.53
138.66
135.10
134.06
131.14
129.32
128.97
128.87
128.83
128.80
127.36
126.33
125.40
124.86
124.82
124.50
122.78
116.53
113.93
110.09
107.26
77.48
77.16
76.84
69.56
55.21
38.43
32.58
24.35

^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P14.

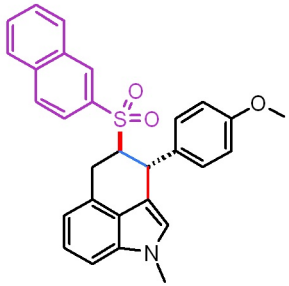




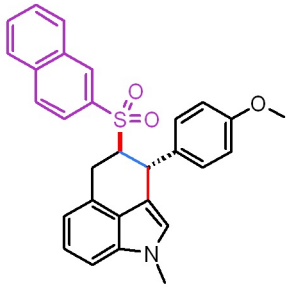
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of P14.



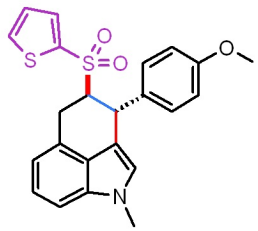
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P15.

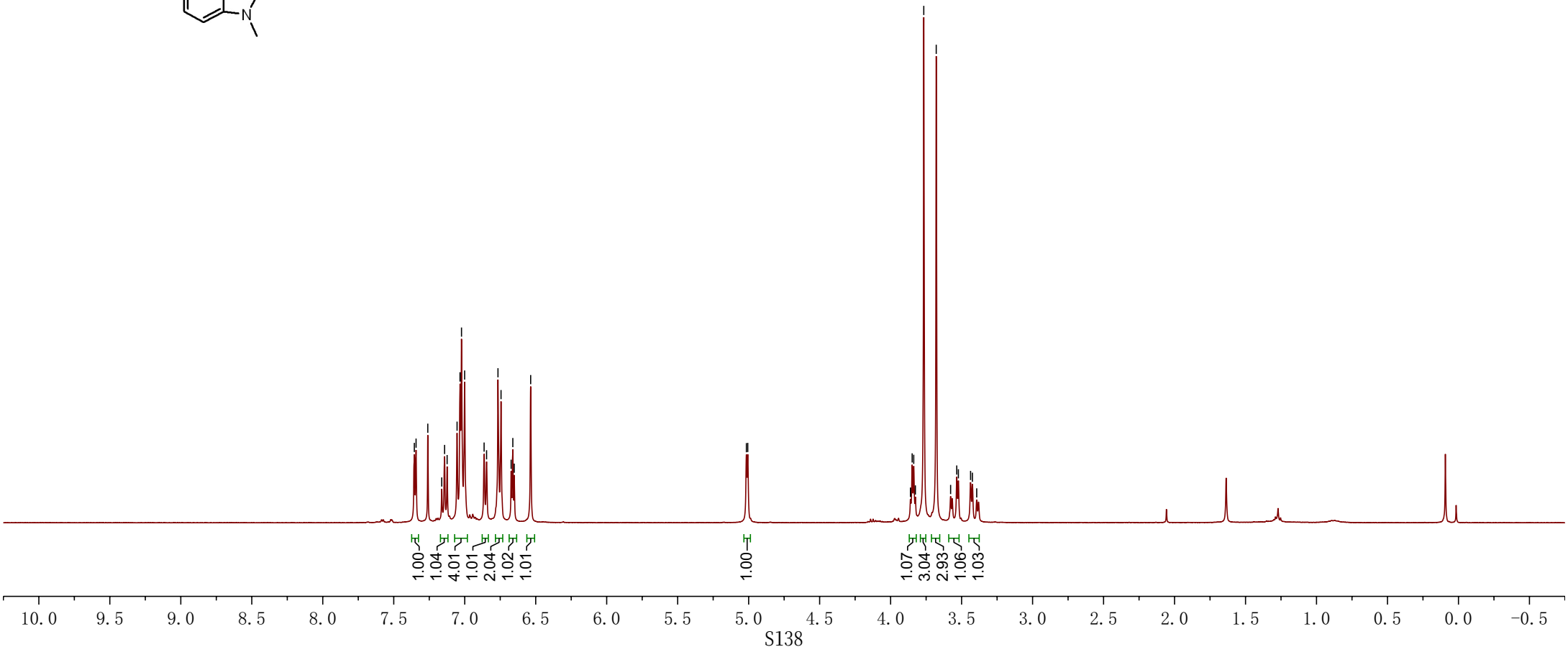


^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P15.

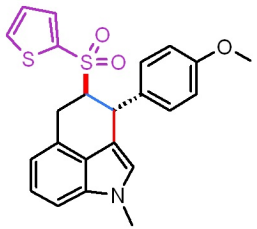


^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P16.

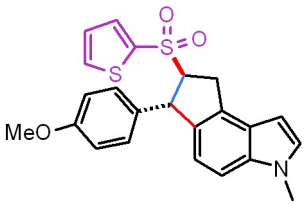


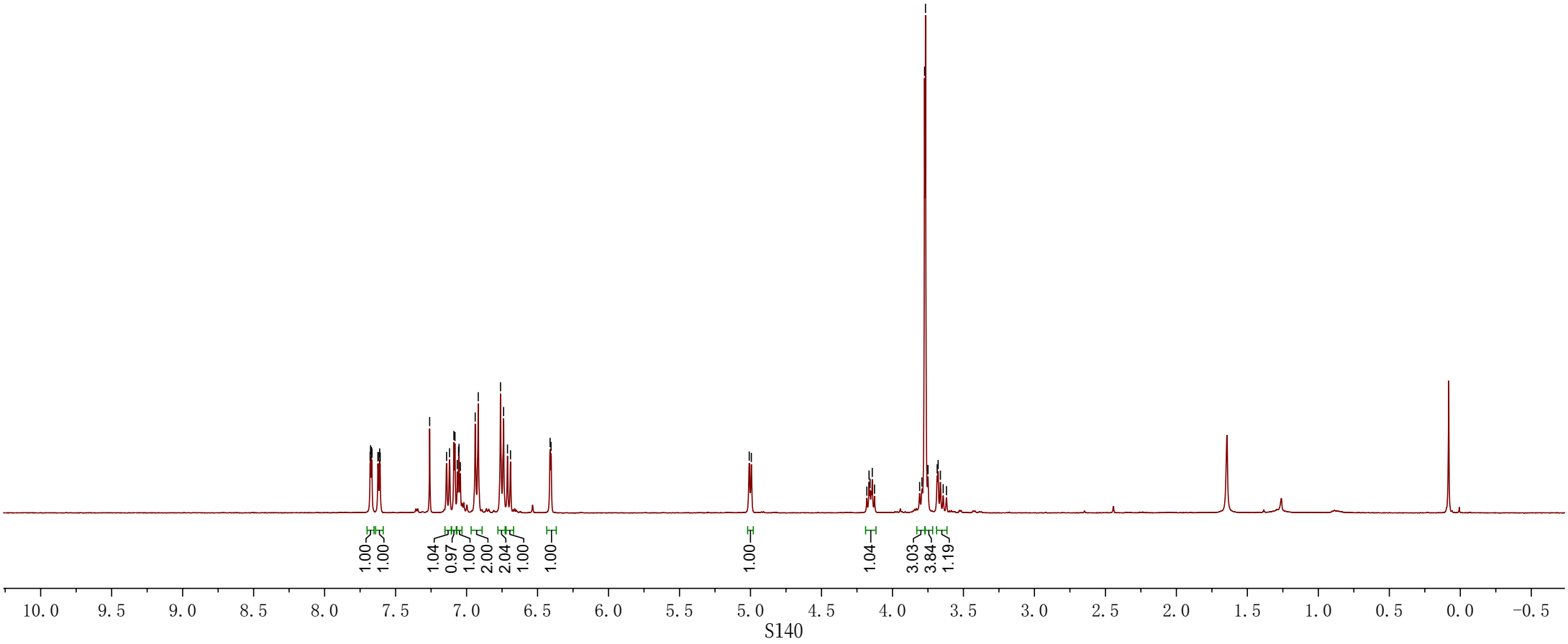


^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P16.



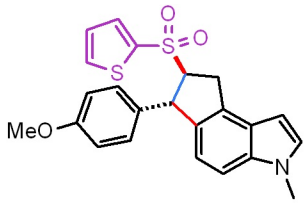
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P16'.

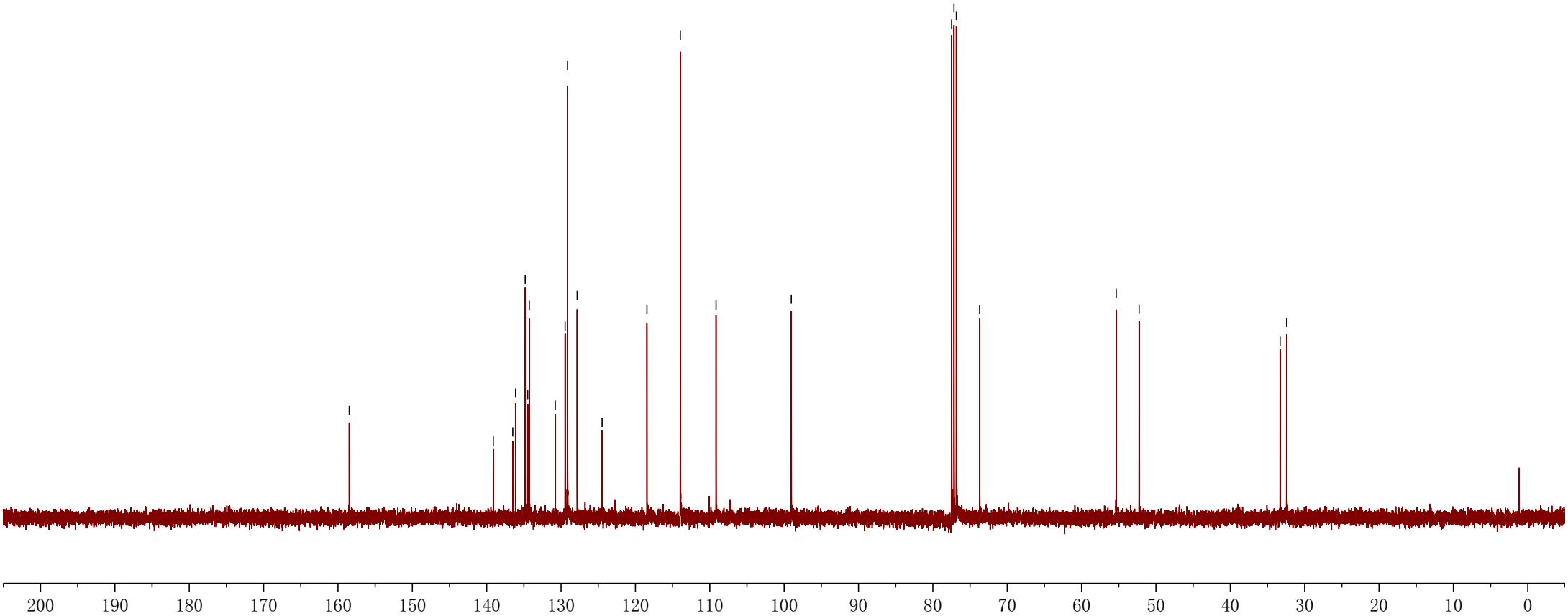


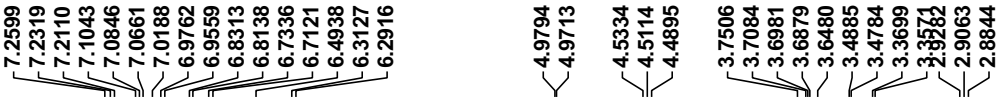


158.48
139.12
136.49
136.12
134.82
134.49
134.27
130.78
129.46
129.13
127.84
124.48
118.45
113.96
109.16
99.04
77.48
77.16
76.84
73.71
55.34
52.26
33.30
32.43

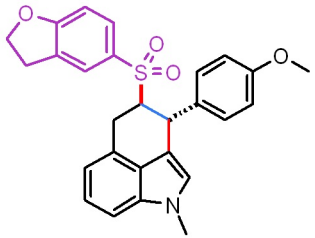
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P16'.

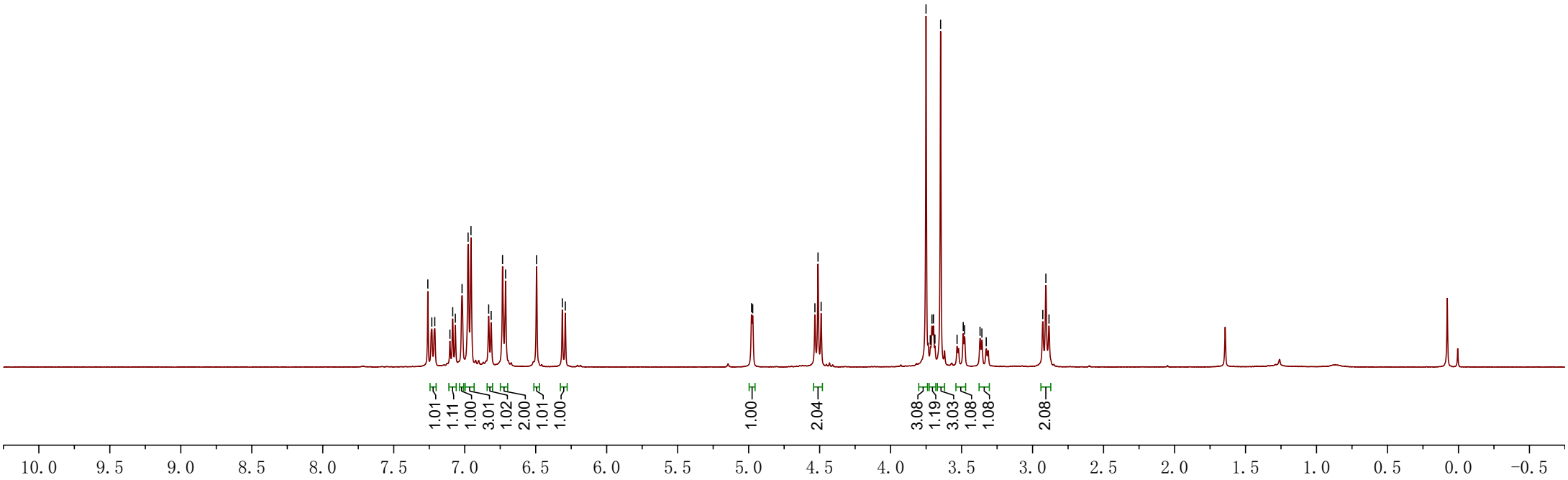




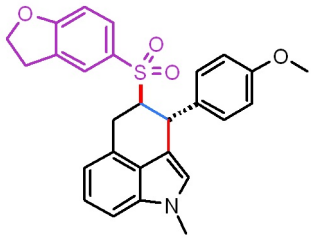


^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P17.

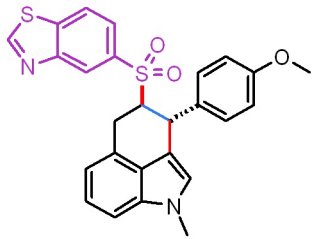


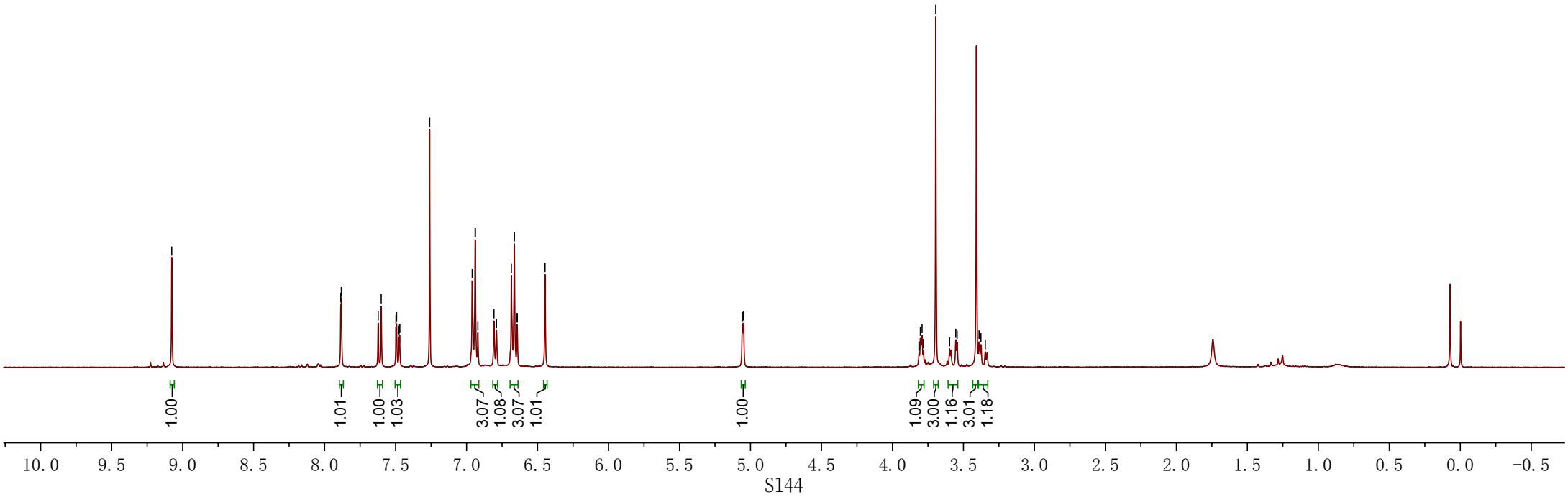


^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P17.

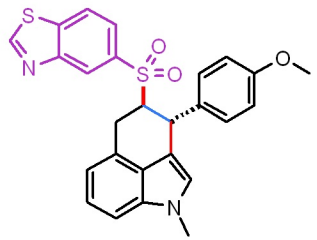


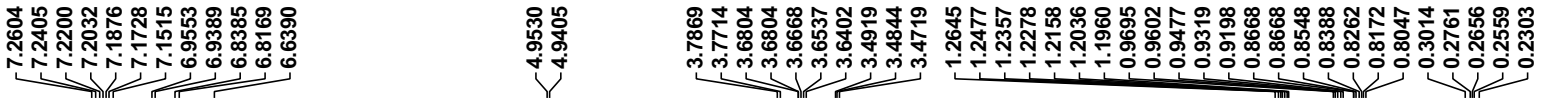
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P18.



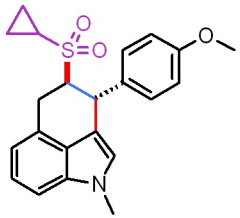


^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P18.

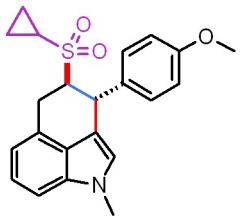




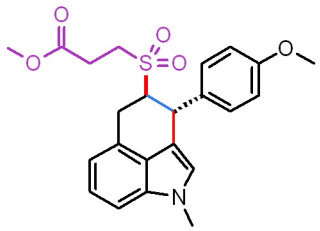
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P19.



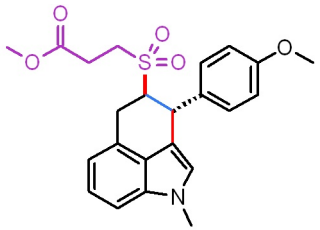
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P19.

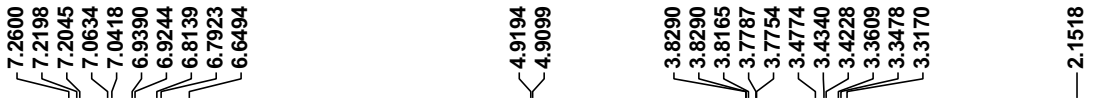


^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P20.

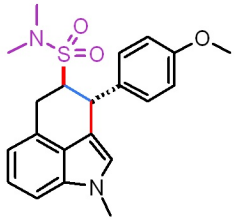


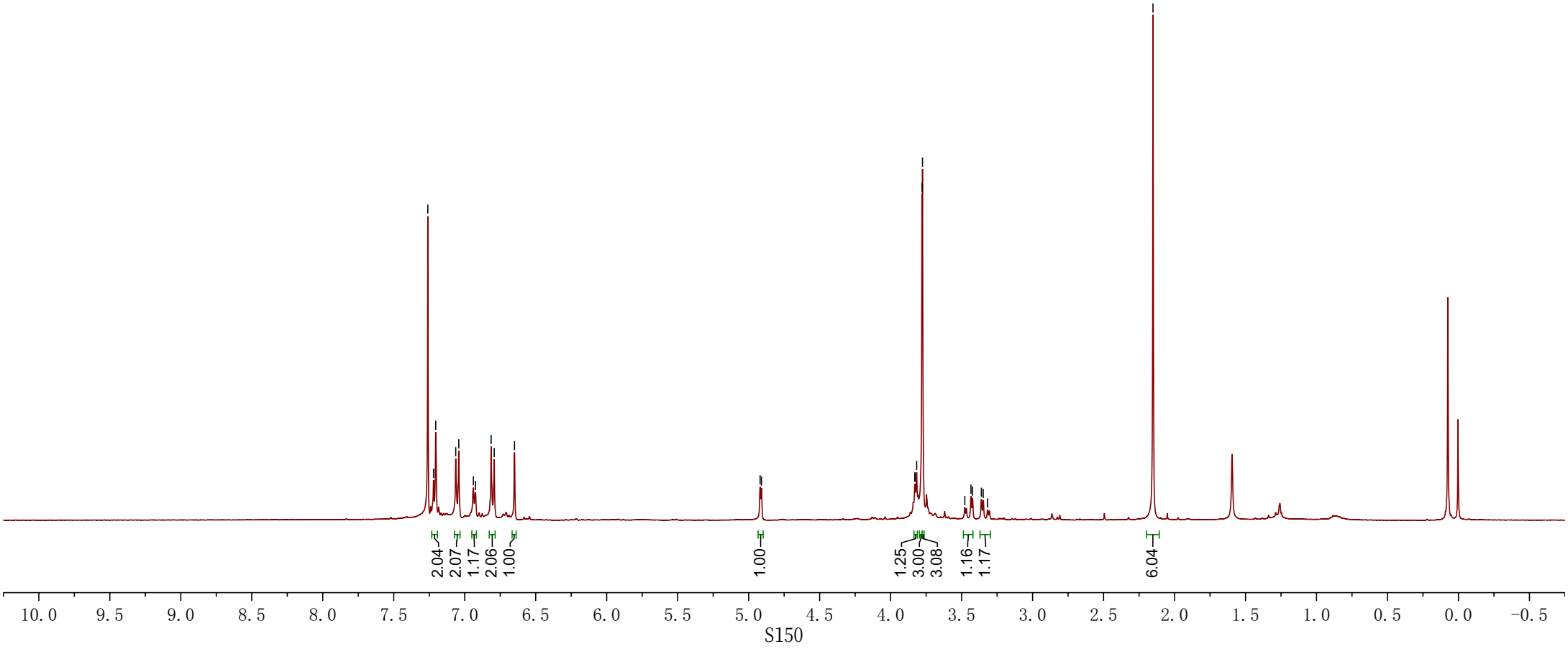
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P20.



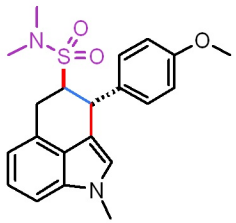


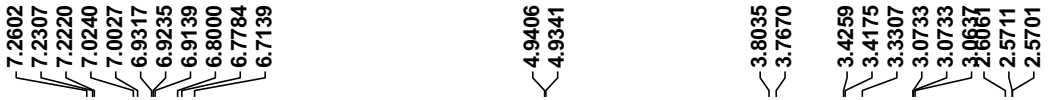
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P21.



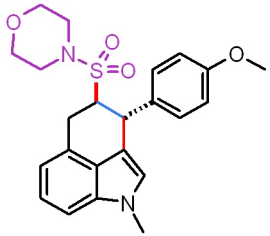


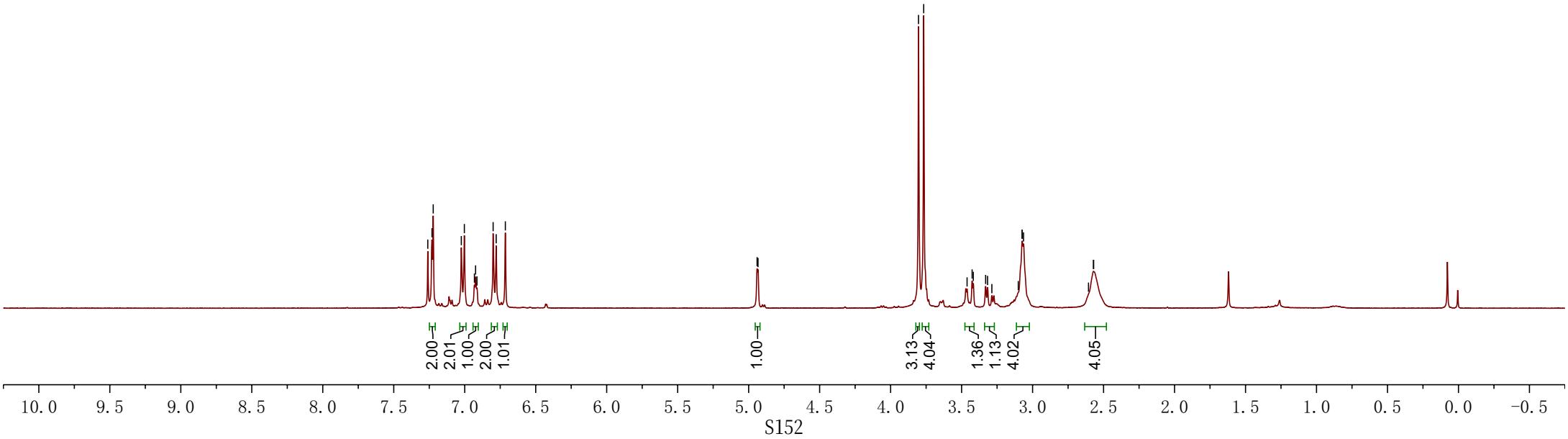
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P21.



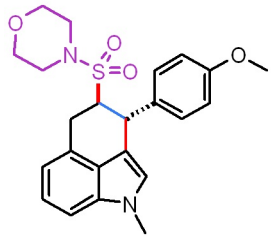


^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P22.

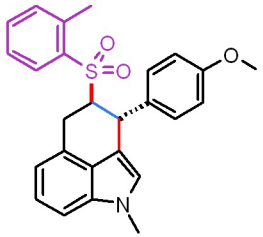


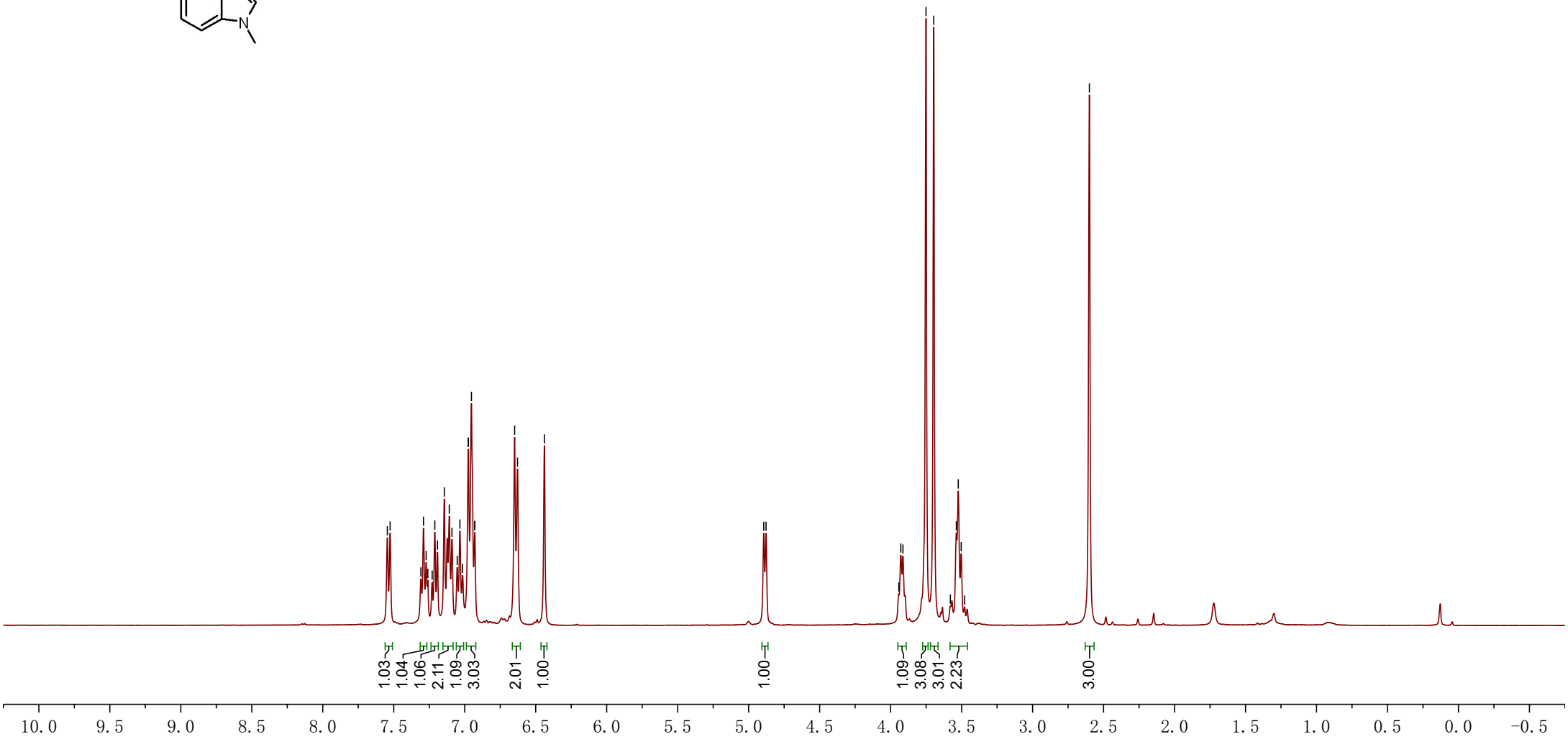


^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P22.

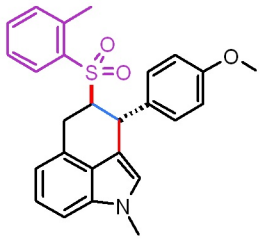


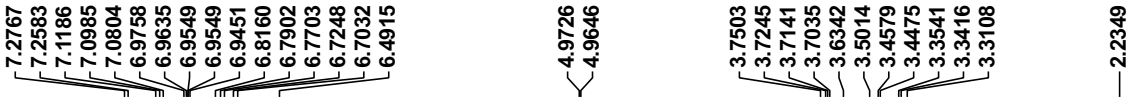
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P23.



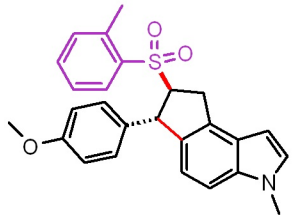


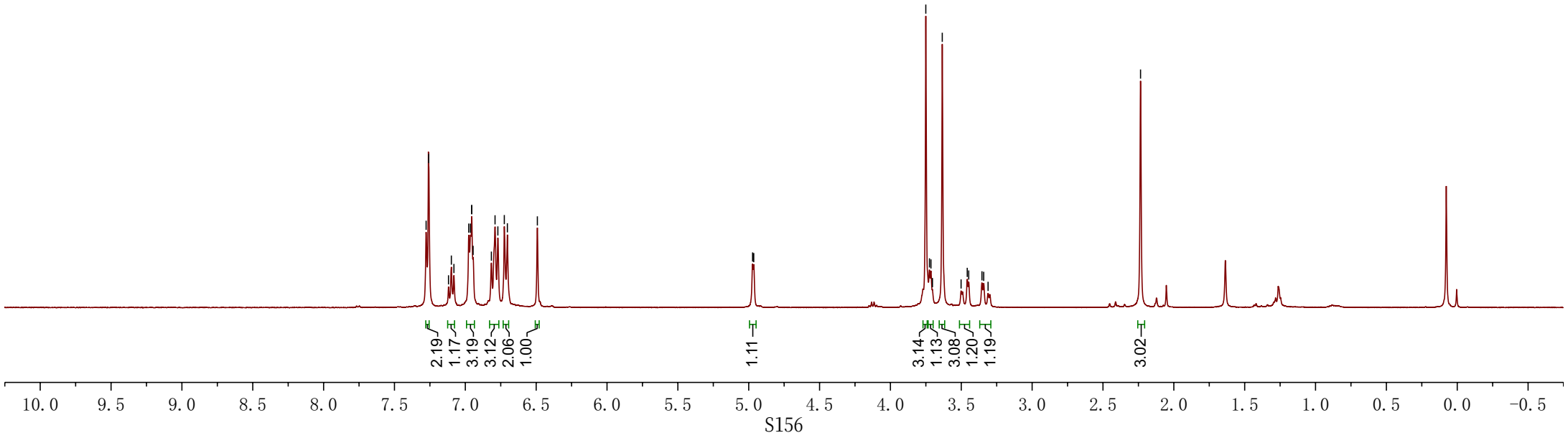
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P23.





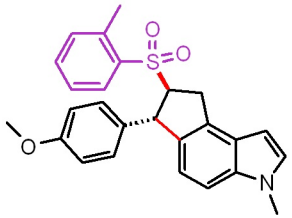
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P23'.

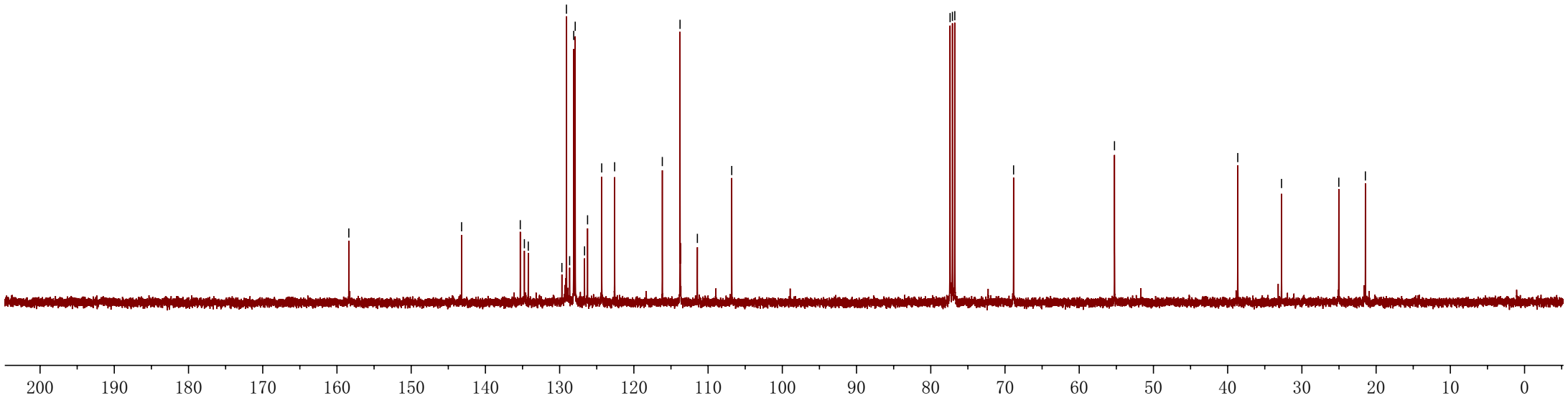


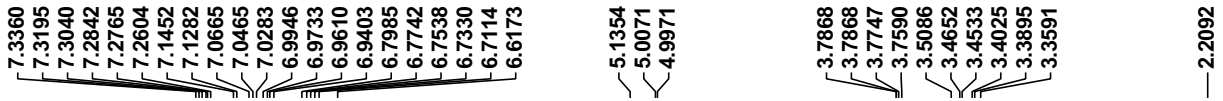


158.40
143.21
135.30
134.75
134.23
129.09
128.10
127.90
126.64
126.24
124.33
122.59
116.17
113.78
111.44
106.81
77.40
77.08
76.76
68.84
55.25
38.64
32.74
25.02
21.45

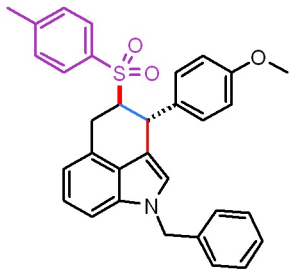
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P23'.

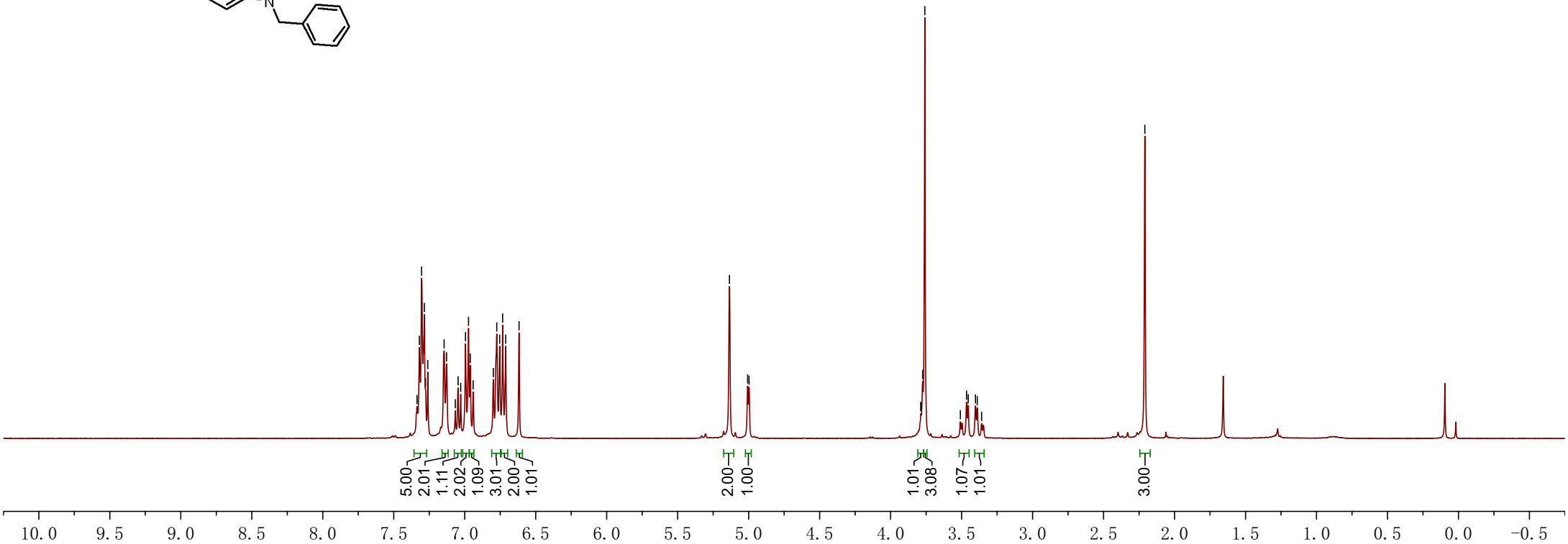






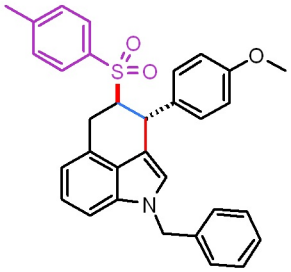
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P24.

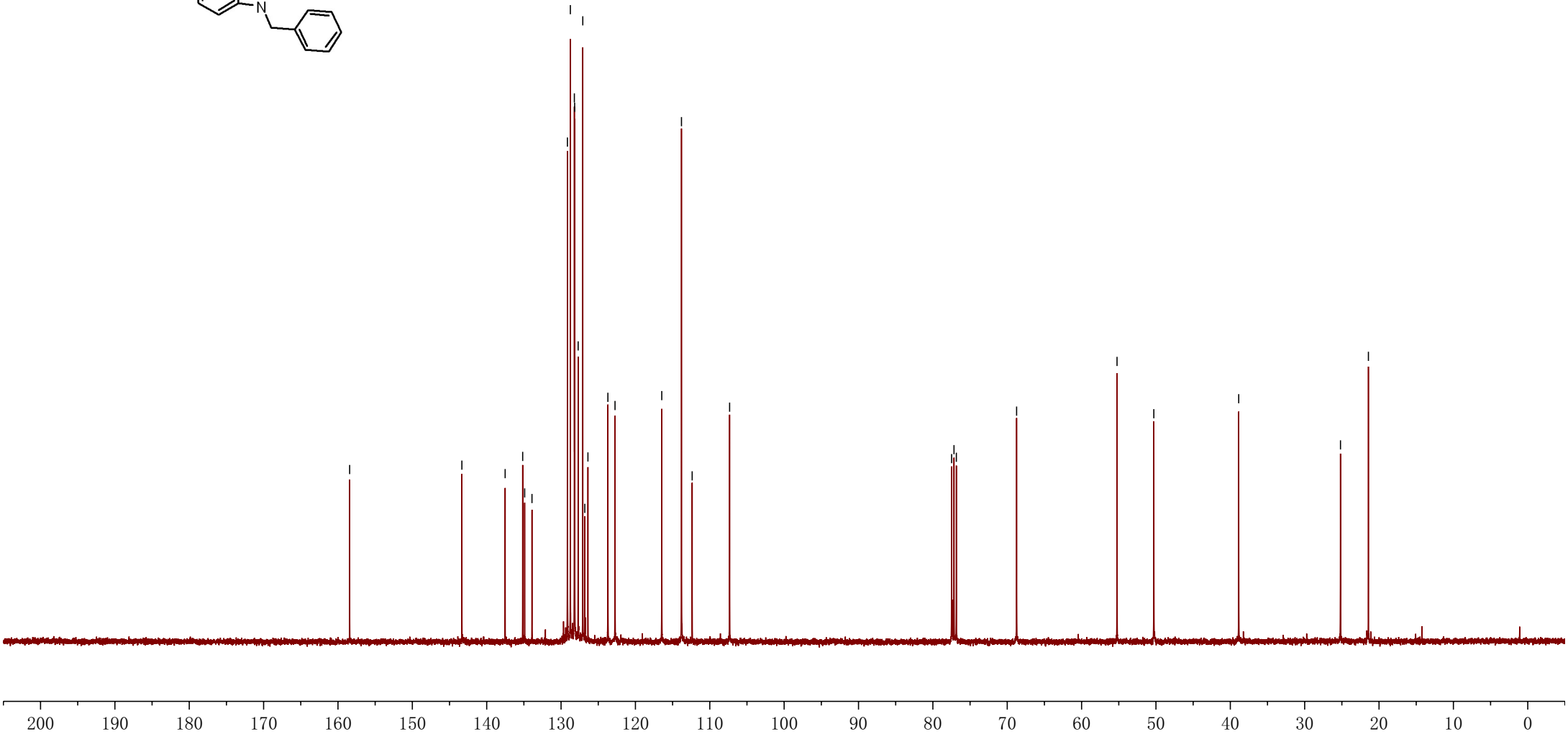




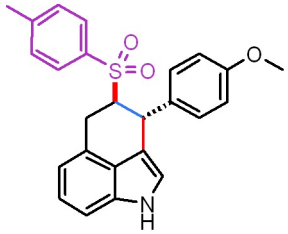
158.43
143.34
135.16
129.14
128.75
128.21
128.17
127.70
127.08
126.39
123.70
122.74
116.46
113.81
112.37
107.33
77.48
77.16
76.84
68.74
55.23
50.28
38.87
25.18
21.43

^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P24.



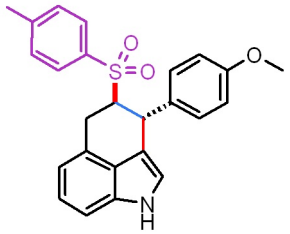


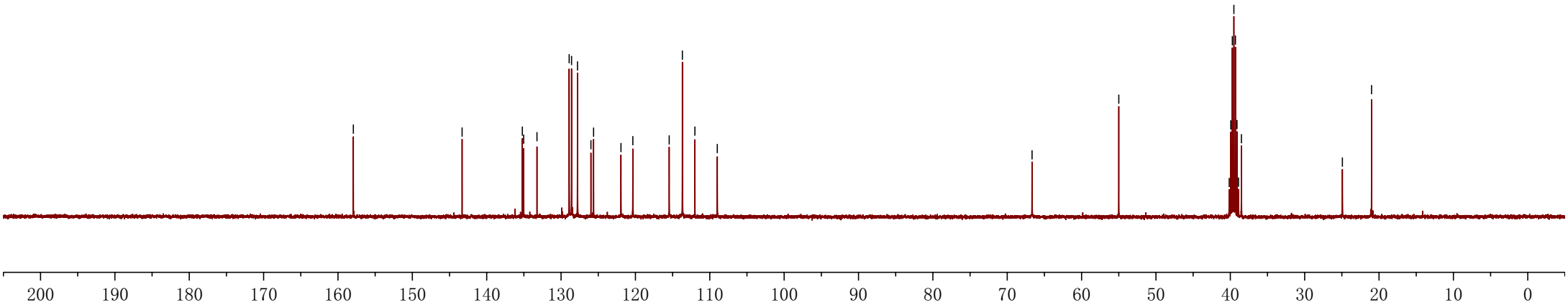
^{1}H NMR (400 MHz, DMSO-*d*6) Spectrum of P25.



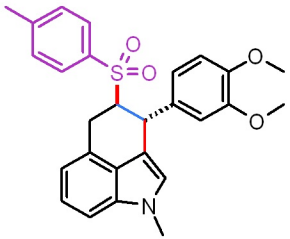
157.93
143.31
135.21
135.03
133.24
128.91
128.59
127.79
125.98
125.63
121.94
120.35
115.46
113.69
112.00
108.99
66.66
55.00
40.15
39.94
39.73
39.52
39.31
39.10
38.89
38.51
24.93
21.01

^{13}C NMR (101 MHz, DMSO-*d*6) Spectrum of P25.



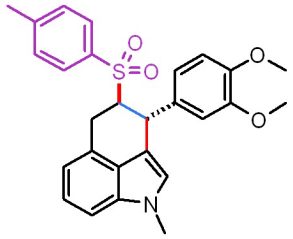


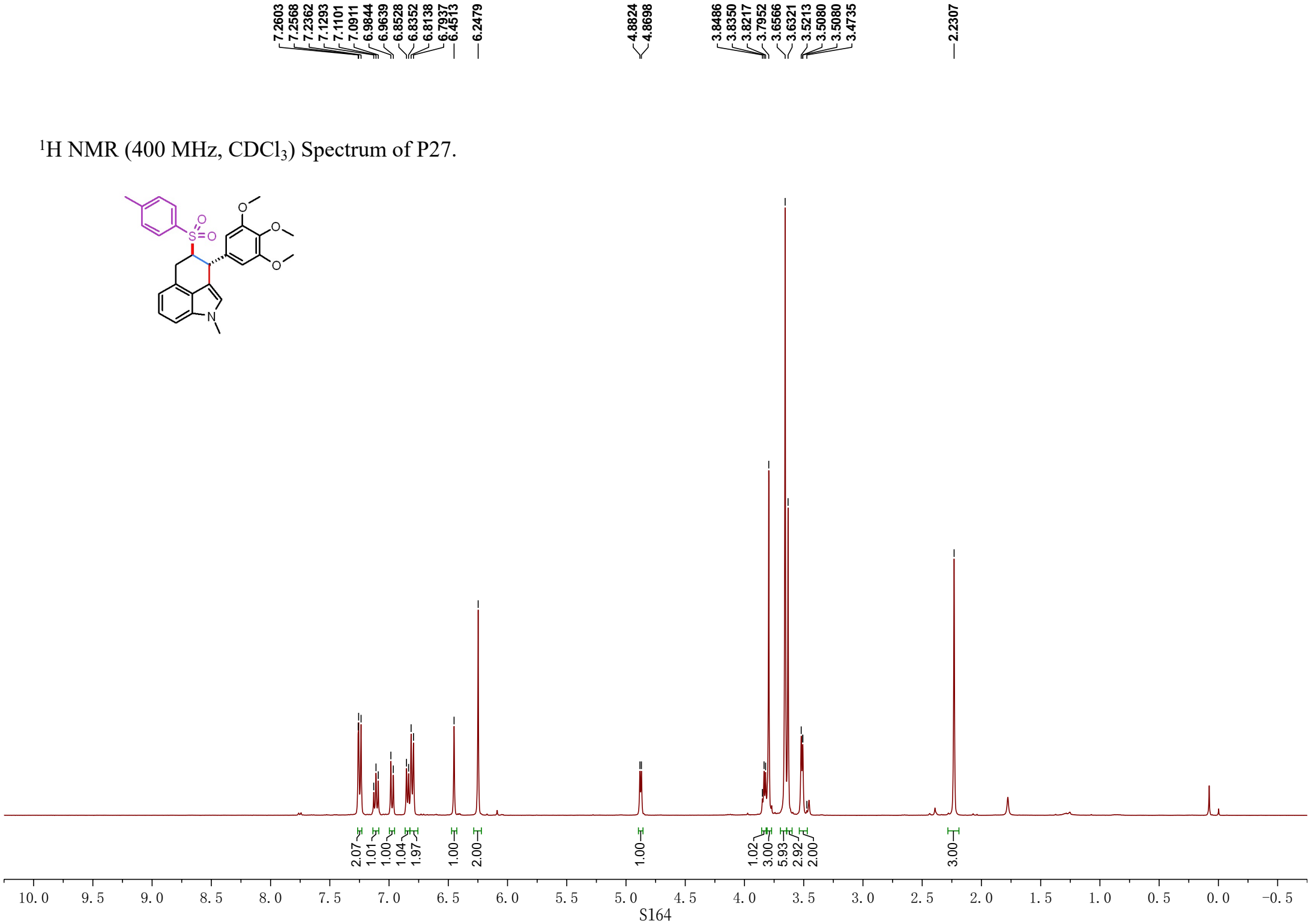
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P26.



148.98
148.05
143.32
135.53
135.21
134.37
128.17
128.02
126.76
126.47
124.52
122.75
120.69
116.32
111.99
111.07
110.92
106.96
77.48
77.16
76.84
68.84
55.97
55.91
39.69
32.86
25.49
21.51

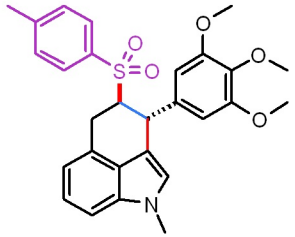
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P26.



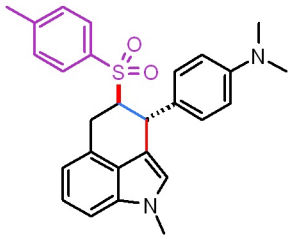


^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P27.

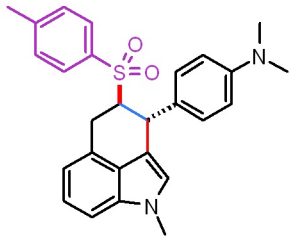
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P27.

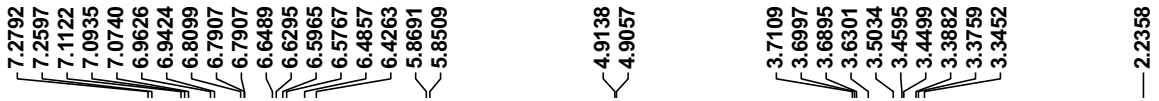


^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P28.

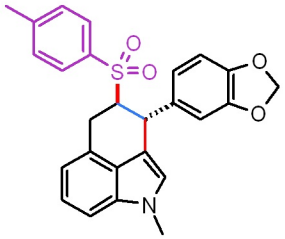


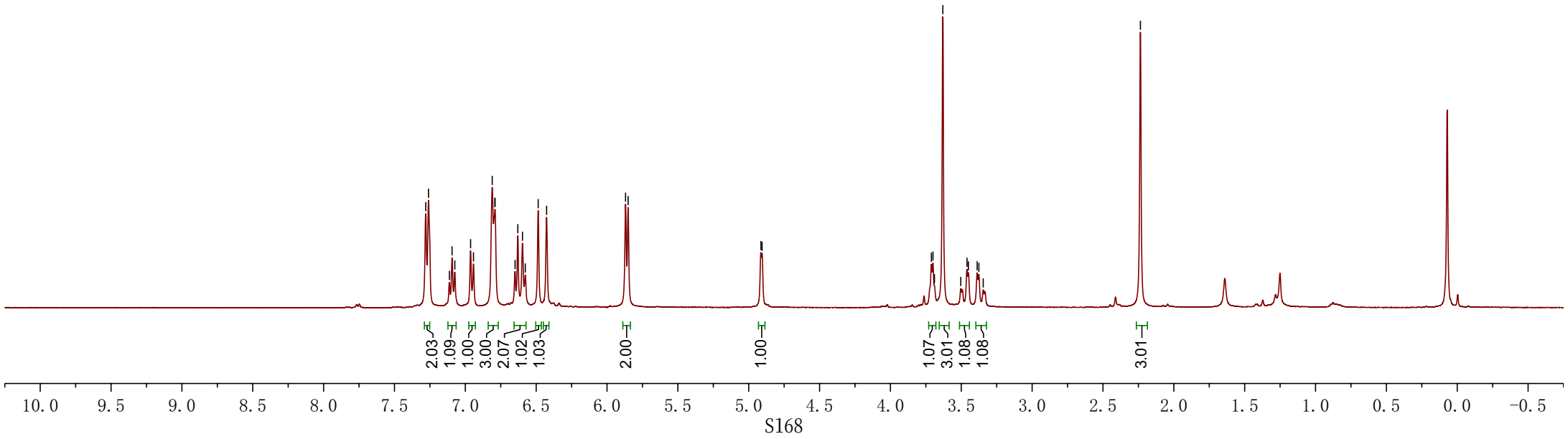
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P28.





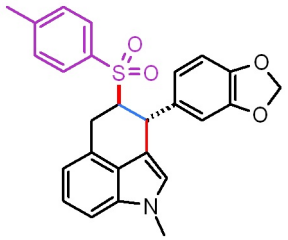
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P29.

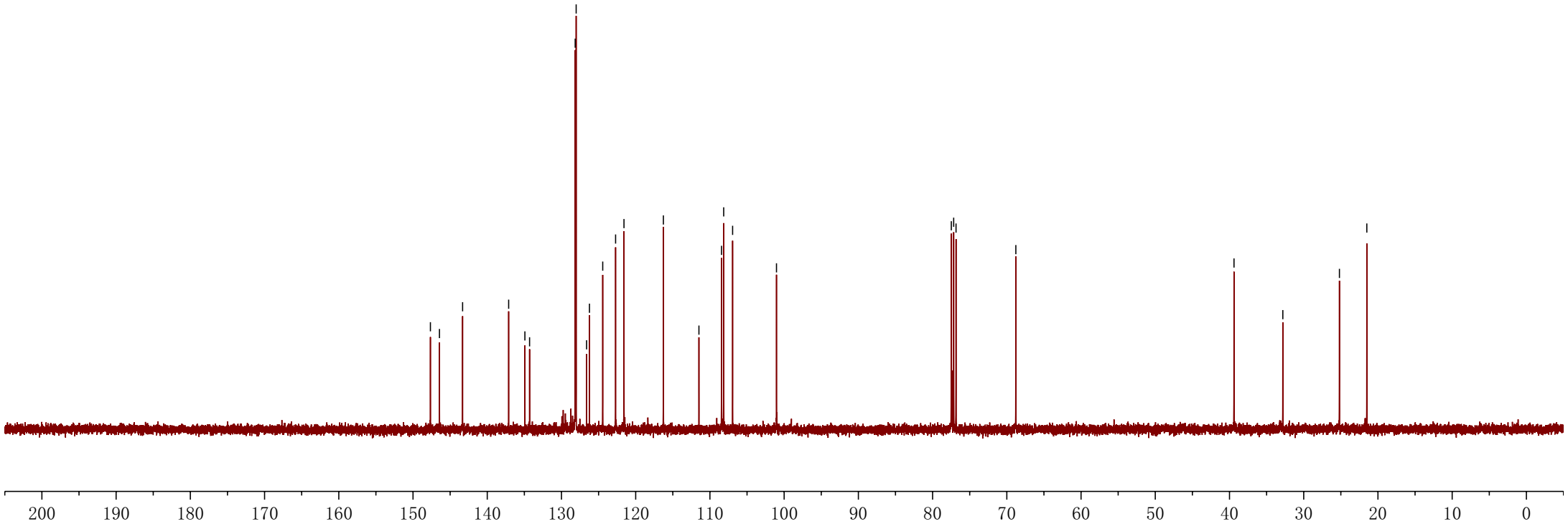




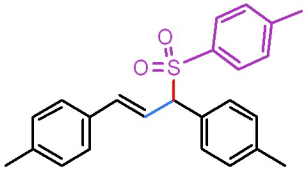
147.66
146.44
143.32
137.12
134.93
134.30
128.15
128.02
126.23
124.44
122.71
121.58
116.27
111.48
108.43
108.14
106.94
101.03
77.48
77.16
76.84
68.78
39.39
32.81
25.19
21.50

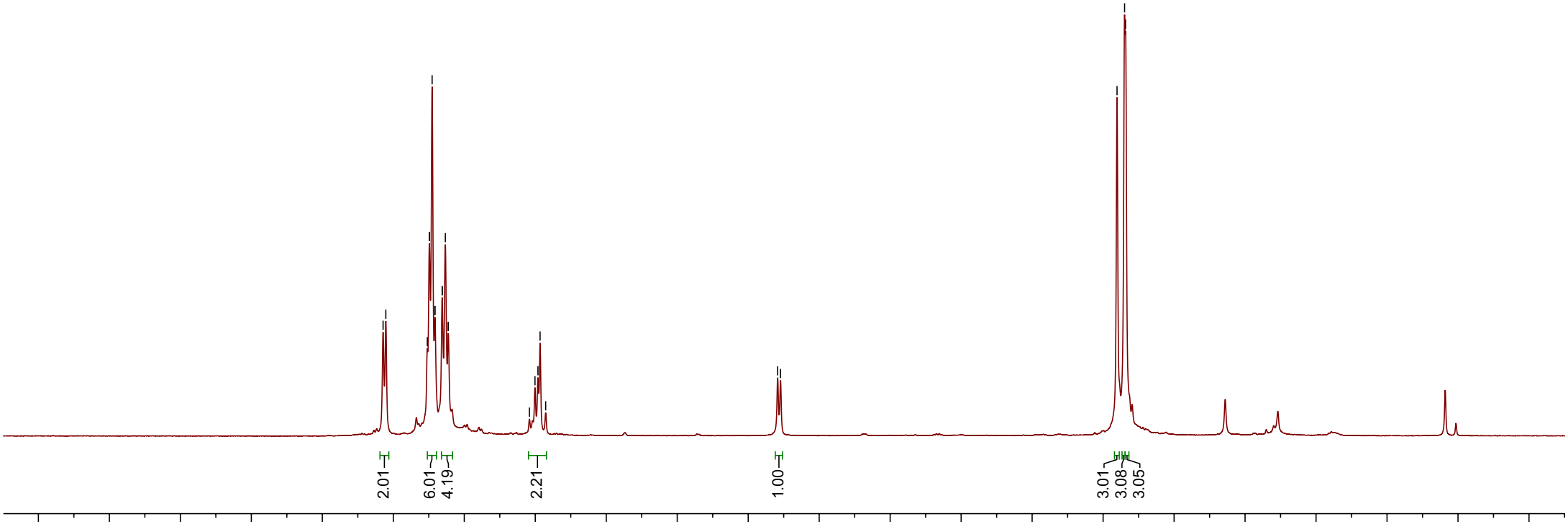
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P29.



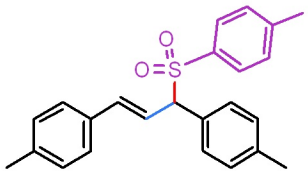


^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P30.

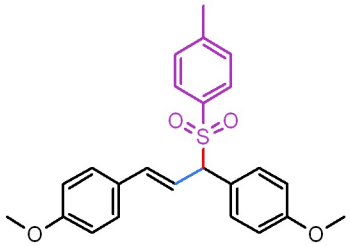




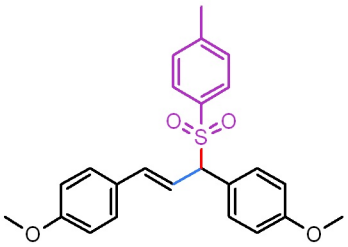
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P30.

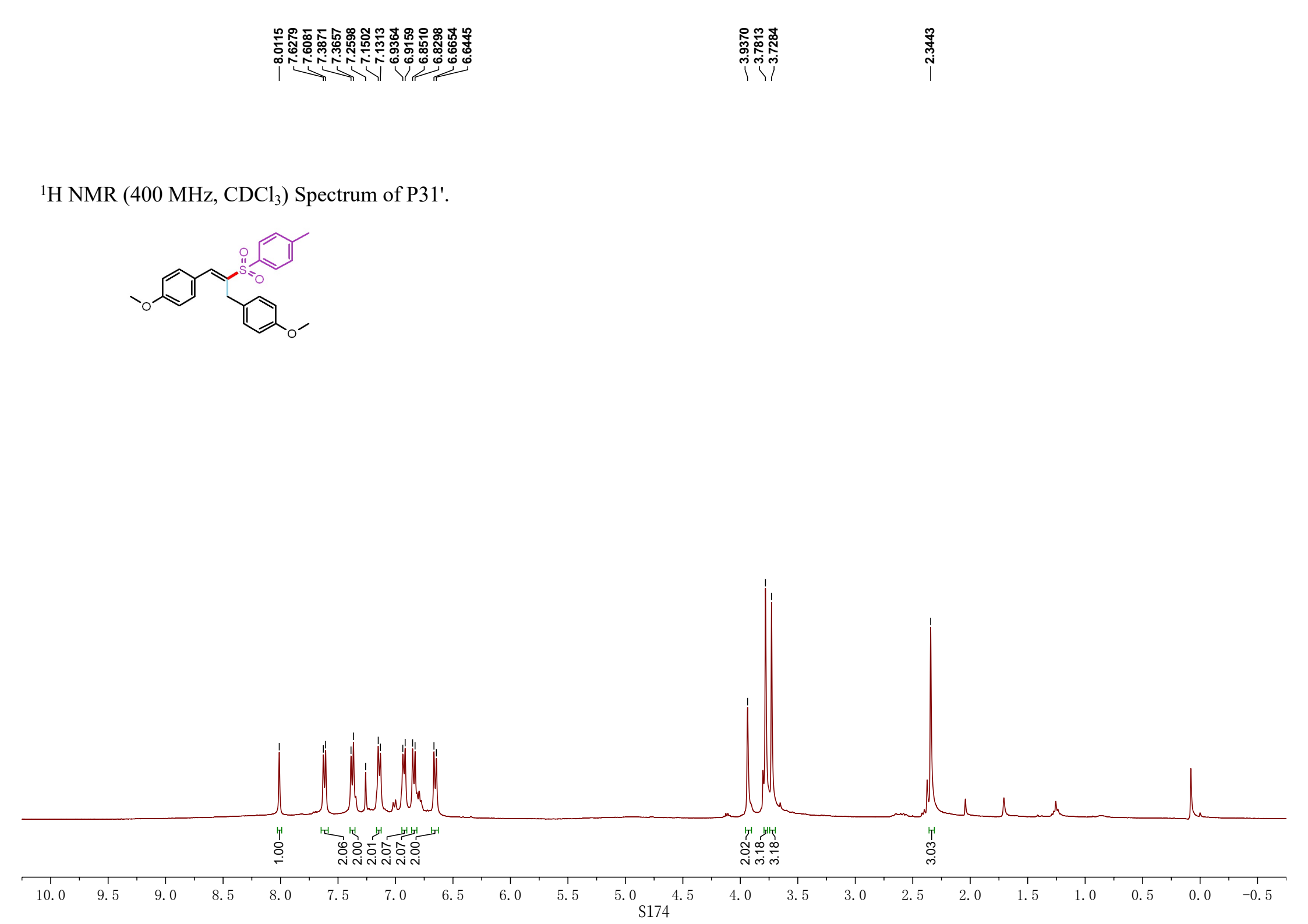


^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P31.

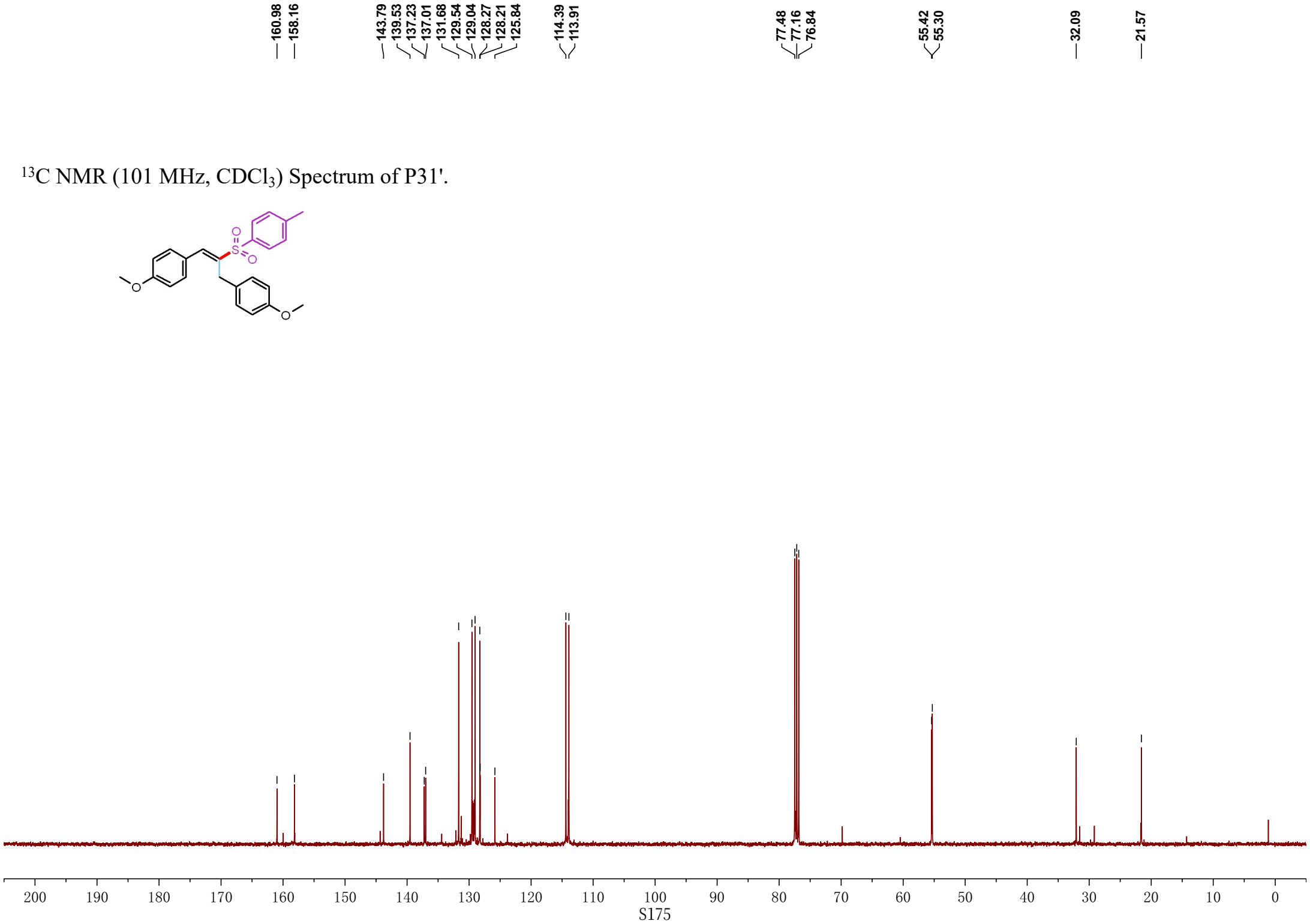


^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P31.

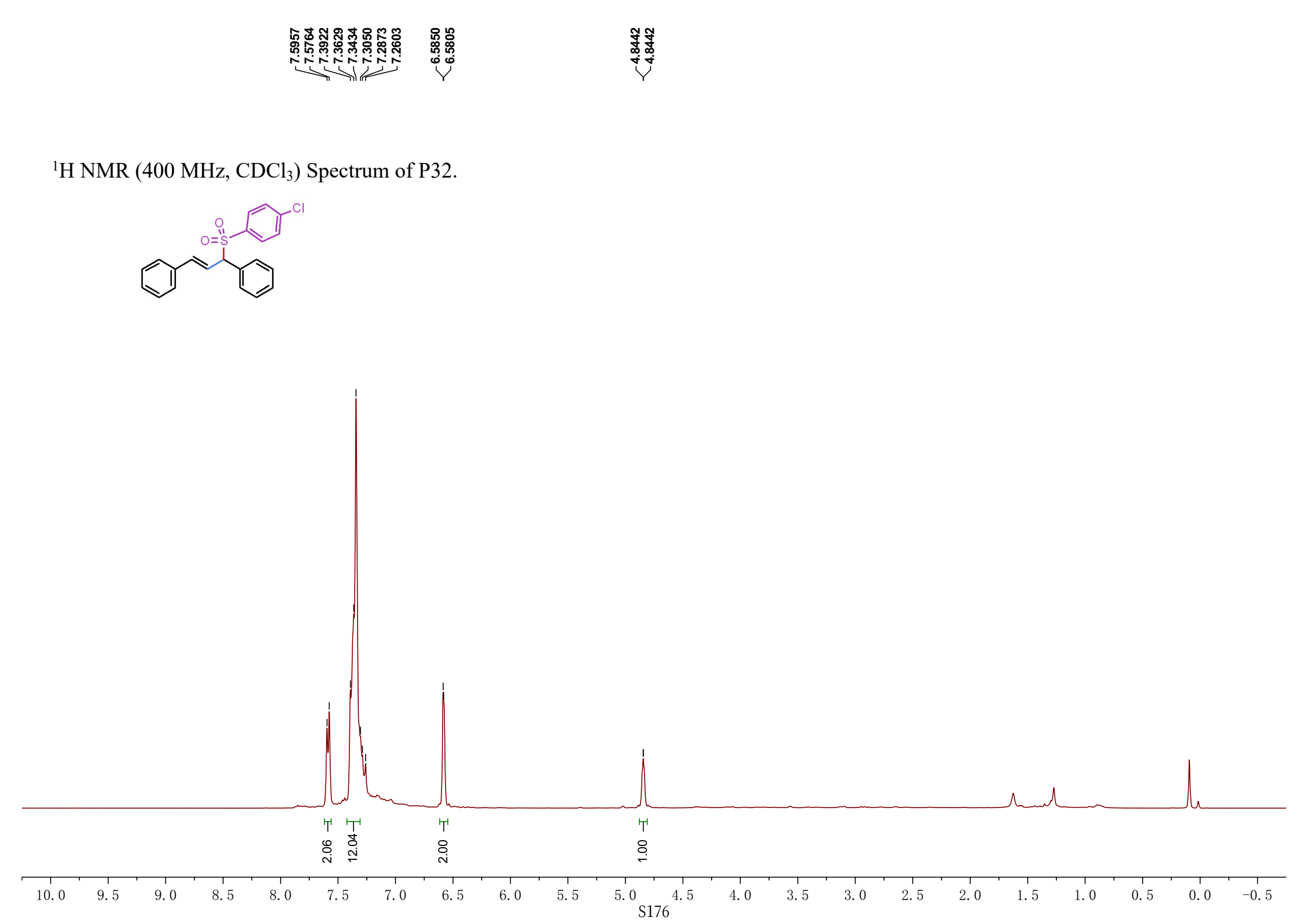




^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P31'.

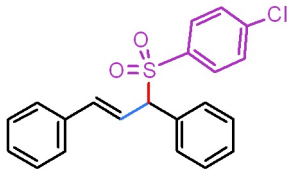


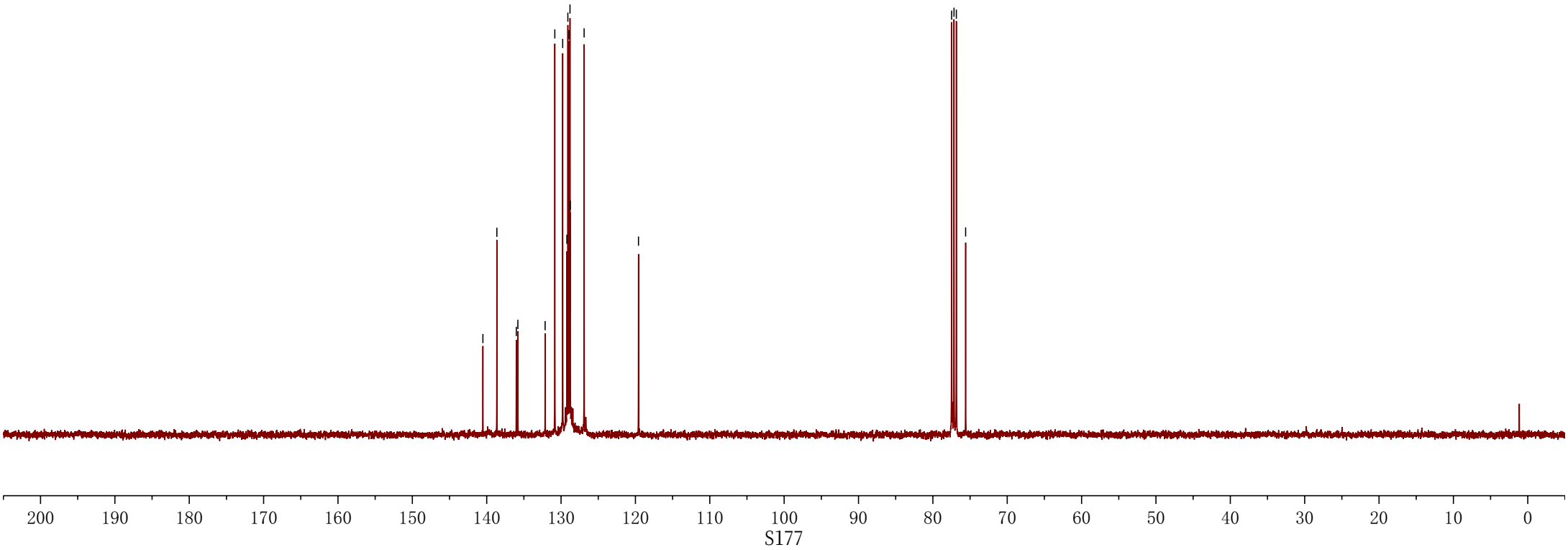
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P31'.



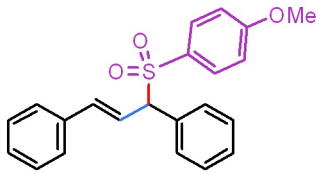
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P32.

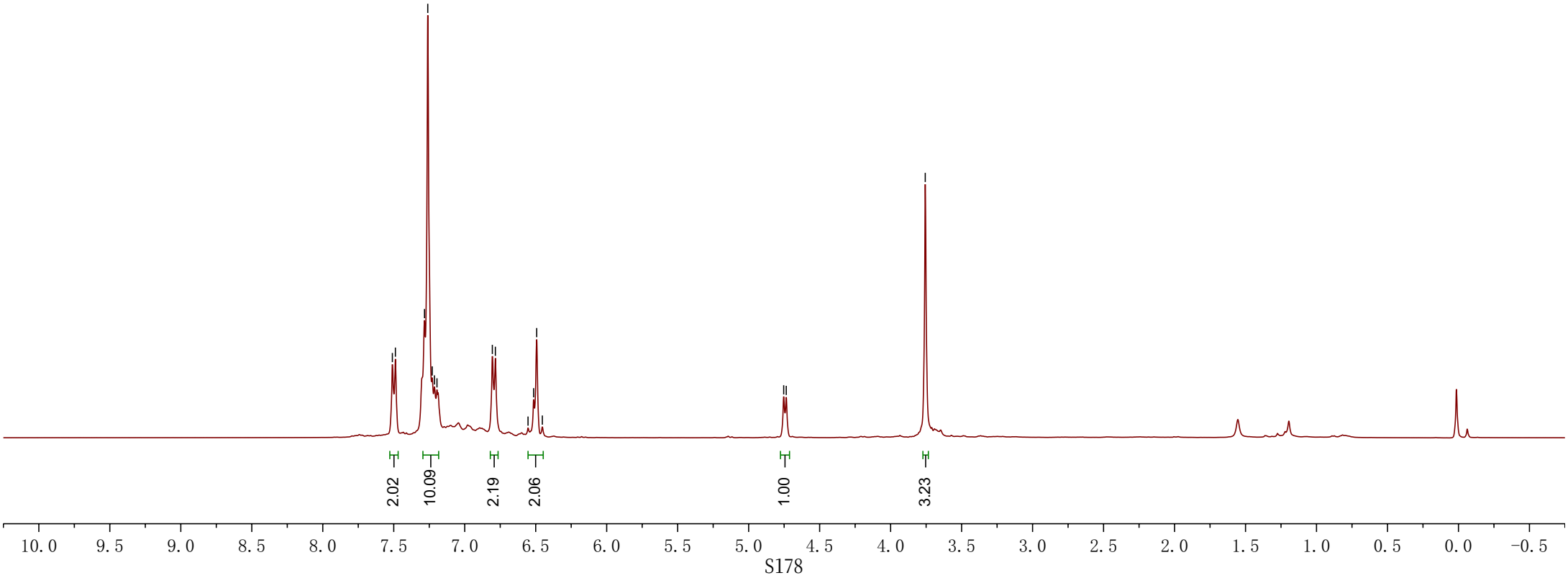
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P32.

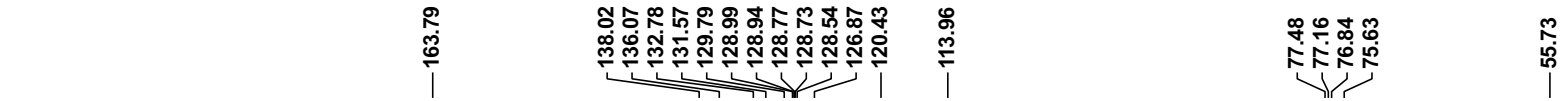




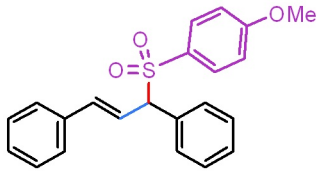
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P33.



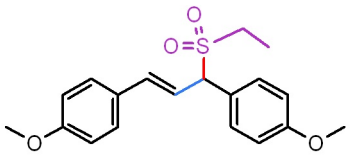


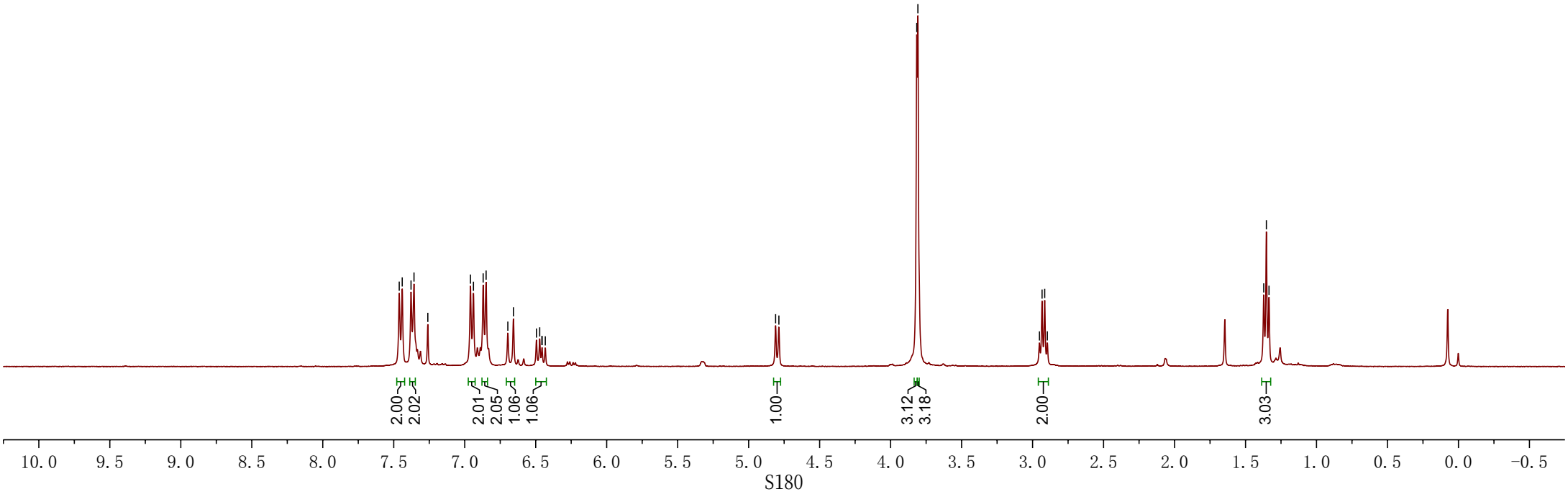


^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P33.

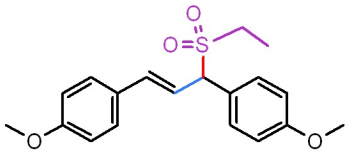


^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P34.

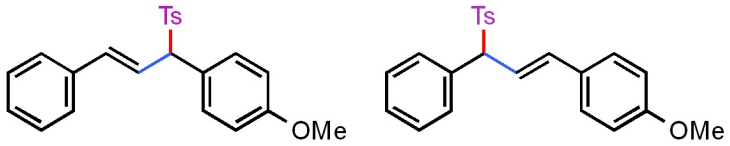


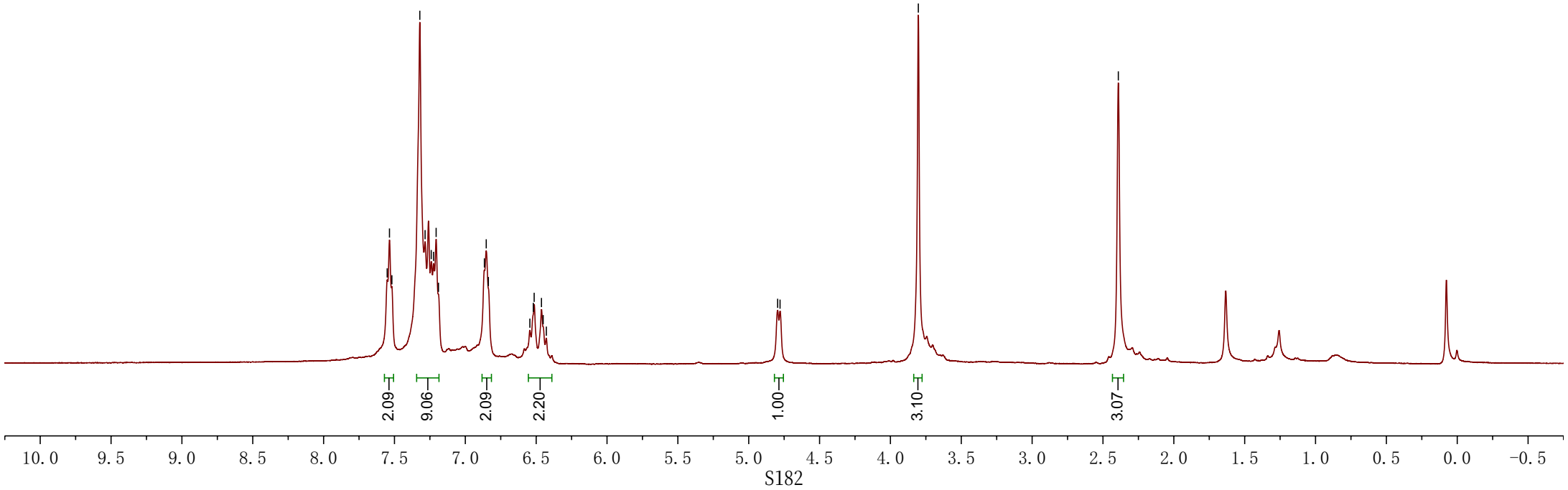


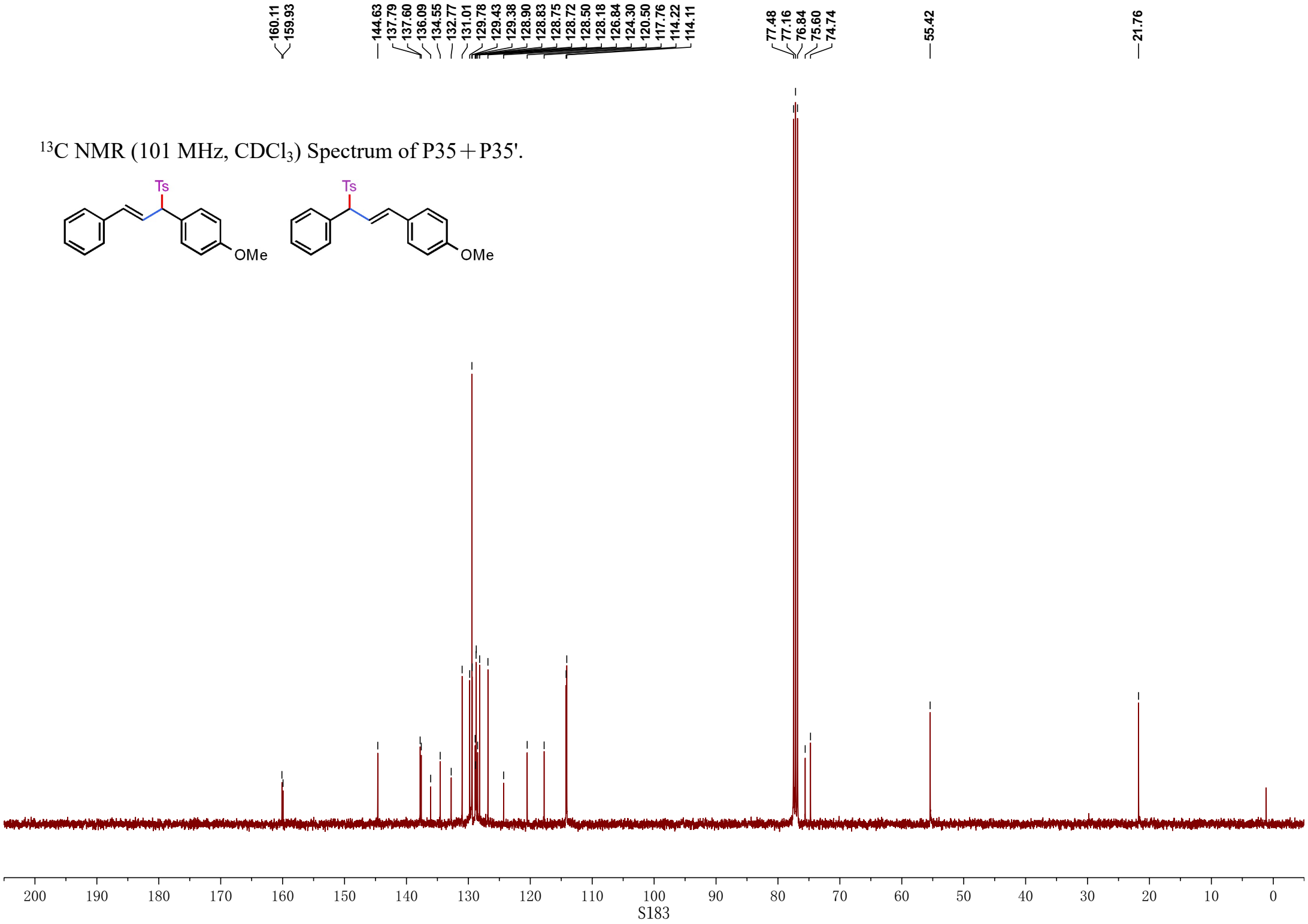
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P34.



^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P35＋P35'.

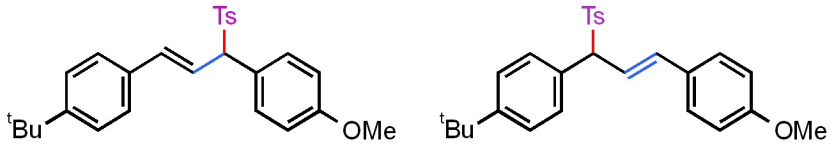


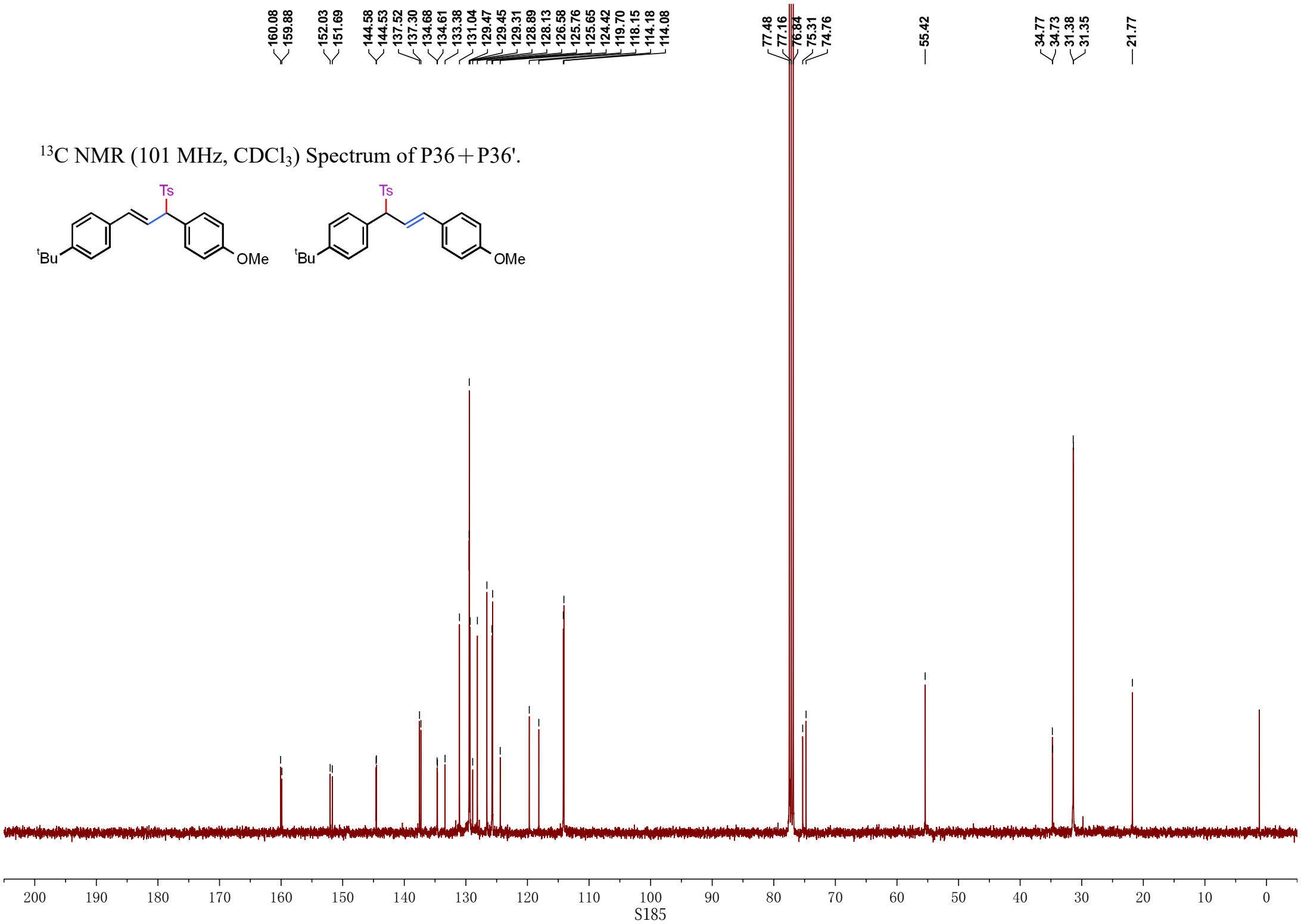




^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P35＋P35'.

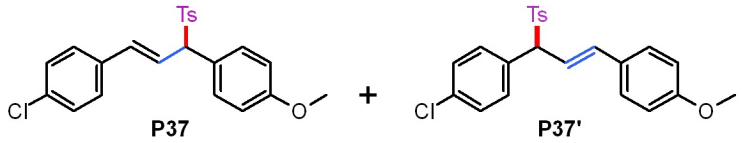
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P36＋P36'.

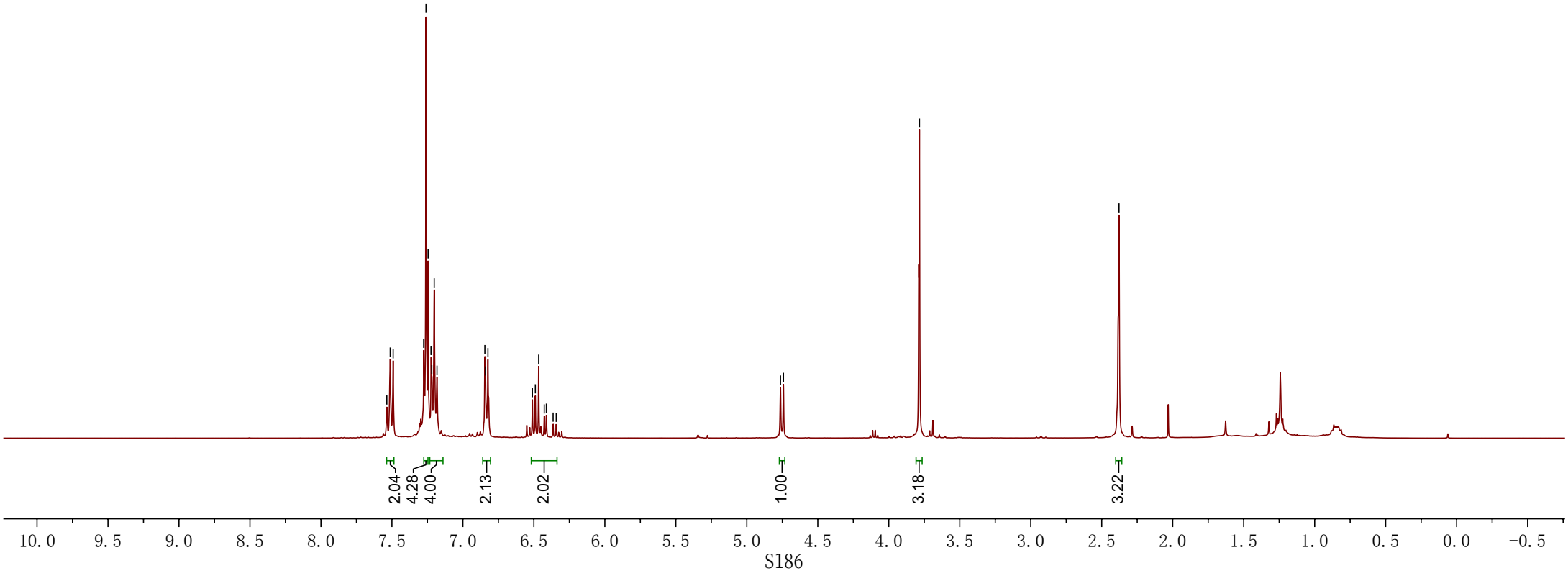




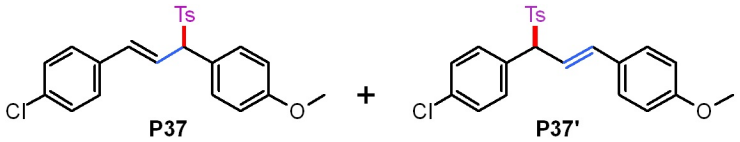
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P36＋P36'.

^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P37＋P37'.

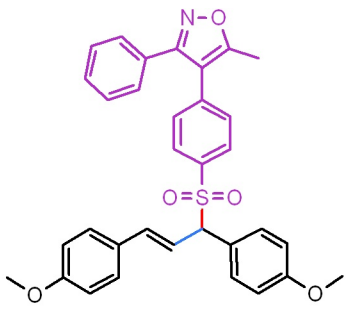




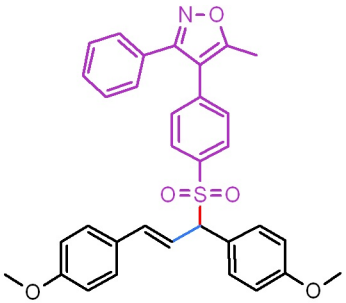
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P37＋P37'.

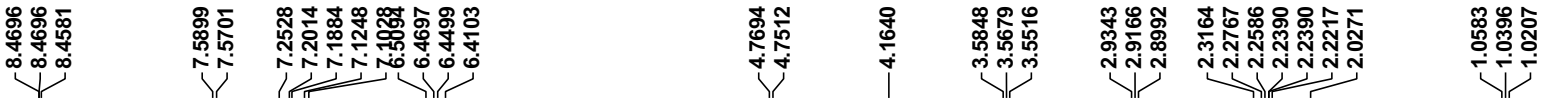


^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P38.

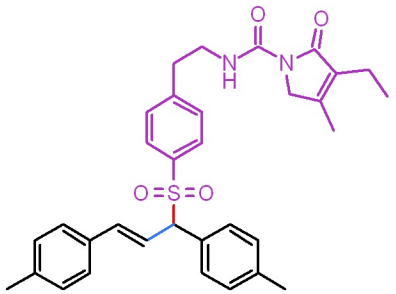


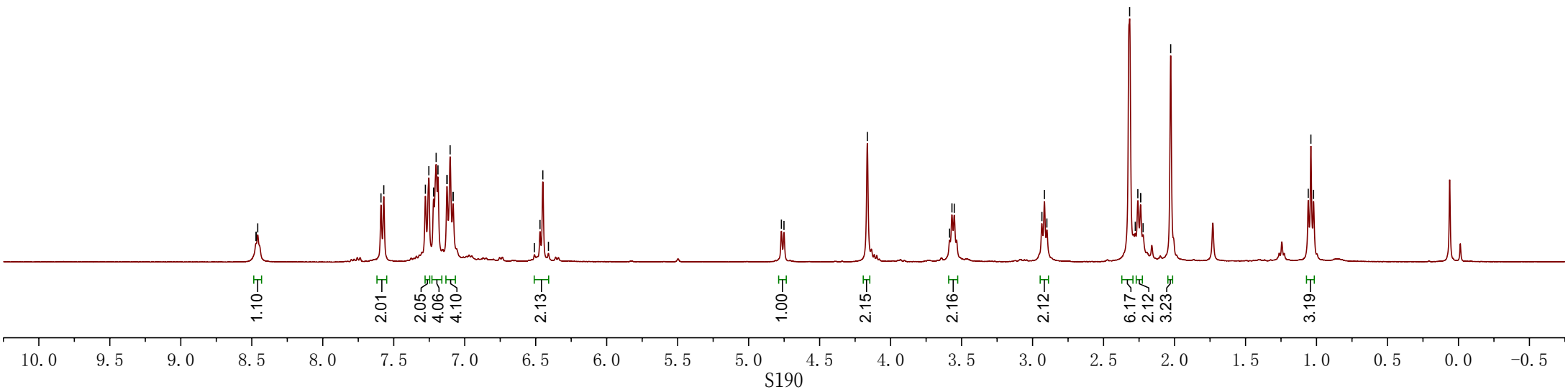
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P38.



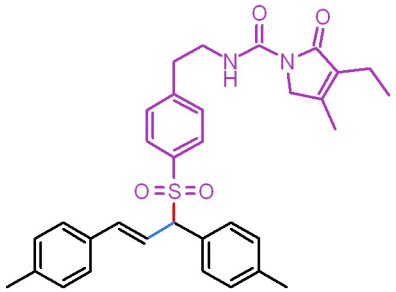


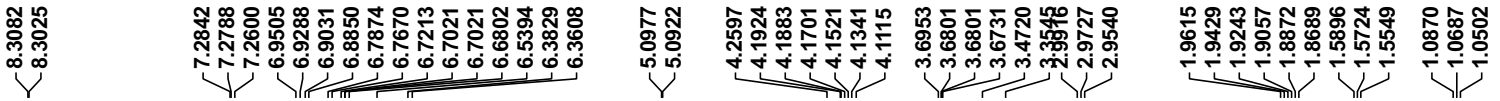
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P39.



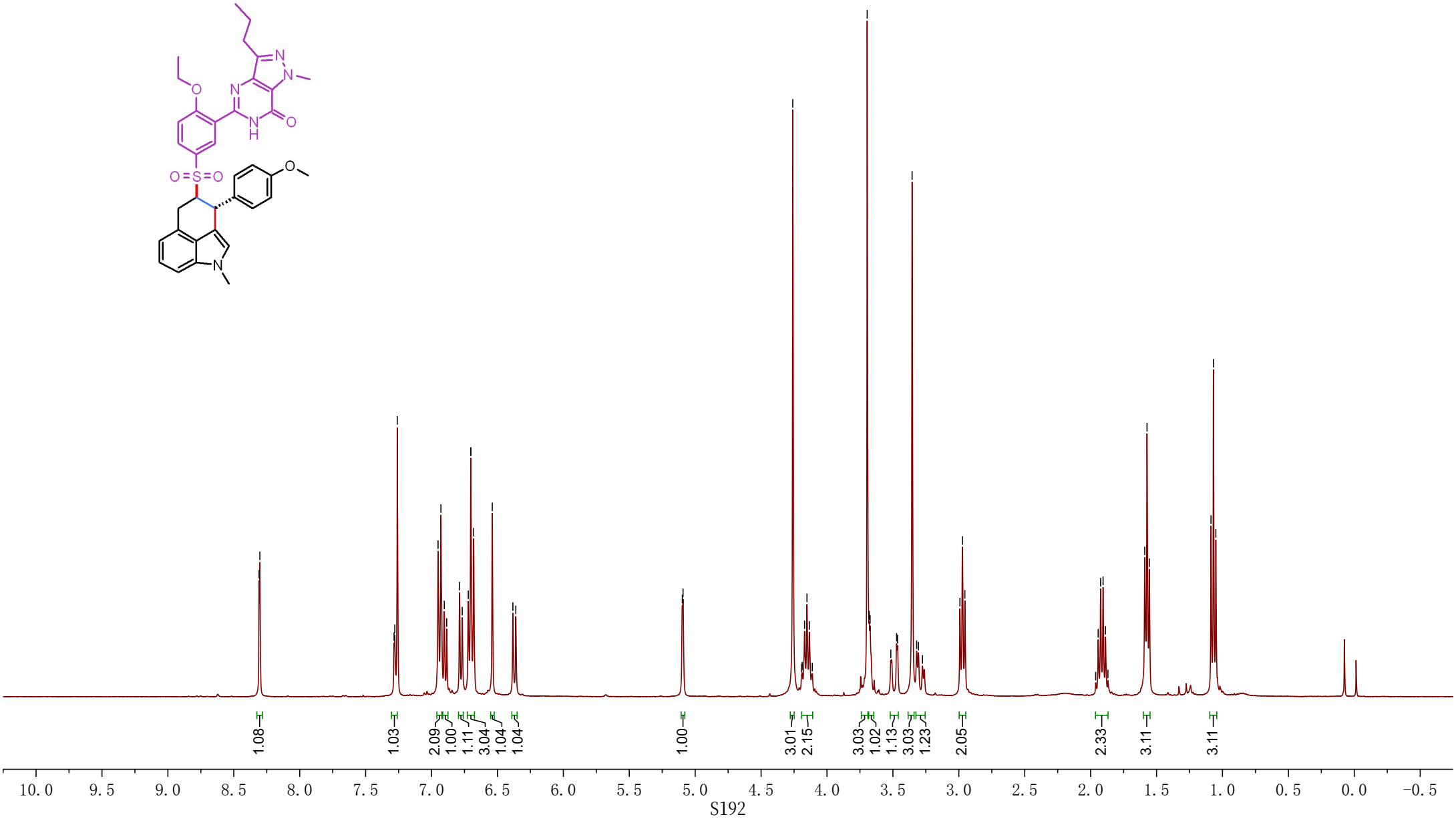


^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P39.

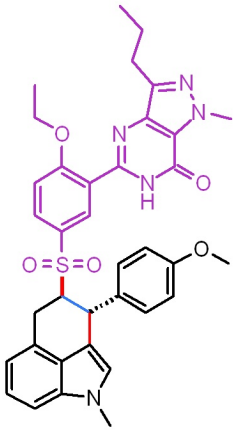




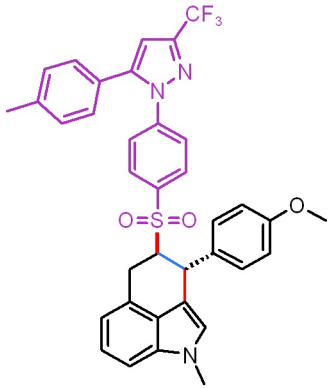
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P40.



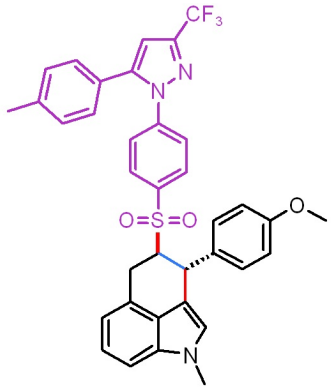
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P40.



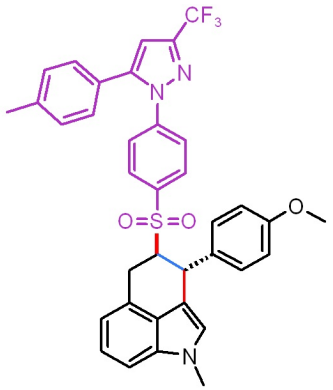
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P41.



^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P41.

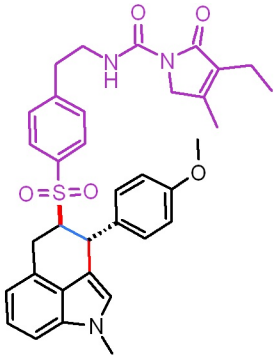


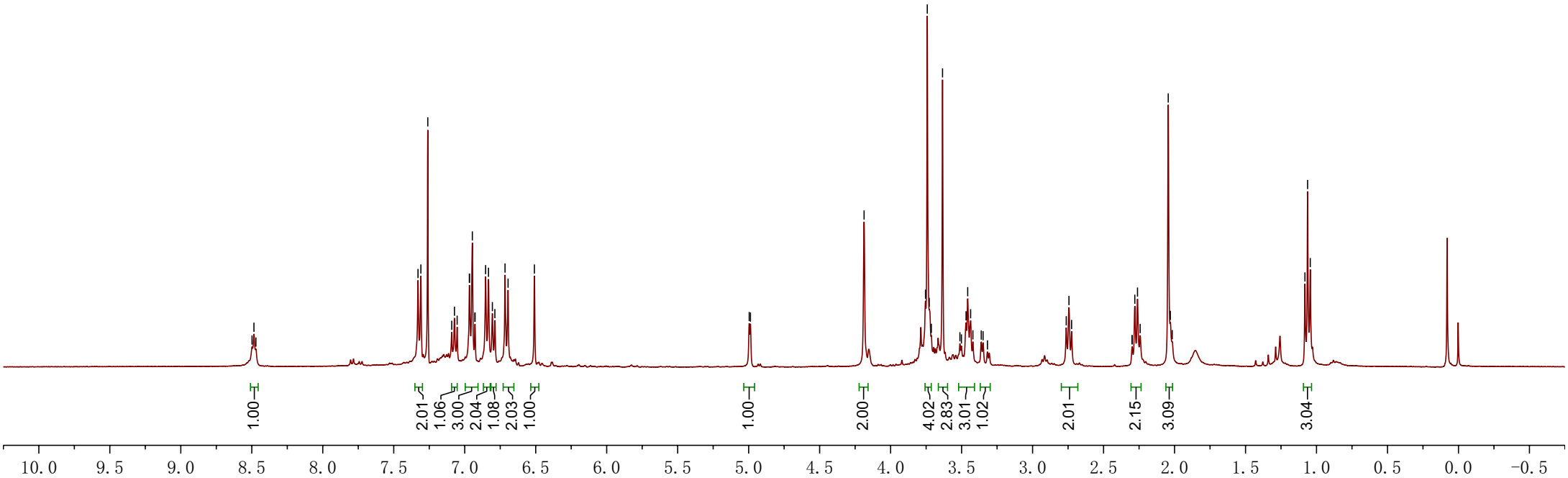
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of P41.

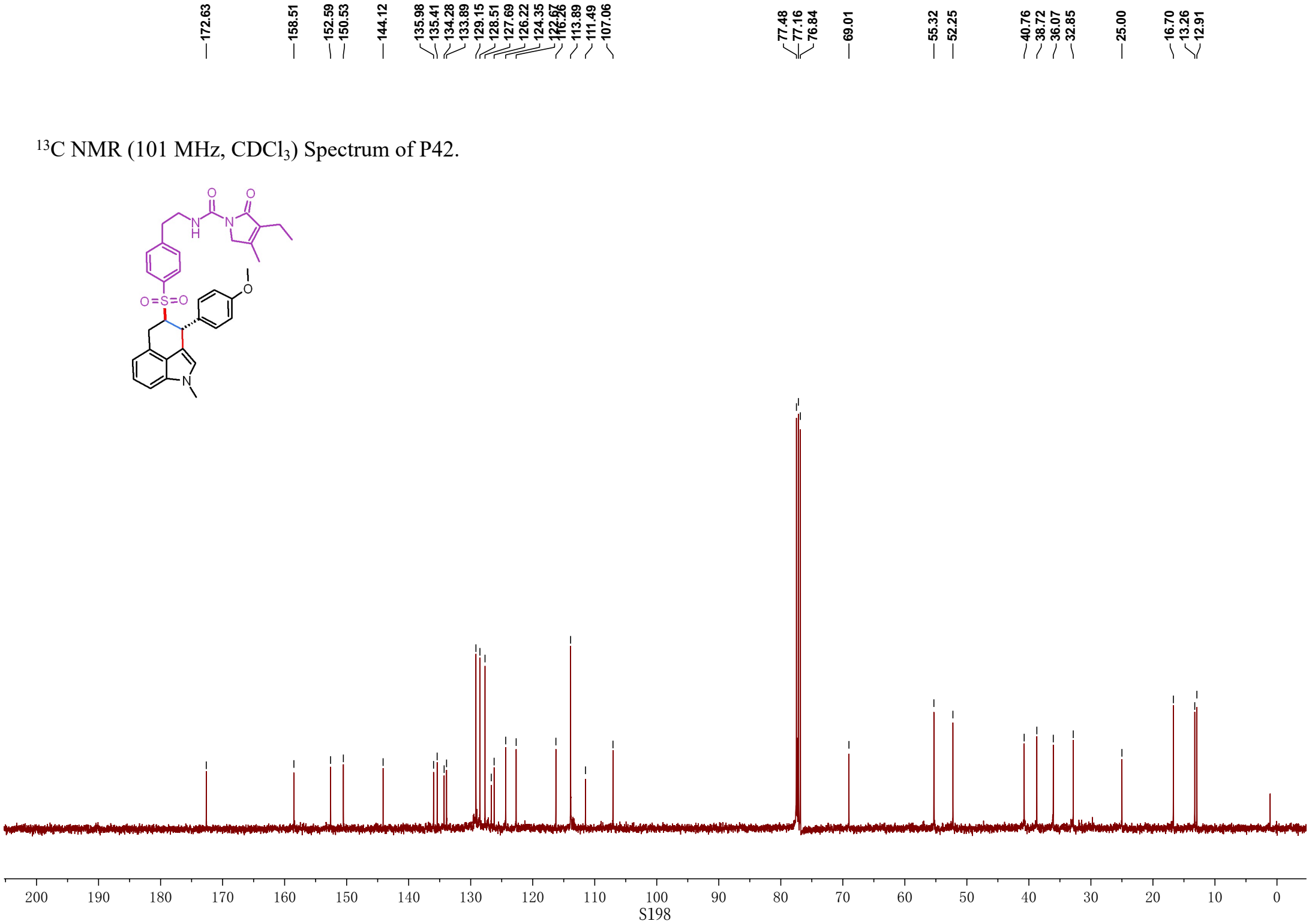


8.4984 8.4848 8.4710 7.3292 7.3089 7.2603 7.0916 7.0724 7.0534 6.9669 6.9669 6.9463 6.9277 6.9277 6.8528 6.8325 6.8052 6.7877 6.7162 6.6947 6.5093 4.9962 4.9875 4.1869 3.7544 3.7418 3.7280 3.7131 3.6343 3.4686 3.4570 3.4364 2.7620 2.7437 2.7251 2.2988 2.2988 2.2799 2.2610 2.2422 2.0444 2.0296 2.0162 1.0816 1.0627 1.0440

^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P42.

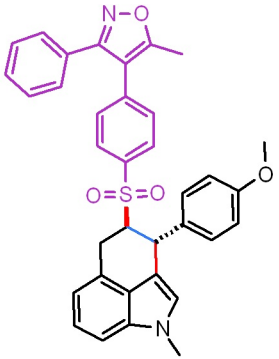


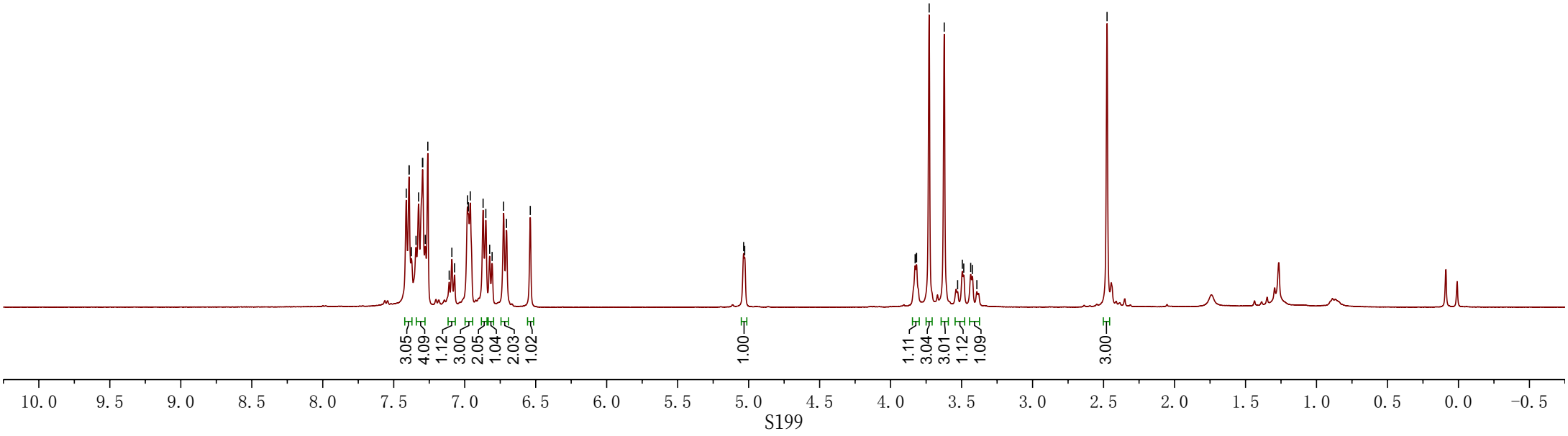




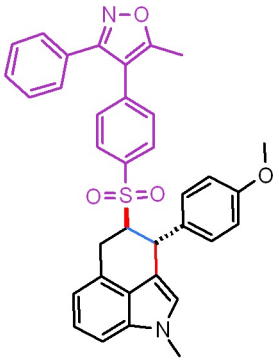
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P42.

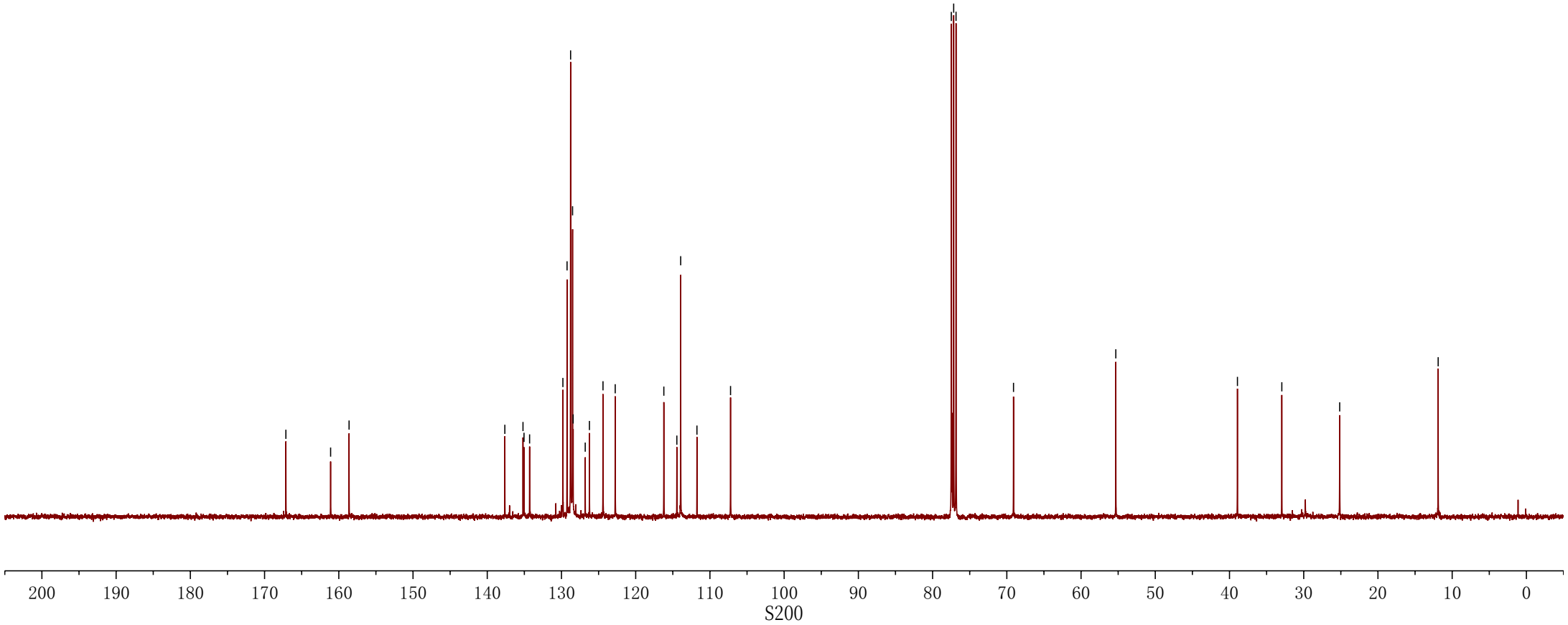
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P43.



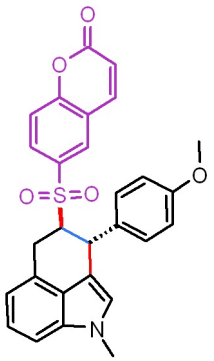


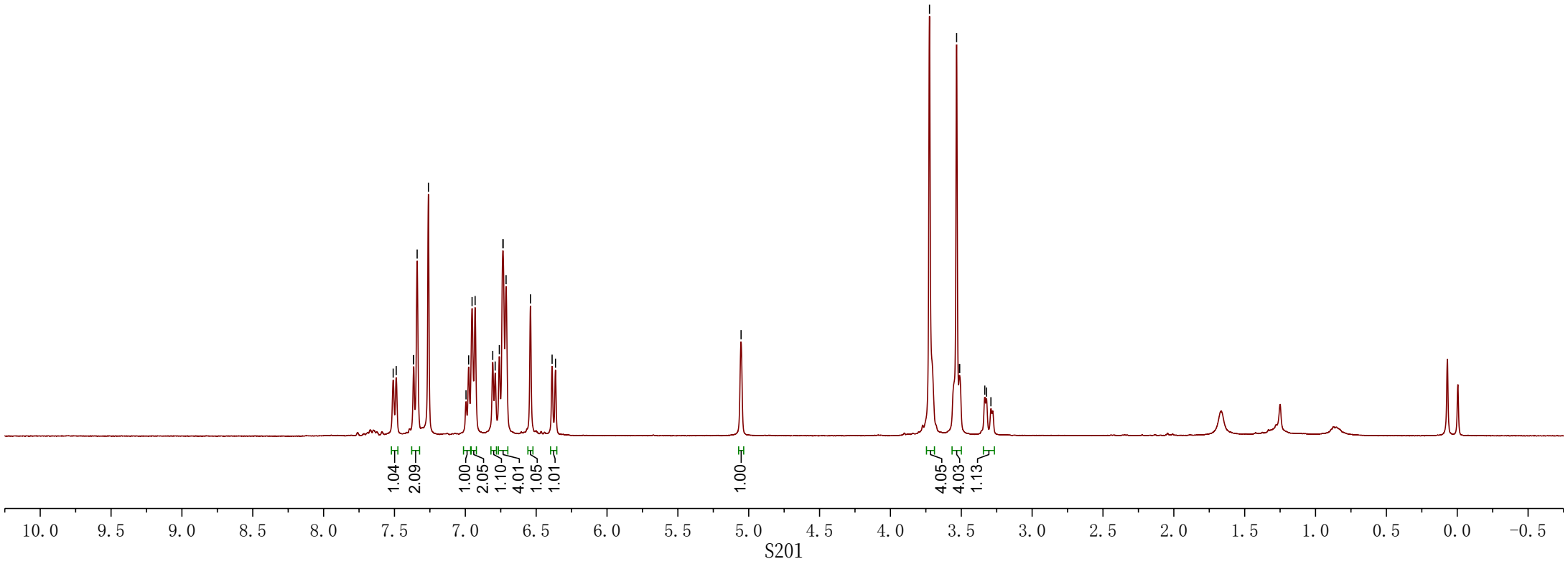
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P43.



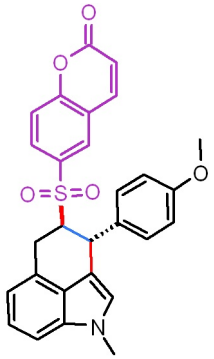


^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P44.

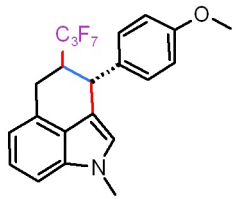


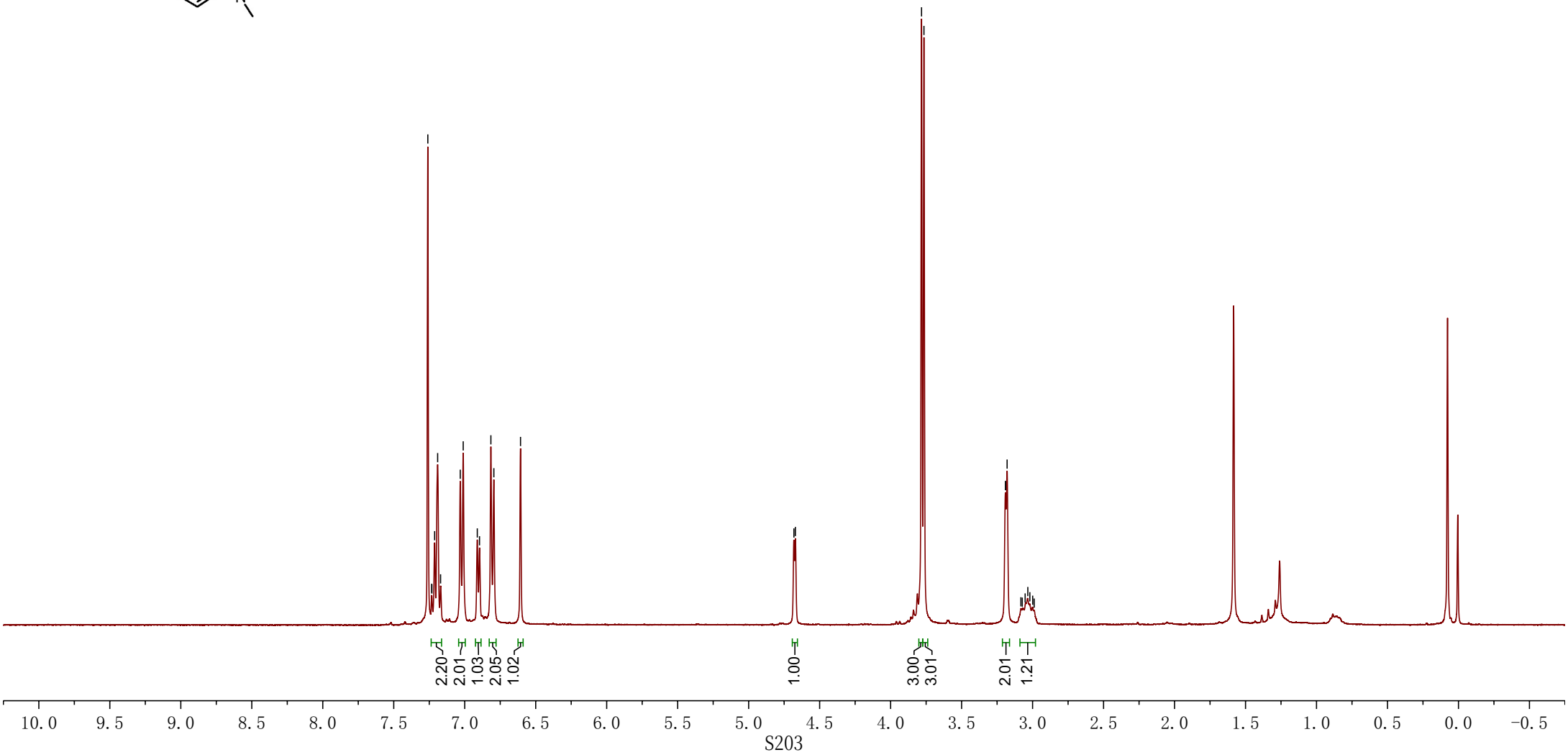


^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P44.

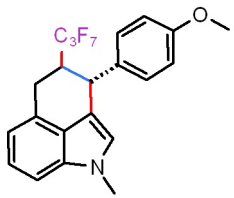


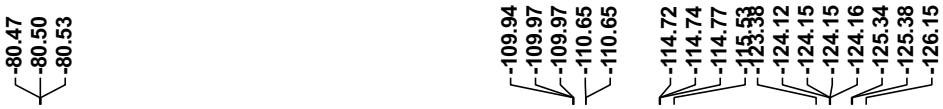
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P45.



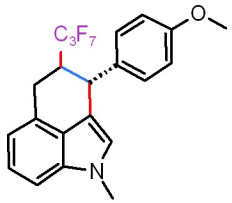


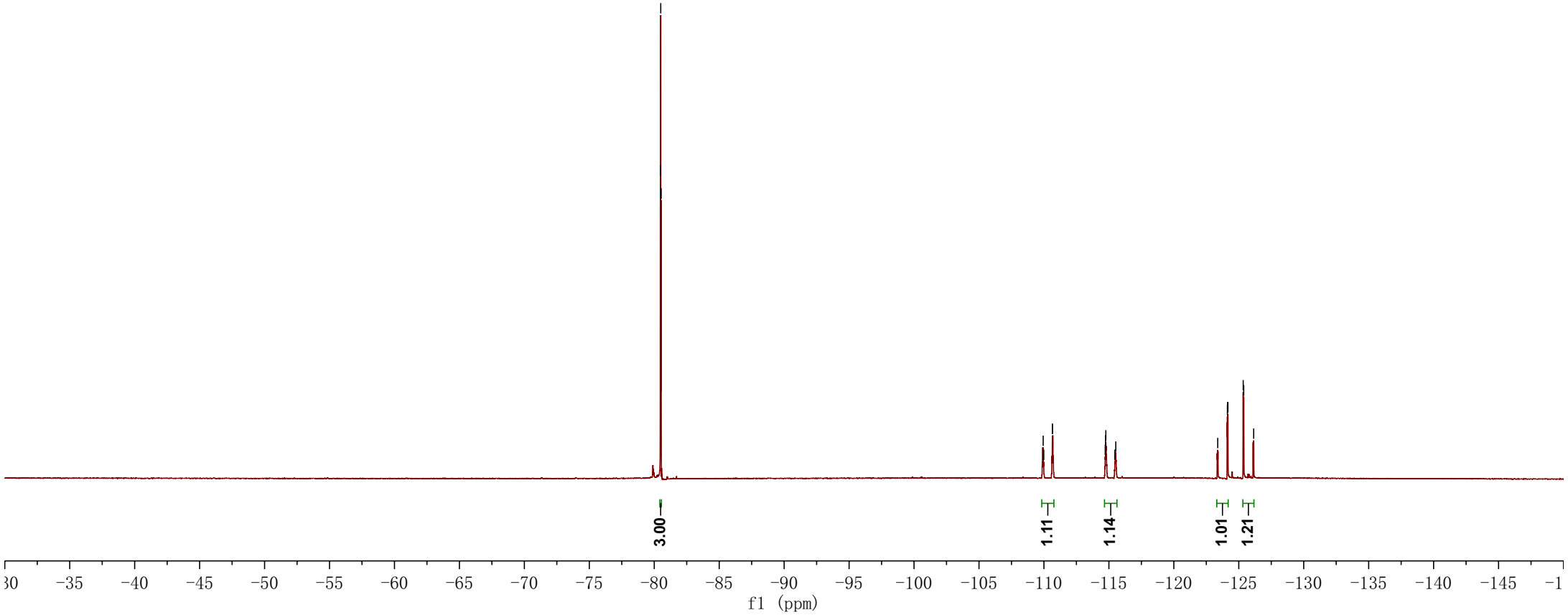
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P45.



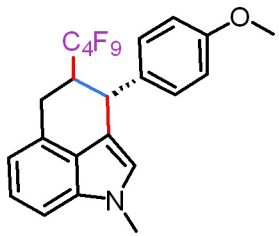


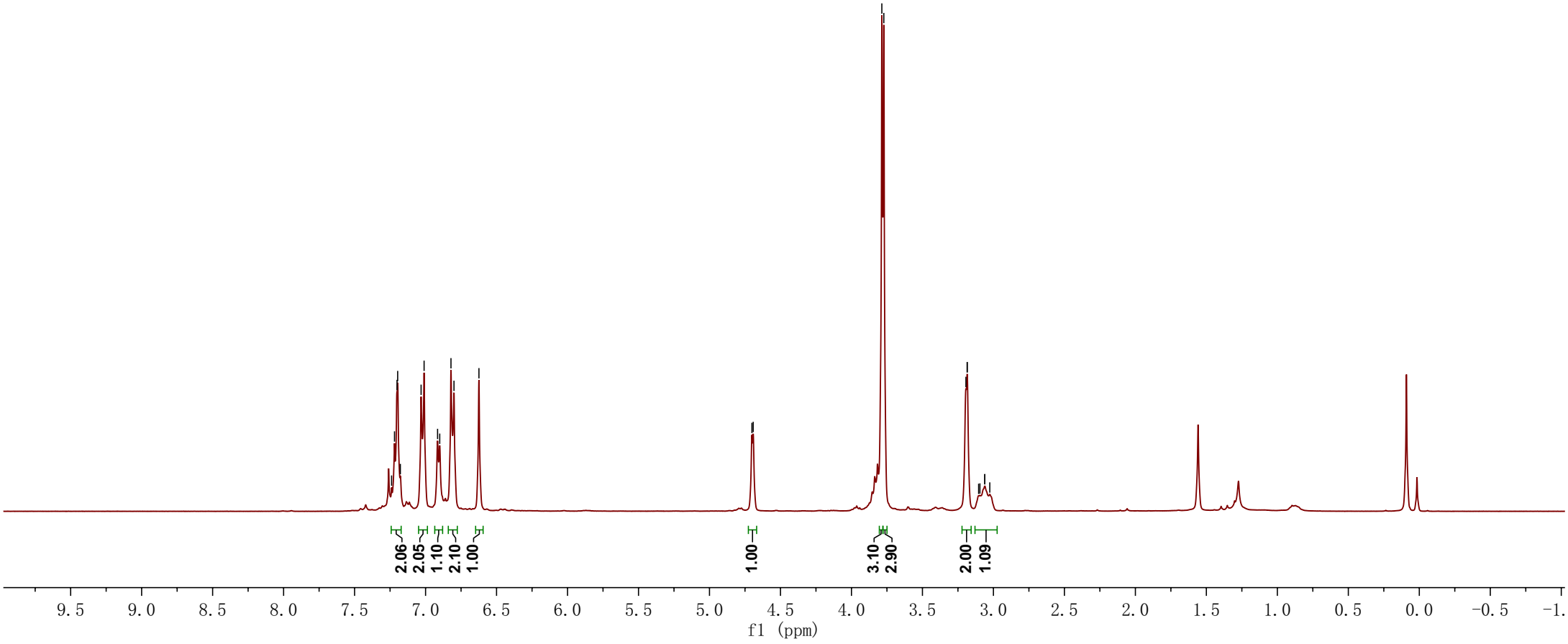
^{19}F NMR (376 MHz, CDCl3) Spectrum of P45.



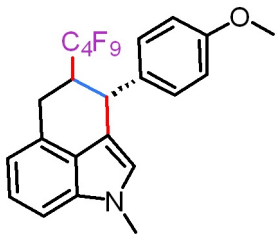


^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P46.

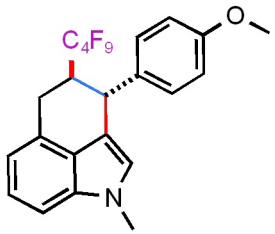


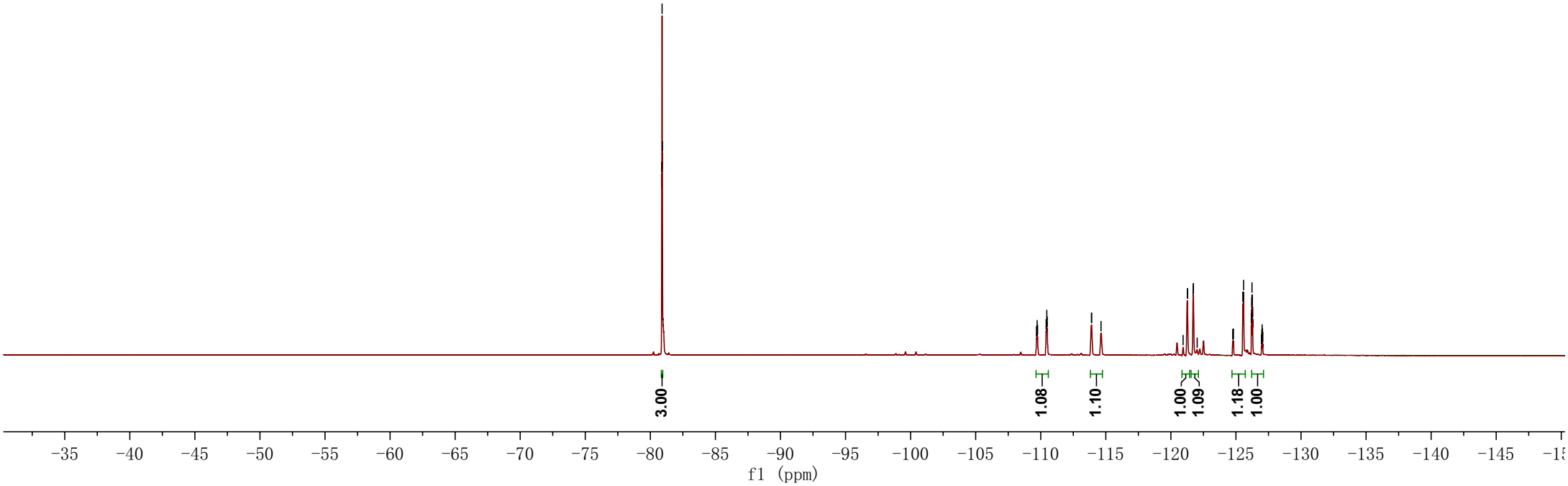


^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P46.

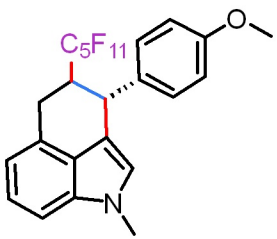


^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of P46.

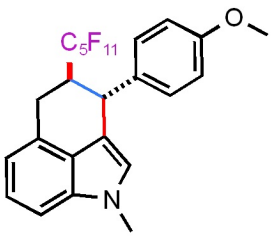




^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P47.



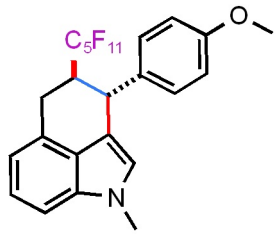
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P47.

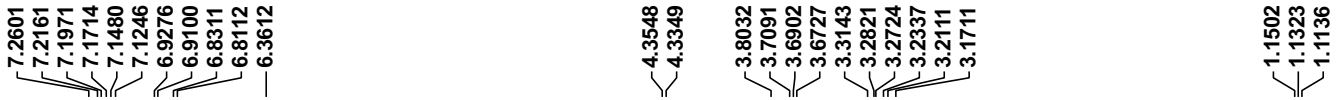


-80.76
-80.79
-80.81

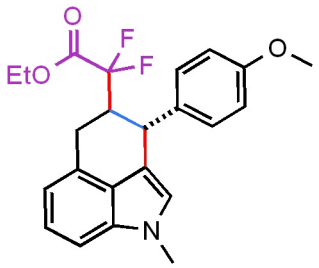
-109.56
-109.58
-110.29
-110.29
-110.31
-113.73
-113.73
-114.48
-119.86
-120.64
-120.66
-120.82
-120.83
-122.32
-122.35
-122.40
-122.80
-122.80
-122.80
-123.57
-125.13
-125.89
-125.91
-126.36
-127.14

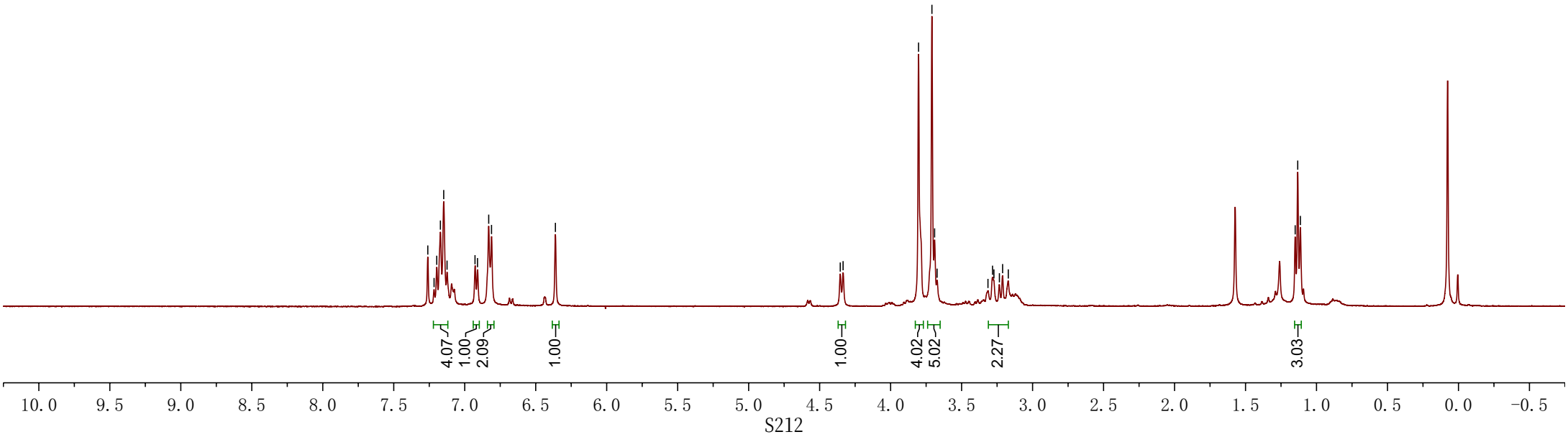
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of P47.



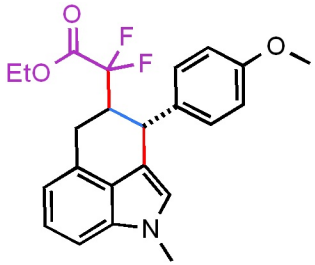


^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P48.



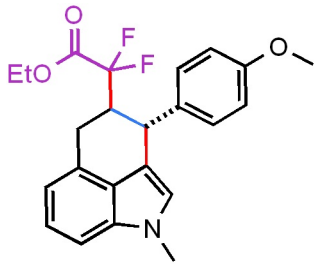


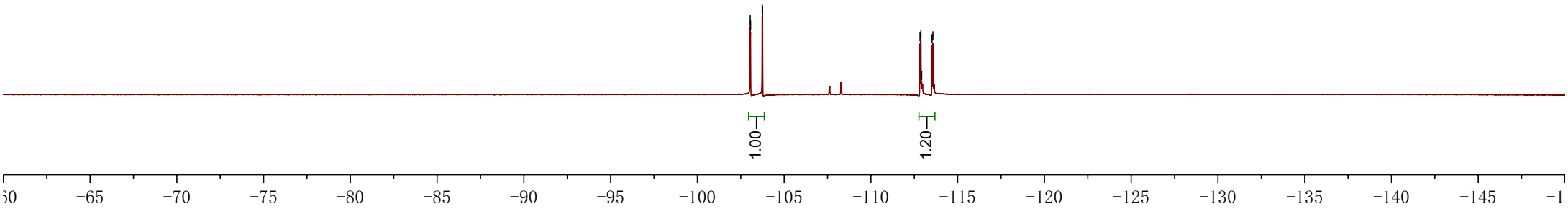
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P48.



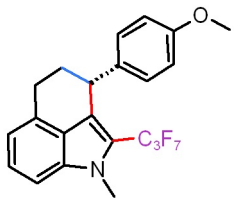
-103.05
-103.06
-103.06
-103.74
-103.75
-112.83
-112.88
-112.93
-113.52
-113.57

^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of P48.

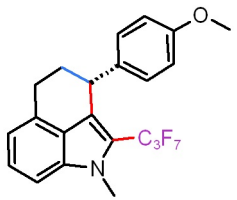


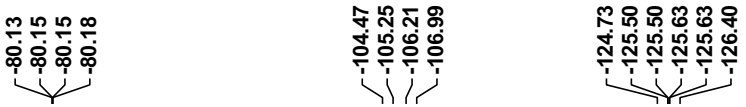


^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P49.

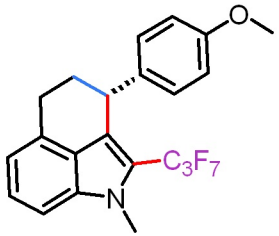


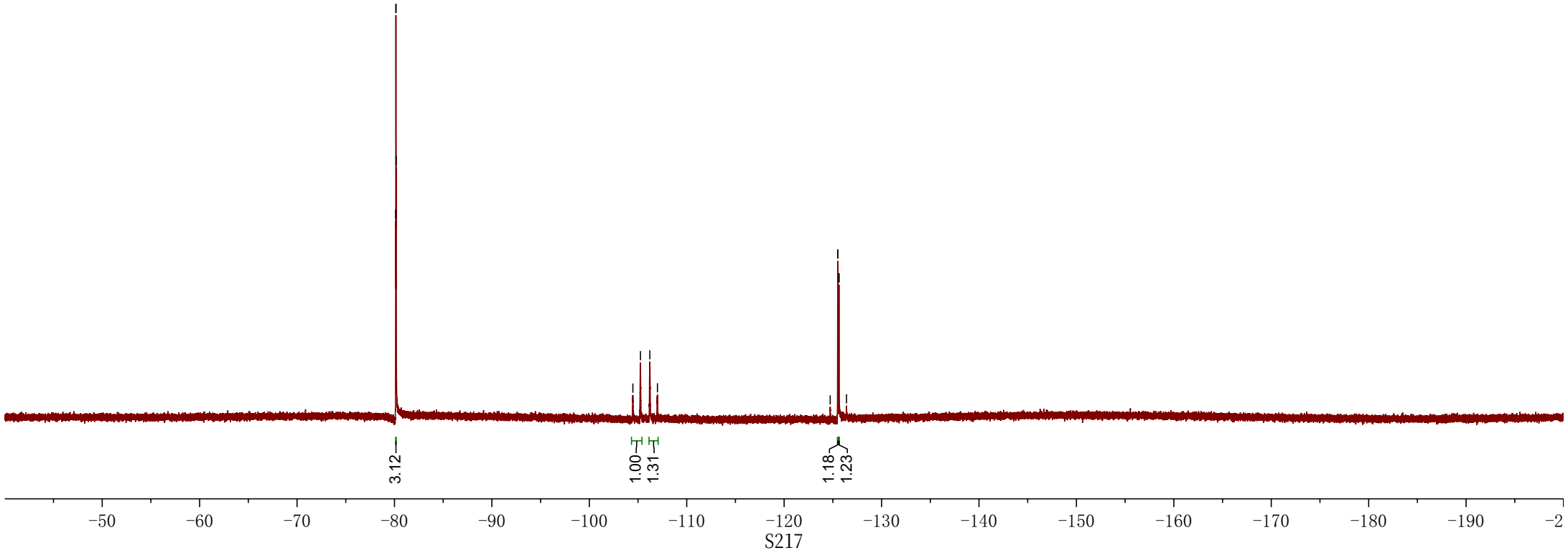
^{13}C NMR (101MHz, $CDCl_3$) Spectrum of P49.



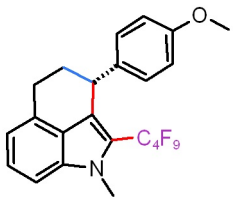


^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of P49.

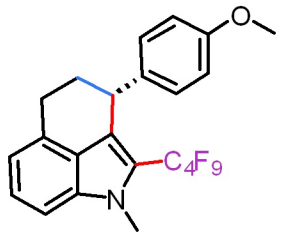


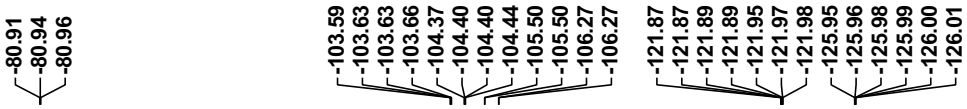


^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P50.

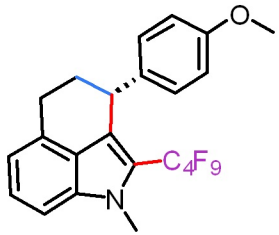


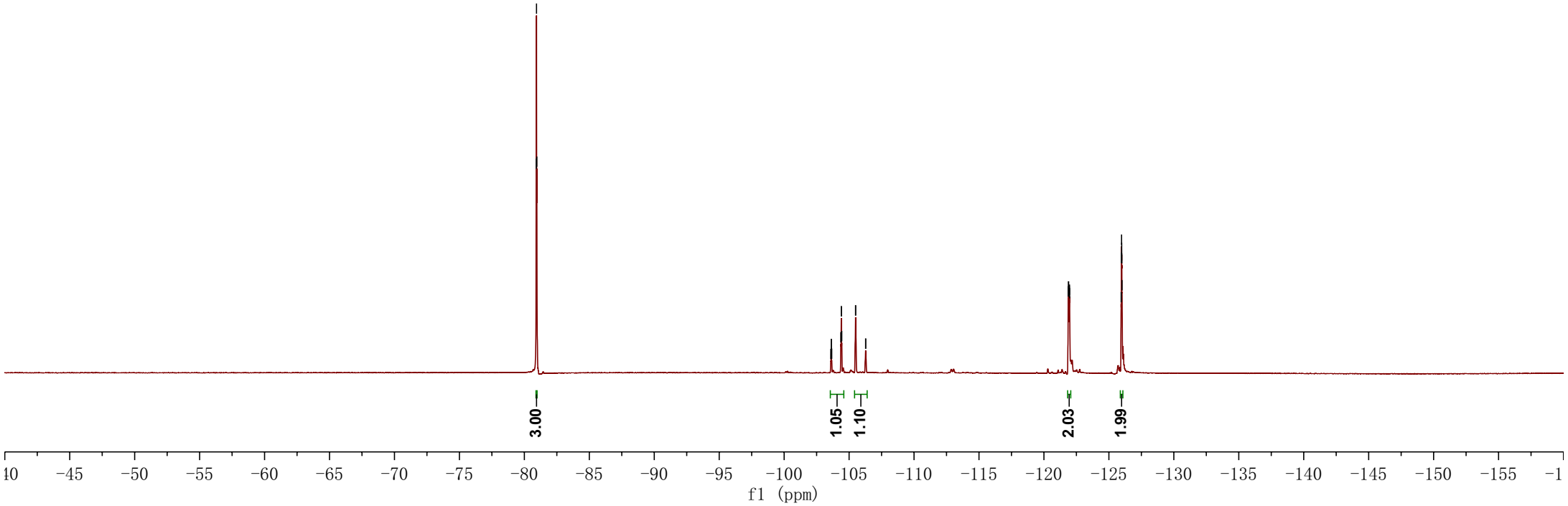
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P50.

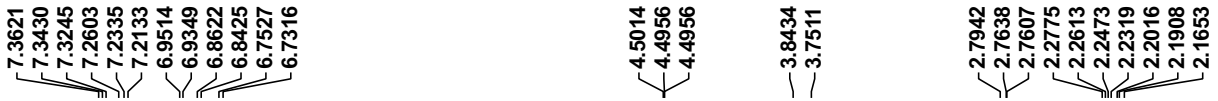




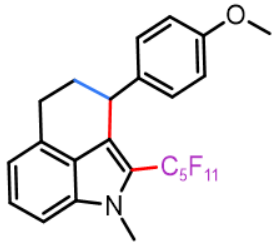
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of P50.

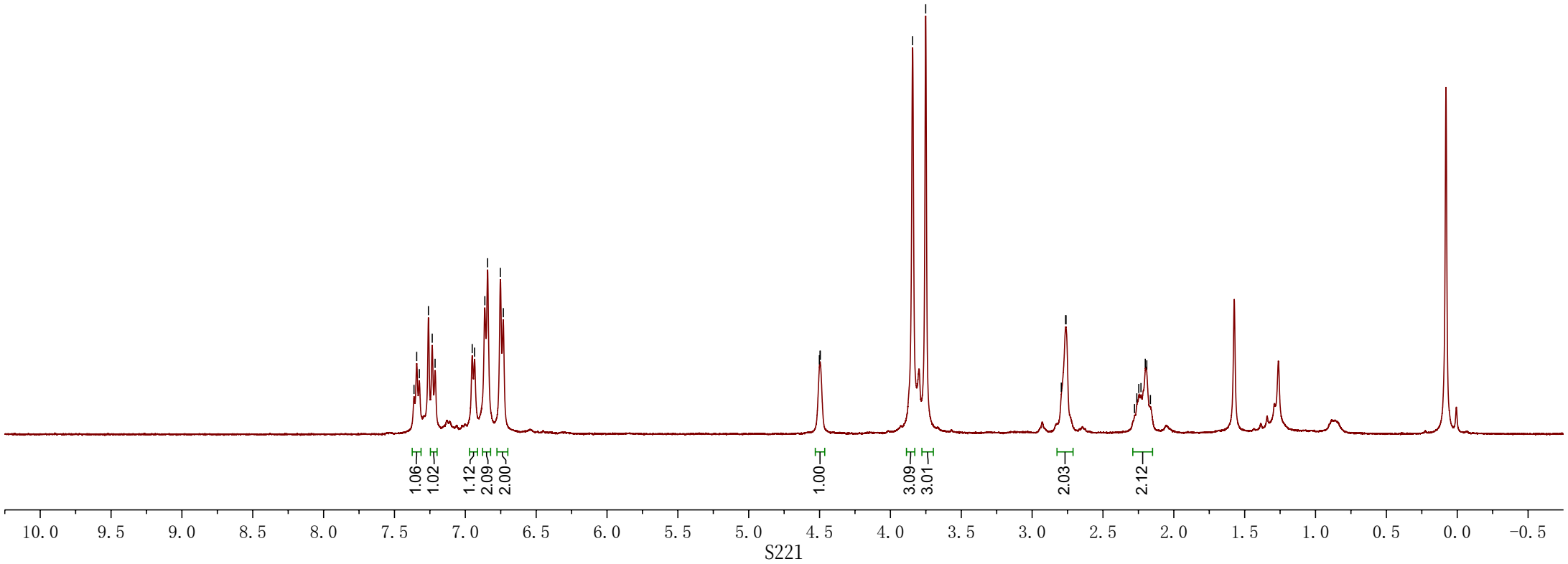




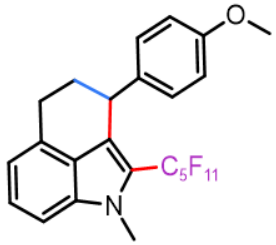


^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P51.



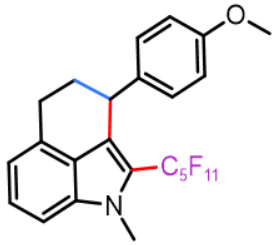


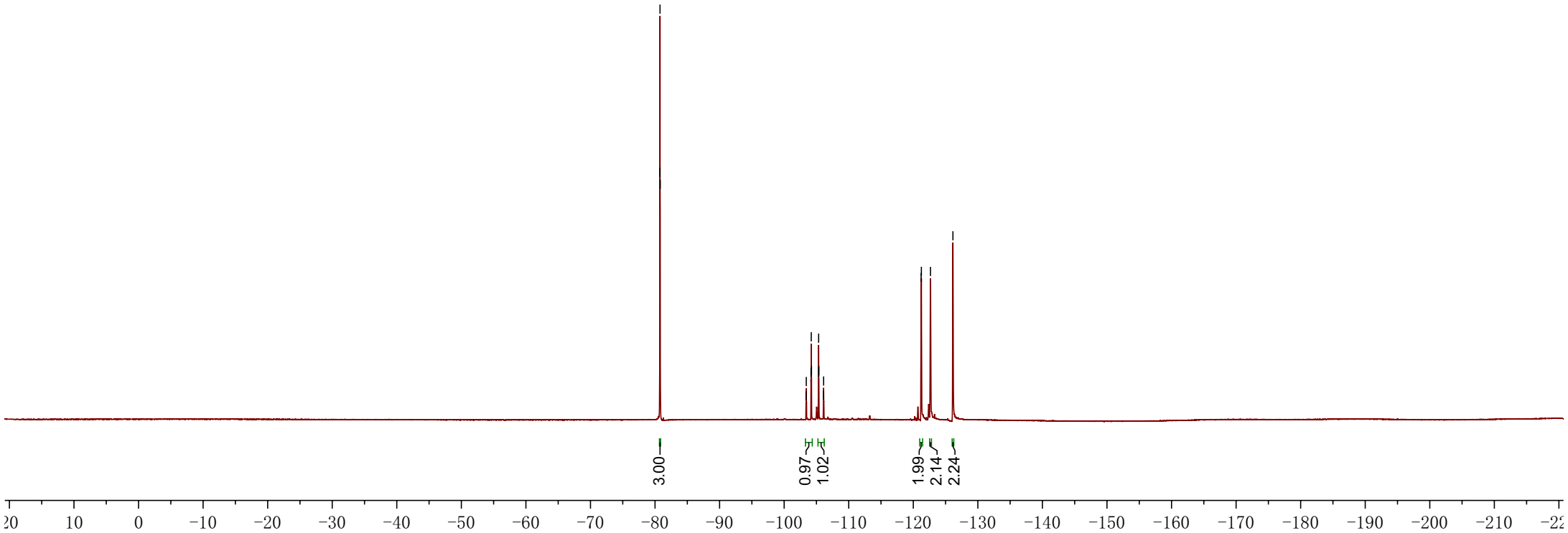
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P51.

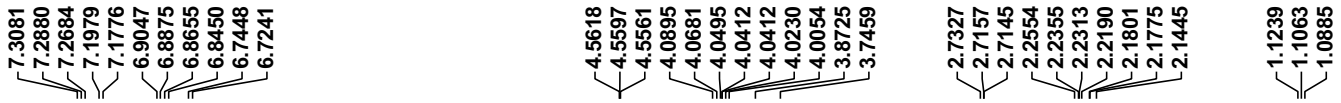


-80.75
-80.77
-80.80
-103.39
-103.42
-104.16
-104.20
-104.23
-105.31
-105.34
-105.38
-106.08
-106.11
-121.21
-121.25
-122.66
-126.14

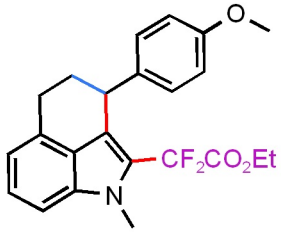
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of P51.

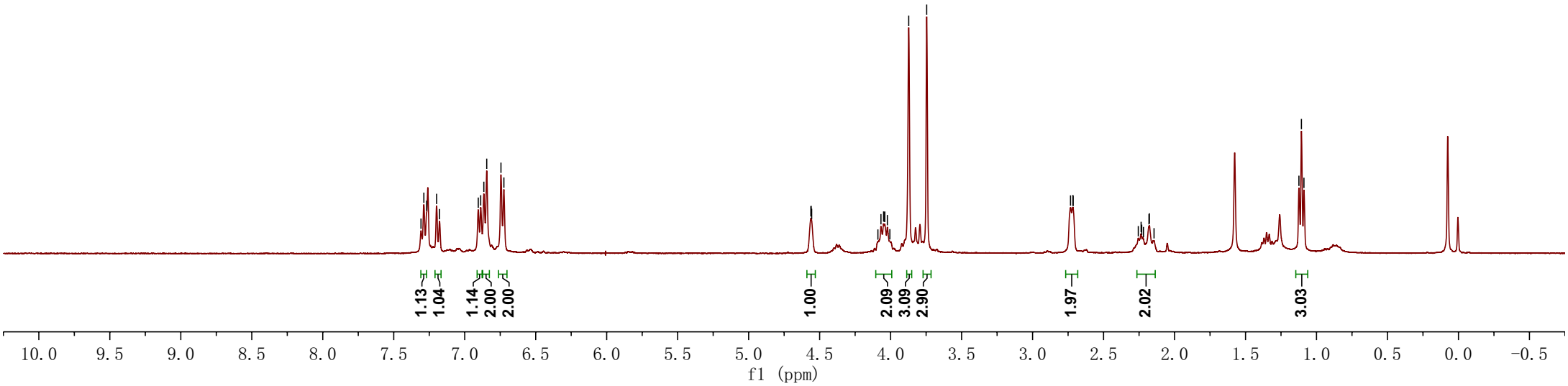




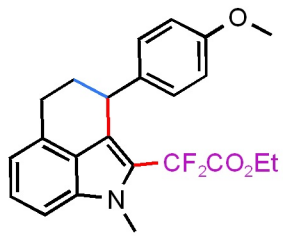


^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P52.



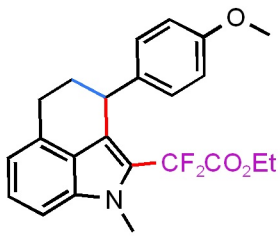


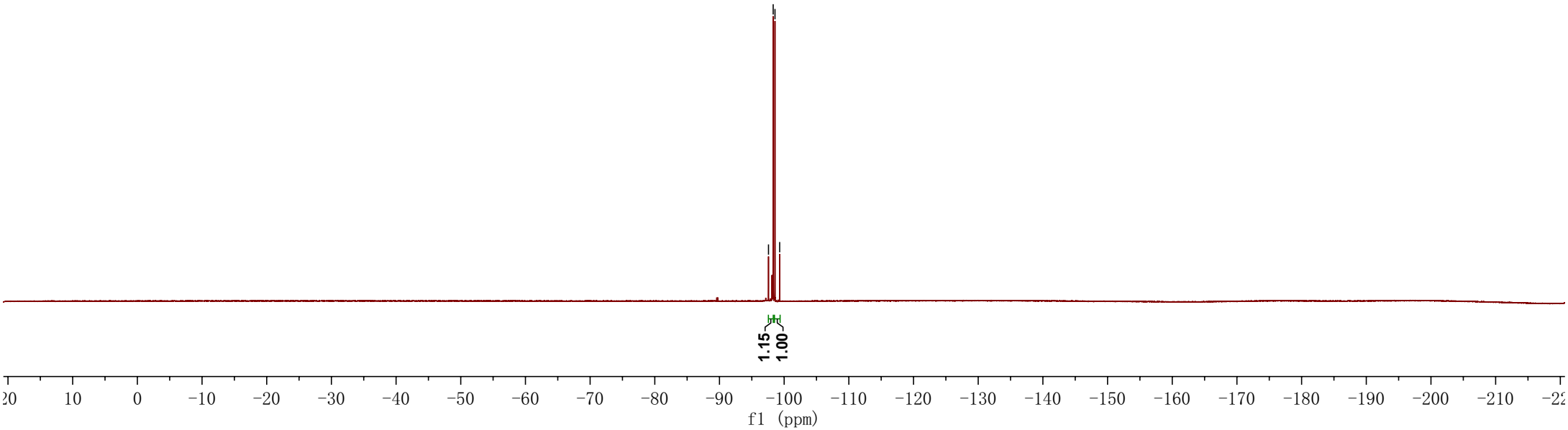
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P52.



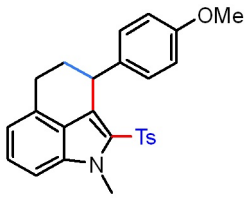
-97.58
-98.30
-98.58
-99.31

^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of P52.

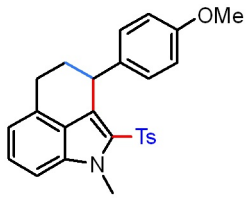




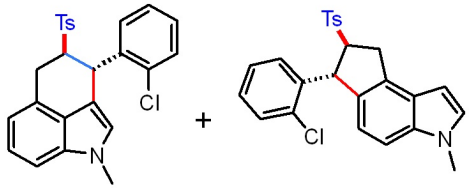
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P56.



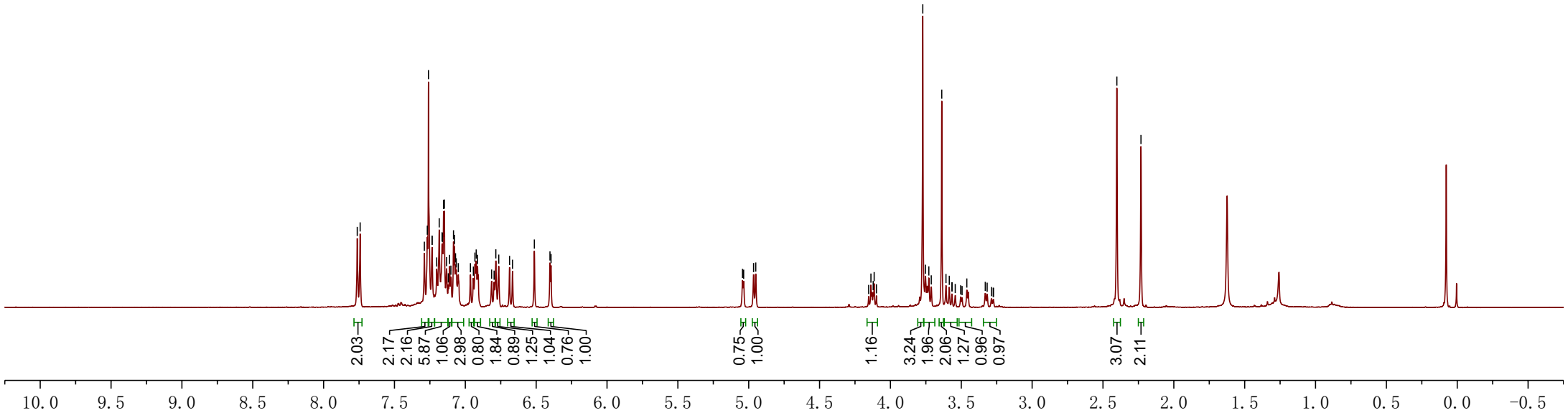
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P56.



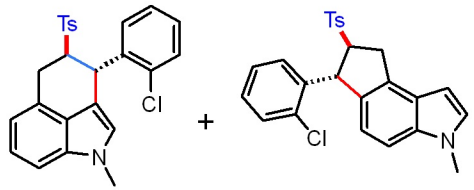
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of P57+P57'.



P57 **P57'**



^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of P57+P57'.



P57 P57'