Calcium(II)-Catalyzed [2+3] Annulation of Enynones: A Sustainable Approach to 9*H*-Pyrrolo[1,2-*a*]indole Frameworks

Supporting Information

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Contents

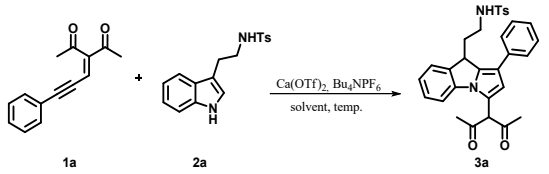
General information

All reactions were carried out under an inert atmosphere of dry N_2 in RBF/sealed tube and were purified by standard method. The proton nuclear magnetic resonance (^{1}H NMR) spectra were determined on a Varian 400 MHz spectrometer (Varian Medical Systems, Inc., Palo Alto, CA, USA). ^{13}C NMR spectra were recorded on a Varian 100 MHz spectrometer. The chemical shifts are provided in parts per million (ppm) downfield with coupling constants in hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d =doublet, t = triplet, q = quartet, m = multiplet. The mass spectra were recorded using high-resolution mass spectrometry (HRMS) (electron ionization MS) on a JMS-700 mass spectrometer (Jeol, Japan) or by HRMS (electrospray ionization MS) on a G2 QTOF mass spectrometer. The products from all reactions were purified by flash column chromatography using silica gel 60 (230–400 mesh Kieselgel 60). Additionally, thin-layer chromatography on 0.25-mm silica plates (E. Merck; silica gel 60 F254) was used to monitor reactions. All reagents were used as received from commercial sources. Melting points were determined in open capillary tubes on an electrothermal apparatus and were uncorrected. X-ray crystallographic data were collected by a Rigaku R-AXIS RAPID diffractometer using graphite monochromate Mo-Ka radiation and single crystal suitable for X-ray diffraction the title (**3z**) compound made in solvent (dichloromethane) at room temperature. Compounds **1**[1] and **2**[2] were prepared according to the literature procedure.

1) a) H. Luo, K. Chen, H. Jiang and S. Zhu, *Org. Lett.*, 2016, **18**, 5208–5211; b) J.-M. Yang, Z.-Q. Li, M.-L. Li, Q. He, S.-F. Zhu and Q.-L. Zhou, *J. Am. Chem. Soc.*, 2017, **139**, 3784–3789; c) B. Song, L. Li, X. Song, Y. Qiu, M. Zhong, P. Zhou and Y. Liang, *Chem. Eur. J.*, 2014, **20**, 5910–5913.

2) a) S. Kinderman, M. M. T. Wekking, J. H. Maarseveen, H. E. Schoemaker, H. Hiemstra and F. P. J. T. Rutjes, *J. Org. Chem.*, 2005, **70**, 5519–5527; b) D.-H. Zhang, X.-Y. Tang, Y. Wei and M. Shi, *Chem. Eur. J.*, 2013, **19**, 13668–13673; c) M. J. Eichberg, R. L. Dorta, K. Lamottke and K. P. C. Vollhardt, *Org. Lett.*, 2000, **2**, 2479–2481; d) J. D. White, Y. Li and D. C. Ihle, *J. Org. Chem.*, 2010, **75**, 3569–3577; e) K. C. Nicolaou, D. Y. K. Chen, X. Huang, T. Ling, M. Bella and S. A. Snyder, *J. Am. Chem. Soc.*, 2004, **126**, 12888–12896; f) D. L. Priebbenow, L. C. Henderson, F. M. Pfeffer and S. G. Stewart, *J. Org. Chem.*, 2010, **75**, 1787–1790; g) A. Kale, S. J. Kwon, J. Lee, J. K. Lee and K. Lee, *Org. Lett.*, 2024, **26**, 1196–1200.

Table 1 Optimization of Reaction Conditions[a]



Entry	Catalyst (mol%)	Solvent	Temp. (° C)	Time	Yield [b] (%) 3a
1	X /Y (5/5)	ACN	rt	12 h	np
2	X /Y (5/5)	ACN	50	12 h	traces
3	X /Y (5/5)	ACN	60	12 h	43
4	X /Y (5/5)	ACN	70	12 h	71
5	X /Y (5/5)	ACN	80	12 h	84
6	X /Y (5/5)	ACN	90	12 h	84
7	X /Y (5/5)	ACN	80	1 h	46
8	**X /Y (5/5)**	**ACN**	**80**	**2h**	**84**
9	X /Y (5/5)	ACN	80	4 h	84
10	-/-	ACN	80	2 h	np
11	X /Y (5/5)	Toluene	80	2 h	81
12	X /Y (5/5)	THF	80	2 h	np
13	X /Y (5/5)	DCE	80	2 h	80
14	X /Y (5/5)	Water	80	2 h	np
15	X /- (5/-)	ACN	80	2 h	np
16	$Ca(NTf_2)_2$/Y (5/5)	ACN	80	2h	78
17	$Cu(OTf)_2$ (5)	ACN	60	2 h	np
18	$Sc(OTf)_2$ (5)	ACN	80	2 h	np
19	$Yb(OTf)_3$ (5)	ACN	80	2 h	np
20	$Zn(OTf)_2$ (5)	ACN	80	2 h	np
21	*p*TSA (5)	ACN	80	2 h	np
22	$CaCl_2$ (5)	ACN	80	2h	np
23	CaF_2 (5)	ACN	80	2h	np

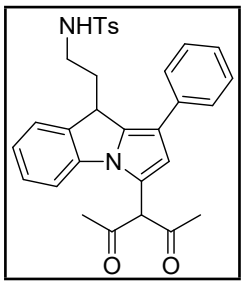
[a] General conditions: **1a** (0.47 mmol, 1.0 equiv.), **2a** (0.47 mmol, 1.0 equiv.), **X**= $Ca(OTf)_2$ (0.023 mmol, 0.05 equiv.), and **Y**= Bu_4NPF_6 (0.023 mmol, 0.05 equiv.) in acetonitrile (5 mL) at 80 ℃ for 2 h; [b] isolated yields, np= no product, - = no catalyst, temp.= temperature and equiv.= equivalent.

General procedure for compound 3

To a magnetically stirred solution of enynone **1** (1.0 equiv.) and tryptamine **2** (1.0 equiv.) in acetonitrile, $Ca(OTf)_2$ (5 mol%) and Bu_4NPF_6 (5 mol%) were added at room temperature. The reaction mixture was then heated to 80 °C and stirred for 2 hours. Upon completion, as monitored by TLC, the reaction mixture was extracted with ethyl acetate (2 × 10 mL). The combined organic layers were dried over $MgSO_4$, concentrated under reduced pressure, and purified by column chromatography to yield the desired compound.

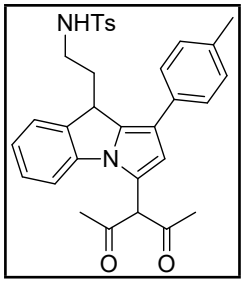
Characterization data for Compound 3

N-(2-(3-(2,4-dioxopentan-3-yl)-1-phenyl-9H-pyrrolo[1,2-a]indol-9-yl)ethyl)-4 methylbenzenesulfonamide (3a):



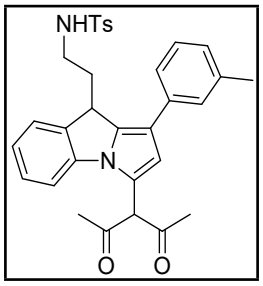
Isolated as yellow solid (141mg, 84%, purification by 10/2, petroleum ether/ethyl acetate); mp 112-114 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 6.8 Hz, 2H), 7.44 – 7.37 (m, 4H), 7.36 (d, *J* = 7.4 Hz, 1H), 7.29 – 7.27 (m, 1H), 7.25 (d, *J* = 3.4 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 3H), 7.08 (d, *J* = 7.9 Hz, 1H), 6.43 (s, 1H), 4.57 (t, *J* = 5.1 Hz, 1H), 4.07 (t, *J* = 7.1, 5.1 Hz, 1H), 2.68 – 2.55 (m, 2H), 2.39 (s, 3H), 2.21 – 2.06 (m, 2H), 1.99 (s, 3H), 1.95 (s, 3H); ^{13}C NMR (126 MHz, CDCl3) δ 193.60, 193.16, 143.22, 140.60, 137.60, 136.64, 134.91, 134.10, 129.56, 128.95, 128.54, 126.94, 126.02, 125.92, 125.29, 123.86, 121.74, 118.74, 114.56, 110.33, 105.09, 39.61, 39.03, 30.82, 24.07, 24.04, 21.50; HRMS calcd for $C_{31}H_{31}N_2O_4S$ [M+H]+: 527.2005, found: 527.1995.

N-(2-(3-(2,4-dioxopentan-3-yl)-1-(p-tolyl)-9H-pyrrolo[1,2-a]indol-9-yl)ethyl)-4-methylbenzenesulfonamide (3b):



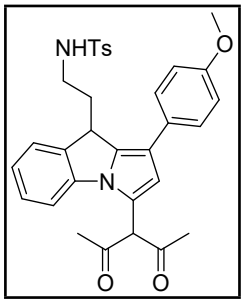
Isolated as yellow solid (139mg, 81%, purification by 10/2, petroleum ether/ethyl acetate); mp 91-93 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.38 (m, 4H), 7.35 (d, *J* = 7.4 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 3H), 7.16 – 7.11 (m, 3H), 7.06 (d, *J* = 7.8 Hz, 1H), 6.39 (s, 1H), 4.55 (t, *J* = 5.0 Hz, 1H), 4.05 (t, *J* = 7.1, 5.1 Hz, 1H), 2.68 – 2.57 (m, 2H), 2.41 (s, 3H), 2.39 (s, 3H), 2.20 – 2.07 (m, 2H), 1.98 (s, 3H), 1.94 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.6, 193.2, 143.2, 140.6, 137.6, 136.7, 135.6, 133.7, 132.0, 129.6, 129.5, 128.5, 126.9, 125.8, 125.3, 123.7, 121.5, 118.7, 114.5, 110.2, 105.1, 39.6, 38.9, 30.7, 24.0, 21.5, 21.2; HRMS calcd for $C_{32}H_{33}N_2O_4S$ [M+H]+: 541.2161, found: 541.2161.

N-(2-(3-(2,4-dioxopentan-3-yl)-1-(m-tolyl)-9H-pyrrolo[1,2-a]indol-9-yl)ethyl)-4-methylbenzenesulfonamide (3c):



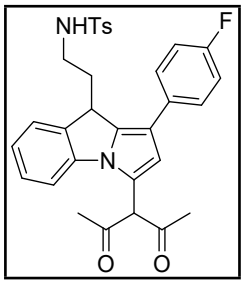
Isolated as yellow solid (136mg, 80%, purification by 10/2, petroleum ether/ethyl acetate); mp 91-93 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.9 Hz, 2H), 7.36 – 7.32 (m, 3H), 7.29 (d, *J* = 7.0 Hz, 1H), 7.27 (s, 1H), 7.15 (d, *J* = 8.1 Hz, 3H), 7.08 (t, *J* = 6.3 Hz, 2H), 6.42 (s, 1H), 4.56 (t, *J* = 5.1 Hz, 1H), 4.05 (t, *J* = 5.9 Hz, 1H), 2.61 (dq, *J* = 21.9, 6.5 Hz, 2H), 2.41 (s, 3H), 2.39 (s, 3H), 2.21 – 2.04 (m, 2H), 1.98 (s, 3H), 1.95 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.5, 193.1, 143.1, 140.6, 138.5, 137.7, 136.7, 134.8, 134.0, 129.5, 128.8, 128.5, 126.9, 126.8, 126.7, 125.2, 123.8, 123.0, 121.6, 118.8, 114.6, 110.3, 105.1, 39.6, 39.0, 30.9, 24.0, 24.0, 21.6, 21.5; HRMS calcd for $C_{32}H_{33}N_2O_4S$ [M+H]+: 541.2161, found: 541.2154.

N-(2-(3-(2,4-dioxopentan-3-yl)-1-(4-methoxyphenyl)-9H-pyrrolo[1,2-a]indol-9-yl)ethyl)-4-methylbenzenesulfonamide (3d):



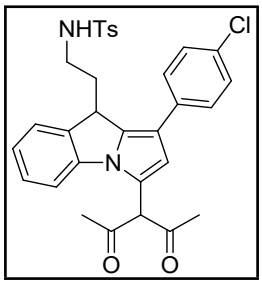
Isolated as brown solid (152mg, 86%, purification by 10/2, petroleum ether/ethyl acetate); mp 106-108 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.7 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 7.4 Hz, 1H), 7.25 (s, 1H), 7.17 – 7.04 (m, 4H), 6.96 (d, *J* = 8.7 Hz, 2H), 6.35 (s, 1H), 4.52 (t, *J* = 5.1 Hz, 1H), 4.17 – 4.11 (m, 1H), 3.87 (s, 3H), 2.67 – 2.55 (m, 2H), 2.39 (s, 3H), 2.16 – 2.03 (m, 2H), 1.99 (s, 3H), 1.94 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.6, 193.1, 158.0, 143.2, 140.6, 137.6, 136.7, 133.2, 129.5, 128.5, 127.5, 127.1, 126.9, 125.2, 123.7, 121.5, 118.4, 114.4, 114.4, 110.2, 105.1, 55.3, 39.6, 38.9, 30.9, 24.0, 24.0, 21.5; HRMS calcd for $C_{32}H_{33}N_2O_5S$ [M+H]+: 557.2110, found: 557.2103.

N-(2-(3-(2,4-dioxopentan-3-yl)-1-(4-fluorophenyl)-9H-pyrrolo[1,2-a]indol-9-yl)ethyl)-4-methylbenzenesulfonamide (3e):



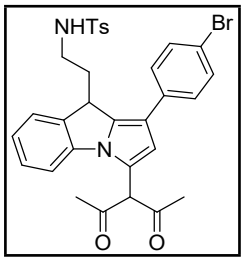
Isolated as brown solid (137mg, 79%, purification by 10/2, petroleum ether/ethyl acetate); mp 104-106 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 10.0 Hz, 1H), 7.07 (dd, *J* = 8.4, 2.3 Hz, 3H), 6.36 (s, 1H), 4.52 (t, *J* = 5.1 Hz, 1H), 4.21 (t, *J* = 5.9 Hz, 1H), 2.62 (tt, *J* = 13.2, 6.7 Hz, 2H), 2.40 (s, 3H), 2.16 – 2.07 (m, 2H), 1.99 (s, 3H), 1.94 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.5, 193.1, 162.4 (d, $^{1}J_{C-F}$ = 246.2 Hz), 160.0, 143.3, 140.55, 137.5, 136.6, 133.8, 131.1, 131.0, 129.5 (d, $^{2}J_{C-F}$ = 22.01 Hz), 128.5, 127.4, 127.3, 126.9, 125.3, 123.9, 121.7, 117.8, 115.8, 115.6, 114.4 (d, $^{3}J_{C-F}$ = 8.6 Hz), 110.3, 105.0, 39.6, 38.8, 31.0, 24.0, 24.0, 21.5; HRMS calcd for $C_{31}H_{30}FN_2O_4S$ [M+H]+: 545.1910, found: 545.1910.

N-(2-(1-(4-chlorophenyl)-3-(2,4-dioxopentan-3-yl)-9H-pyrrolo[1,2-a]indol-9-yl)ethyl)-4-methylbenzenesulfonamide (3f):



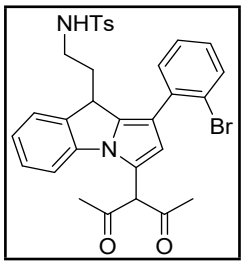
Isolated as yellow solid (145mg, 81%, purification by 10/2, petroleum ether/ethyl acetate); mp 106-108 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 12.4, 8.4 Hz, 4H), 7.36 (d, *J* = 8.6 Hz, 3H), 7.28 (d, *J* = 1.2 Hz, 1H), 7.17 (t, *J* = 7.2 Hz, 3H), 7.08 (d, *J* = 7.9 Hz, 1H), 6.39 (s, 1H), 4.53 (t, *J* = 5.1 Hz, 1H), 4.04 (t, *J* = 6.2 Hz, 1H), 2.63 (dt, *J* = 21.8, 6.6 Hz, 2H), 2.40 (s, 3H), 2.11 (dt, *J* = 14.1, 7.1 Hz, 2H), 1.98 (s, 3H), 1.95 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.5, 193.1, 143.3, 140.4, 137.4, 136.6, 134.2, 133.4, 131.5, 129.6, 129.0, 128.6, 127.1, 126.8, 125.3, 124.0, 121.9, 117.6, 114.3, 110.4, 39.5, 39.0, 30.8, 24.0, 24.0, 21.5; HRMS calcd for $C_{31}H_{30}ClN_2O_4S$ [M+H]+: 561.1615, found: 561.1624.

N-(2-(1-(4-bromophenyl)-3-(2,4-dioxopentan-3-yl)-9H-pyrrolo[1,2-a]indol-9-yl)ethyl)-4-methylbenzenesulfonamide (3g):



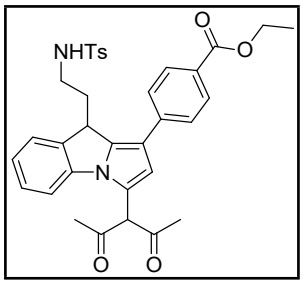
Isolated as yellow solid (160mg, 83%, purification by 10/2, petroleum ether/ethyl acetate); mp 108-110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 3H), 7.37 (d, *J* = 7.0 Hz, 2H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.16 (dd, *J* = 15.5, 8.1 Hz, 3H), 7.08 (d, *J* = 7.9 Hz, 1H), 6.39 (s, 1H), 4.53 (t, *J* = 5.0 Hz, 1H), 4.04 (t, *J* = 6.1 Hz, 1H), 2.66 – 2.56 (m, 2H), 2.41 (s, 3H), 2.09 (q, *J* = 6.5 Hz, 2H), 1.98 (s, 3H), 1.95 (s, 3H);^{13}C NMR (101 MHz, $CDCl_3$) δ 193.7, 193.0, 143.3, 140.7, 137.8, 136.7, 136.5, 135.4, 133.2, 131.2, 129.5, 128.4, 128.3, 127.5, 126.9, 125.1, 123.7, 123.1, 120.6, 118.2, 117.2, 110.3, 105.0, 39.8, 39.2, 32.0, 24.1, 24.0, 21.5; HRMS calcd for $C_{31}H_{30}BrN_2O_4S$ [M+H]+: 605.1110, found: 605.1107.

N-(2-(1-(2-bromophenyl)-3-(2,4-dioxopentan-3-yl)-9H-pyrrolo[1,2-a]indol-9-yl)ethyl)-4-methylbenzenesulfonamide (3h):



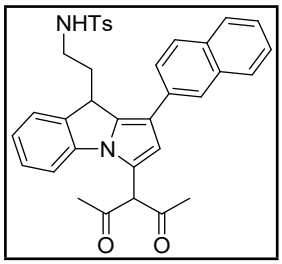
Isolated as white solid (162mg, 84%, purification by 10/2, petroleum ether/ethyl acetate); mp 165-167 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 6.8 Hz, 1H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.35 – 7.28 (m, 2H), 7.26 – 7.14 (m, 4H), 7.14 – 7.01 (m, 2H), 6.28 (s, 1H), 4.40 (t, *J* = 5.4 Hz, 1H), 3.98 (t, *J* = 6.2 Hz, 1H), 2.65 – 2.52 (m, 2H), 2.41 (s, 3H), 1.99 (s, 6H), 1.89 (q, *J* = 6.2 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$δ 193.7, 193.0, 143.3, 140.7, 137.8, 136.7, 136.5, 135.4, 133.2, 131.2, 129.5, 128.4, 128.3, 127.5, 126.9, 125.1, 123.7, 123.1, 120.6, 118.2, 117.2, 110.3, 105.0, 105.0, 39.8, 39.2, 32.0, 24.1, 24.0, 21.5; HRMS calcd for $C_{31}H_{30}BrN_2O_4S$ [M+H]+: 605.1110, found: 605.1129.

ethyl 4-(3-(2,4-dioxopentan-3-yl)-9-(2-(4-methylphenylsulfonamido)ethyl)-9H-pyrrolo[1,2-a]indol-1-yl)benzoate (3i):



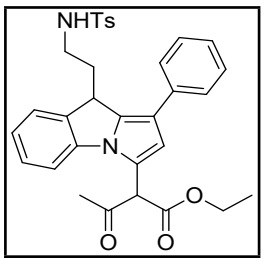
Isolated as pink solid (135mg, 71%, purification by 10/2, petroleum ether/ethyl acetate); mp 112-114 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (t, *J* = 1.8 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.46 (dt, *J* = 7.7, 4.0 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 1H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.17 – 7.12 (m, 1H), 7.08 (d, *J* = 7.8 Hz, 1H), 6.49 (s, 1H), 5.06 (dd, *J* = 8.2, 4.3 Hz, 1H), 4.72 (dd, *J* = 7.1, 3.8 Hz, 1H), 4.46 (q, *J* = 7.1 Hz, 2H), 3.02 – 2.93 (m, 1H), 2.77 – 2.70 (m, 1H), 2.40 (s, 3H), 2.27 – 2.21 (m, 1H), 2.06 – 2.00 (m, 1H), 1.99 (s, 3H), 1.96 (s, 3H), 1.45 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.5, 193.2, 167.1, 143.2, 140.2, 138.2, 136.9, 135.4, 135.2, 130.8, 129.7, 129.5, 129.0, 128.4, 126.9, 126.7, 126.4, 125.6, 124.0, 121.8, 117.2, 113.9, 110.3, 105.0, 61.3, 40.1, 38.4, 30.7, 24.0, 24.0, 21.5, 14.4; HRMS calcd for $C_{34}H_{35}N_2O_6S$ [M+H]+: 599.2216, found: 599.2216.

N-(2-(3-(2,4-dioxopentan-3-yl)-1-(naphthalen-2-yl)-9H-pyrrolo[1,2-a]indol-9-yl)ethyl)-4-methylbenzenesulfonamide (3j):



Isolated as yellow solid (147mg, 80%, purification by 10/2, petroleum ether/ethyl acetate); mp 160-162 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 8.6 Hz, 1H), 7.83 (d, *J* = 9.5 Hz, 1H), 7.52 (q, *J* = 8.3, 7.2 Hz, 4H), 7.30 (t, *J* = 8.2 Hz, 4H), 7.13 (d, *J* = 7.6 Hz, 4H), 6.39 (s, 1H), 4.31 (t, *J* = 5.9 Hz, 1H), 3.54 (t, *J* = 6.2 Hz, 1H), 2.56 – 2.49 (m, 1H), 2.39 (s, 3H), 2.30 – 2.23 (m, 1H), 2.08 (s, 3H), 2.04 (s, 3H), 1.77 – 1.70 (m, 1H), 1.65 – 1.60 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.6, 193.1, 143.1, 140.7, 138.0, 136.7, 135.9, 133.9, 133.6, 131.3, 129.4, 128.7, 128.4, 127.2, 126.7, 126.6, 126.3, 126.0, 125.7, 125.7, 125.2, 123.7, 121.1, 117.5, 117.2, 110.3, 105.2, 39.9, 38.7, 32.7, 24.2, 24.1, 21.4; HRMS calcd for $C_{35}H_{33}N_2O_4S$ [M+H]+: 577.2161, found: 577.2155.

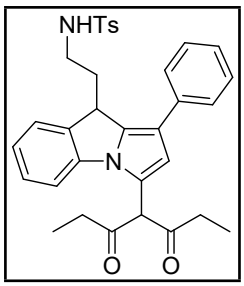
ethyl 2-(9-(2-(4-methylphenylsulfonamido)ethyl)-1-phenyl-9H-pyrrolo[1,2-a]indol-3-yl)-3-oxobutanoate (3k):



Isolated as light pink solid (135mg, 76%, purification by 10/2, petroleum ether/ethyl acetate); mp 105-107 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 7.9 Hz, 1H), 7.31 (q, *J* = 8.7, 7.8 Hz, 4H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.18 – 7.08 (m, 3H), 7.06 (t, *J* = 7.3 Hz, 1H), 6.30 (s, 1H), 5.63 (s, 1H), 4.33 (t, *J* = 6.4 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.17 (tt, *J* = 12.7, 6.4 Hz, 2H), 2.94 (t, *J* = 6.4 Hz, 2H), 2.55 (s, 3H), 2.38 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9, 159.3, 152.4, 143.2, 139.1, 136.9, 135.5, 133.9, 129.6, 128.9, 128.0, 127.8, 127.5, 127.0, 122.2, 119.8, 118.4, 114.2, 111.0, 109.2, 108.6, 60.2, 43.21,

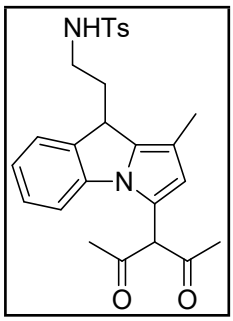
41.9, 24.8, 21.5, 14.3, 13.9; HRMS calcd for $C_{32}H_{33}N_2O_5S$ [M+H]+: 557.2110, found: 557.2121.

N-(2-(3-(3,5-dioxoheptan-4-yl)-1-phenyl-9H-pyrrolo[1,2-a]indol-9-yl)ethyl)-4-methylbenzenesulfonamide (3l):



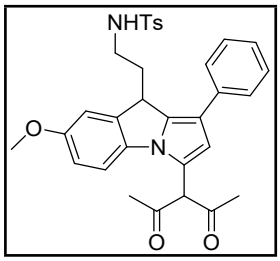
Isolated as white solid (145mg, 86%, purification by 10/2, petroleum ether/ethyl acetate); mp 113-115 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.0 Hz, 2H), 7.41 (dd, *J* = 7.9, 6.0 Hz, 4H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.27 (d, *J* = 1.2 Hz, 1H), 7.24 (d, *J* = 1.3 Hz, 1H), 7.17 – 7.12 (m, 3H), 7.07 (d, *J* = 7.8 Hz, 1H), 6.42 (s, 1H), 4.56 (t, *J* = 5.1 Hz, 1H), 4.09 (t, 1H), 2.66 – 2.56 (m, 2H), 2.39 (s, 3H), 2.30 (dd, *J* = 15.8, 7.6 Hz, 2H), 2.23 – 2.09 (m, 4H), 1.00 (td, *J* = 7.5, 4.5 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.8, 196.3, 143.2, 140.6, 137.6, 136.6, 134.9, 134.1, 129.5, 128.9, 128.4, 126.9, 125.9, 125.9, 125.3, 123.8, 121.2, 118.7, 114.7, 110.5, 103.6, 39.6, 39.0, 30.9, 29.9, 29.8, 21.5, 9.3, 9.3; HRMS calcd for $C_{33}H_{35}N_2O_4S$ [M+H]+: 555.2318, found: 555.2326.

N-(2-(3-(2,4-dioxopentan-3-yl)-1-methyl-9H-pyrrolo[1,2-a]indol-9-yl)ethyl)-4-methylbenzenesulfonamide (3m):



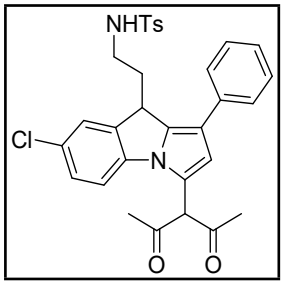
Isolated as white solid (120mg, 81%, purification by 10/2, petroleum ether/ethyl acetate); mp 107-109 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.3 Hz, 2H), 7.21 (dd, *J* = 17.7, 7.8 Hz, 4H), 7.07 – 7.03 (m, 1H), 6.97 (d, *J* = 7.8 Hz, 1H), 5.96 (s, 1H), 4.25 (t, *J* = 6.2 Hz, 1H), 4.12 (t, *J* = 5.2 Hz, 1H), 2.74 (d, *J* = 6.7 Hz, 2H), 2.41 (s, 3H), 2.26 – 2.17 (m, 2H), 2.12 (d, *J* = 1.3 Hz, 3H), 1.95 (s, 3H), 1.85 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.60, 192.91, 143.43, 141.08, 137.74, 136.81, 134.21, 129.64, 128.32, 127.00, 125.15, 123.06, 120.18, 117.37, 112.57, 109.86, 105.46, 39.81, 37.71, 32.23, 29.71, 23.97, 23.95, 21.50, 11.21; HRMS calcd for $C_{26}H_{29}N_2O_4S$ [M+H]+: 465.1848, found: 465.1836.

N-(2-(3-(2,4-dioxopentan-3-yl)-7-methoxy-1-phenyl-9H-pyrrolo[1,2-a]indol-9-yl)ethyl)-4-methylbenzenesulfonamide (3p):



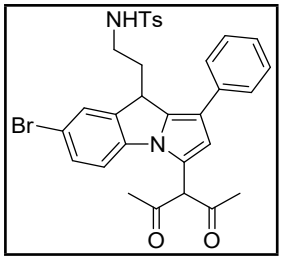
Isolated as brown solid (130mg, 80%, purification by 10/2, petroleum ether/ethyl acetate); mp 94-96 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.8 Hz, 2H), 7.41 (dd, *J* = 7.8, 4.6 Hz, 4H), 7.25 (s, 1H), 7.15 (d, *J* = 7.9 Hz, 2H), 6.97 (d, *J* = 8.9 Hz, 2H), 6.77 (s, 1H), 6.38 (s, 1H), 4.53 (d, *J* = 5.4 Hz, 1H), 4.08 – 4.04 (m, 1H), 3.83 (s, 3H), 2.67 – 2.56 (m, 2H), 2.39 (s, 3H), 2.22 – 2.12 (m, 2H), 1.98 (s, 3H), 1.95 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.2, 156.7, 139.2, 136.6, 135.0, 133.8, 129.5, 128.9, 126.9, 125.8, 121.3, 113.7, 112.6, 112.3, 110.5, 55.8, 39.5, 39.2, 30.9, 24.0, 21.5; HRMS calcd for $C_{32}H_{33}N_2O_5S$ [M+H]+: 557.2110, found: 557.2095.

N-(2-(7-chloro-3-(2,4-dioxopentan-3-yl)-1-phenyl-9H-pyrrolo[1,2-a]indol-9-yl)ethyl)-4-methylbenzenesulfonamide (3q):



Isolated as white solid (135mg, 83%, purification by 10/2, petroleum ether/ethyl acetate); mp 104-106 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.0 Hz, 2H), 7.47 – 7.35 (m, 4H), 7.28 (d, *J* = 2.7 Hz, 2H), 7.23 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.19 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 8.3 Hz, 1H), 6.43 (s, 1H), 4.54 (t, *J* = 5.1 Hz, 1H), 4.08 (t, 1H), 2.69 – 2.55 (m, 2H), 2.41 (s, 3H), 2.25 – 2.04 (m, 2H), 1.98 (s, 3H), 1.96 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.5, 193.2, 143.4, 139.6, 139.1, 136.5, 134.6, 133.8, 129.6, 129.2, 129.0, 128.5, 127.0, 126.2, 126.0, 125.6, 121.8, 119.1, 114.9, 110.9, 104.7, 39.5, 38.9, 30.8, 24.0, 24.0, 21.5; HRMS calcd for $C_{31}H_{30}ClN_2O_4S$ [M+H]+: 561.1615, found: 561.1622.

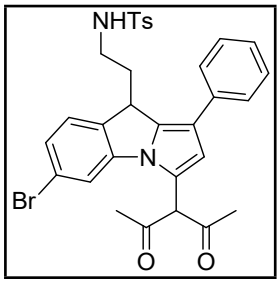
N-(2-(7-bromo-3-(2,4-dioxopentan-3-yl)-1-phenyl-9H-pyrrolo[1,2-a]indol-9-yl)ethyl)-4-methylbenzenesulfonamide (3r):



Isolated as yellow solid (125mg, 81%, purification by 10/2, petroleum ether/ethyl acetate); mp 109-111 ^{o}C; ^{1}H

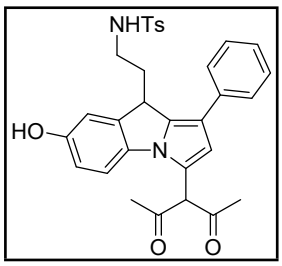
NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.4 Hz, 2H), 7.47 – 7.41 (m, 4H), 7.39 (d, *J* = 11.4 Hz, 2H), 7.28 (d, *J* = 7.4 Hz, 1H), 7.19 (d, *J* = 7.9 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 1H), 6.43 (s, 1H), 4.54 (t, *J* = 5.1 Hz, 1H), 4.06 (t, *J* = 6.3 Hz, 1H), 2.66 – 2.57 (m, 2H), 2.41 (s, 3H), 2.18 – 2.05 (m, 2H), 1.97 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.5, 193.2, 143.4, 139.9, 136.5, 134.6, 133.7, 131.4, 129.6, 129.0, 128.4, 127.0, 126.2, 126.0, 121.8, 116.6, 115.1, 111.4, 104.7, 39.5, 38.8, 30.8, 24.0, 21.5; HRMS calcd for $C_{31}H_{30}BrN_2O_4S$ [M+H]+: 605.1110, found: 605.1121.

N-(2-(6-bromo-3-(2,4-dioxopentan-3-yl)-1-phenyl-9H-pyrrolo[1,2-a]indol-9-yl)ethyl)-4-methylbenzenesulfonamide (3s):



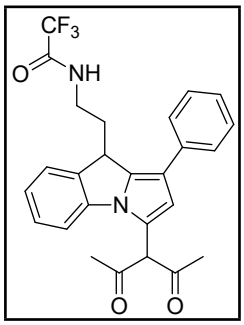
Isolated as yellow solid (120mg, 80%, purification by 10/2, petroleum ether/ethyl acetate); mp 115-117 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.5 Hz, 2H), 7.42 (dd, *J* = 7.9, 5.1 Hz, 4H), 7.29 – 7.27 (m, 1H), 7.23 (d, *J* = 12.1 Hz, 2H), 7.19 – 7.14 (m, 3H), 6.43 (s, 1H), 4.53 (t, *J* = 5.2 Hz, 1H), 4.05 (t, *J* = 6.2 Hz, 1H), 2.59 (dt, *J* = 18.2, 6.6 Hz, 2H), 2.40 (s, 3H), 2.17 – 2.08 (m, 2H), 1.99 (s, 3H), 1.95 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.5, 193.1, 143.4, 141.7, 136.8, 136.4, 134.5, 134.4, 129.6, 128.9, 126.9, 126.7, 126.5, 126.2, 125.9, 121.9, 121.9, 119.1, 115.3, 113.5, 104.6, 39.6, 38.6, 31.6, 30.8, 24.0, 21.5; HRMS calcd for $C_{31}H_{30}BrN_2O_4S$ [M+H]+: 605.1110, found: 605.1125.

N-(2-(3-(2,4-dioxopentan-3-yl)-7-hydroxy-1-phenyl-9H-pyrrolo[1,2-a]indol-9-yl)ethyl)-4-methylbenzenesulfonamide (3t):



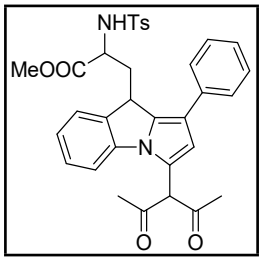
Isolated as dark brown solid (125mg, 76%, purification by 10/2, petroleum ether/ethyl acetate); mp 120-122 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.6 Hz, 2H), 7.45 – 7.37 (m, 4H), 7.23 (d, *J* = 7.4 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 6.72 (dd, *J* = 8.4, 2.5 Hz, 1H), 6.37 (s, 1H), 5.20 (s, 1H), 4.52 (t, *J* = 5.1 Hz, 1H), 4.13 – 4.09 (m, 1H), 2.69 – 2.58 (m, 2H), 2.39 (s, 3H), 2.14 – 2.05 (m, 2H), 1.98 (s, 3H), 1.94 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.7, 193.2, 152.7, 143.4, 139.4, 136.4, 135.0, 134.3, 133.8, 129.6, 128.9, 126.9, 125.8, 125.8, 121.2, 118.5, 114.6, 113.6, 113.3, 110.7, 105.1, 39.6, 39.1, 31.6, 30.7, 24.1, 22.6, 21.5; HRMS calcd for $C_{31}H_{31}N_2O_5S$ [M+H]+: 543.1954, found: 543.1951.

N-(2-(3-(2,4-dioxopentan-3-yl)-1-phenyl-9H-pyrrolo[1,2-a]indol-9-yl)ethyl)-2,2,2-trifluoroacetamide (3u):



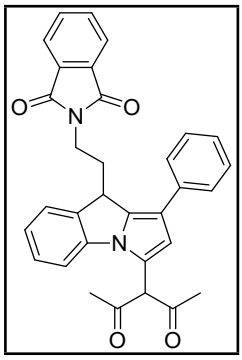
Isolated as dark yellow solid (150mg, 81%, purification by 10/2, petroleum ether/ethyl acetate); mp 134-136 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.0 Hz, 2H), 7.47 – 7.41 (m, 3H), 7.30 (t, *J* = 7.7 Hz, 2H), 7.17 (d, *J* = 7.5 Hz, 1H), 7.11 (d, *J* = 7.8 Hz, 1H), 6.48 (s, 1H), 5.90 (s, 1H), 4.67 (t, *J* = 4.7 Hz, 1H), 3.19 (dd, *J* = 13.7, 6.7 Hz, 1H), 2.83 (dd, *J* = 13.5, 7.0 Hz, 1H), 2.49 (t, *J* = 5.6 Hz, 1H), 2.30 (dd, *J* = 13.9, 4.2 Hz, 1H), 2.00 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.4, 193.3, 156.9 (q, $^2J_{C\text{-}F}$ = 35.7 Hz), 156.5, 140.6, 137.3, 134.6, 133.6, 129.0, 128.8, 126.2, 125.8, 125.1, 124.1, 122.0, 118.9, 114.6 (q, $^1J_{C\text{-}F}$ = 286.5 Hz), 110.4, 105.0, 39.4, 36.4, 29.0, 24.0, 23.8; HRMS calcd for $C_{26}H_{24}F_3N_2O_3$ [M+H]+: 469.1739, found: 469.1736.

methyl 3-(3-(2,4-dioxopentan-3-yl)-1-phenyl-9H-pyrrolo[1,2-a]indol-9-yl)-2-(4-methylphenylsulfonamido)propanoate (3v):



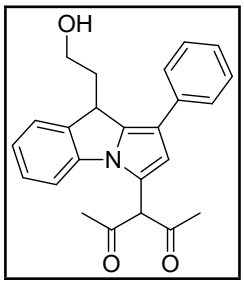
Isolated as yellow solid (128mg, 80%, purification by 10/2, petroleum ether/ethyl acetate); mp 104-106 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (q, *J* = 6.5 Hz, 5H), 7.39 (t, *J* = 6.8 Hz, 2H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 6.9 Hz, 1H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 7.9 Hz, 1H), 6.43 (s, 1H), 4.69 (d, *J* = 9.4 Hz, 1H), 4.54 (t, *J* = 5.4 Hz, 1H), 3.92 – 3.87 (m, 1H), 3.18 (s, 3H), 2.54 – 2.47 (m, 1H), 2.37 (s, 3H), 2.29 (dd, *J* = 14.0, 6.7 Hz, 1H), 2.11 (s, 3H), 1.96 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.6, 193.5, 171.4, 143.5, 140.8, 136.8, 136.5, 134.8, 133.5, 129.4, 128.8, 128.6, 127.1, 125.9, 125.8, 123.5, 121.7, 118.7, 114.6, 110.4, 105.2, 53.7, 52.2, 38.5, 34.0, 24.1, 24.1, 21.5; HRMS calcd for $C_{33}H_{33}N_2O_6S$ [M+H]+: 585.2059, found: 585.2056.

2-(2-(3-(2,4-dioxopentan-3-yl)-1-phenyl-9H-pyrrolo[1,2-a]indol-9-yl)ethyl)isoindoline-1,3-dione (3w):



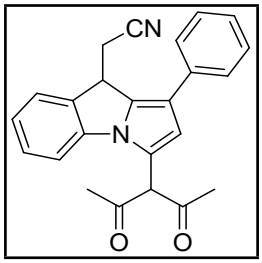
Isolated as yellow solid (135mg, 78%, purification by 10/2, petroleum ether/ethyl acetate); mp 203-205 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 4H), 7.48 (d, *J* = 7.9 Hz, 1H), 7.43 (d, *J* = 7.0 Hz, 2H), 7.30 (t, *J* = 7.7 Hz, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.10 (d, *J* = 16.0 Hz, 1H), 7.04 (d, *J* = 7.7 Hz, 1H), 6.97 (t, *J* = 7.4 Hz, 1H), 6.40 (s, 1H), 4.56 (dd, *J* = 5.7, 4.1 Hz, 1H), 3.54 – 3.38 (m, 2H), 2.63 – 2.48 (m, 2H), 2.25 (s, 3H), 1.93 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.9, 192.4, 166.6, 139.7, 136.6, 133.9, 132.7, 132.5, 130.8, 127.6, 127.0, 124.8, 124.6, 123.9, 122.3, 121.8, 120.5, 117.7, 113.5, 109.3, 104.3, 38.5, 33.4, 26.7, 23.1; HRMS calcd for $C_{32}H_{27}N_2O_4$ [M+H]+: 503.1971, found: 503.1964.

3-(9-(2-hydroxyethyl)-1-phenyl-9H-pyrrolo[1,2-a]indol-3-yl)pentane-2,4-dione (3x):



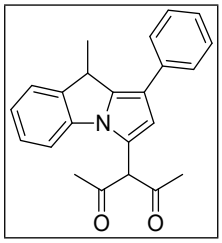
Isolated as yellow solid (180mg, 79%, purification by 10/2, petroleum ether/ethyl acetate); mp 109-111 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.7 Hz, 2H), 7.47 (d, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.27 (s, 1H), 7.22 (t, *J* = 5.8 Hz, 1H), 7.13 (t, *J* = 7.4 Hz, 1H), 7.09 (d, *J* = 7.9 Hz, 1H), 6.45 (s, 1H), 4.65 (t, *J* = 5.5 Hz, 1H), 3.48 – 3.38 (m, 2H), 2.27 (q, *J* = 6.1 Hz, 2H), 2.01 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.7, 193.1, 140.5, 138.7, 135.2, 135.2, 128.8, 128.2, 125.9, 125.8, 125.4, 123.6, 121.3, 118.4, 114.4, 110.2, 105.3, 59.8, 38.6, 34.2, 31.6, 24.1, 24.0, 22.6, 14.1; HRMS calcd for $C_{34}H_{24}N_1O_3$ [M+H]+: 374.1756, found: 374.1756.

2-(3-(2,4-dioxopentan-3-yl)-1-phenyl-9H-pyrrolo[1,2-a]indol-9-yl)acetonitrile (3y):



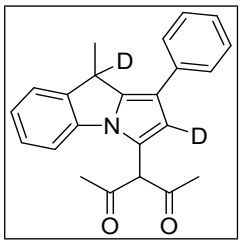
Isolated as brown solid (190mg, 82%, purification by 10/2, petroleum ether/ethyl acetate); mp 110-112 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.5 Hz, 1H), 7.54 (d, *J* = 7.0 Hz, 2H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.31 – 7.26 (m, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.12 (d, *J* = 7.9 Hz, 1H), 6.46 (s, 1H), 4.70 (dd, *J* = 8.0, 3.6 Hz, 1H), 3.12 (dd, *J* = 16.7, 3.7 Hz, 1H), 2.75 (dd, *J* = 16.7, 7.9 Hz, 1H), 2.02 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.8, 193.1, 140.6, 135.7, 134.4, 131.8, 129.5, 129.1, 128.4, 126.5, 125.6, 125.5, 124.1, 122.4, 119.8, 117.1, 114.6, 110.6, 104.9, 37.4, 24.1, 24.0, 20.7; HRMS calcd for $C_{24}H_{21}N_2O_2$ [M+H]+: 369.1603, found: 369.1626.

3-(9-methyl-1-phenyl-9H-pyrrolo[1,2-a]indol-3-yl)pentane-2,4-dione (3z):



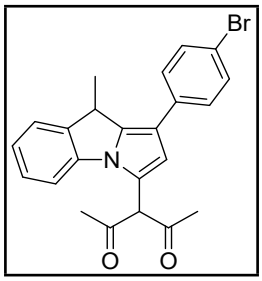
Isolated as brown solid (220mg, 84%, purification by 10/1, petroleum ether/ethyl acetate); mp 78-80 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (s, 2H), 7.44 – 7.39 (m, 3H), 7.25 – 7.18 (m, 2H), 7.17 – 7.12 (m, 1H), 7.09 (d, *J* = 7.8 Hz, 1H), 6.47 (s, 1H), 4.46 (q, *J* = 7.1 Hz, 1H), 2.04 (s, 3H), 2.02 (s, 3H), 1.55 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.50, 193.50, 140.9, 137.3, 135.2, 128.7, 127.9, 125.69, 125.5, 124.9, 123.5, 120.8, 114.1, 110.1, 36.4, 24.1, 17.2; HRMS calcd for $C_{23}H_{22}NO_2$ [M+H]+: 344.1651, found: 344.1658.

(D-3-(9-methyl-1-phenyl-9H-pyrrolo[1,2-a]indol-3-yl)pentane-2,4-dione (D-3z):



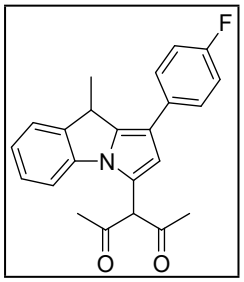
Isolated as light yellow solid (222mg, 84%, purification by 10/1, petroleum ether/ethyl acetate); mp 79-81 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.7 Hz, 2H), 7.43 – 7.38 (m, 3H), 7.24 – 7.19 (m, 2H), 7.13 (t, *J* = 7.0 Hz, 1H), 7.07 (d, *J* = 7.8 Hz, 1H), 2.02 (s, 6H), 1.55 (d, *J* = 4.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.5, 193.4, 140.8, 140.1, 137.3, 135.2, 128.7, 127.9, 125.6, 125.5, 124.9, 123.5, 120.8, 117.8, 114.1, 110.1, 105.4, 36.5, 26.7, 24.6, 24.1, 24.1, 17.2, 17.1; HRMS calcd for $C_{23}H_{20}D_2NO_2$ [M+H]+: 346.1776, found: 346.1772.

3-(1-(4-bromophenyl)-9-methyl-9H-pyrrolo[1,2-a]indol-3-yl)pentane-2,4-dione (3aa):



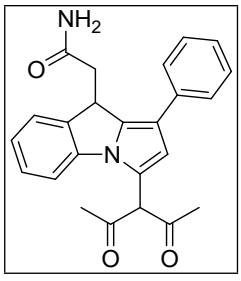
Isolated as yellow solid (250mg, 79%, purification by 20/1, petroleum ether/ethyl acetate); mp 138-140 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.6 Hz, 2H), 7.46 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 7.4 Hz, 1H), 7.23 (d, *J* = 7.7 Hz, 1H), 7.14 (t, *J* = 7.0 Hz, 1H), 7.08 (d, *J* = 7.8 Hz, 1H), 6.41 (s, 1H), 4.40 (q, *J* = 7.2 Hz, 1H), 2.02 (s, 3H), 2.00 (s, 3H), 1.52 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.45, 193.45, 140.7, 139.9, 137.5, 134.2, 131.7, 127.9, 127.2, 124.9, 123.6, 121.1, 118.8, 116.8, 113.9, 110.1, 105.2, 105.2, 36.4, 24.1, 24.1, 17.1; HRMS calcd for $C_{23}H_{21}BrNO_2$ [M+H]+: 422.0756, found: 422.0745.

3-(1-(4-fluorophenyl)-9-methyl-9H-pyrrolo[1,2-a]indol-3-yl)pentane-2,4-dione (3ab):



Isolated as yellow solid (220mg, 80%, purification by 20/1, petroleum ether/ethyl acetate); mp 132-134 °C; ^{1}H NMR (400 MHz, $CDCl_3$)) δ 7.55 (dd, *J* = 8.4, 5.3 Hz, 2H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.15 – 7.10 (m, 2H), 7.10 – 7.07 (m, 2H), 6.39 (s, 1H), 4.41 (q, *J* = 7.1 Hz, 1H), 2.02 (s, 3H), 2.00 (s, 3H), 1.51 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.4, 193.4, 140.7 (d, $^1J_{C\text{-}F}$ = 246.2 Hz), 140.0, 139.4, 137.0, 131.4, 127.9 (d, $^2J_{C\text{-}F}$ = 22.01 Hz), 127.1, 127.0, 124.9, 123.5, 120.9, 117.0, 115.6, 115.4, 114.0 (d, $^3J_{C\text{-}F}$ = 8.6 Hz), 110.1, 105.3, 36.3, 24.1, 17.2; HRMS calcd for $C_{23}H_{21}FNO_2$ [M+H]+: 362.1556, found: 362.1542.

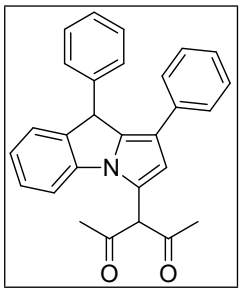
N-(2-(3-(2,4-dioxopentan-3-yl)-1-phenyl-9H-pyrrolo[1,2-a]indol-9-yl)ethyl)acetamide (3ac):



Isolated as yellow solid (230mg, 78%, purification by 20/1, petroleum ether/ethyl acetate); mp 236-238 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 14.2, 7.2 Hz, 3H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.22 (d, *J* = 7.6 Hz, 2H), 7.14 – 7.07 (m, 2H), 6.46 (s, 1H), 5.21 (d, *J* = 25.1 Hz, 2H), 4.98 (dd, *J* = 9.4, 3.5 Hz, 1H), 3.15 (dd, *J* = 15.4, 3.6 Hz,

1H), 2.37 – 2.31 (m, 1H), 2.01 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.4, 193.3, 172.5, 140.2, 138.2, 134.7, 134.3, 129.0, 128.5, 126.1, 125.9, 125.6, 123.8, 121.6, 118.2, 114.3, 110.2, 37.7, 37.2, 24.1; HRMS calcd for $C_{24}H_{22}N_2O_3$ [M+H]+: 387.1709, found: 387.1721.

3-(1,9-diphenyl-9H-pyrrolo[1,2-a]indol-3-yl)pentane-2,4-dione (3ad):



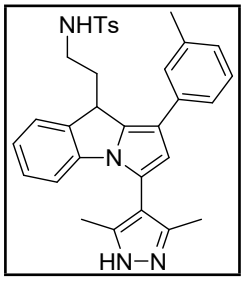
Isolated as white solid (150mg, 76%, purification by 20/1, petroleum ether/ethyl acetate); mp 202-204 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.1 Hz, 2H), 7.25 (d, *J* = 5.7 Hz, 4H), 7.19 (dd, *J* = 13.8, 6.7 Hz, 5H), 7.12 (d, *J* = 7.8 Hz, 1H), 7.08 – 7.01 (m, 2H), 6.60 (s, 1H), 5.35 (s, 1H), 2.10 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.89, 192.96, 140.22, 140.16, 139.38, 135.14, 134.36, 129.01, 128.36, 128.17, 127.57, 127.24, 126.01, 125.61, 125.39, 123.80, 121.58, 119.00, 114.20, 110.15, 105.36, 48.05, 24.21, 24.09; HRMS calcd for $C_{28}H_{24}NO_2$ [M+H]+: 406.1807, found: 406.1795.

General procedure for compound 4a

To a magnetically stirred solution of compound **3c** (1.0 mmol) and hydrazine hydrate (1.0 mmol) in ethanol, the reaction mixture was heated to 50 °C and stirred for 12 hours. Upon completion, as confirmed by TLC, ethanol was removed by distillation. The crude product was then purified by column chromatography to obtain the desired compound.

Characterization data for compound 4a

N-(2-(3-(3,5-dimethyl-1H-pyrazol-4-yl)-1-(m-tolyl)-9H-pyrrolo[1,2-a]indol-9-yl)ethyl)-4-methylbenzenesulfonamide (4a):



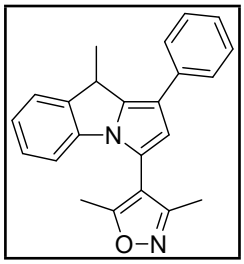
Isolated as brown solid (0.045g, 91%, purification by 10/2, petroleum ether/ethyl acetate); mp 226-228 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.1 Hz, 2H), 7.36 (d, J = 8.9 Hz, 2H), 7.30 (t, J = 7.8 Hz, 2H), 7.15 (d, J = 8.0 Hz, 3H), 7.07 (dq, J = 6.6, 4.0, 3.1 Hz, 2H), 6.72 (d, J = 7.8 Hz, 1H), 6.41 (s, 1H), 4.55 (t, J = 5.1 Hz, 1H), 4.16 (t, J = 5.5 Hz, 1H), 2.61 – 2.73 (m, 2H), 2.40 (d, J = 9.4 Hz, 6H), 2.19 (s, 3H), 2.18 (s, 3H), 2.06 (dq, J = 11.8, 6.3 Hz, 2H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 140.8, 138.4, 137.7, 136.8, 135.1, 134.4, 129.5, 128.8, 128.1, 126.9, 126.8, 126.7, 124.9, 123.5, 123.1, 118.6, 114.0, 110.8, 39.8, 38.9, 31.2, 21.6, 21.5, 11.4, 11.3; HRMS calcd for $C_{32}H_{33}N_4O_2S$ [M+H]+: 537.2324, found: 537.2322.

General procedure for compound 4b

To a magnetically stirred solution of compound **3y** (1.0 mmol) and hydroxylamine hydrochloride (1.0 mmol) in ethanol, the reaction mixture was heated to 50 °C and stirred for 12 hours. Upon completion, as confirmed by TLC, ethanol was removed by distillation. The crude product was then purified by column chromatography to obtain the desired compound.

Characterization data for compound 4b

3,5-dimethyl-4-(9-methyl-1-phenyl-9H-pyrrolo[1,2-a]indol-3-yl)isoxazole (4b):



Isolated as brown solid (0.095g, 95%, purification by 10/2, petroleum ether/ethyl acetate); mp 212-214 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.3 Hz, 2H), 7.40 (t, *J* = 7.7 Hz, 3H), 7.21 (s, 1H), 7.16 (d, *J* = 7.4 Hz, 1H), 7.13 – 7.09 (m, 1H), 6.77 (d, *J* = 6.6 Hz, 1H), 6.50 (d, *J* = 4.5 Hz, 1H), 4.46 (q, *J* = 7.3 Hz, 1H), 2.38 (d, *J* = 22.6 Hz, 3H), 2.21 (d, *J* = 20.2 Hz, 3H), 1.54 (t, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 160.5, 140.8, 140.0,

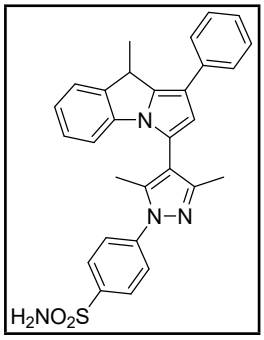
138.3, 135.0, 128.7, 127.7, 125.8, 125.6, 124.9, 123.6, 118.2, 114.3, 110.3, 108.8, 36.4, 31.6, 22.69, 17.02, 14.17, 11.8, 10.7.; HRMS calcd for $C_{23}H_{21}N_2O$ [M+H]+: 341.1654, found: 341.1649.

General procedure for compound 4c

To a magnetically stirred solution of compound **3y** (1.0 mmol) and hydrazineylbenzenesulfonamide hydrochloride (1.0 mmol) in ethanol, the reaction mixture was heated to 50 °C and stirred for 12 hours. Upon completion, as confirmed by TLC, ethanol was removed by distillation. The crude product was then purified by column chromatography to obtain the desired compound.

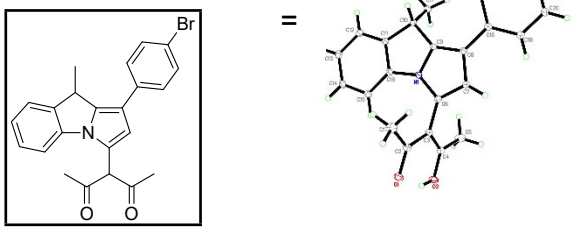
Characterization data for compound 4c

4-(3,5-dimethyl-4-(9-methyl-1-phenyl-9H-pyrrolo[1,2-a]indol-3-yl)-1H-pyrazol-1-yl)benzenesulfonamide (4c):



Isolated as brown solid (0.12g, 85%, purification by 10/2, petroleum ether/ethyl acetate); mp 218-220 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 5.0 Hz, 2H), 7.74 (d, *J* = 5.7 Hz, 2H), 7.64 (d, *J* = 7.6 Hz, 2H), 7.42 (d, *J* = 7.3 Hz, 3H), 7.21 (dd, *J* = 17.5, 9.8 Hz, 2H), 7.11 (d, *J* = 7.4 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 6.52 (s, 1H), 5.13 (s, 2H), 4.47 (q, *J* = 7.2, 6.5 Hz, 1H), 2.37 (d, *J* = 20.8 Hz, 3H), 2.27 (d, *J* = 17.7 Hz, 3H), 1.57 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.9, 150.7, 143.3, 140.9, 140.9, 140.3, 140.2, 139.4, 139.2, 137.9, 135.3, 128.7, 128.7, 127.7, 127.7, 127.6, 125.8, 125.7, 125.4, 124.7, 124.1, 124.1, 123.4, 117.9, 117.8, 117.4, 114.1, 113.8, 110.5, 36.4, 17.1, 16.9, 12.7, 12.6, 12.3, 12.2; HRMS calcd for $C_{29}H_{27}N_4O_2S$ [M+H]+: 495.1855, found: 495.1847.

X ray crystallographic data for compound 3aa

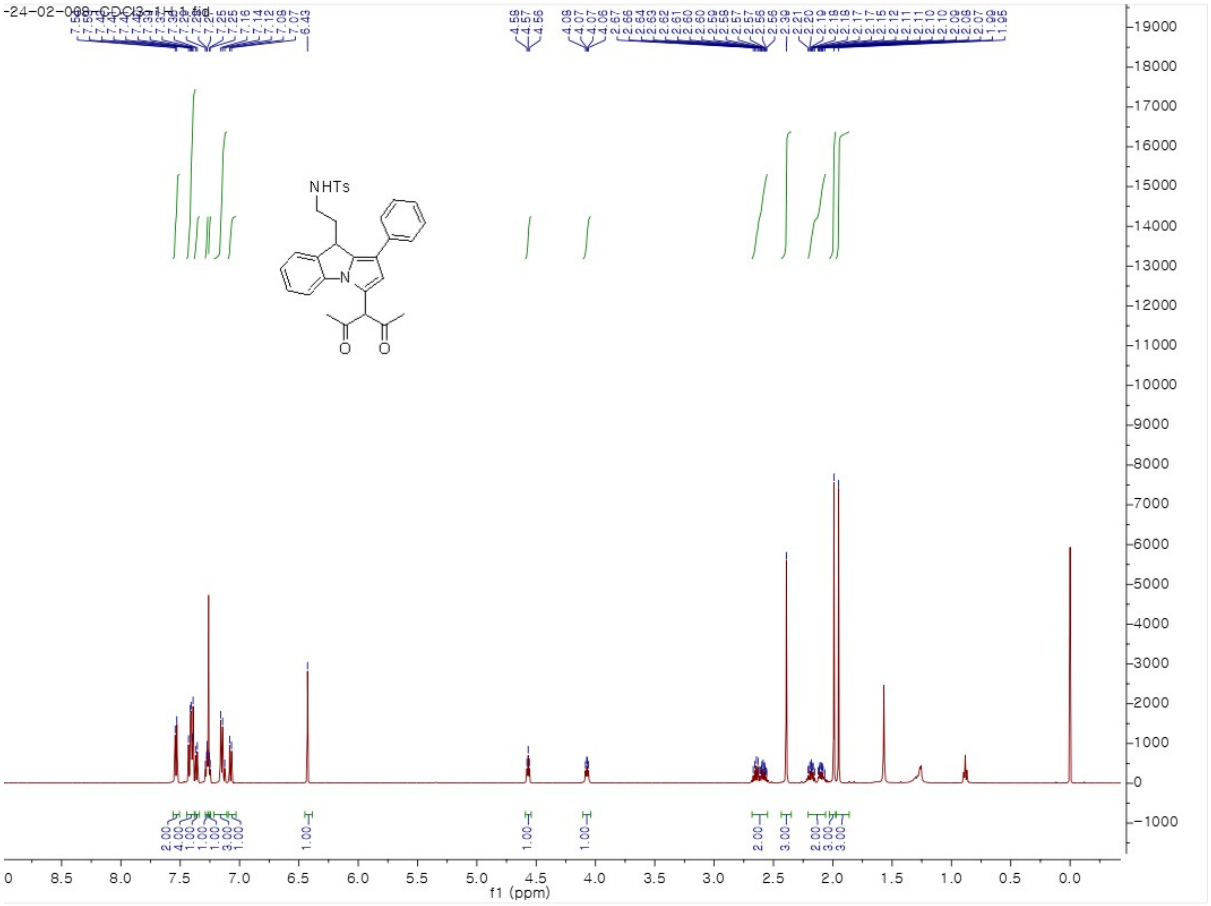


3aa

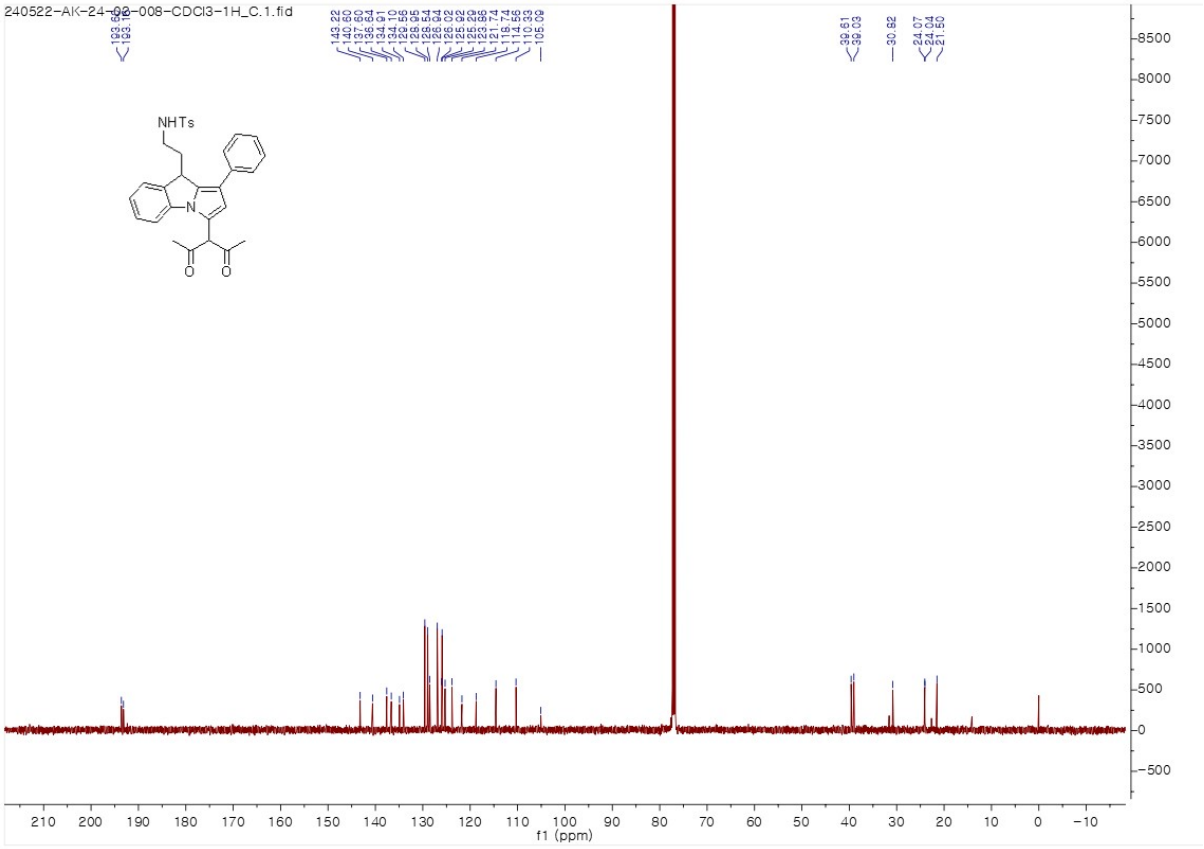
Identification code	20241203LT_0m	
Empirical formula	C23 H20 Br N O2	
Formula weight	422.31	
Temperature	100(1) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.0636(4) Å	α= 62.853(2)°
	b = 10.5318(5) Å	β= 85.644(3)°
	c = 11.2940(5) Å	γ = 85.833(3)°
Volume	955.67(8) Å³	
Z	2	
Density (calculated)	1.468 Mg/m³	
Absorption coefficient	2.168 mm⁻¹	
F(000)	432	
Crystal size	0.180 x 0.160 x 0.060 mm³	
Theta range for data collection	2.029 to 27.968°	
Index ranges	-11<=h<=11, -13<=k<=13, -14<=l<=14	
Reflections collected	17803	
Independent reflections	4562 [R(int) = 0.0312]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	

Max. and min. transmission	0.88 and 0.77
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4562 / 2 / 247
Goodness-of-fit on F^2	1.057
Final R indices [I>2sigma(I)]	R1 = 0.0328, wR2 = 0.0863
R indices (all data)	R1 = 0.0381, wR2 = 0.0886
Extinction coefficient	n/a
Largest diff. peak and hole	0.772 and -0.427 e.$Å^{-3}$

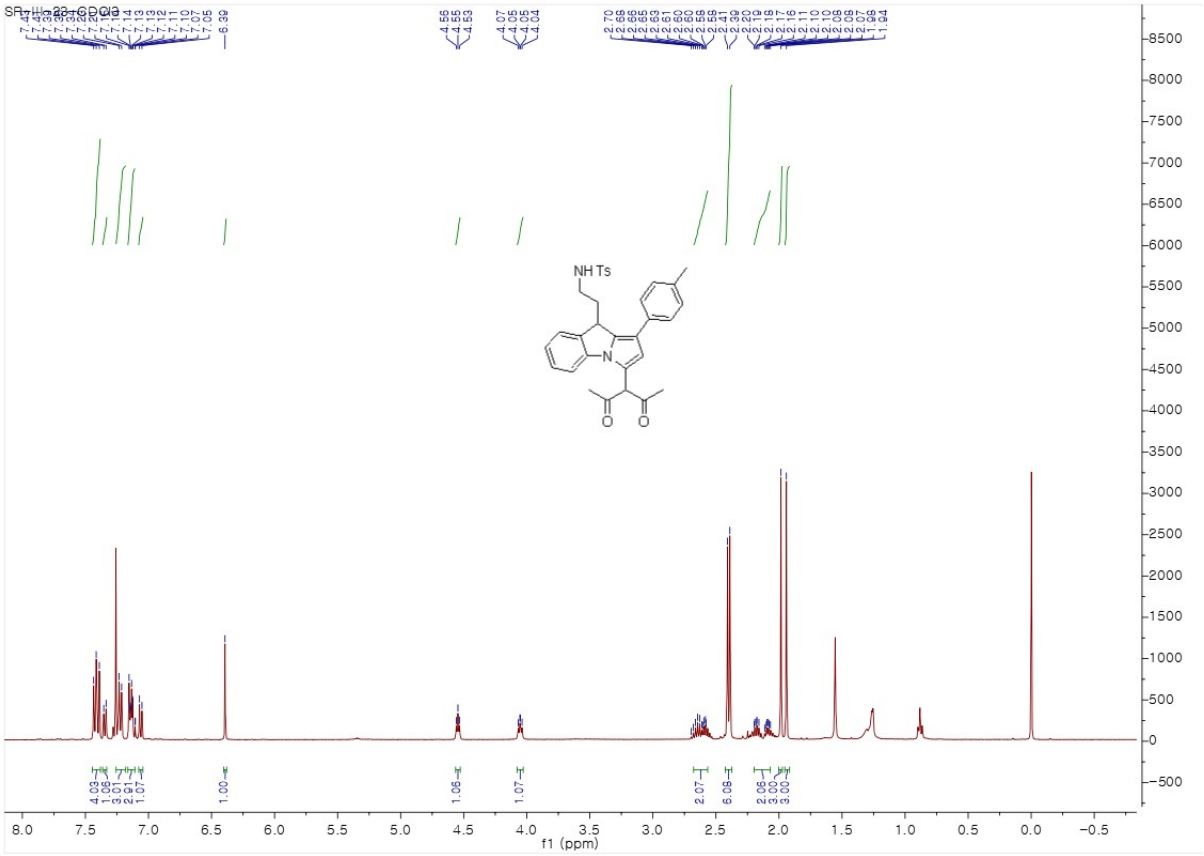
NMR copies of compound 3



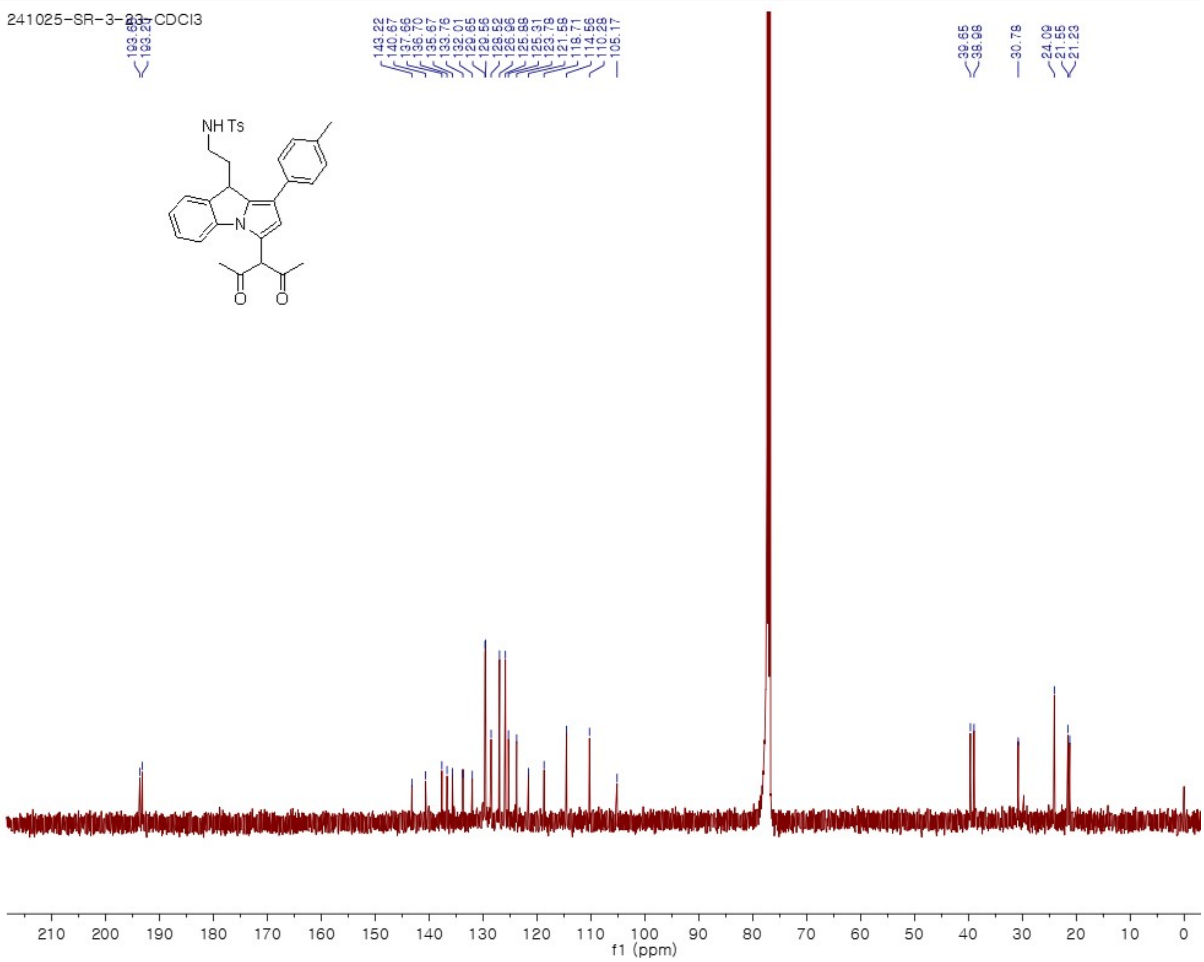
^{1}H NMR spectra of compound 3a (500MHz, $CDCl_3$)



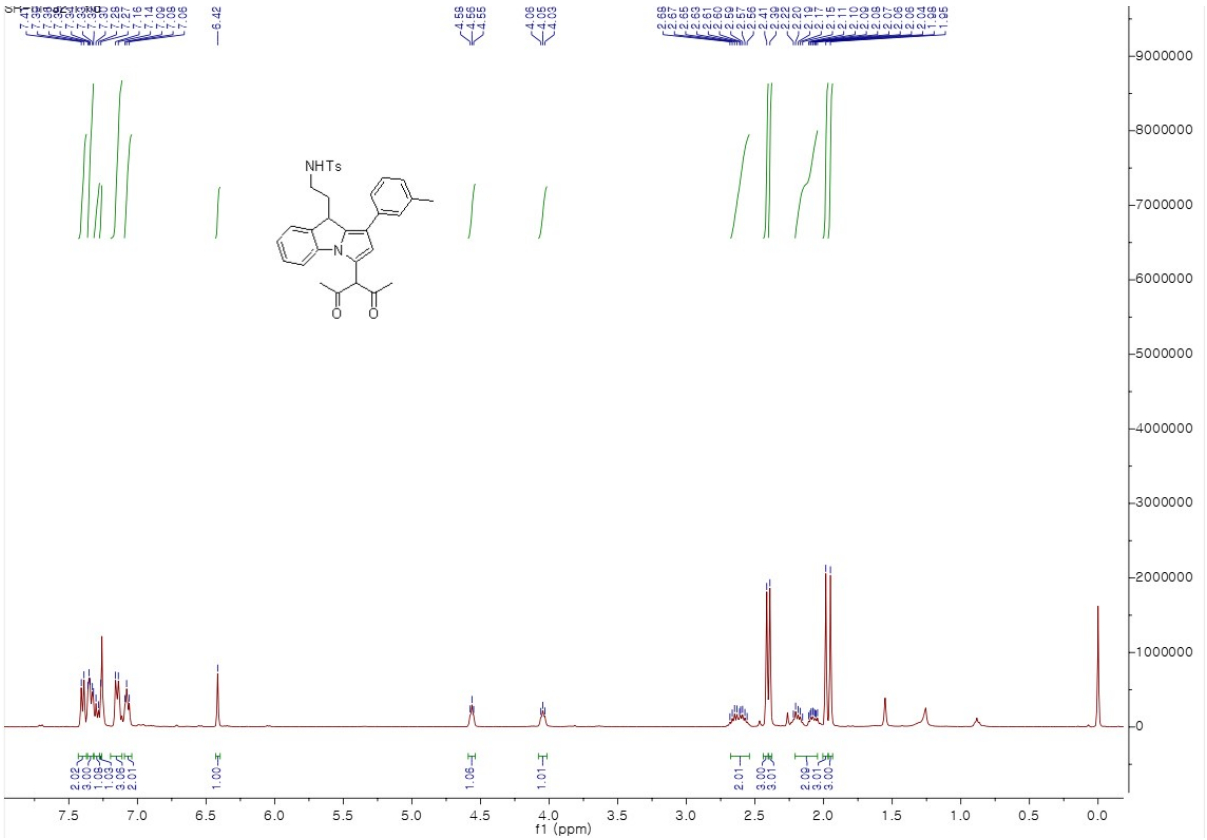
^{13}C NMR spectra of compound 3a (126MHz, $CDCl_3$)



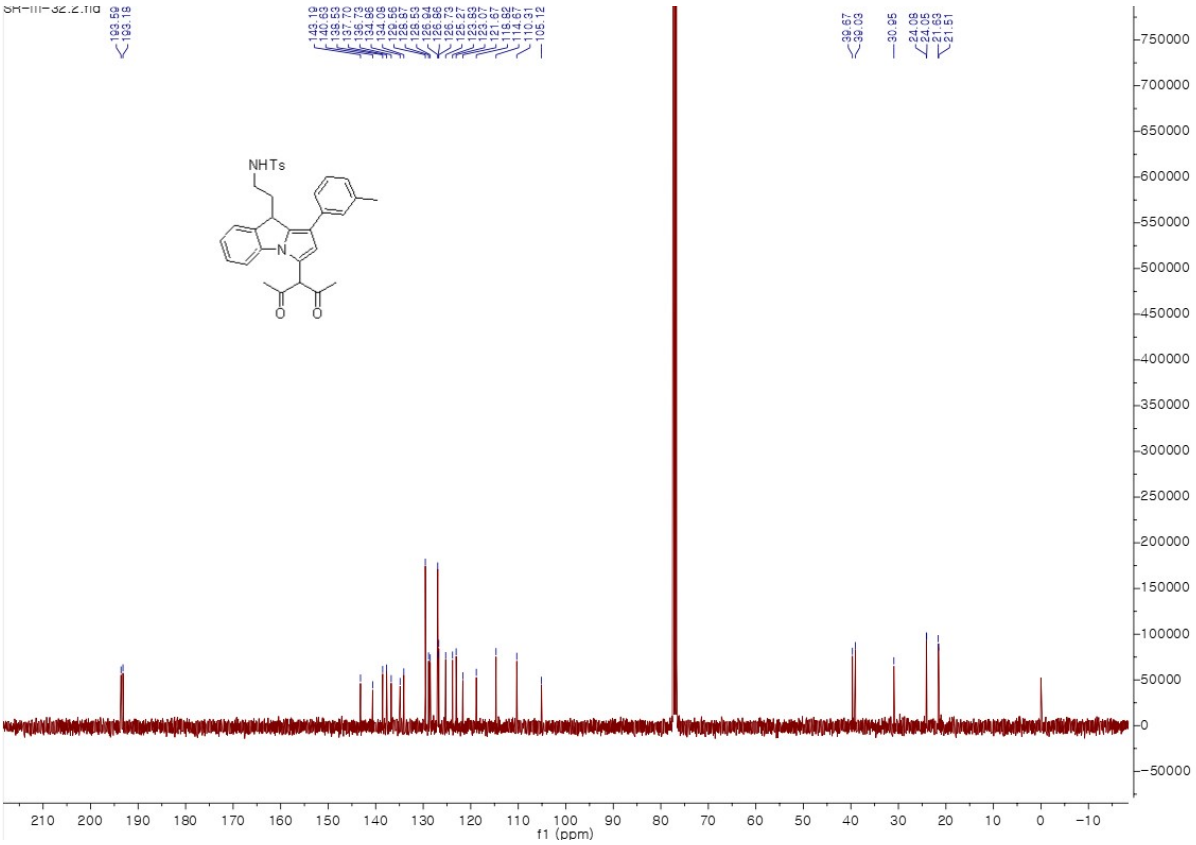
^{1}H NMR spectra of compound 3b (400MHz, $CDCl_3$)



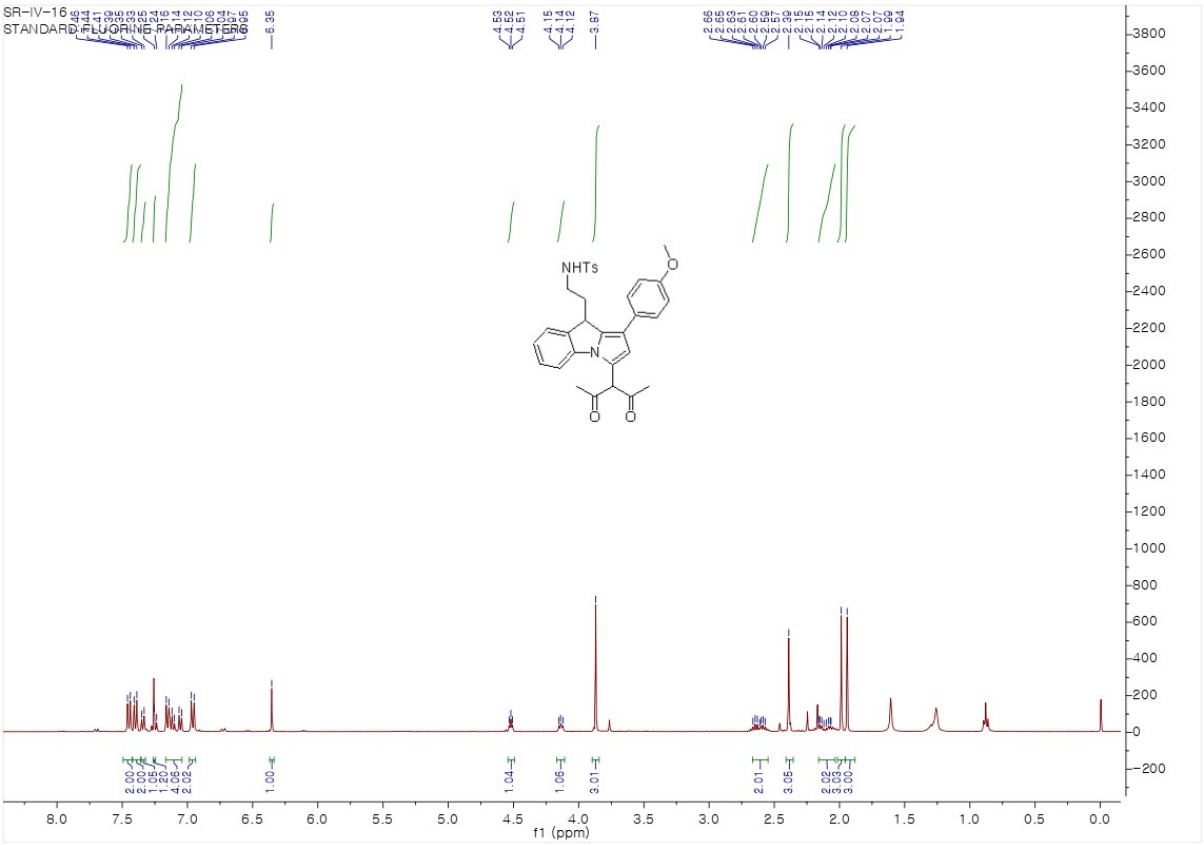
^{13}C NMR spectra of compound 3b (126MHz, $CDCl_3$)



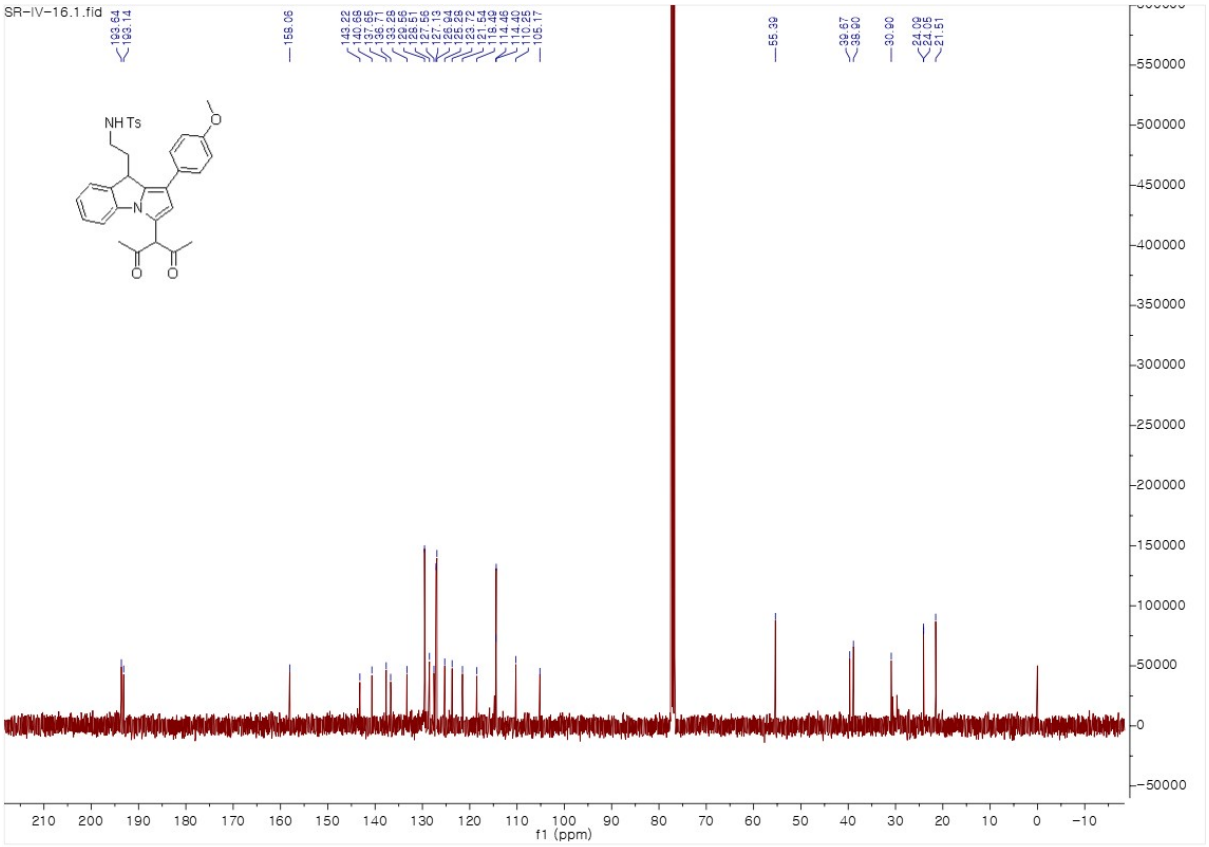
^{1}H NMR spectra of compound 3c (400MHz, $CDCl_3$)



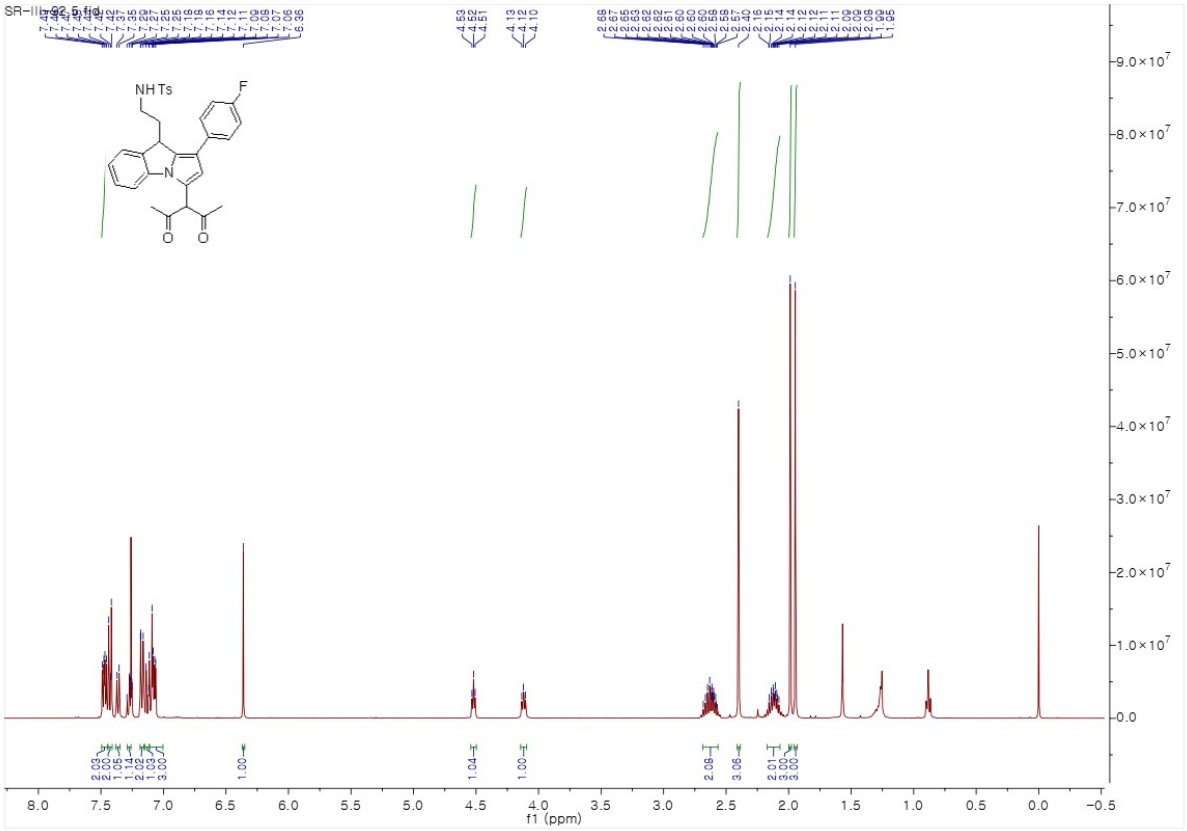
^{13}C NMR spectra of compound 3c (126MHz, $CDCl_3$)



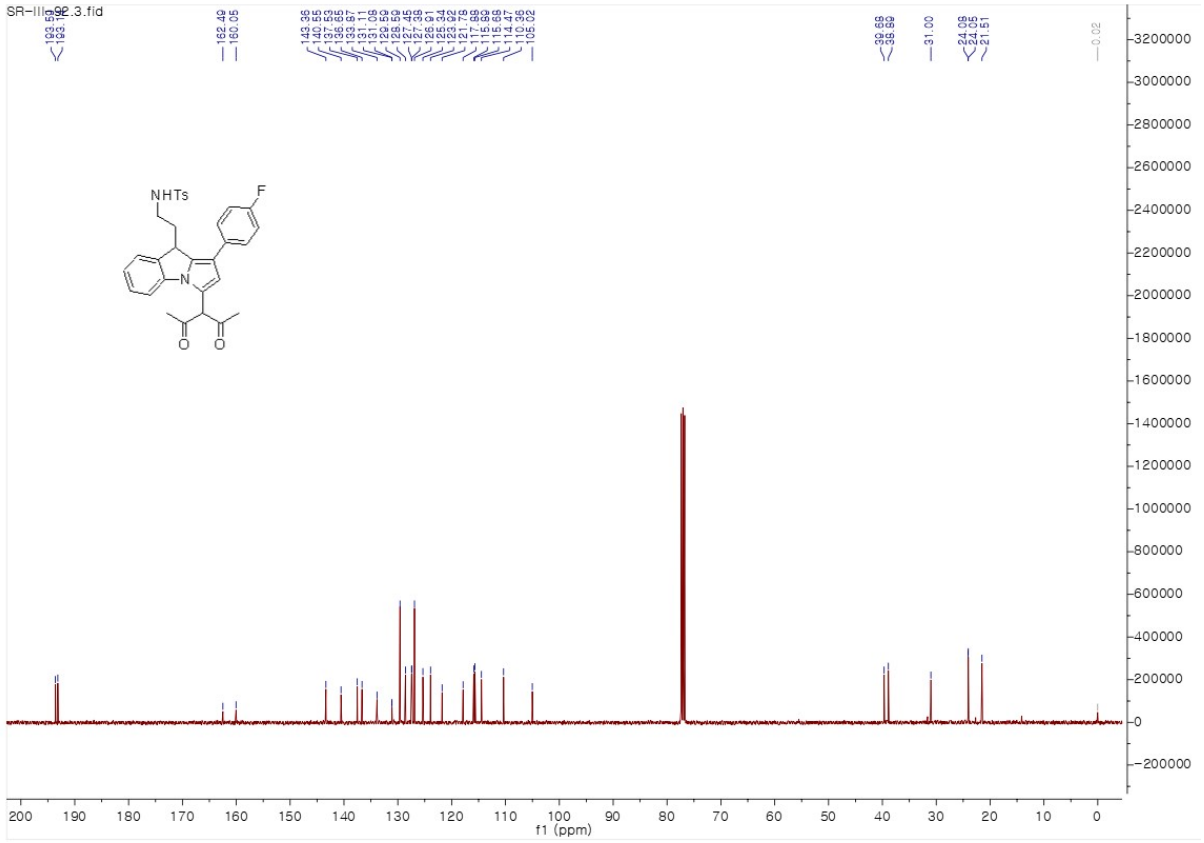
^{1}H NMR spectra of compound 3d (400MHz, $CDCl_3$)



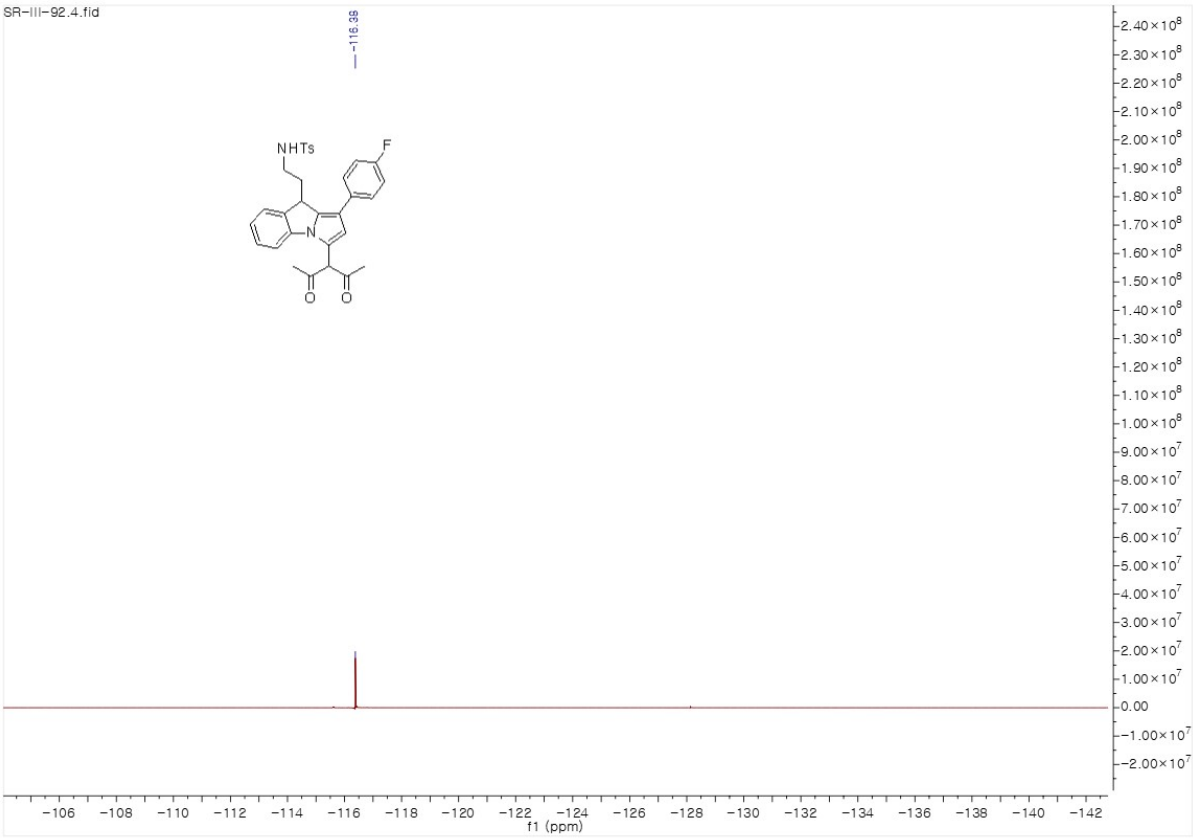
^{13}C NMR spectra of compound 3d (101MHz, $CDCl_3$)



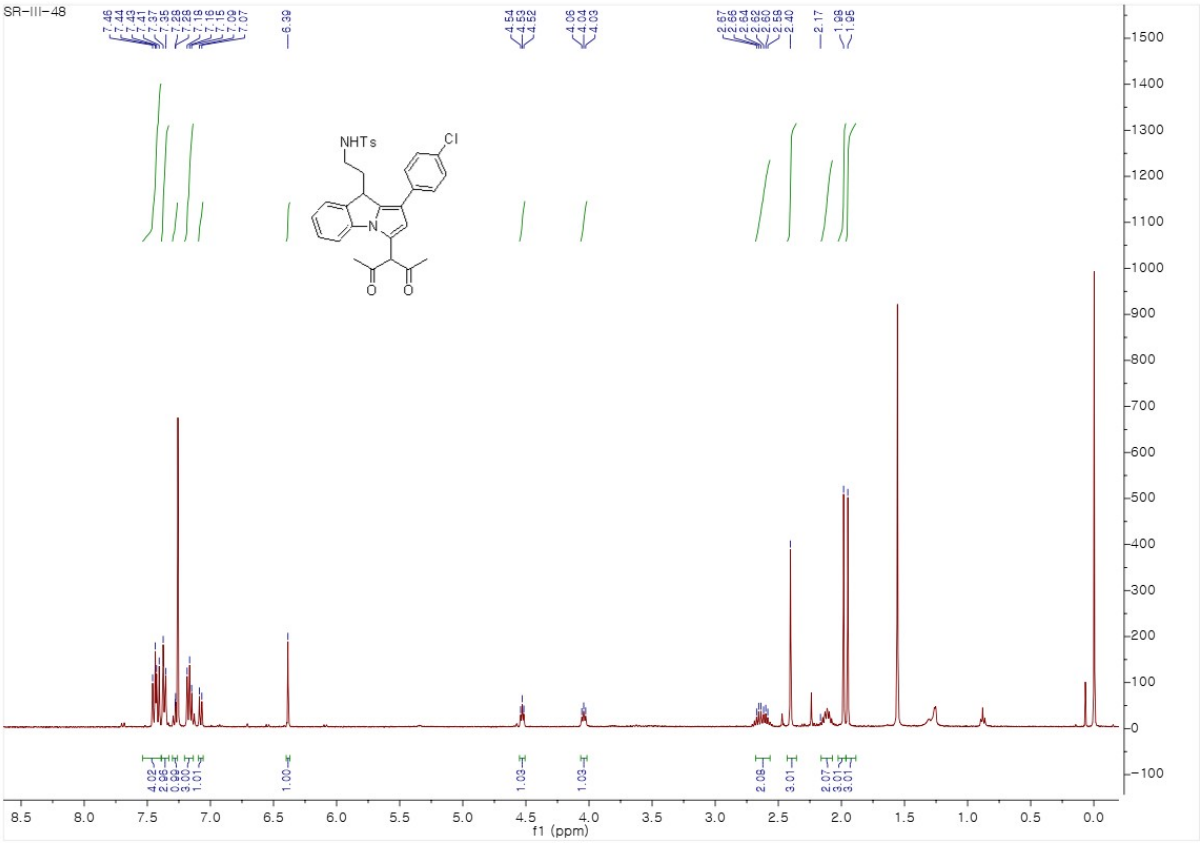
^{1}H NMR spectra of compound 3e (400MHz, $CDCl_3$)



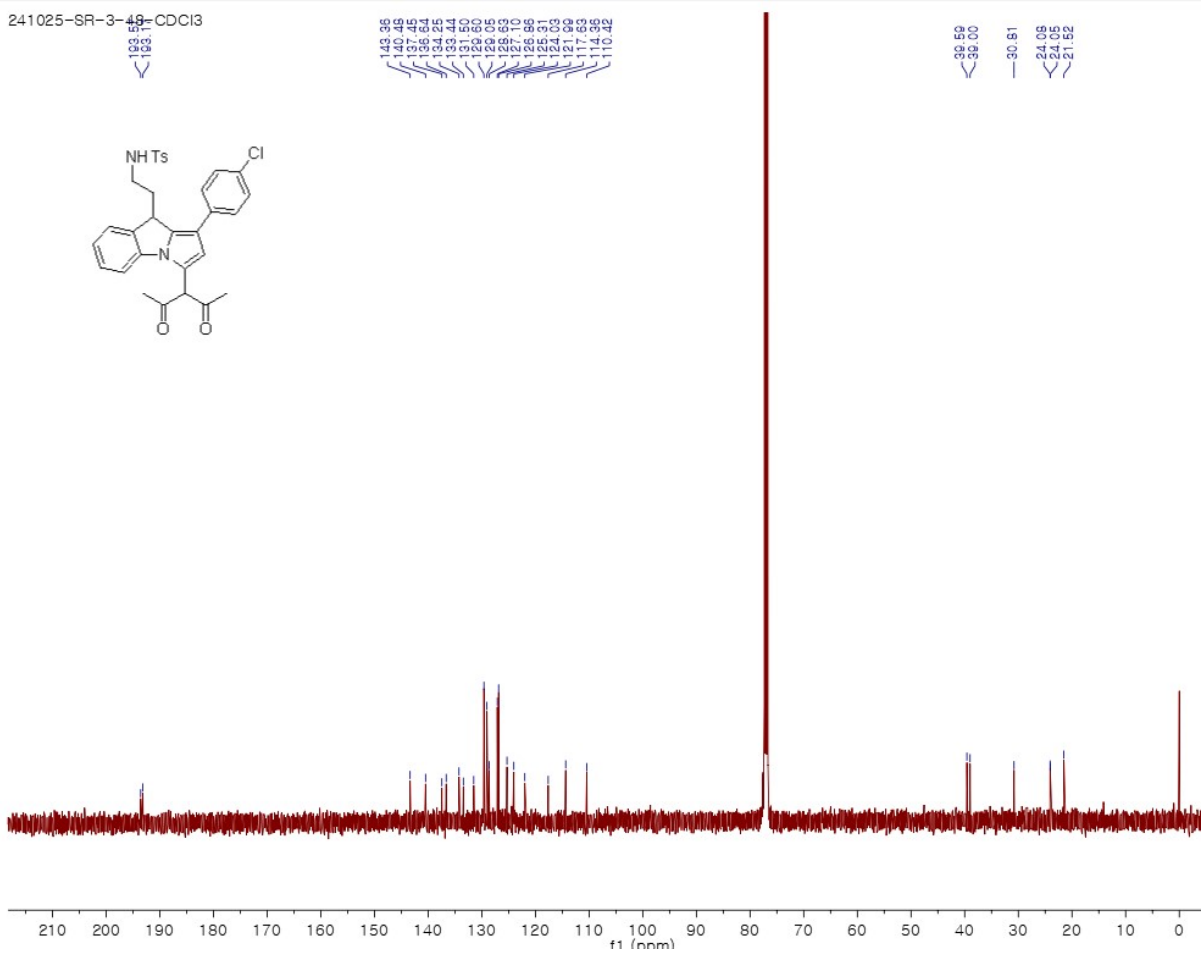
^{13}C NMR spectra of compound 3e (126MHz, $CDCl_3$)



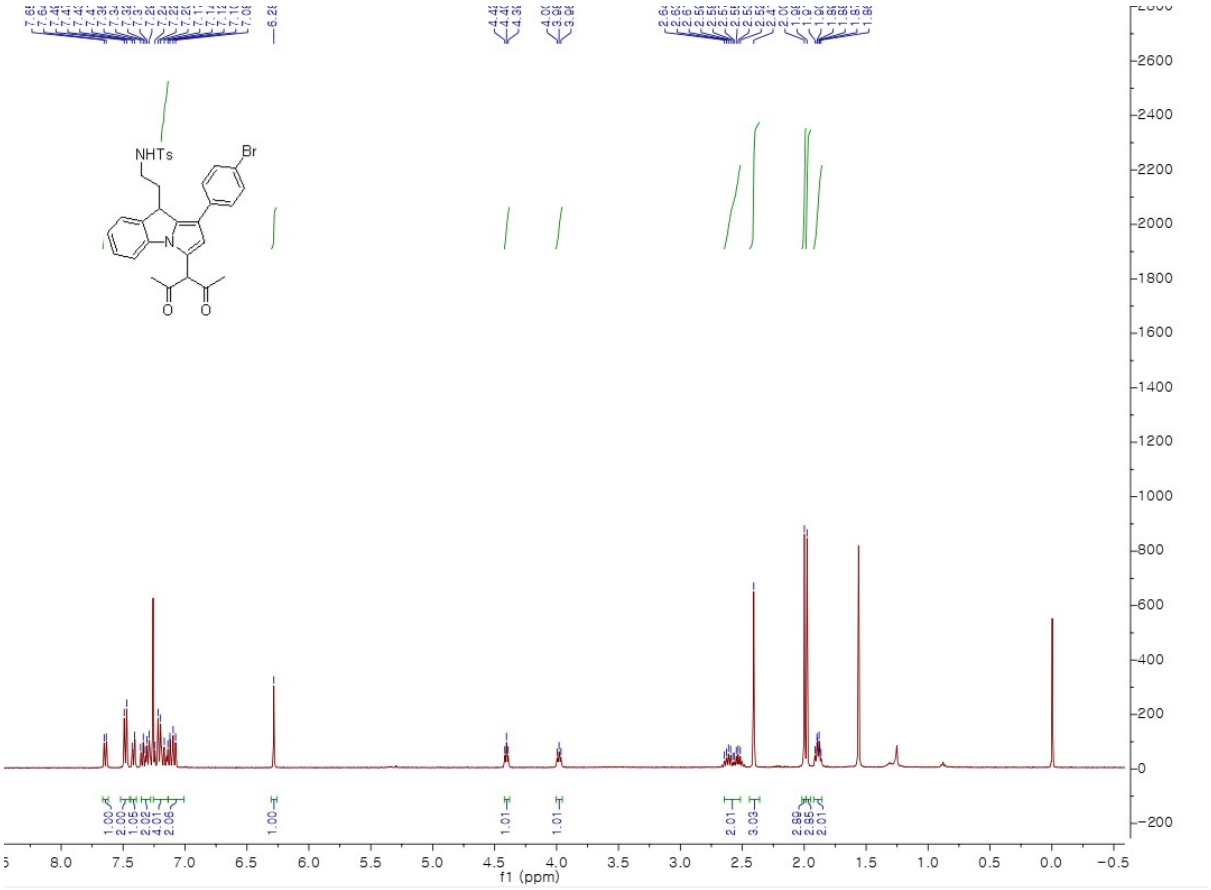
^{19}F NMR spectra of compound 3e (400Hz, $CDCl_3$)



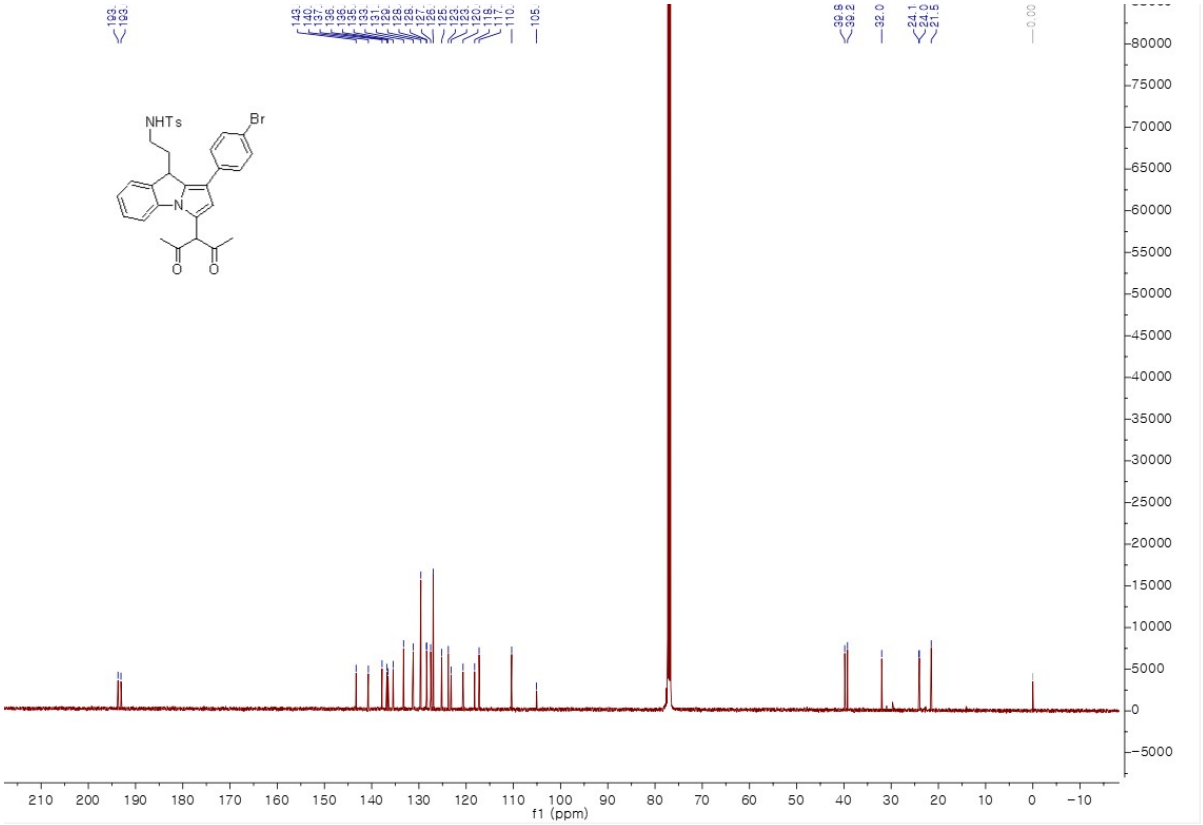
^{1}H NMR spectra of compound 3f (400MHz, $CDCl_3$)



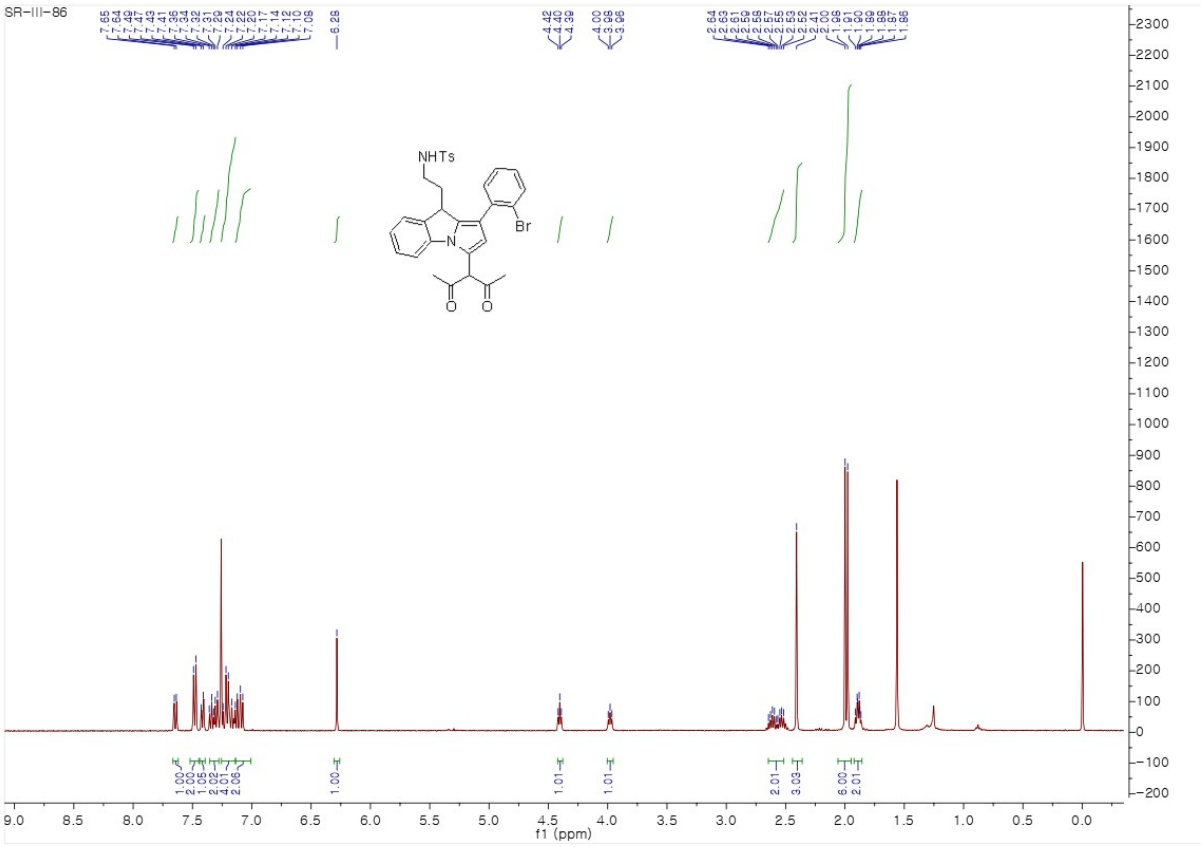
^{13}C NMR spectra of compound 3f (126MHz, $CDCl_3$)



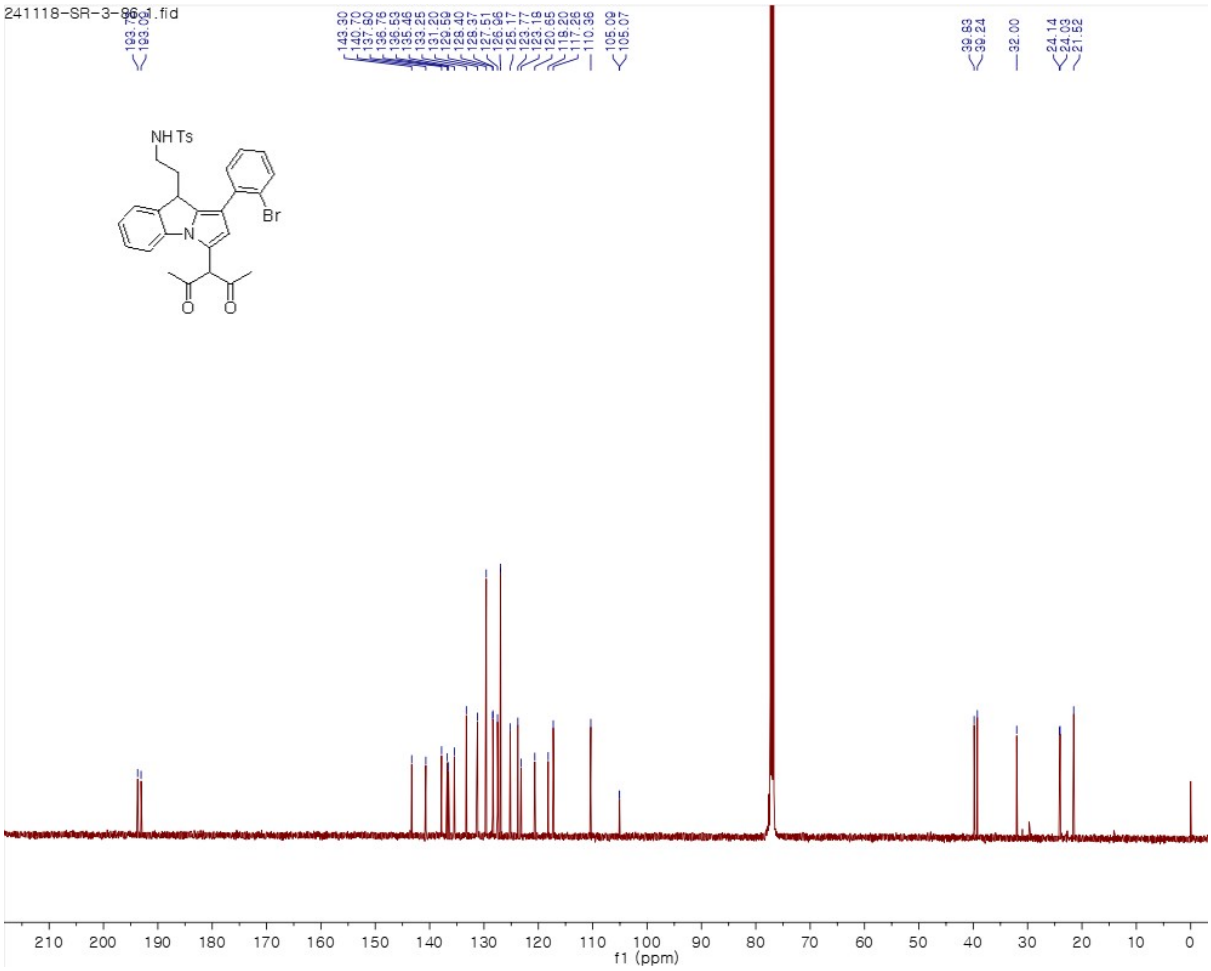
^{1}H NMR spectra of compound 3g (400MHz, $CDCl_3$)



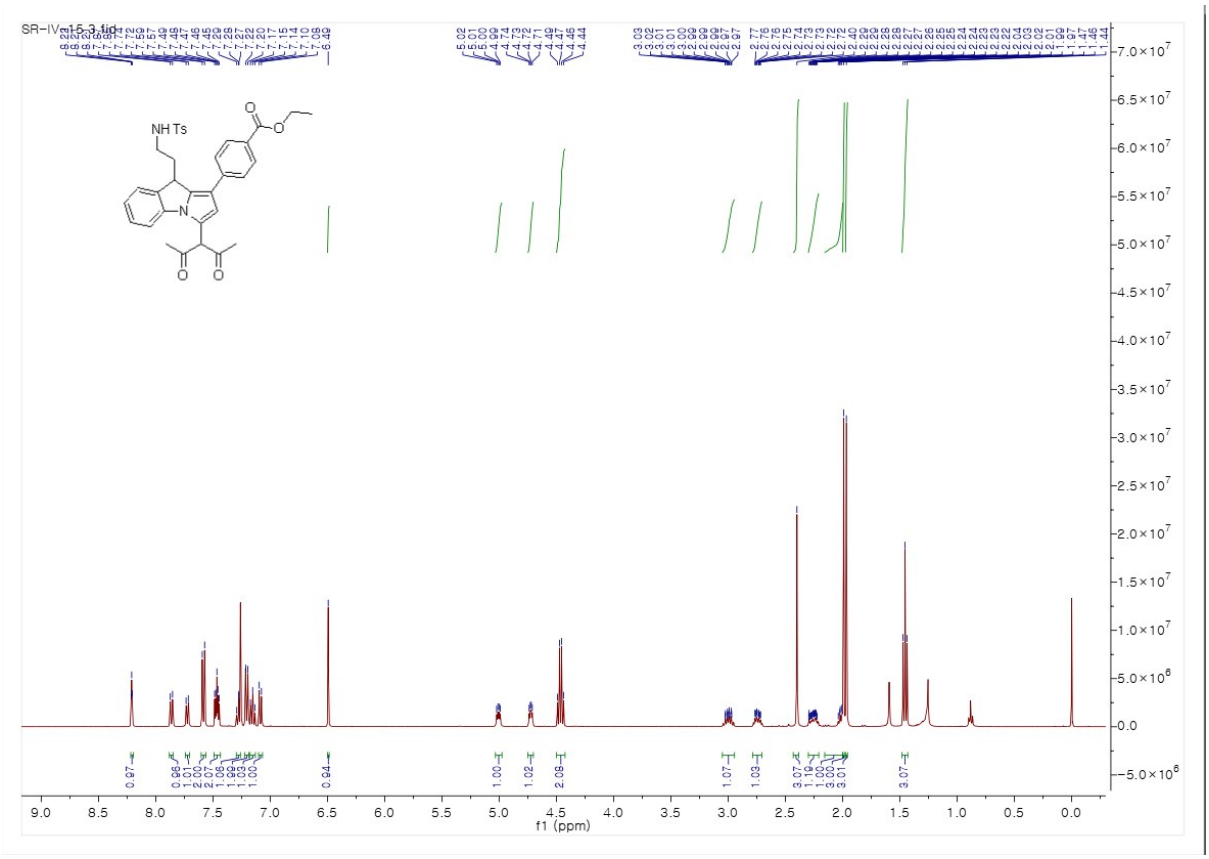
^{13}C NMR spectra of compound 3g (101MHz, $CDCl_3$)



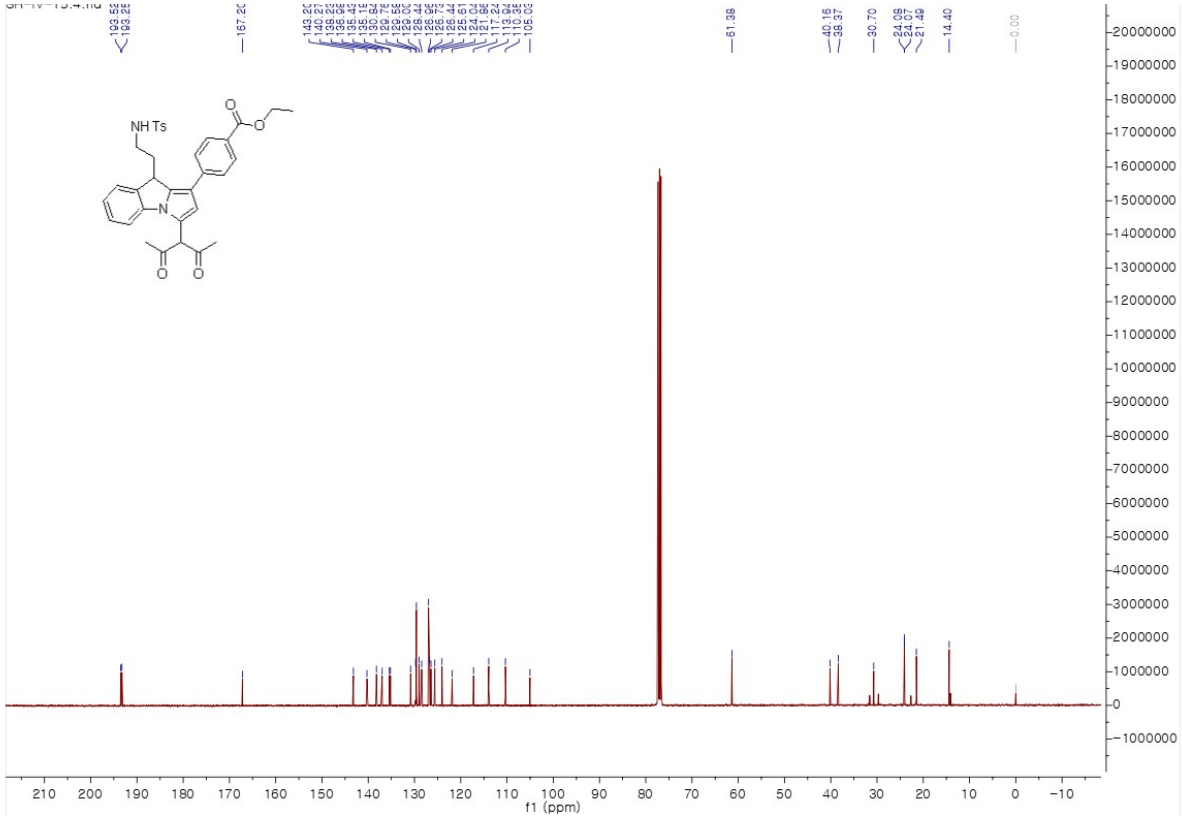
^{1}H NMR spectra of compound 3h (400MHz, $CDCl_3$)



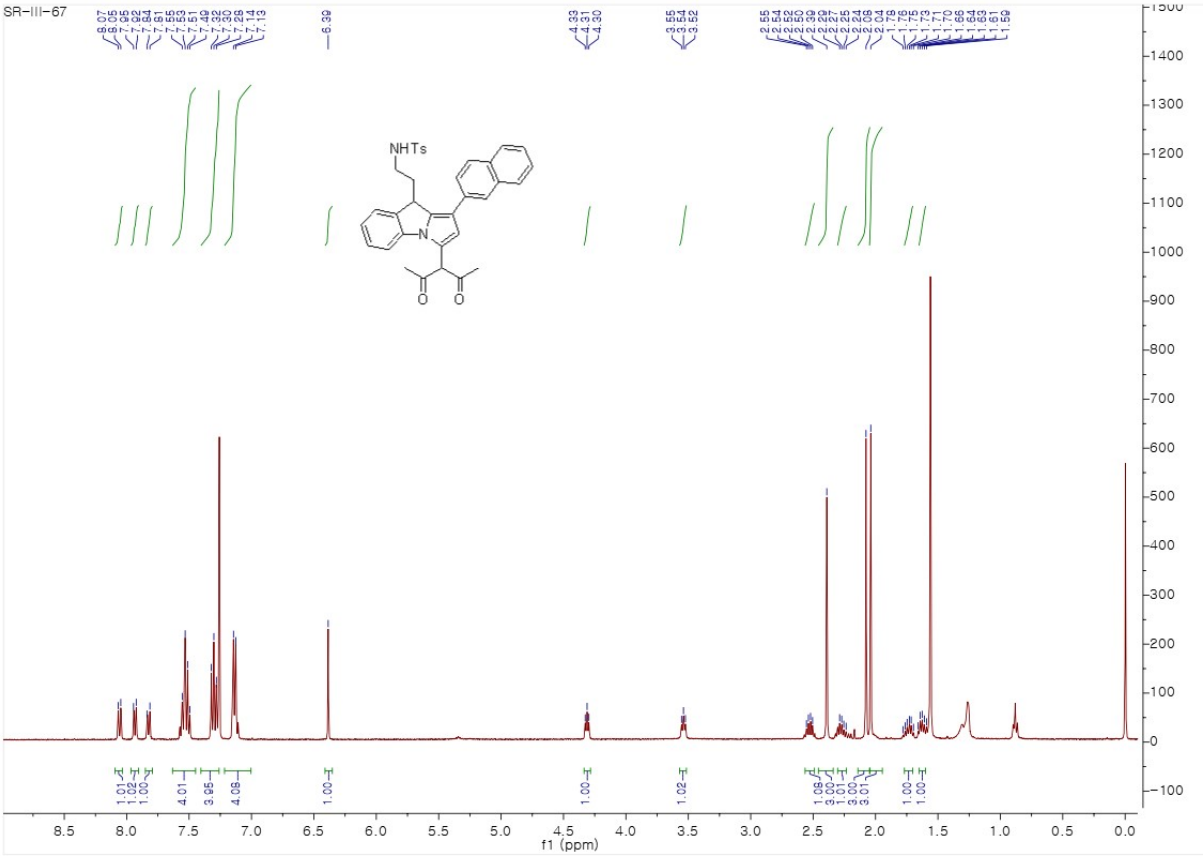
^{13}C NMR spectra of compound 3h (126MHz, $CDCl_3$)



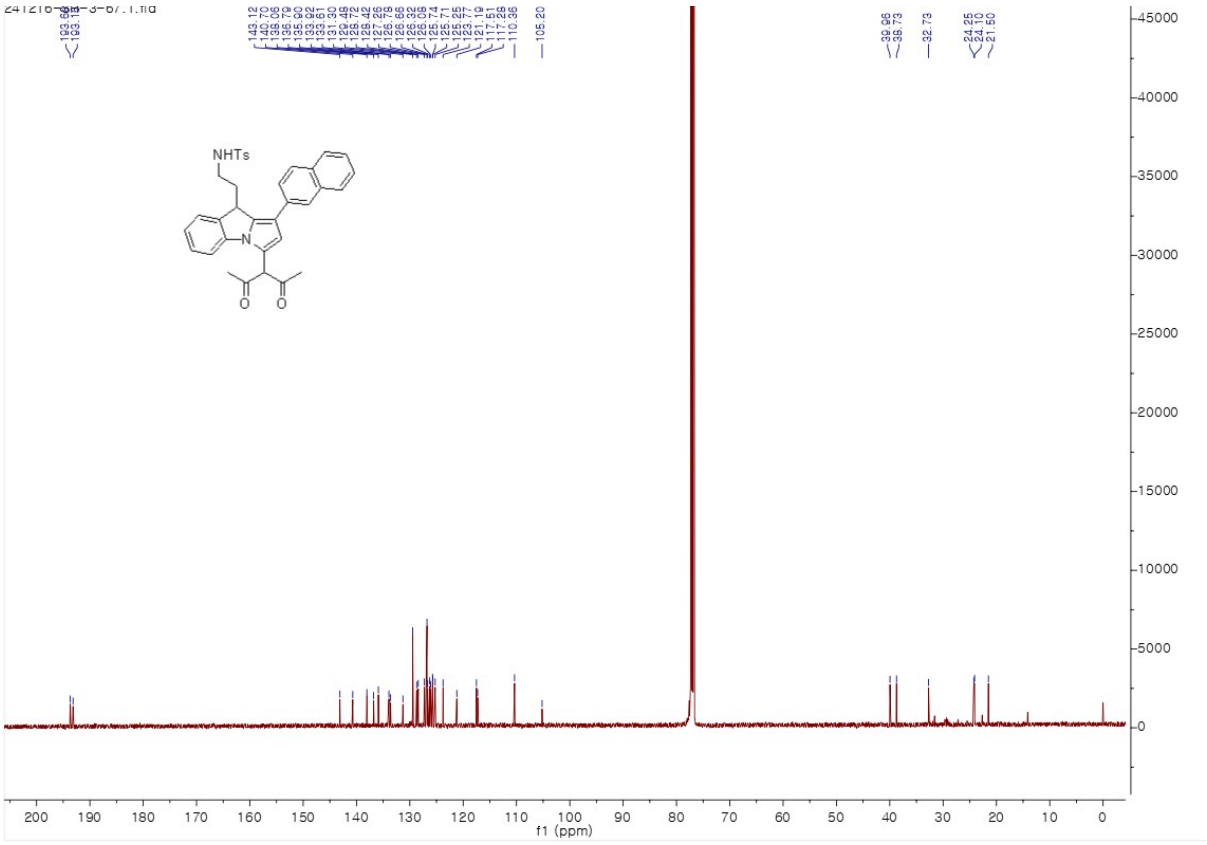
^{1}H NMR spectra of compound 3i (400MHz, $CDCl_3$)



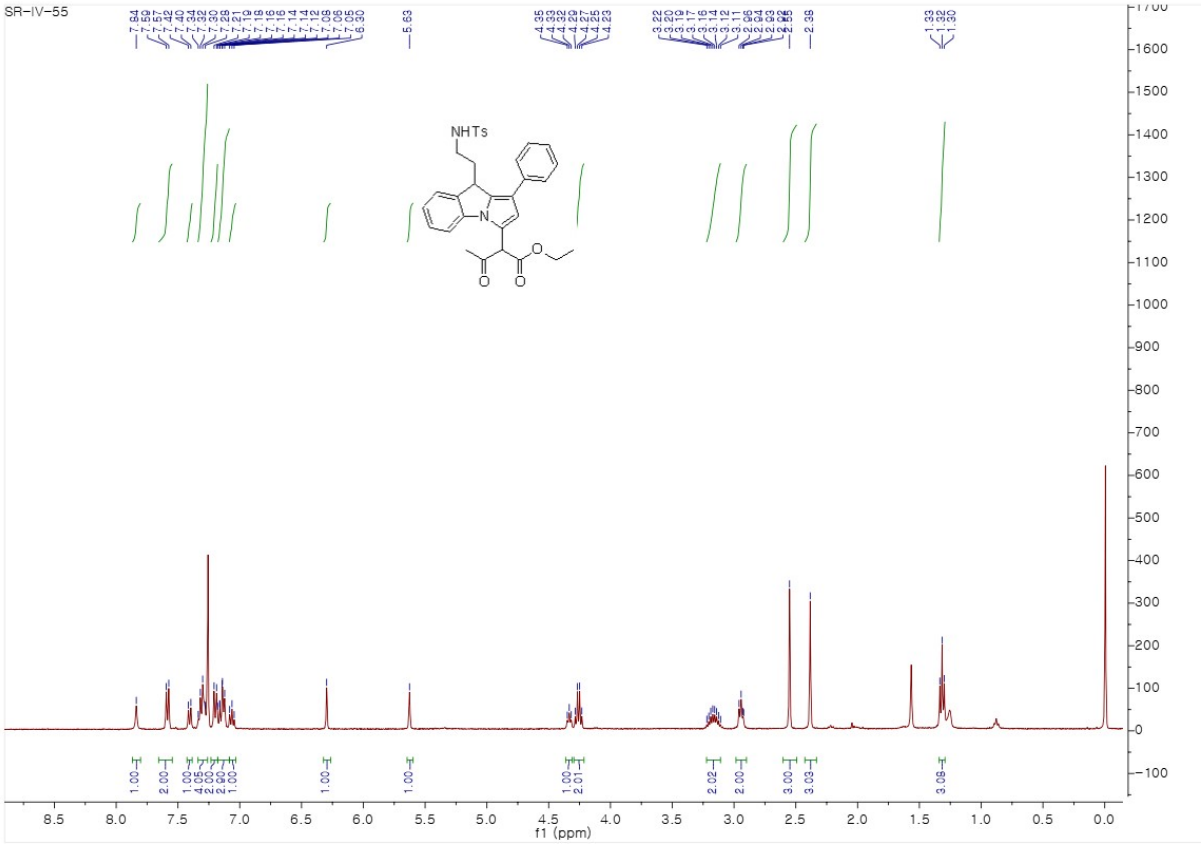
^{13}C NMR spectra of compound 3i (101MHz, $CDCl_3$)



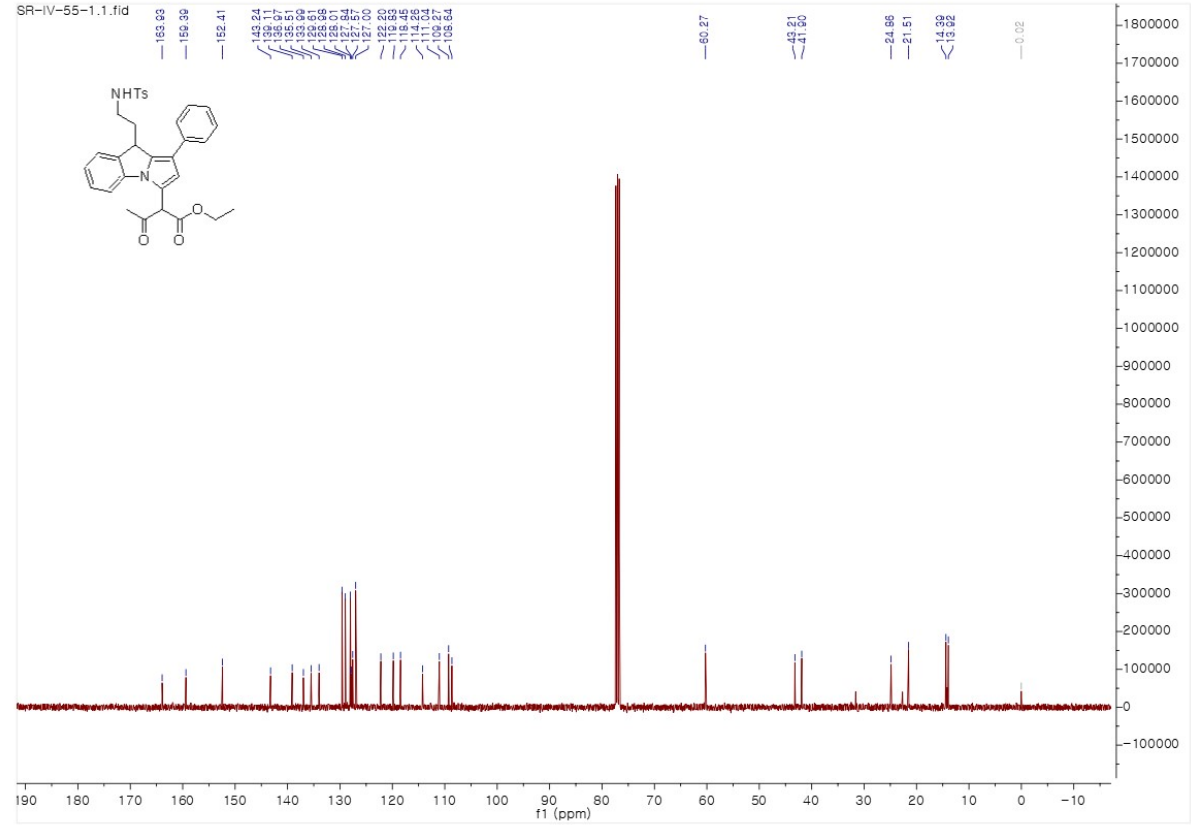
^{1}H NMR spectra of compound 3j (400MHz, $CDCl_3$)



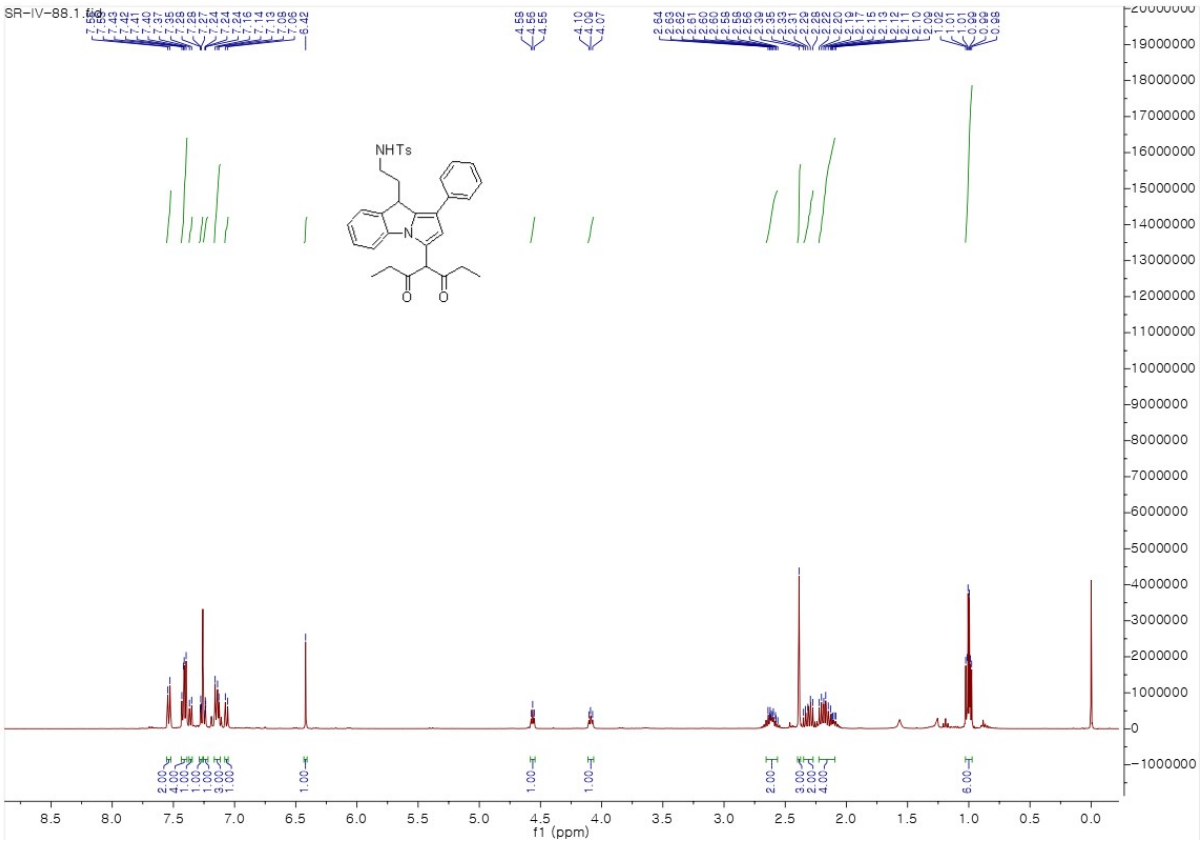
^{13}C NMR spectra of compound 3j (400MHz, $CDCl_3$)



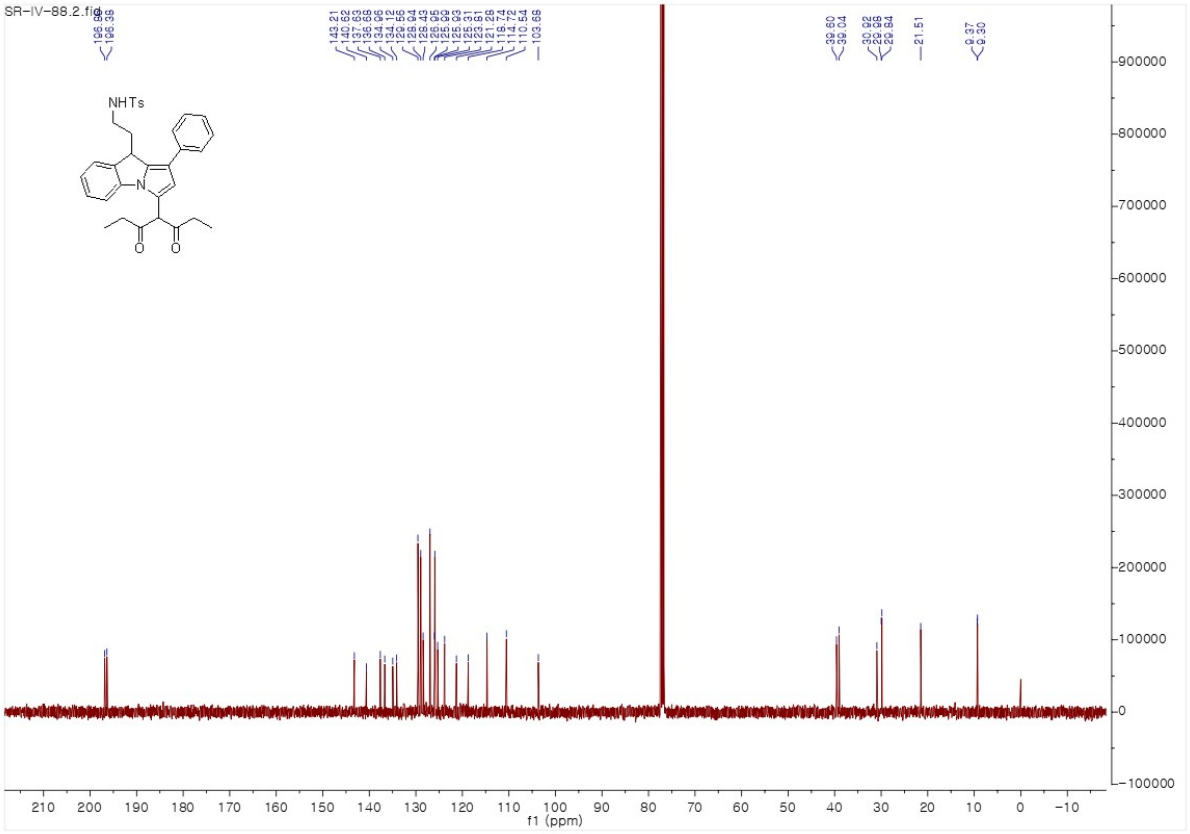
^{1}H NMR spectra of compound 3k (400MHz, $CDCl_3$)



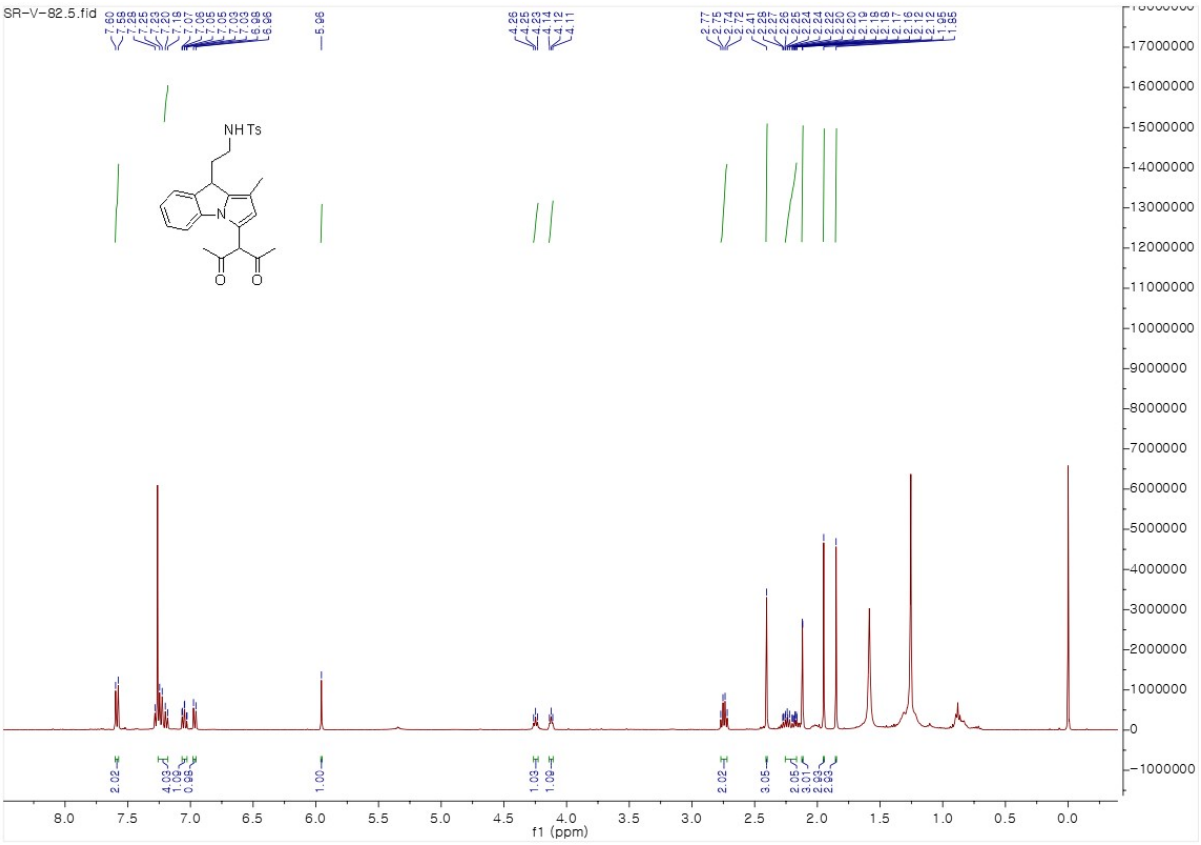
^{13}C NMR spectra of compound 3k (101MHz, $CDCl_3$)



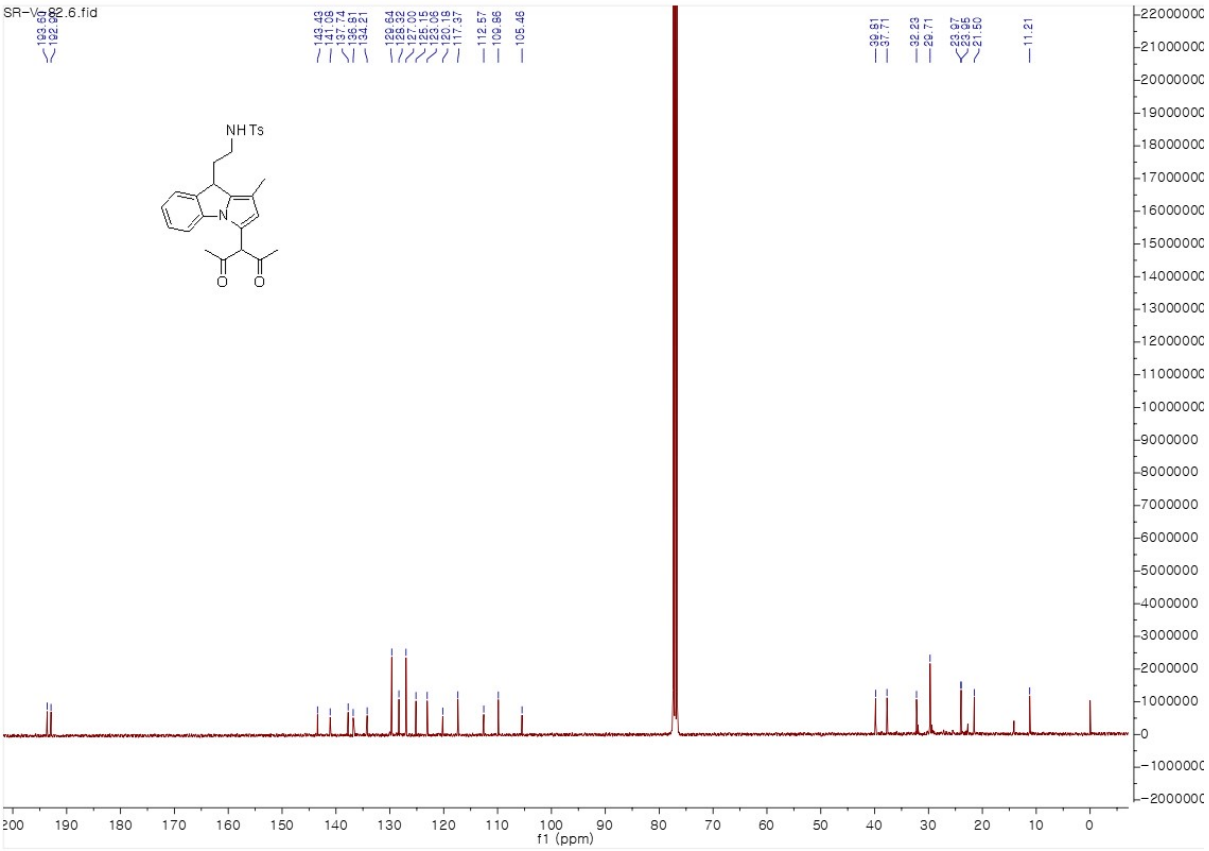
^{1}H NMR spectra of compound 3l (400MHz, $CDCl_3$)



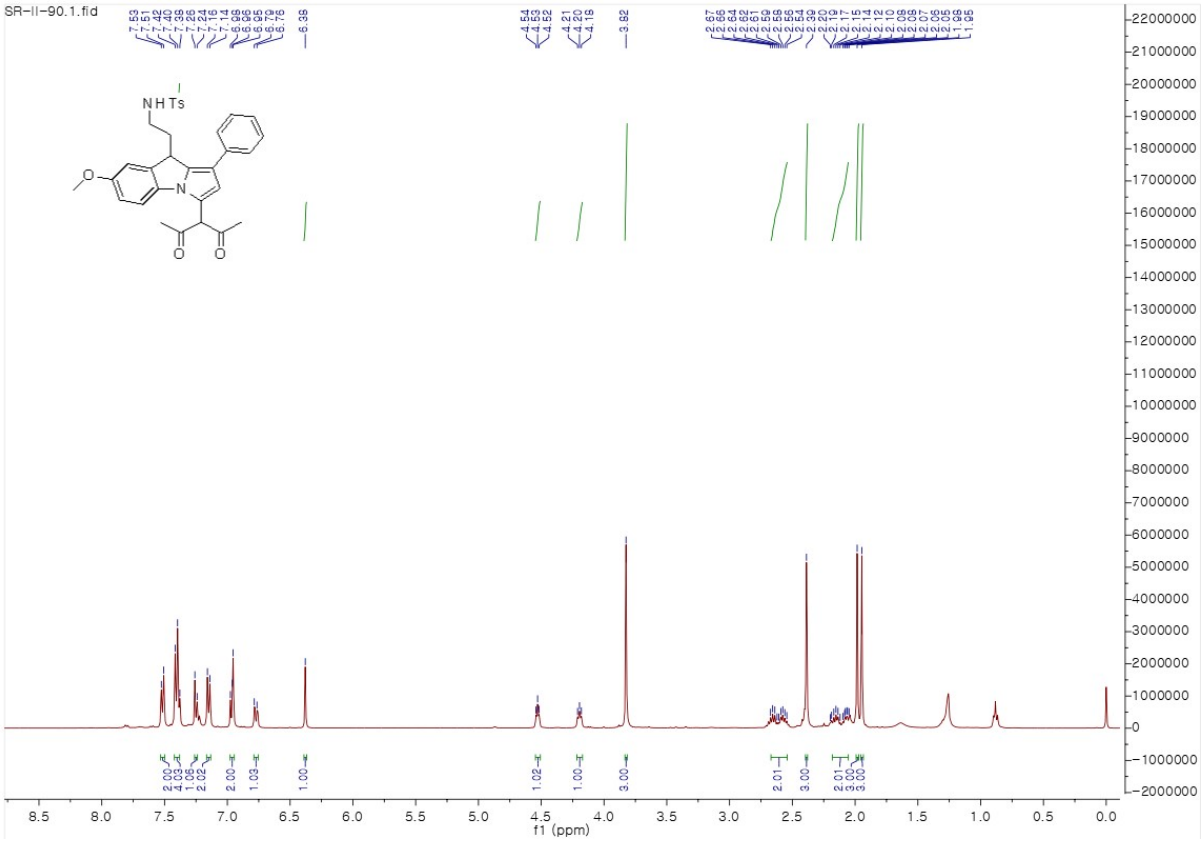
^{13}C NMR spectra of compound 3l (101MHz, $CDCl_3$)



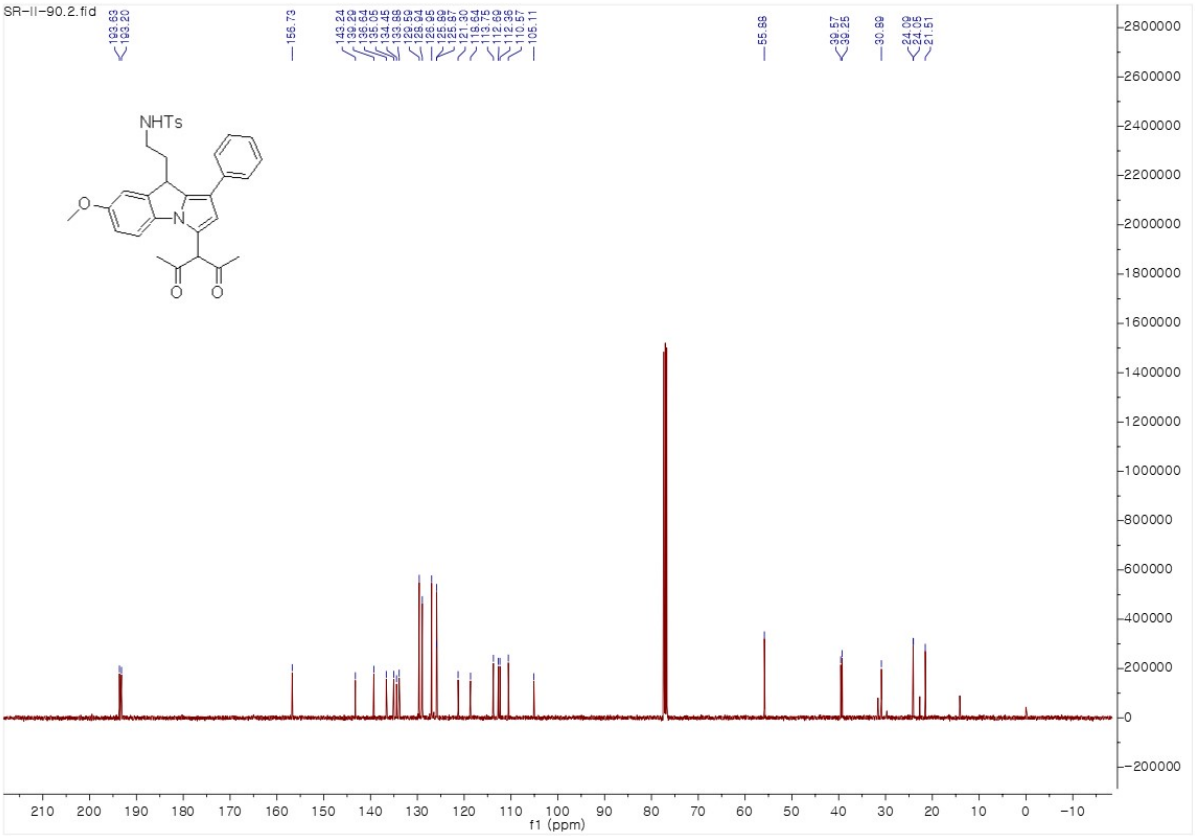
^{1}H NMR spectra of compound 3m (400MHz, $CDCl_3$)



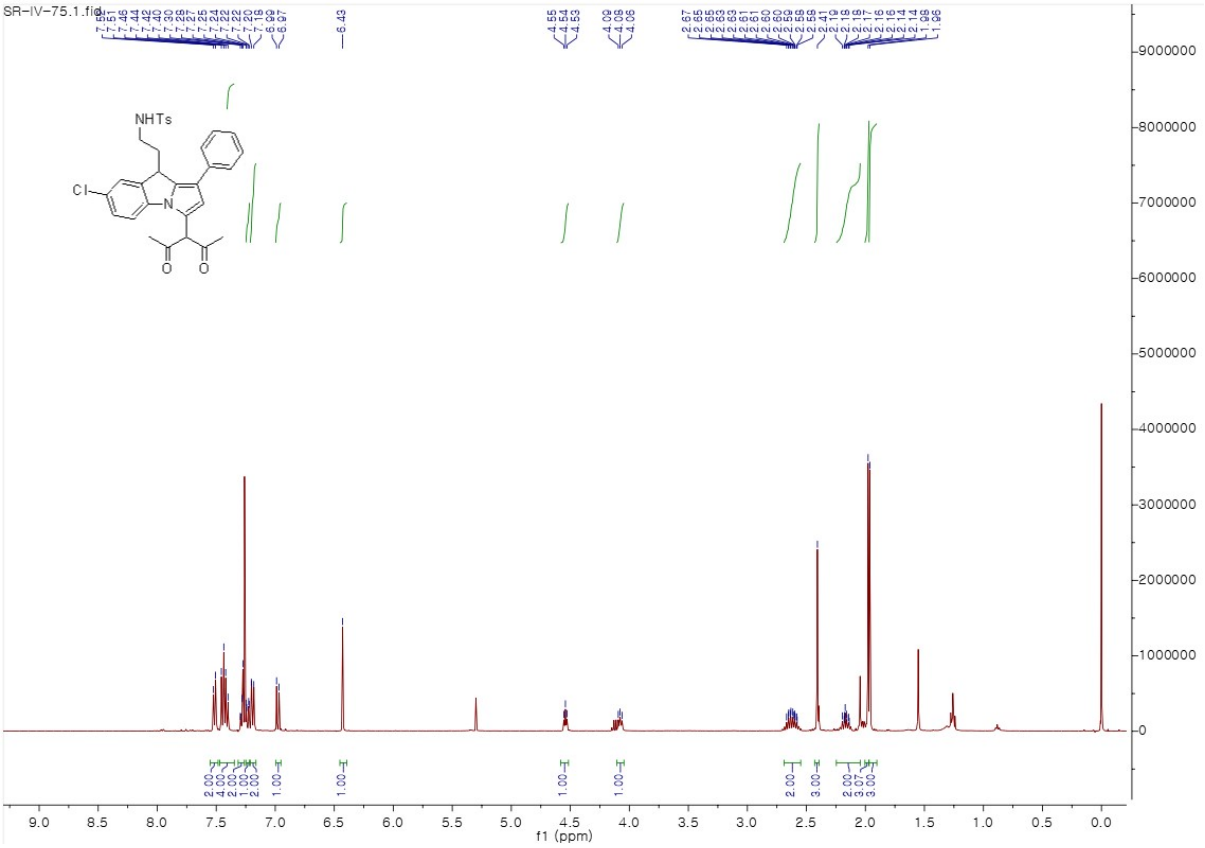
^{13}C NMR spectra of compound 3l (101MHz, $CDCl_3$)



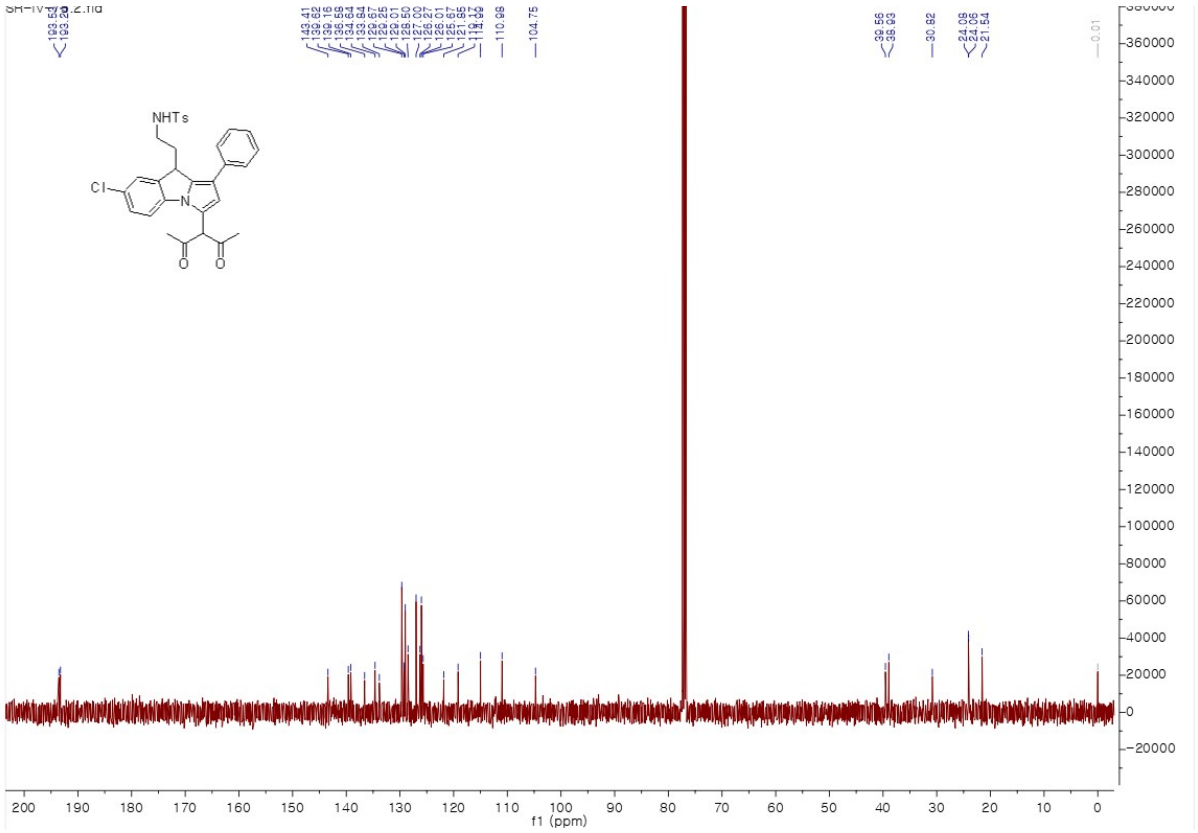
^{1}H NMR spectra of compound 3p (400MHz, $CDCl_3$)



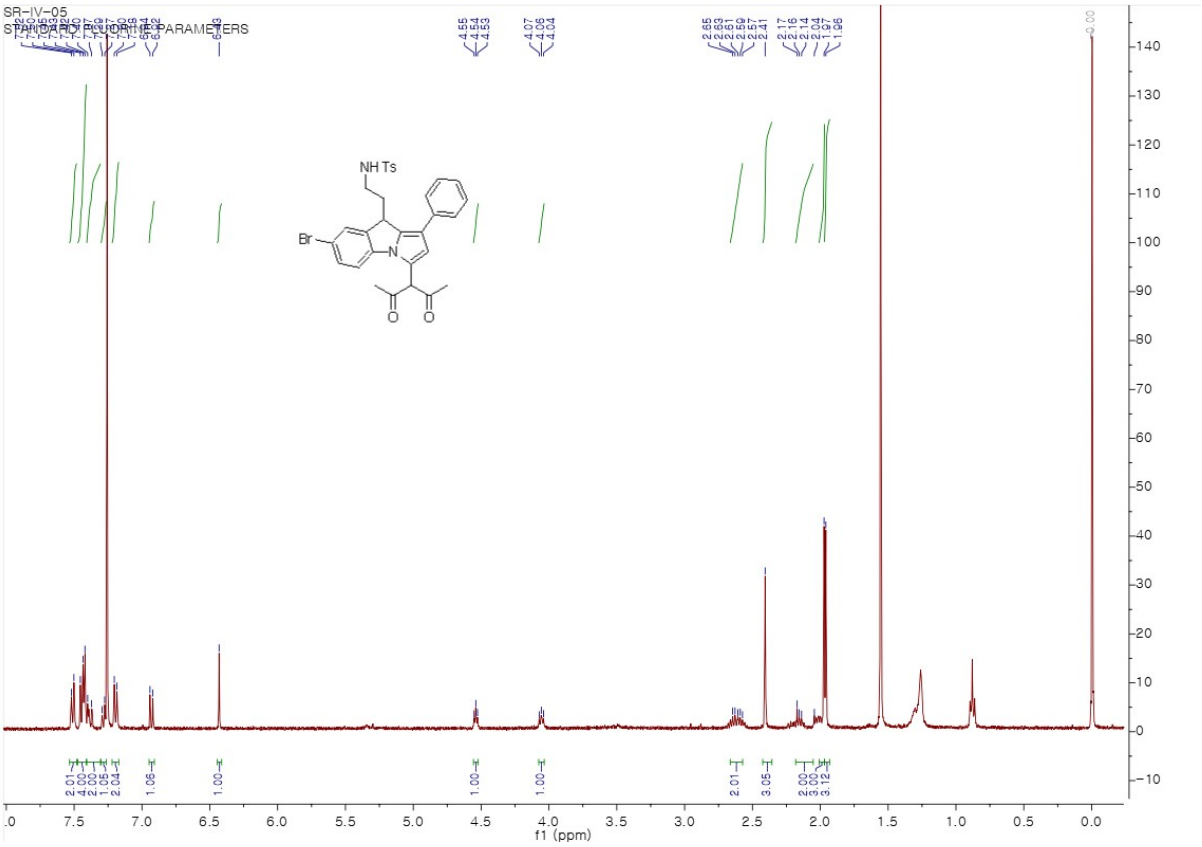
^{13}C NMR spectra of compound 3p (126MHz, $CDCl_3$)



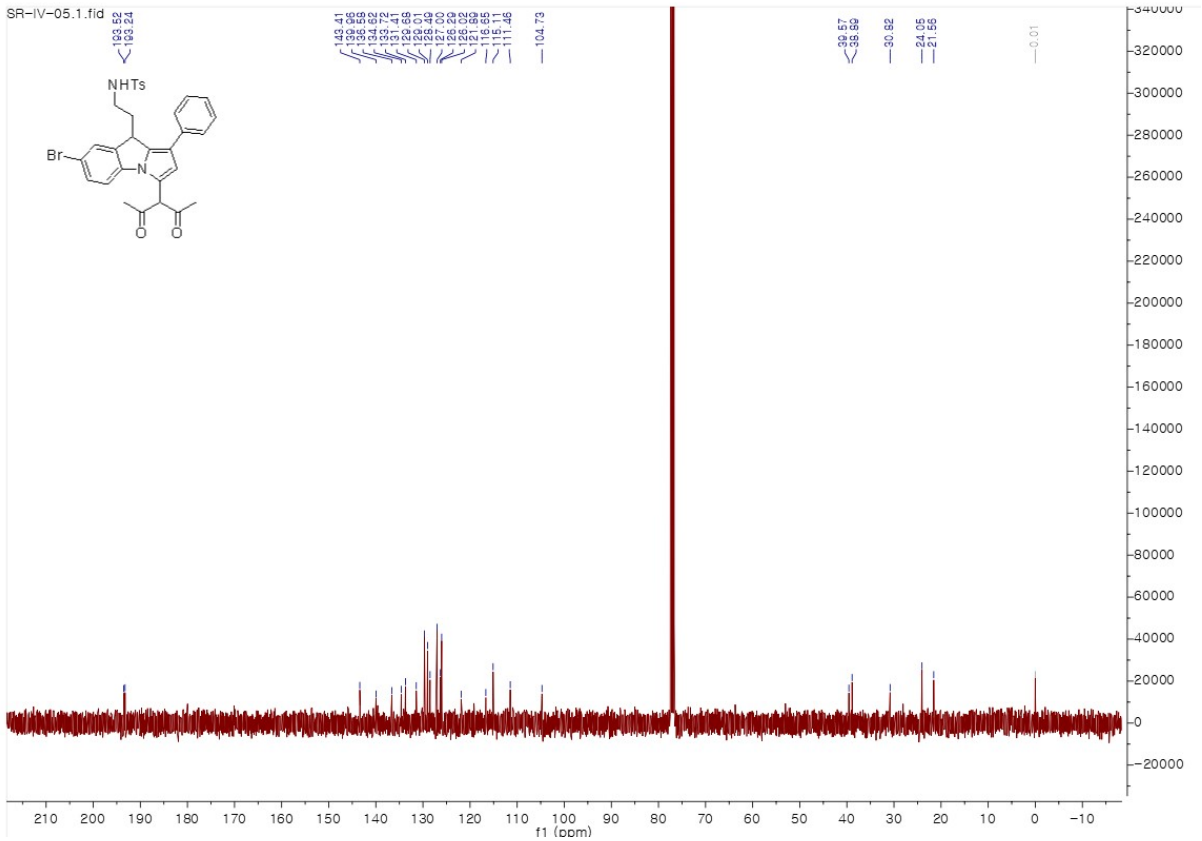
^{1}H NMR spectra of compound 3q (400MHz, $CDCl_3$)



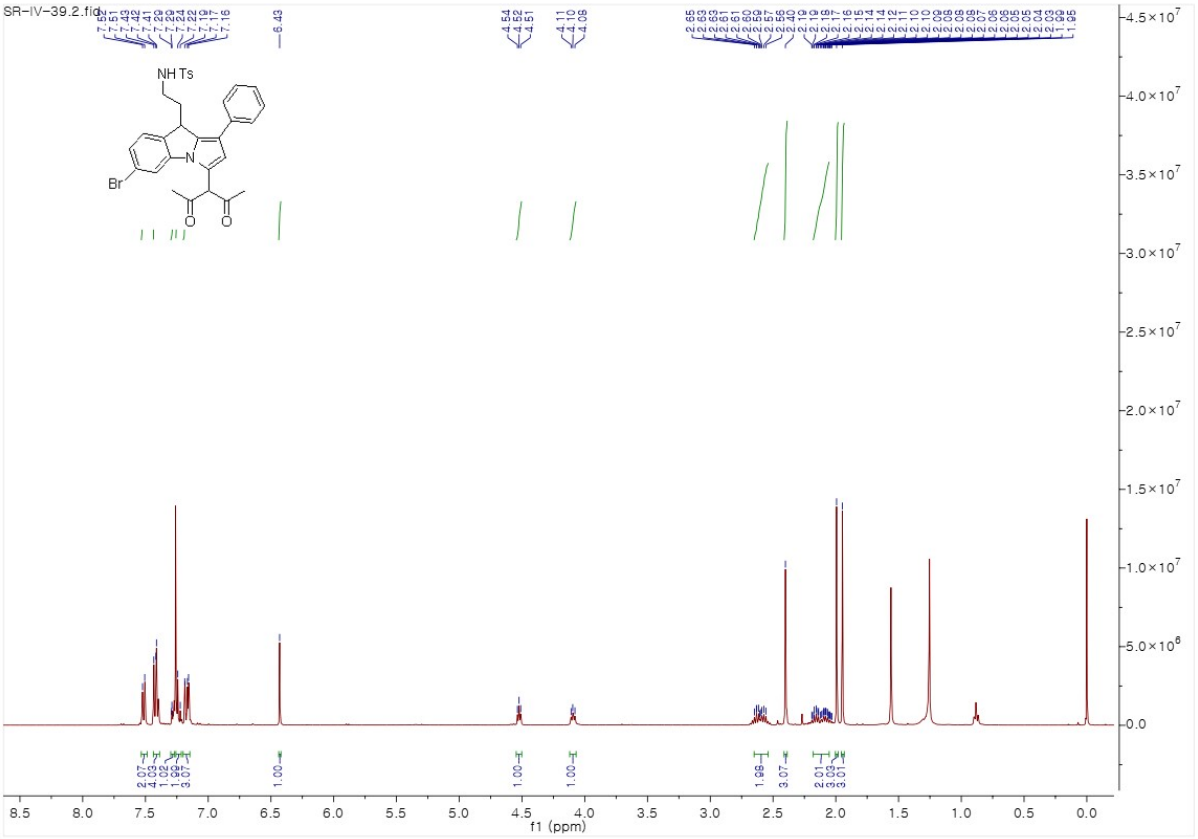
^{13}C NMR spectra of compound 3q (101MHz, $CDCl_3$)



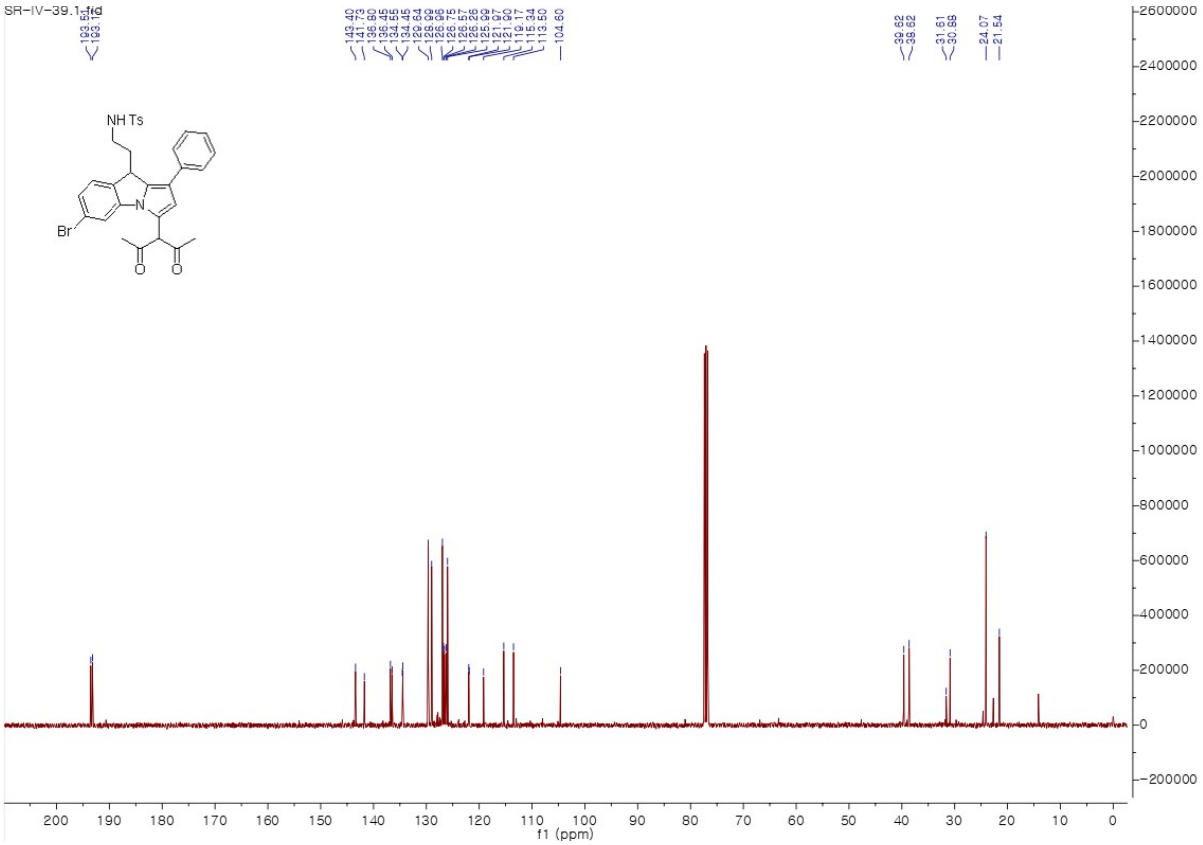
^{1}H NMR spectra of compound 3r (400MHz, $CDCl_3$)



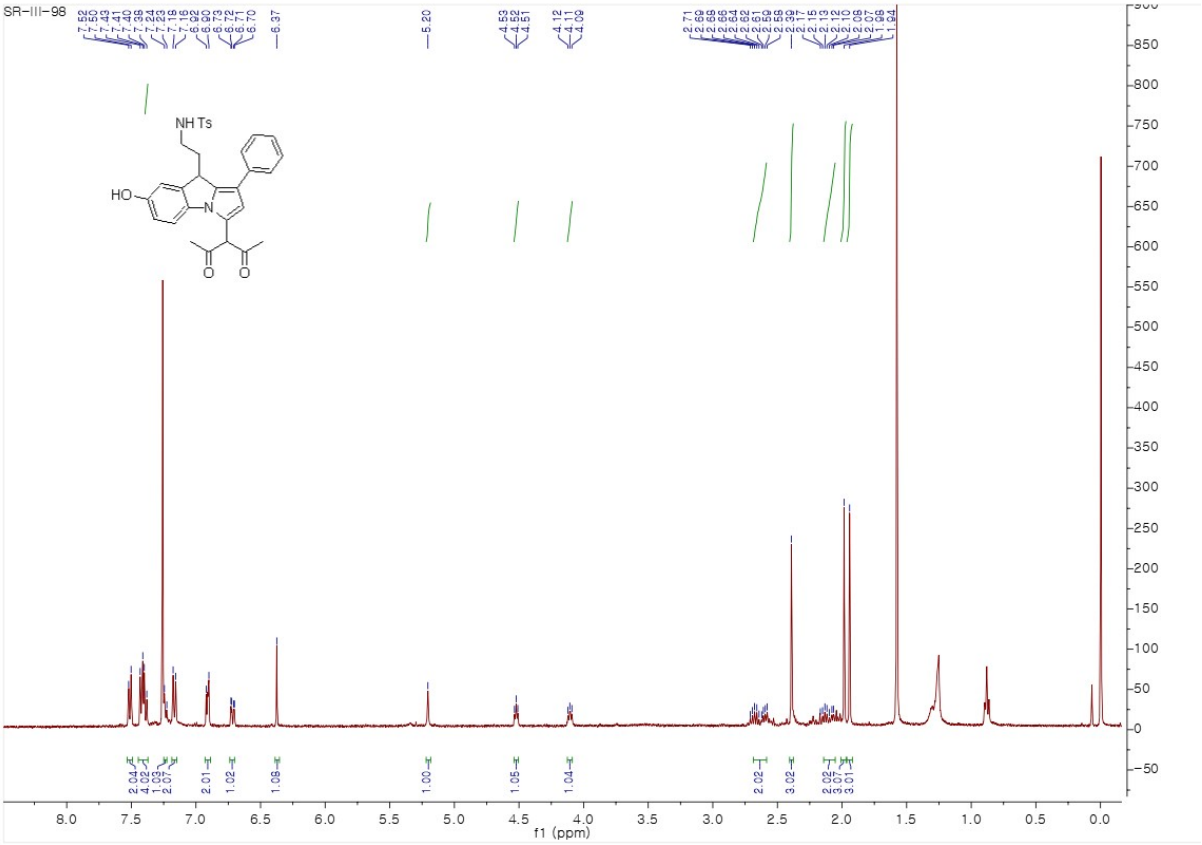
^{13}C NMR spectra of compound 3r (101MHz, $CDCl_3$)



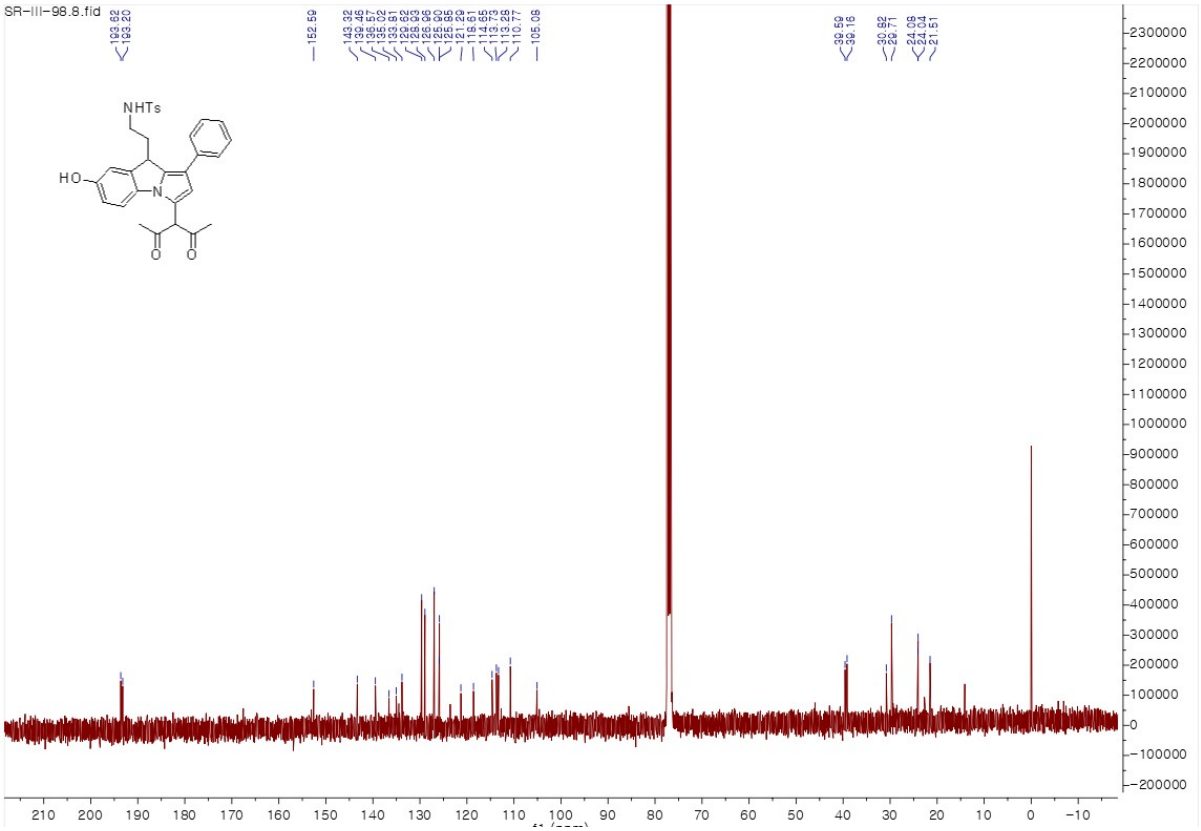
^{1}H NMR spectra of compound 3s (400MHz, $CDCl_3$)



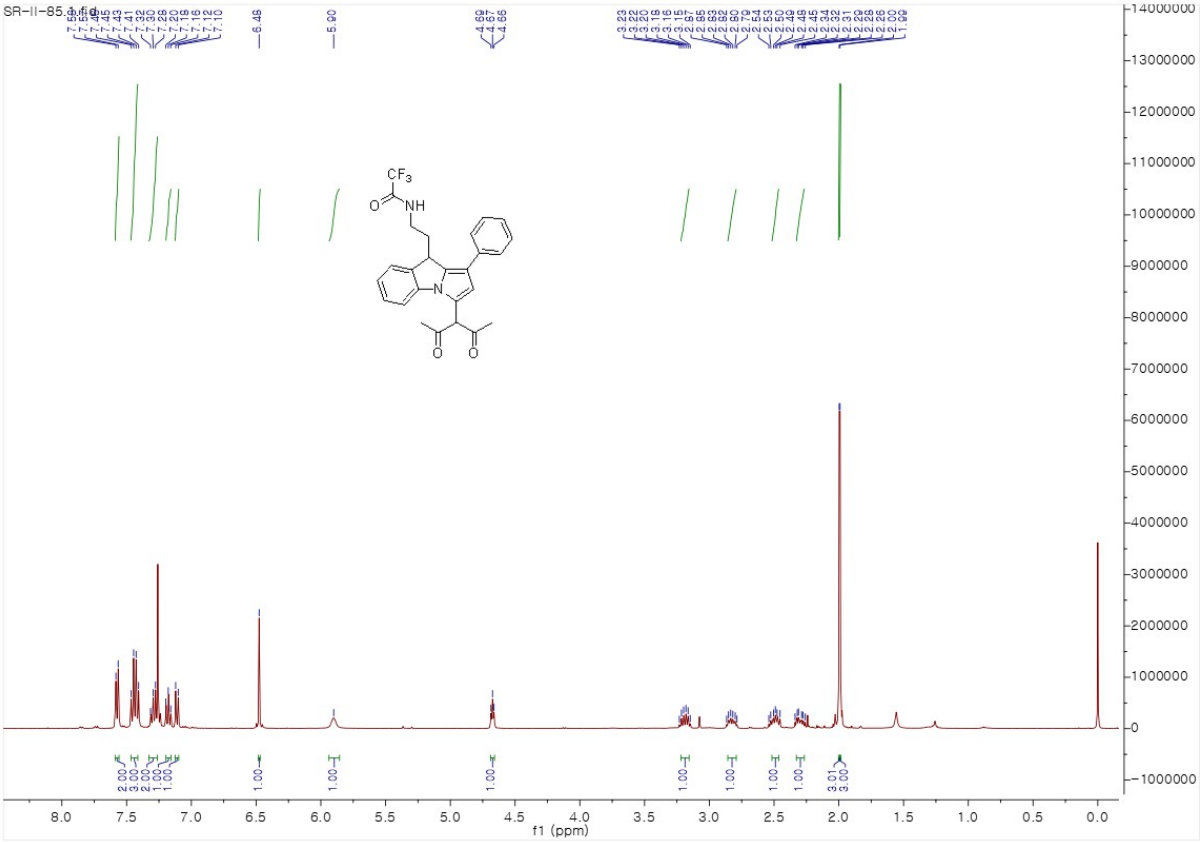
^{13}C NMR spectra of compound 3s (126MHz, $CDCl_3$)



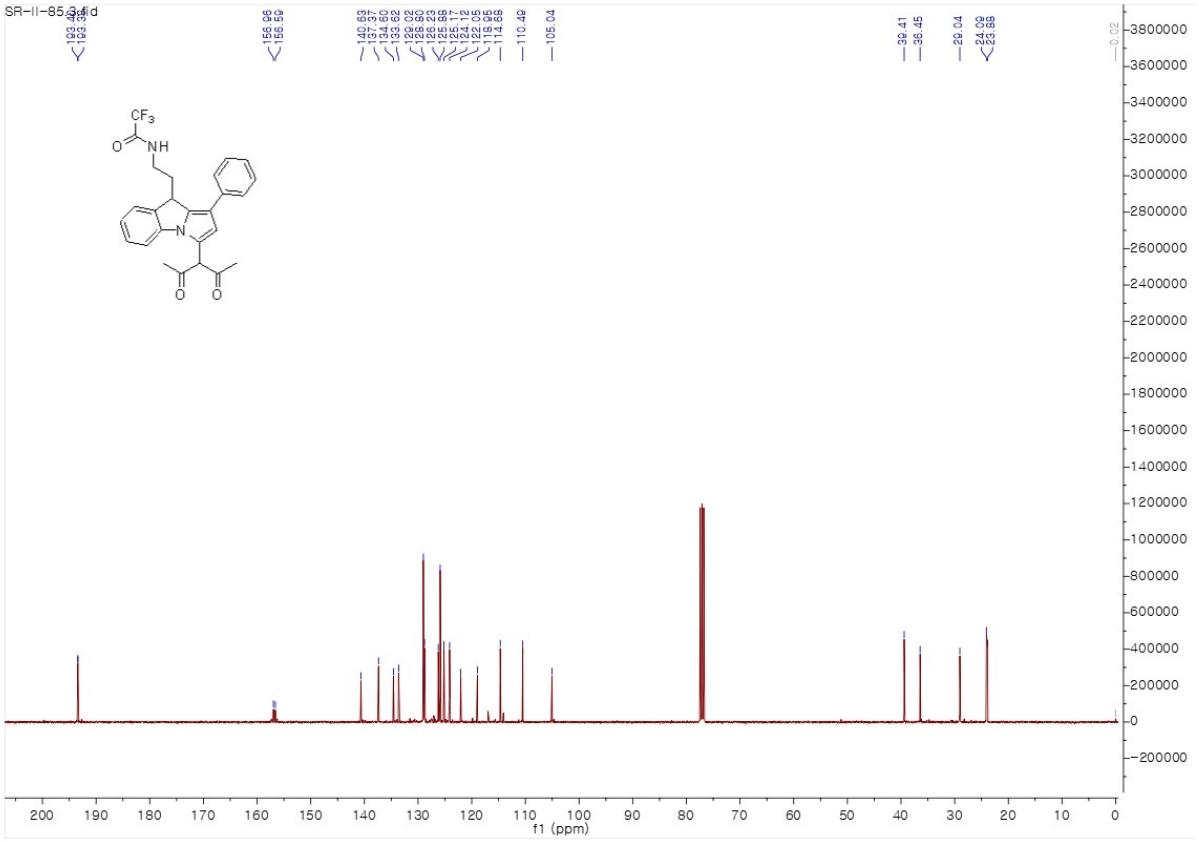
^{1}H NMR spectra of compound 3t (400MHz, $CDCl_3$)



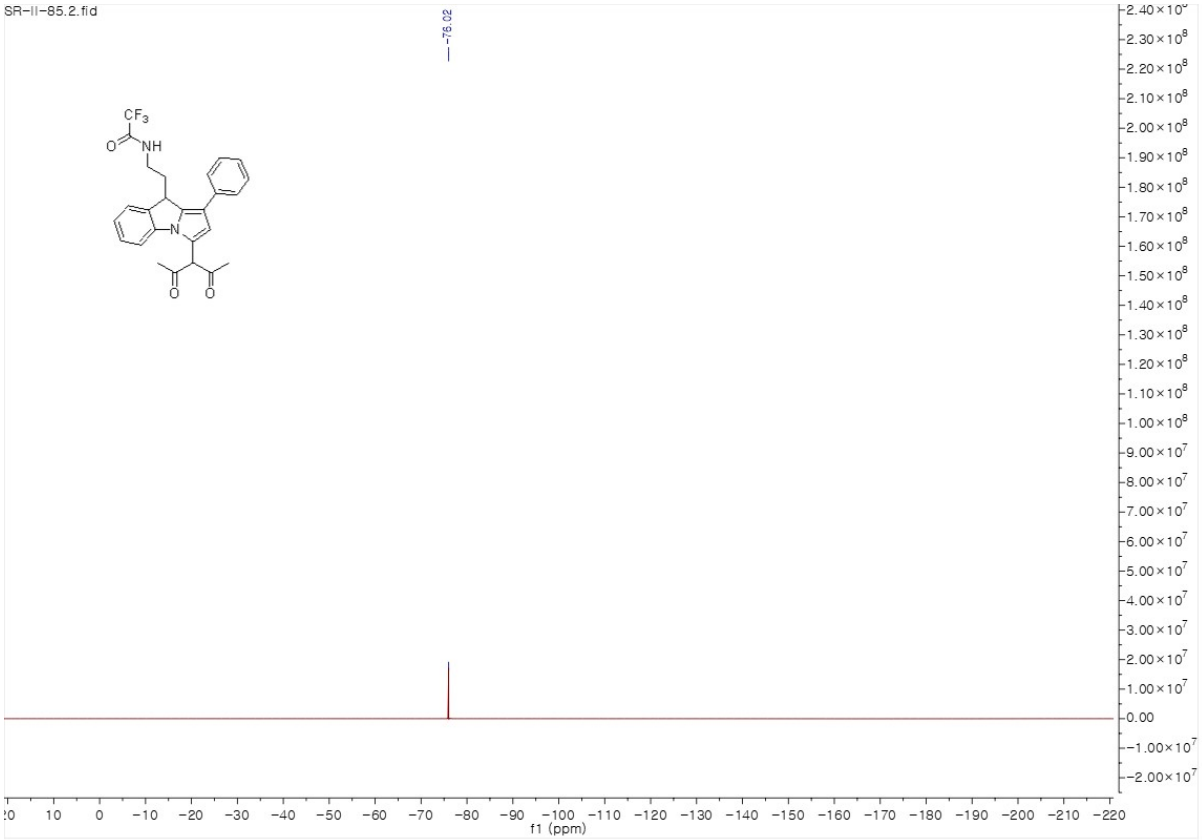
^{13}C NMR spectra of compound 3t (126MHz, $CDCl_3$)



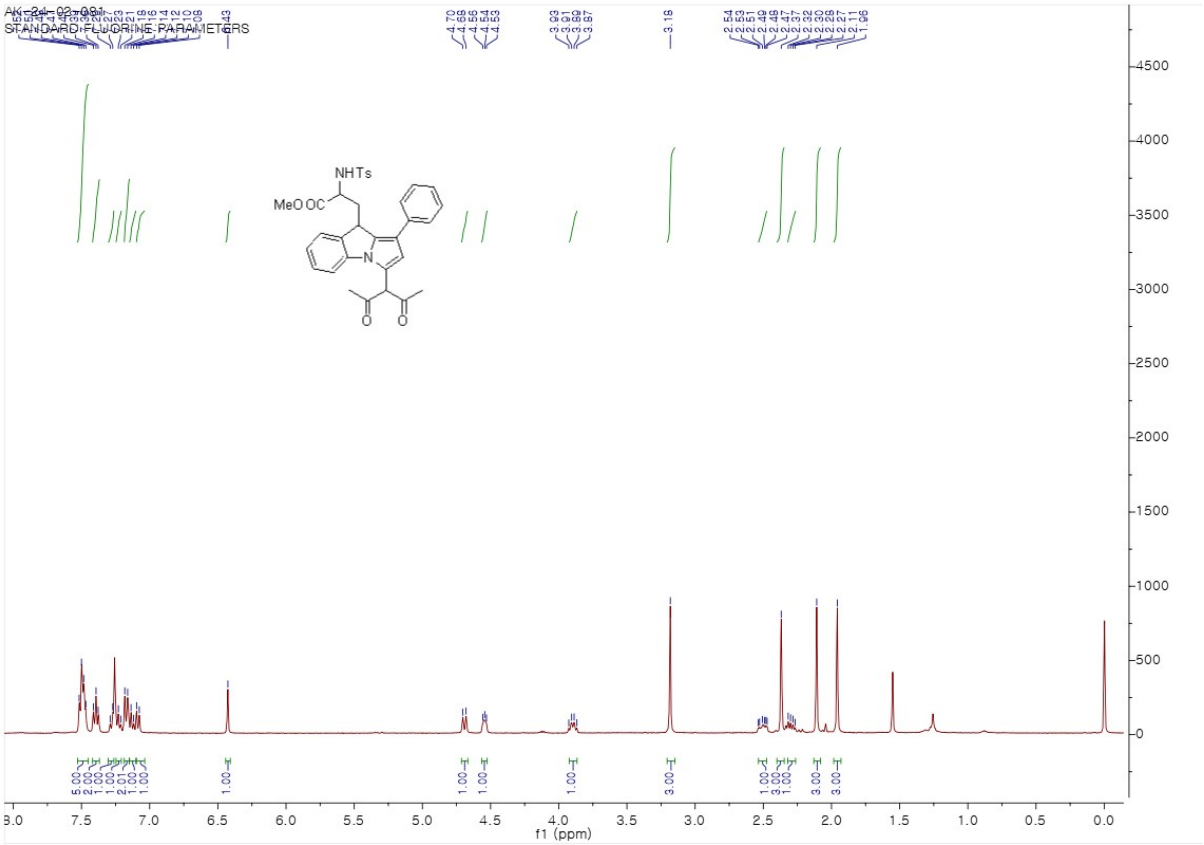
^{1}H NMR spectra of compound 3u (400MHz, $CDCl_3$)



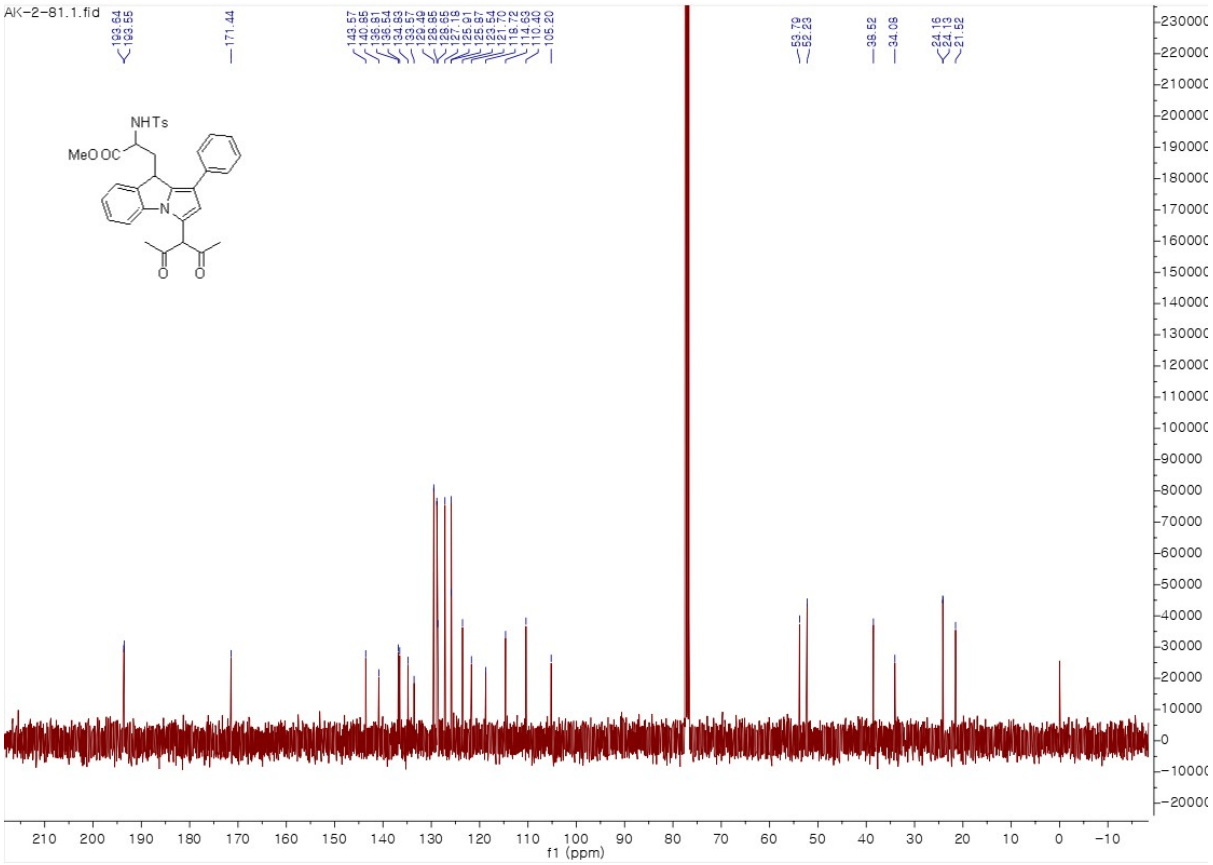
^{13}C NMR spectra of compound 3u (126MHz, $CDCl_3$)



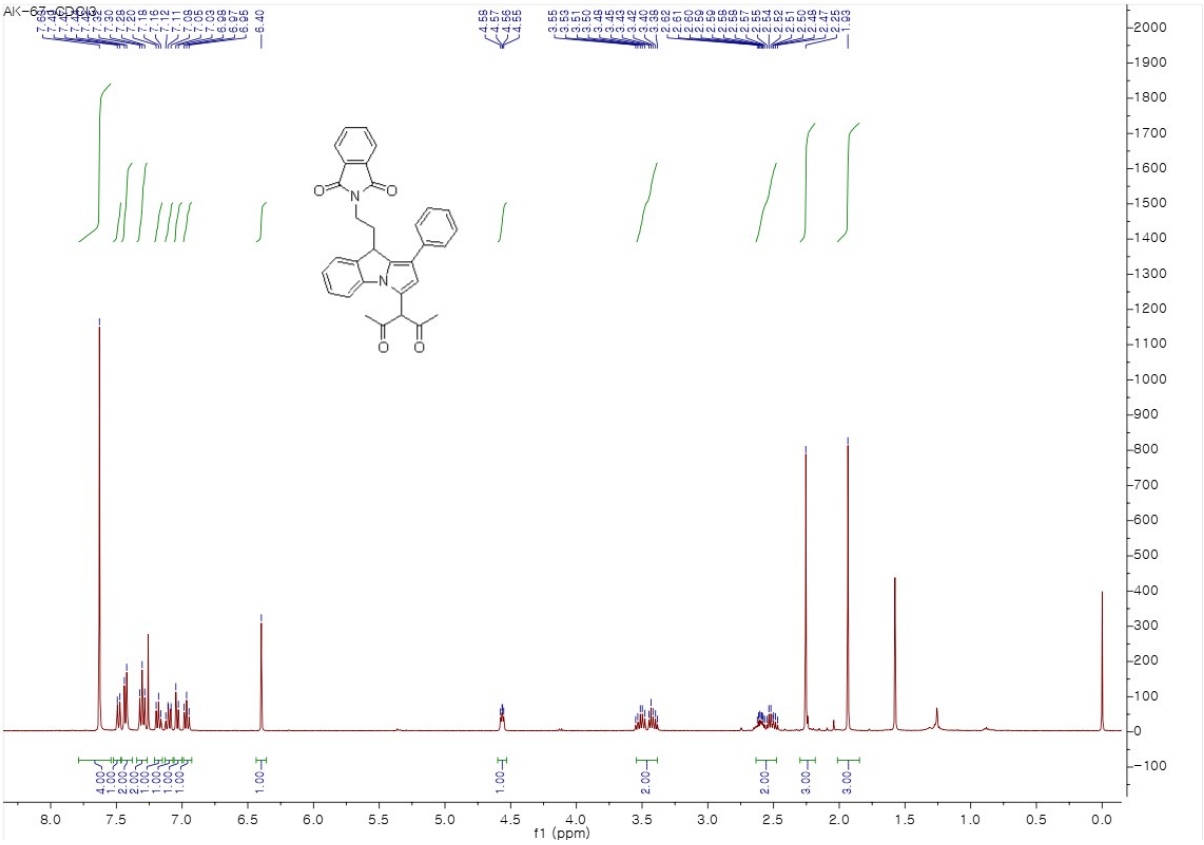
^{19}F NMR spectra of compound 3u (400MHz, $CDCl_3$)



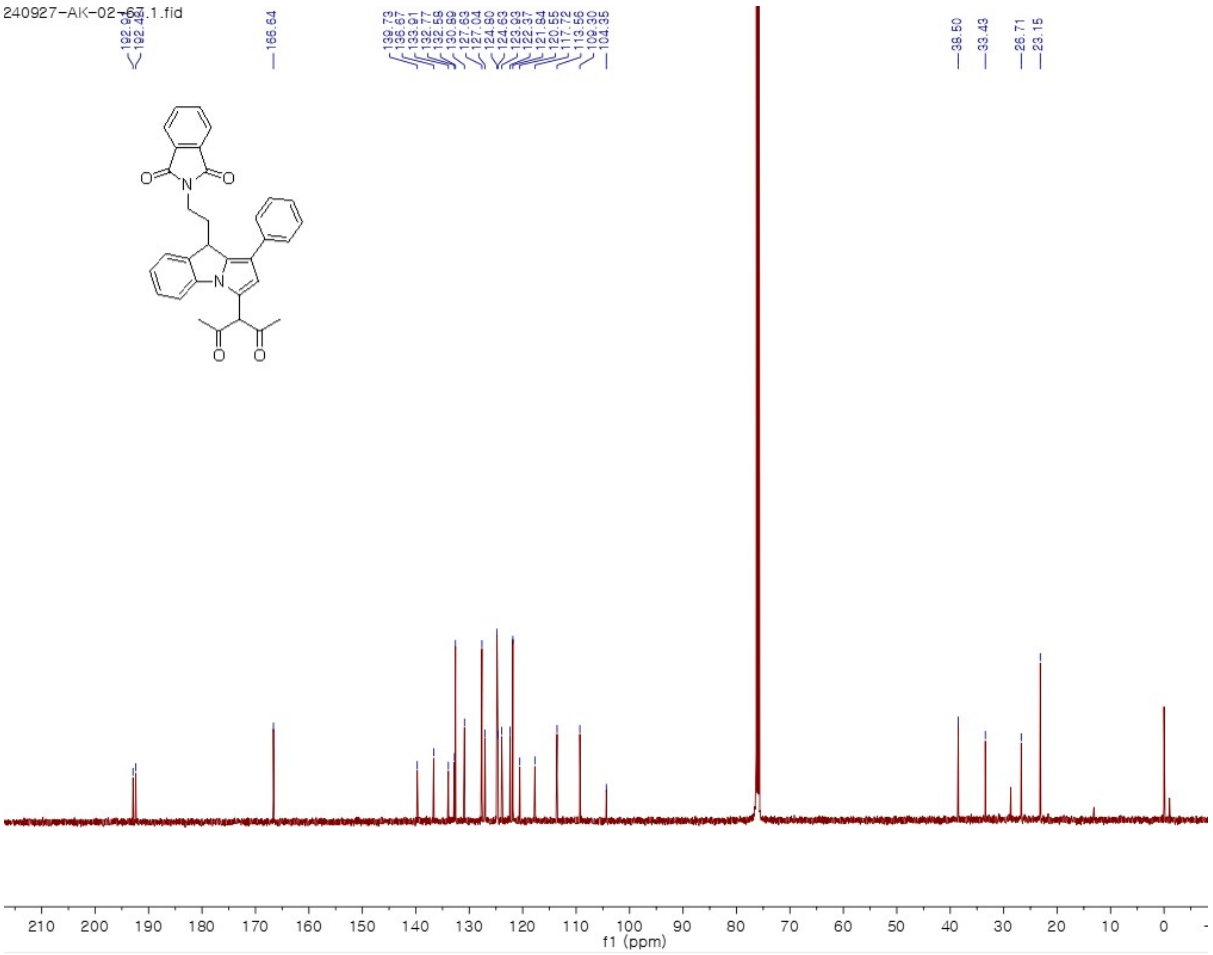
^{1}H NMR spectra of compound 3v (400MHz, $CDCl_3$)



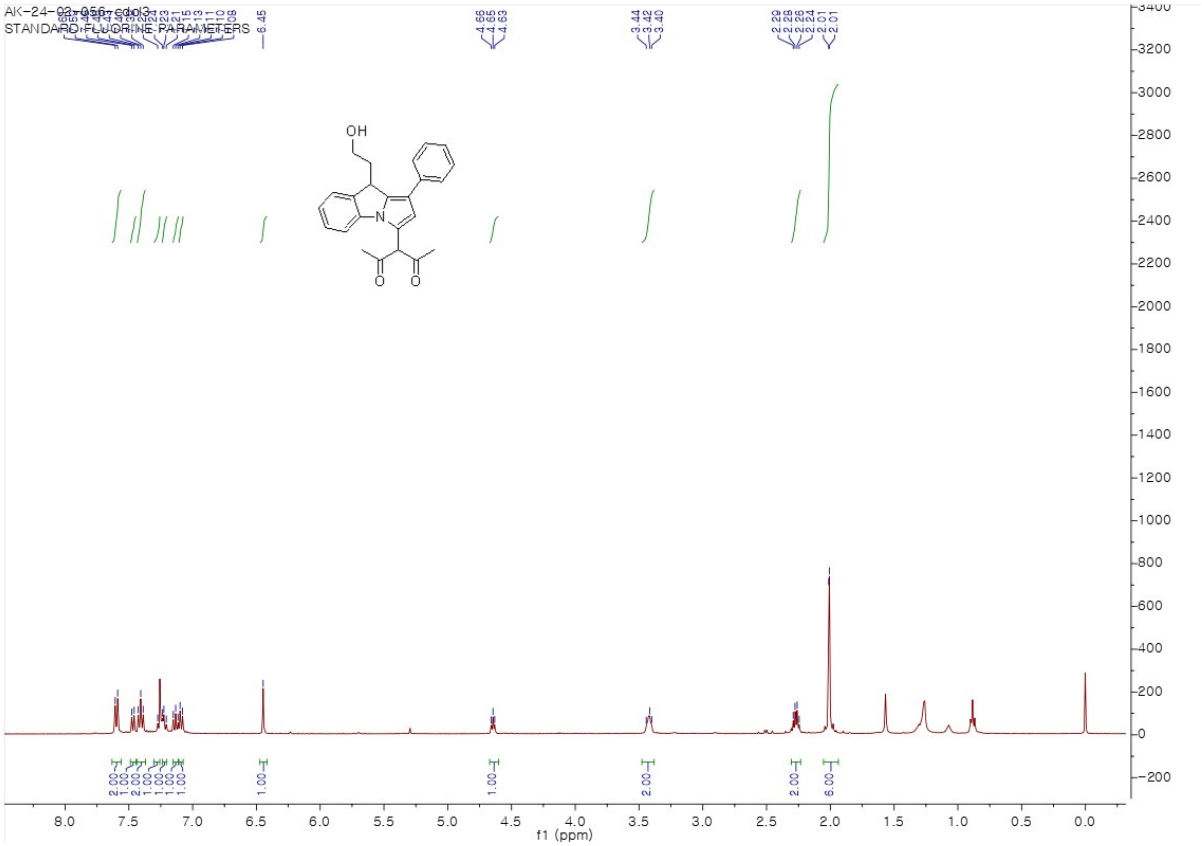
^{13}C NMR spectra of compound 3v (101MHz, $CDCl_3$)



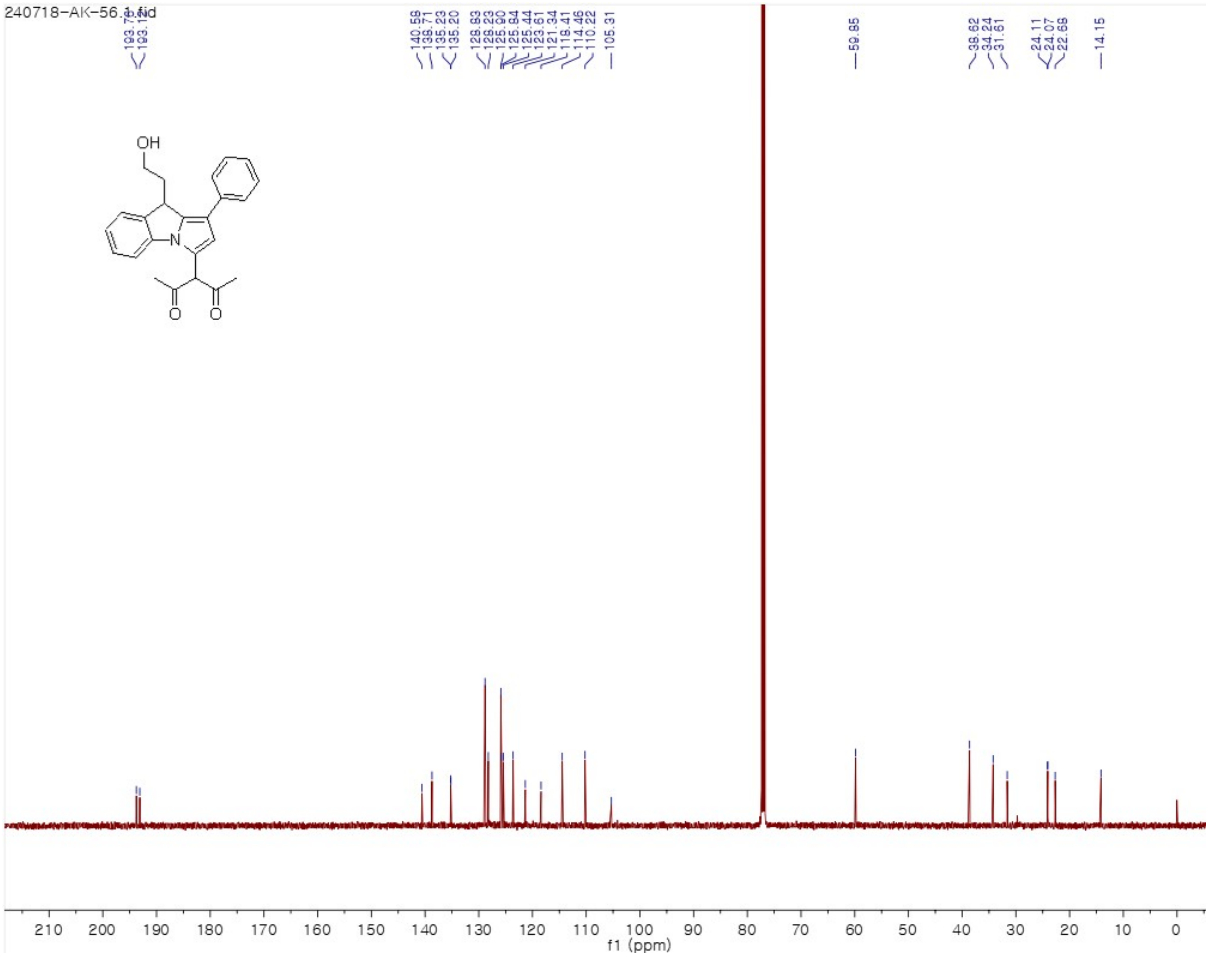
^{1}H NMR spectra of compound 3w (400MHz, $CDCl_3$)



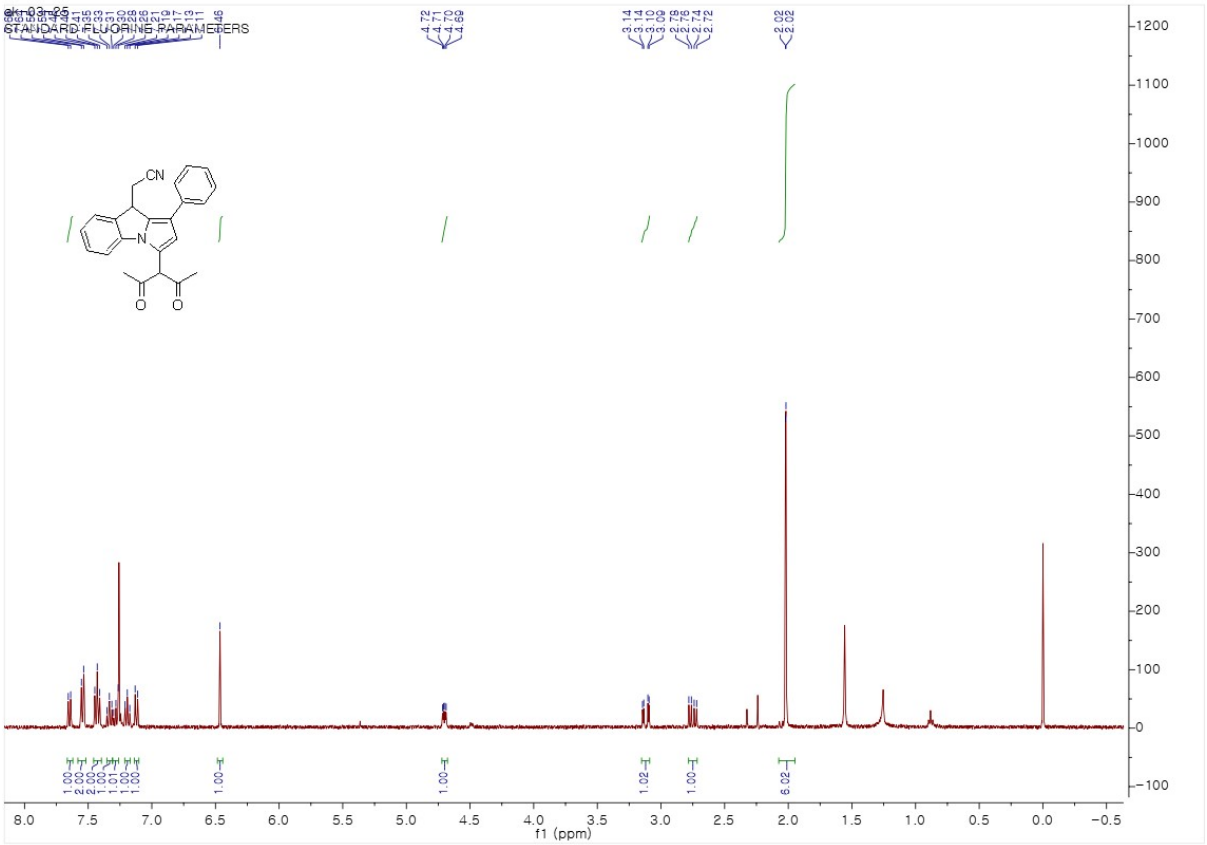
^{13}C NMR spectra of compound 3w (126MHz, $CDCl_3$)



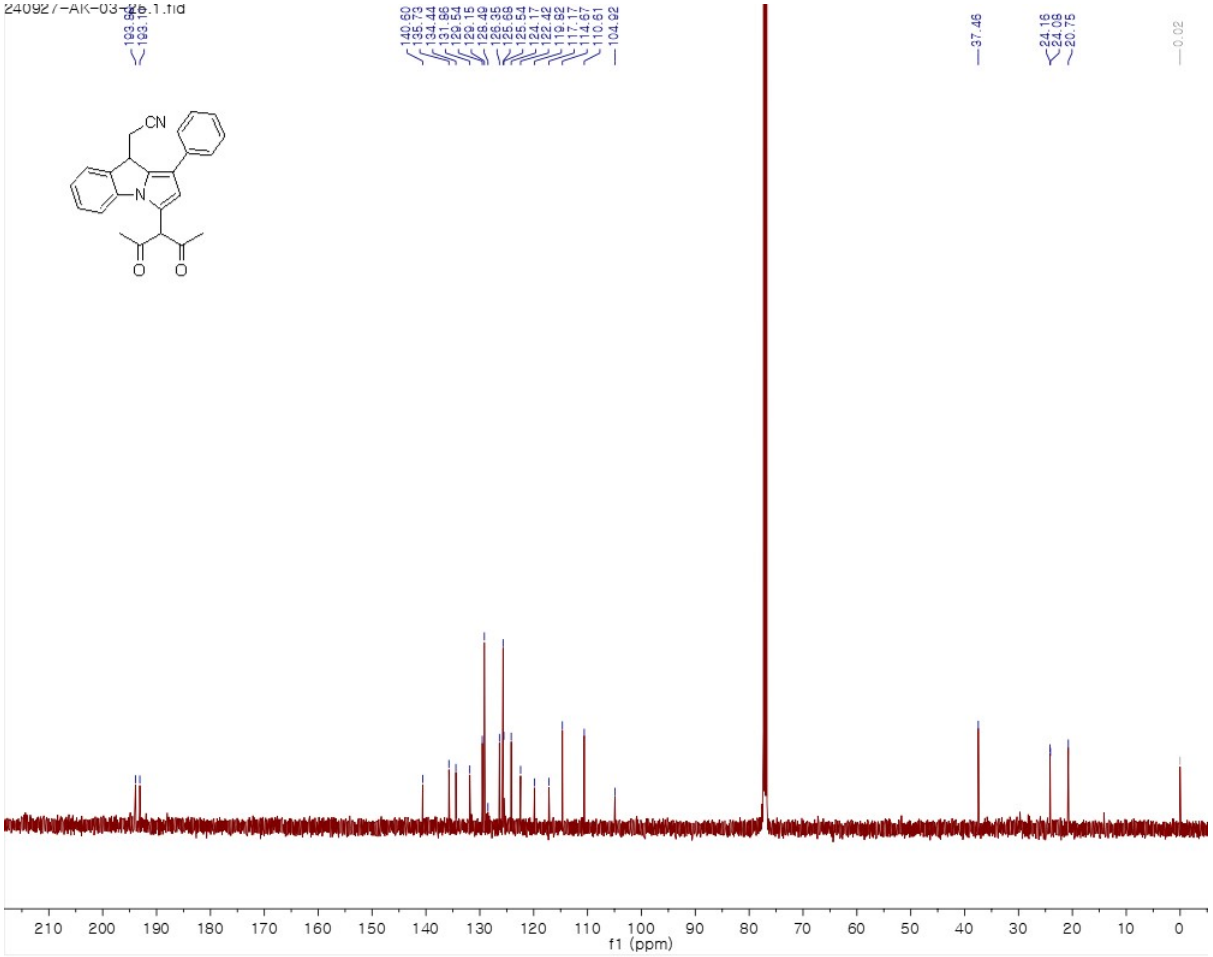
^{1}H NMR spectra of compound 3x (400MHz, $CDCl_3$)



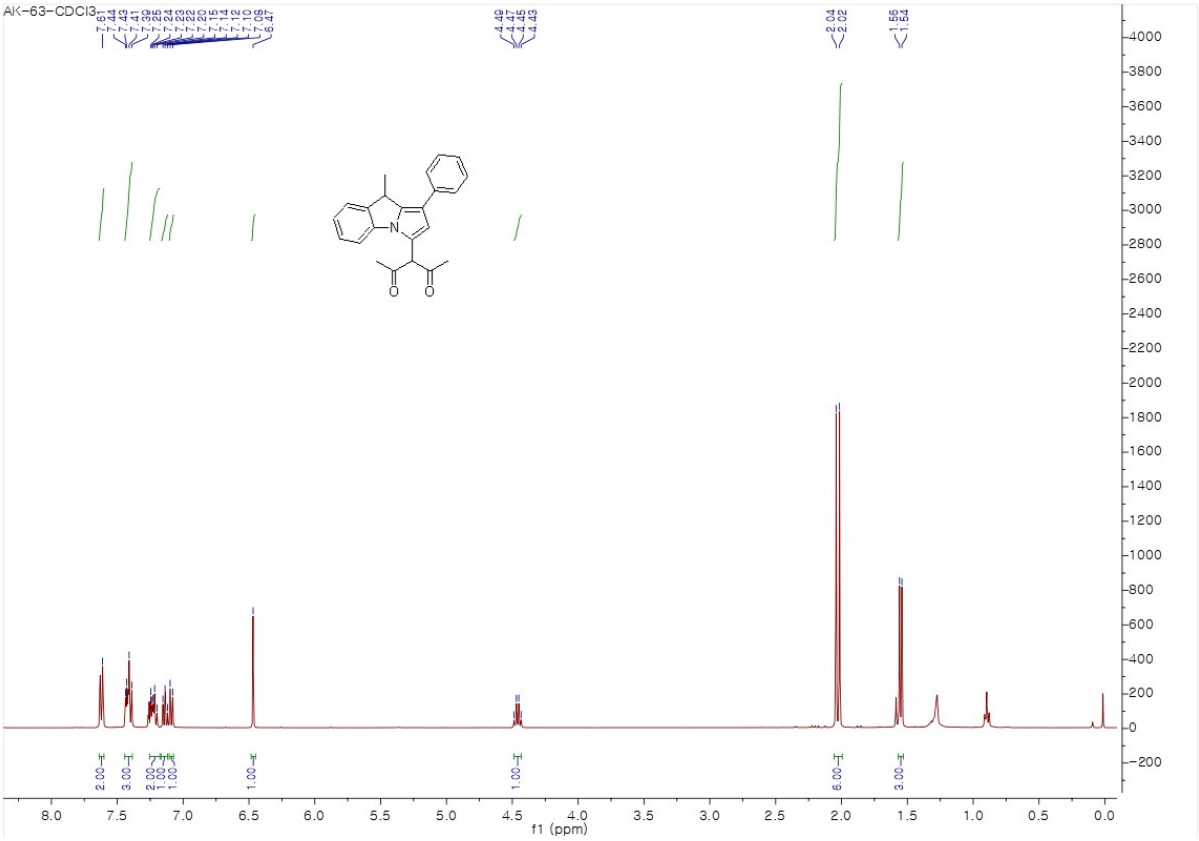
^{13}C NMR spectra of compound 3x (126MHz, $CDCl_3$)



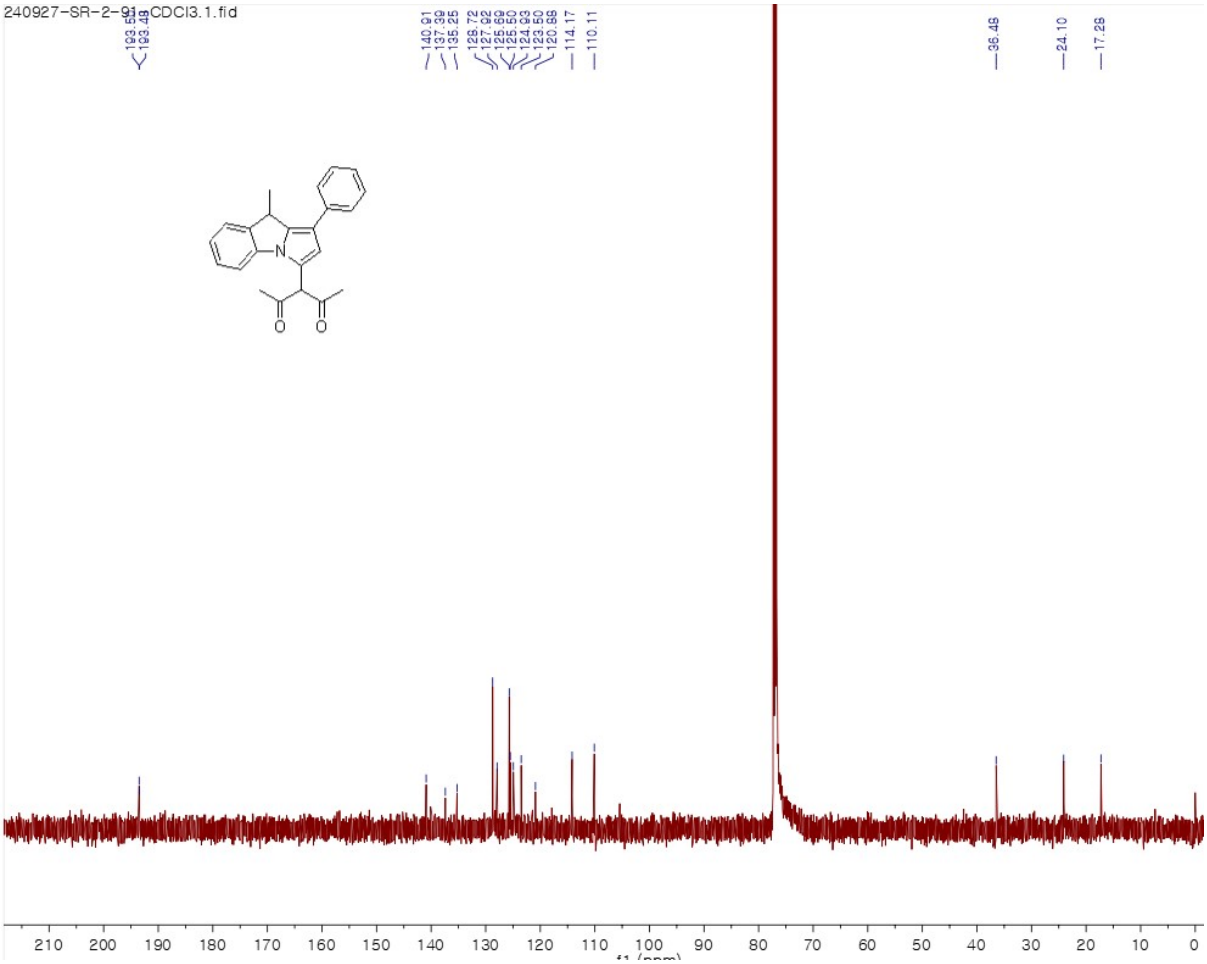
^{1}H NMR spectra of compound 3y (400MHz, $CDCl_3$)



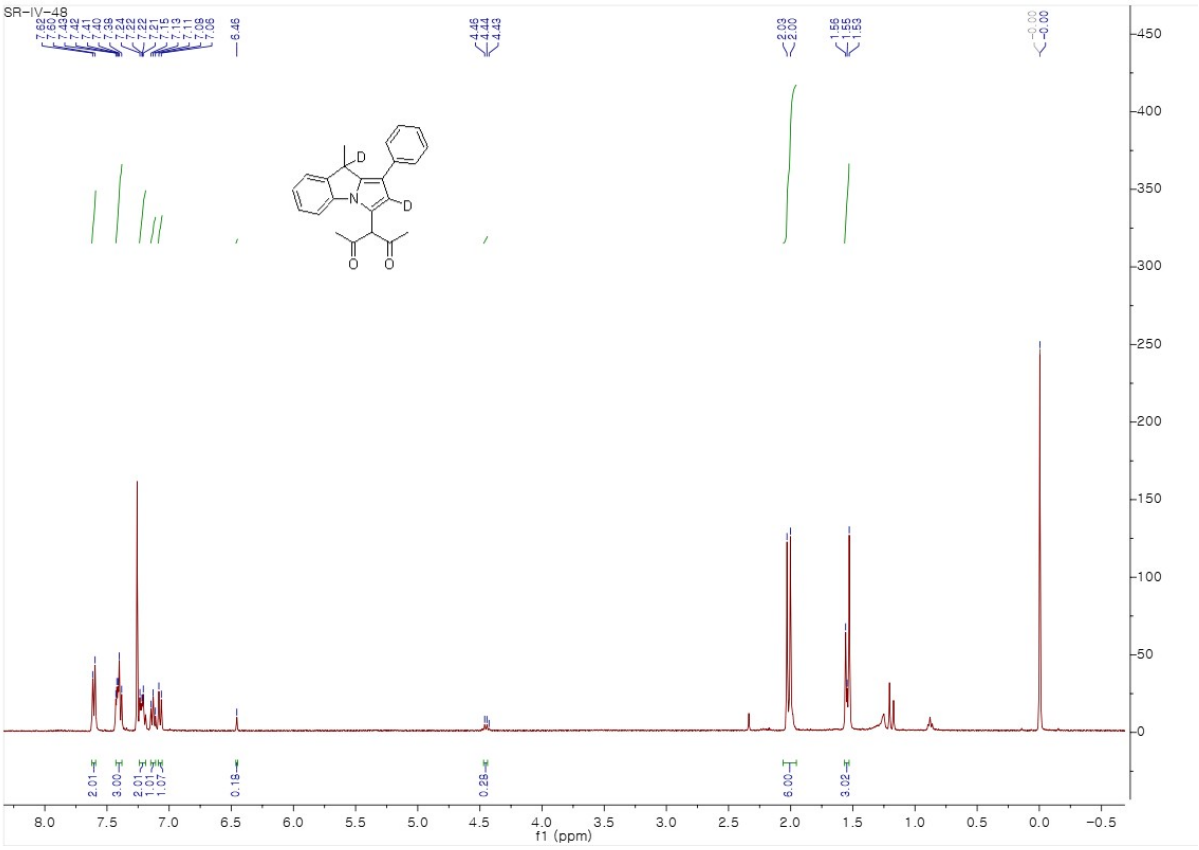
^{13}C NMR spectra of compound 3y (126MHz, $CDCl_3$)



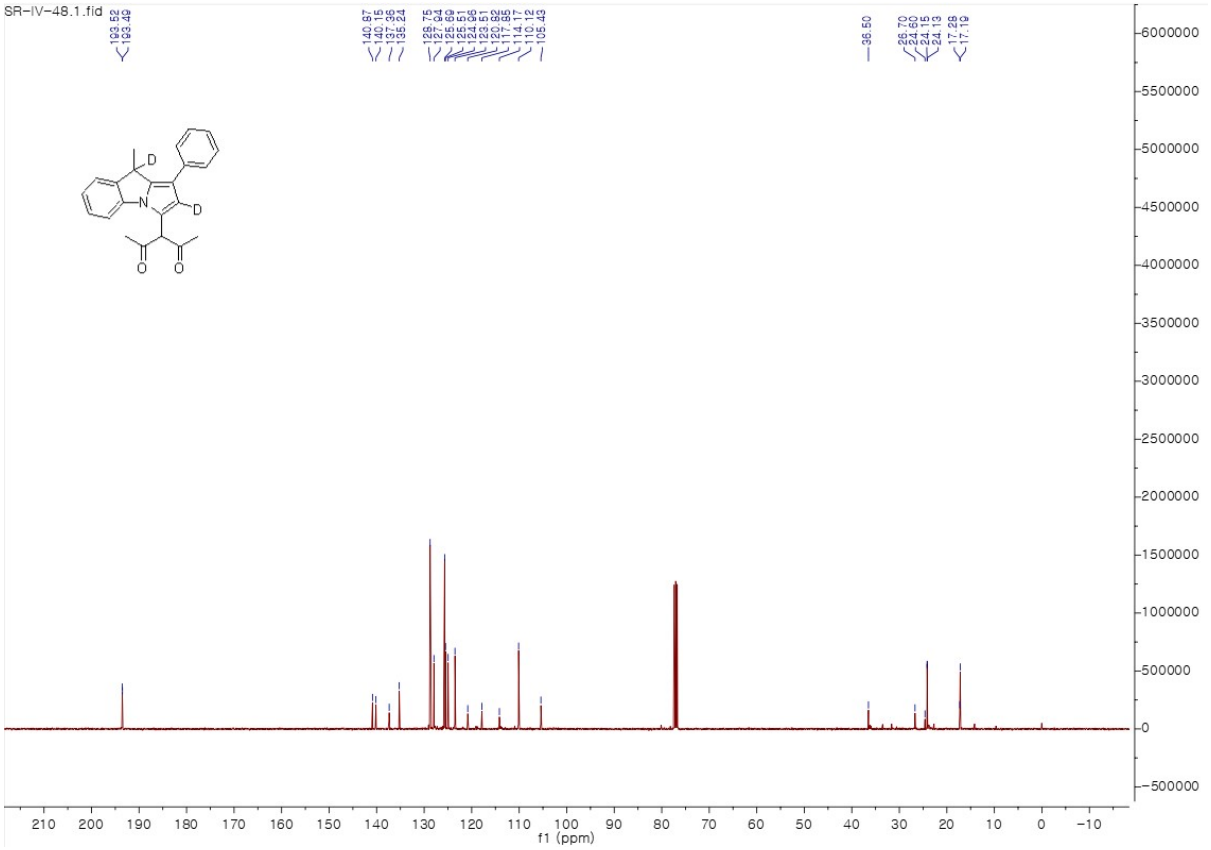
^{1}H NMR spectra of compound 3z (400MHz, $CDCl_3$)



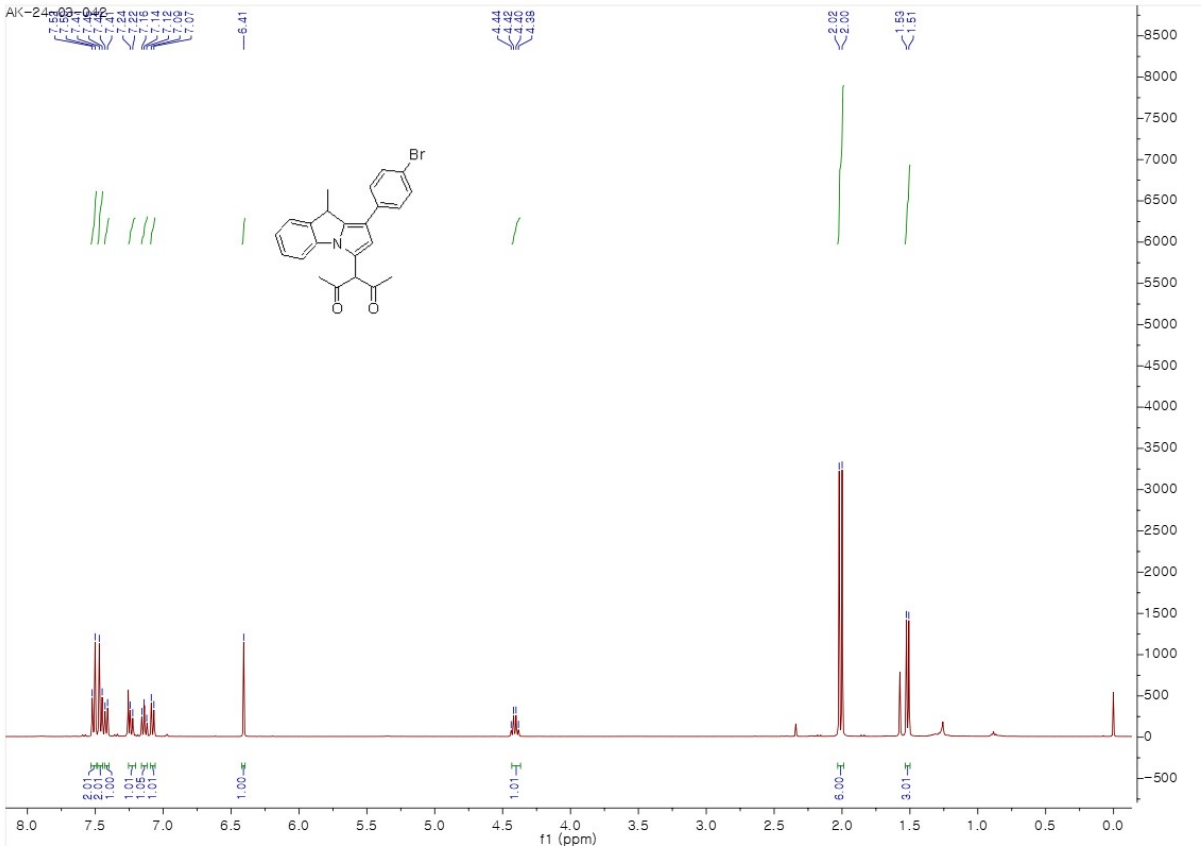
^{1}H NMR spectra of compound 3z (126MHz, $CDCl_3$)



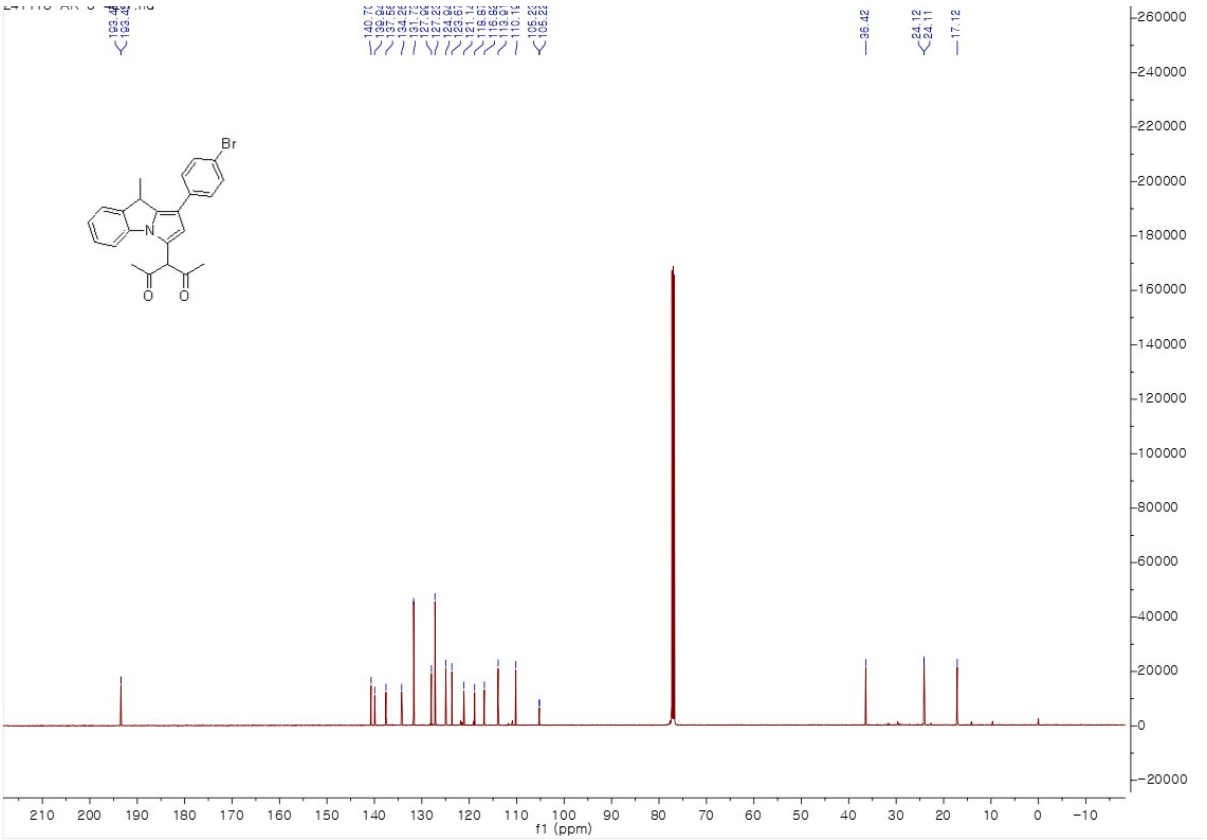
^{1}H NMR spectra of compound [D]-3z (400MHz, $CDCl_3$)



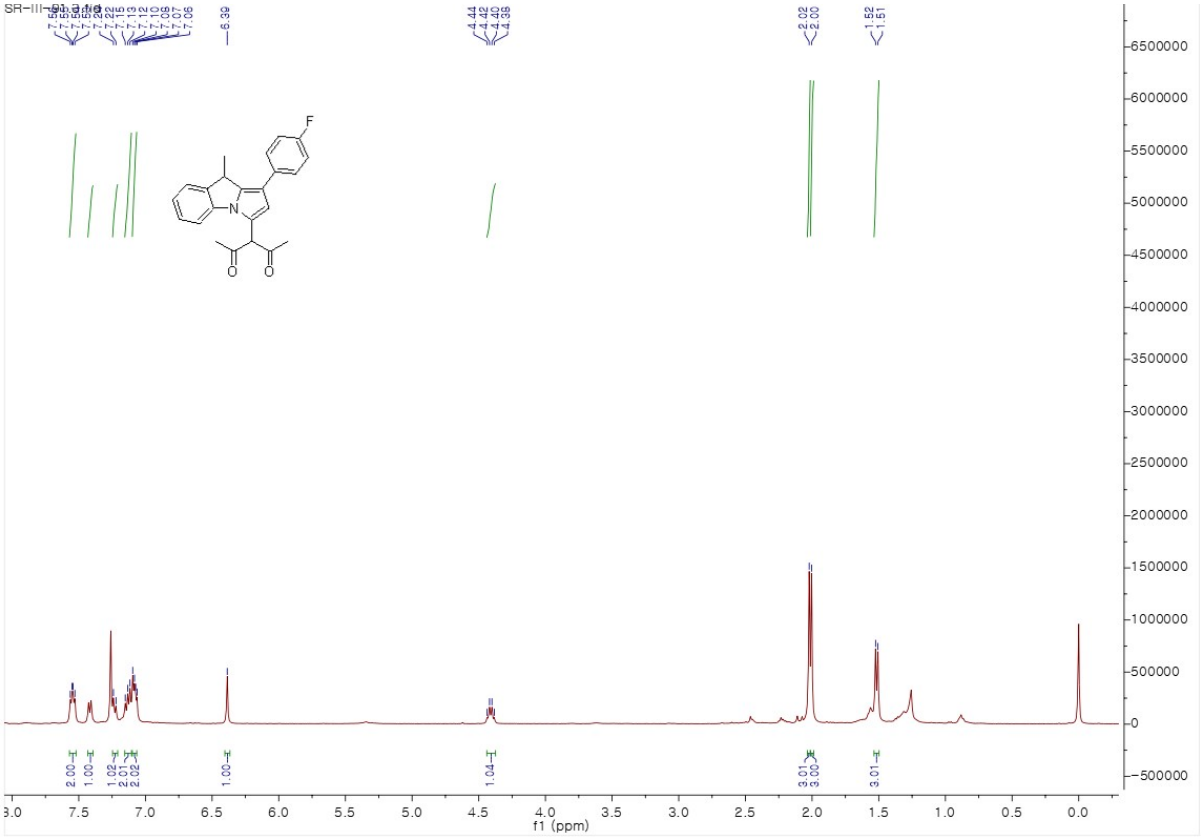
^{13}C NMR spectra of compound [D]-3z (101MHz, $CDCl_3$)



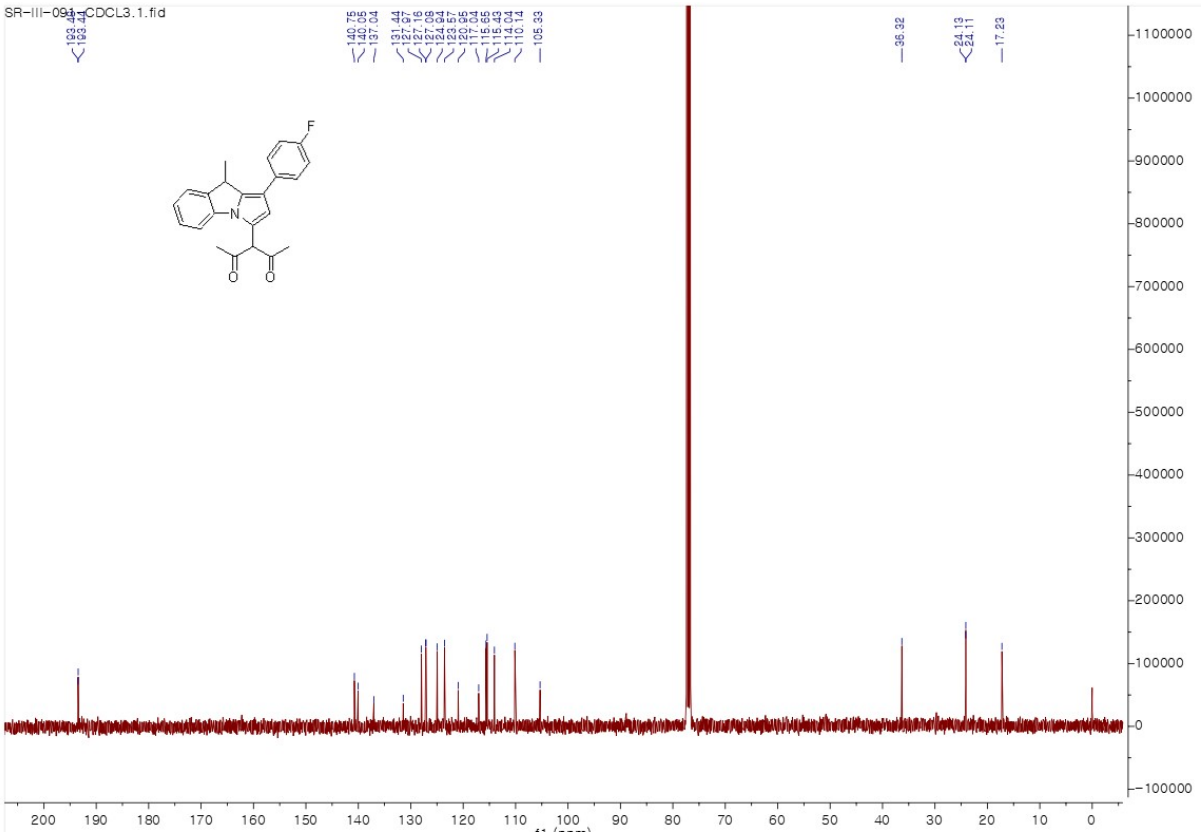
^{1}H NMR spectra of compound 3aa (400MHz, $CDCl_3$)



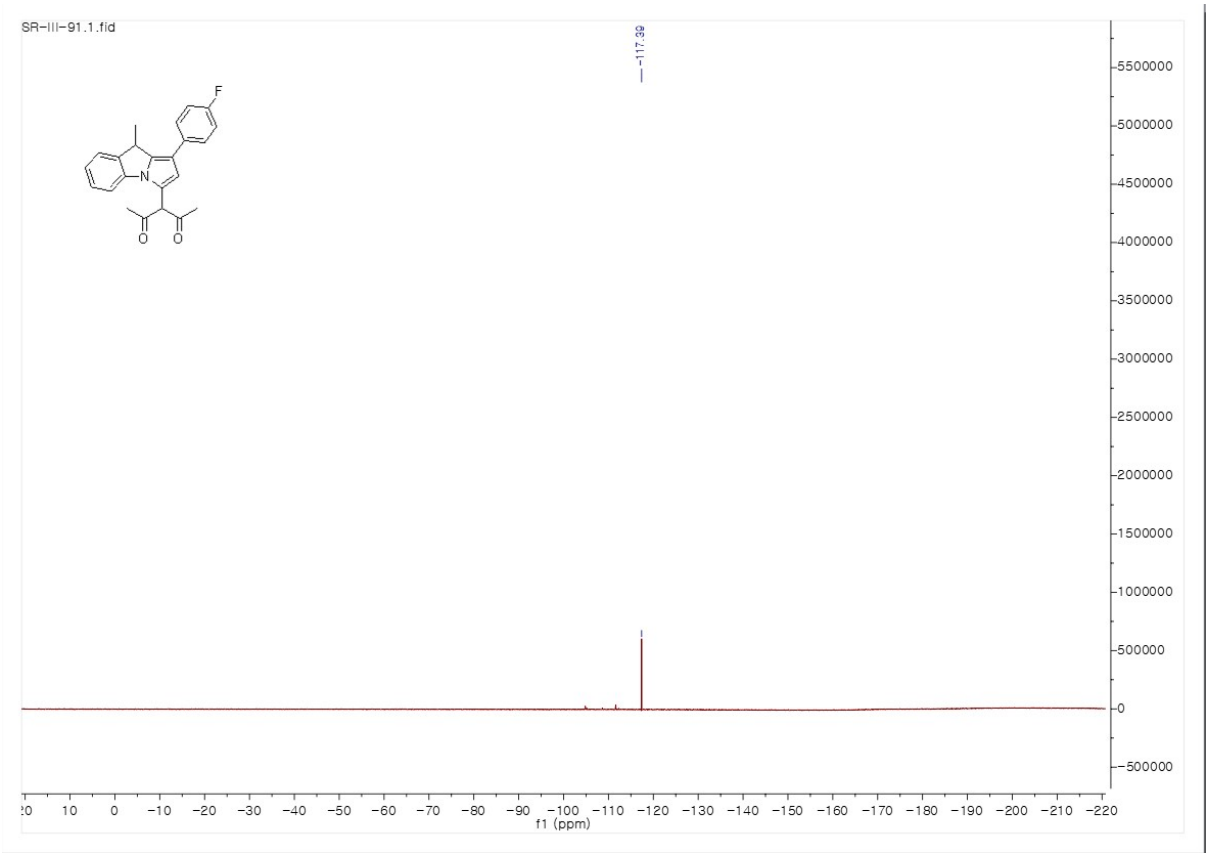
^{13}C NMR spectra of compound 3aa (400MHz, $CDCl_3$)



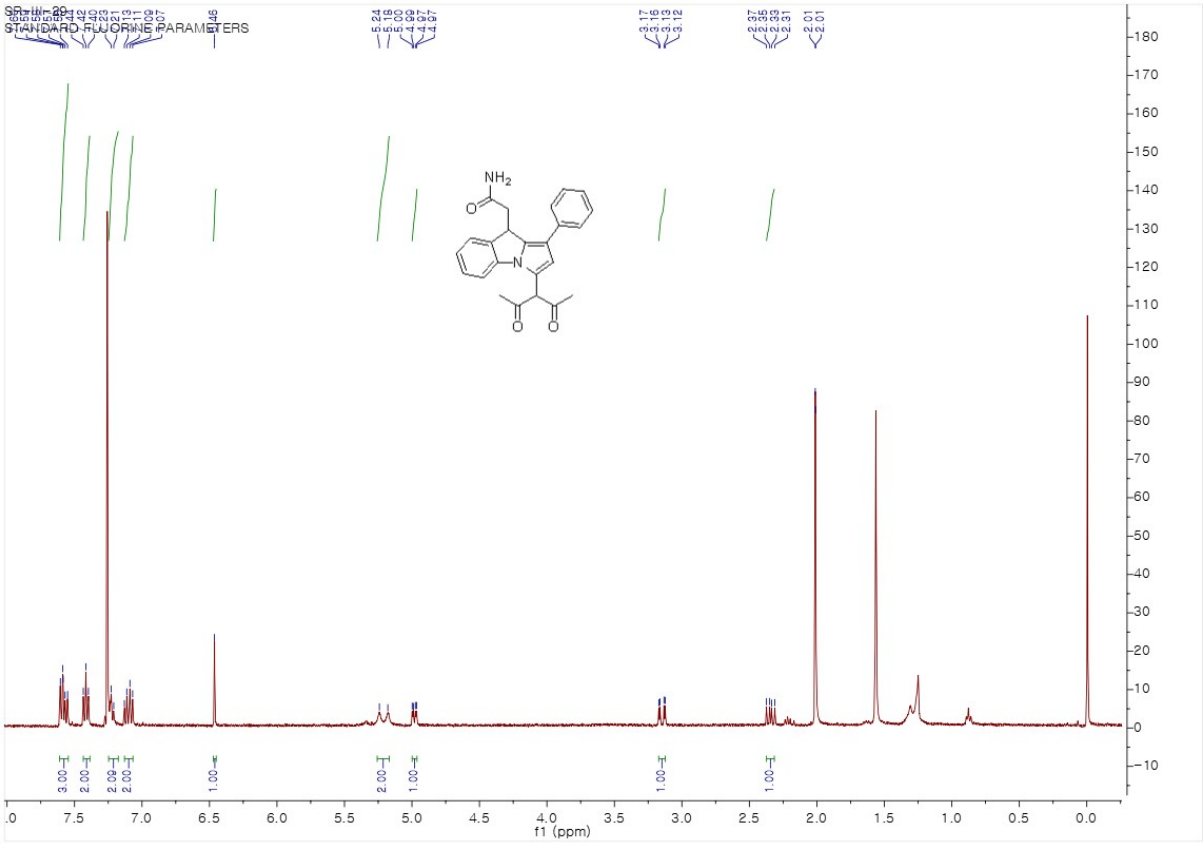
^{1}H NMR spectra of compound 3ab (400MHz, $CDCl_3$)



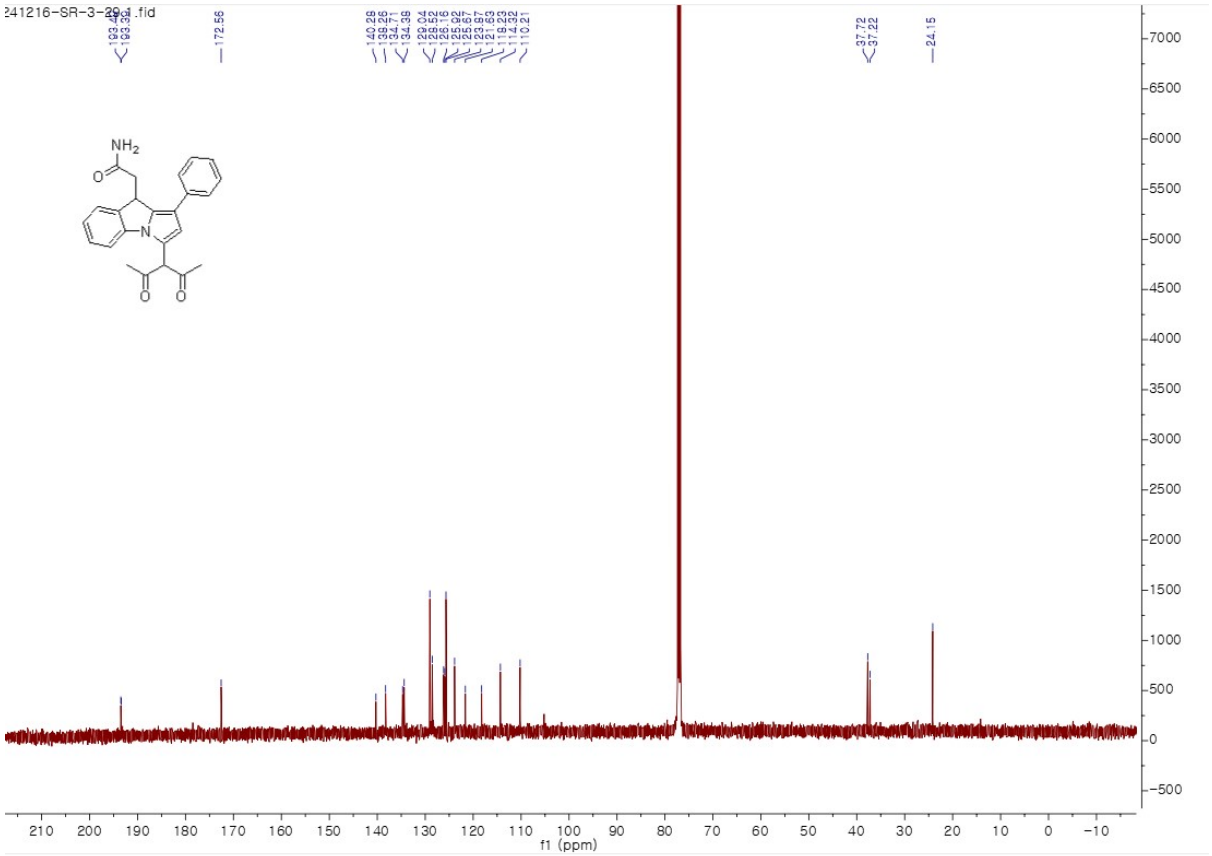
^{13}C NMR spectra of compound 3ab (101MHz, $CDCl_3$)



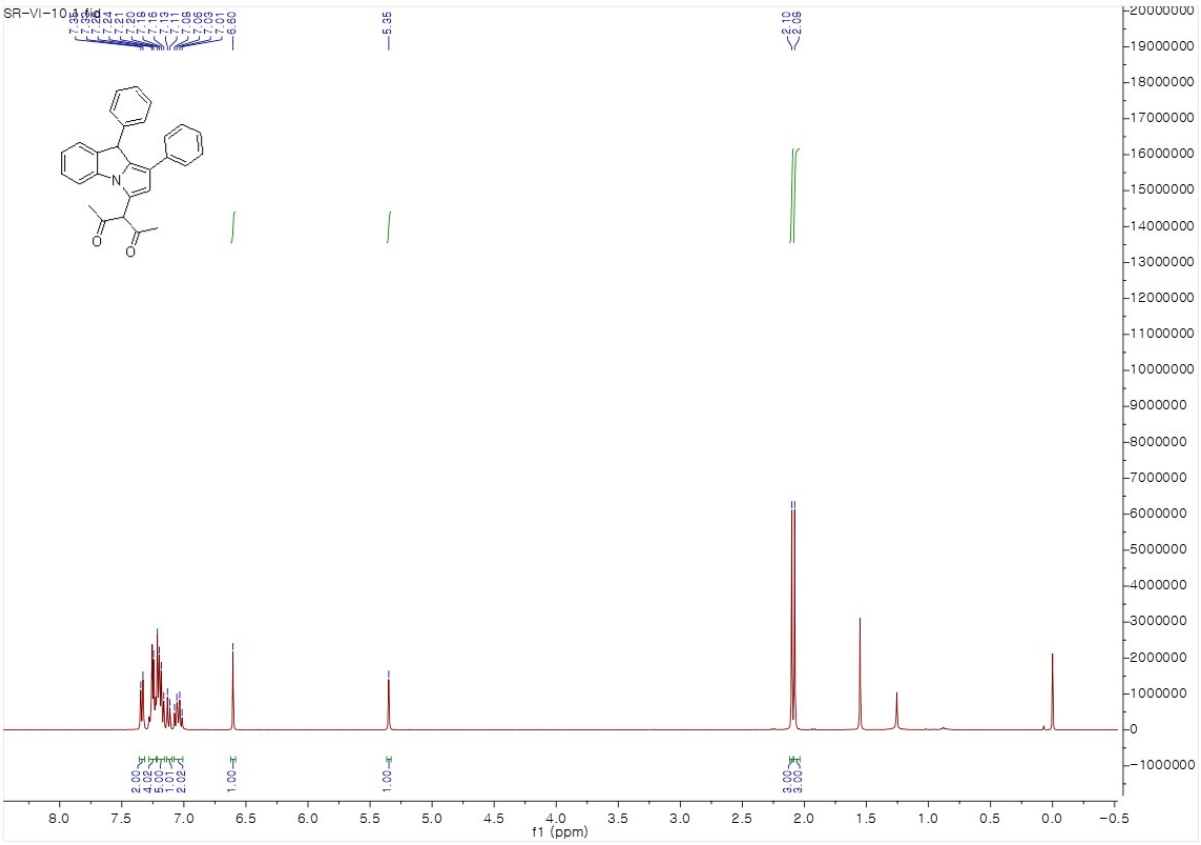
^{19}F NMR spectra of compound 3ab (400MHz, $CDCl_3$)



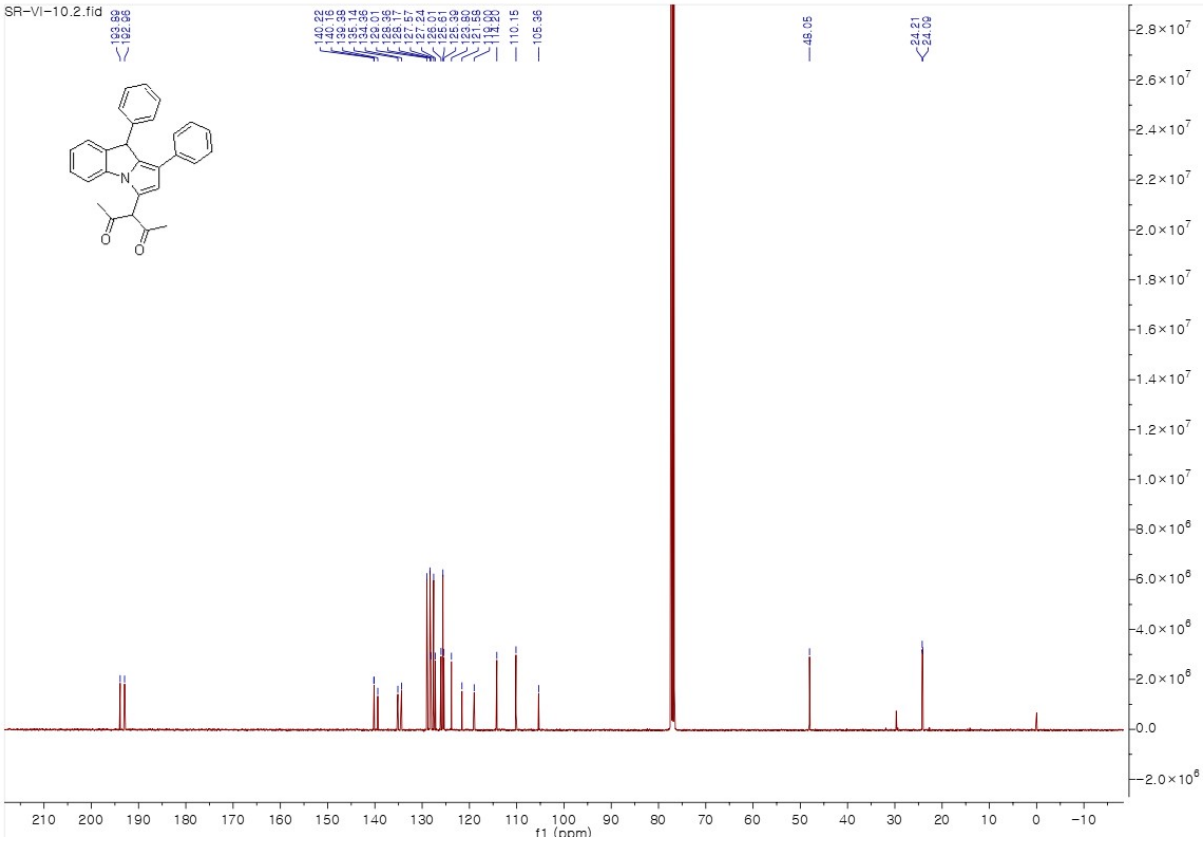
^{1}H NMR spectra of compound 3ac (400MHz, $CDCl_3$)



^{13}C NMR spectra of compound 3ac (126MHz, $CDCl_3$)

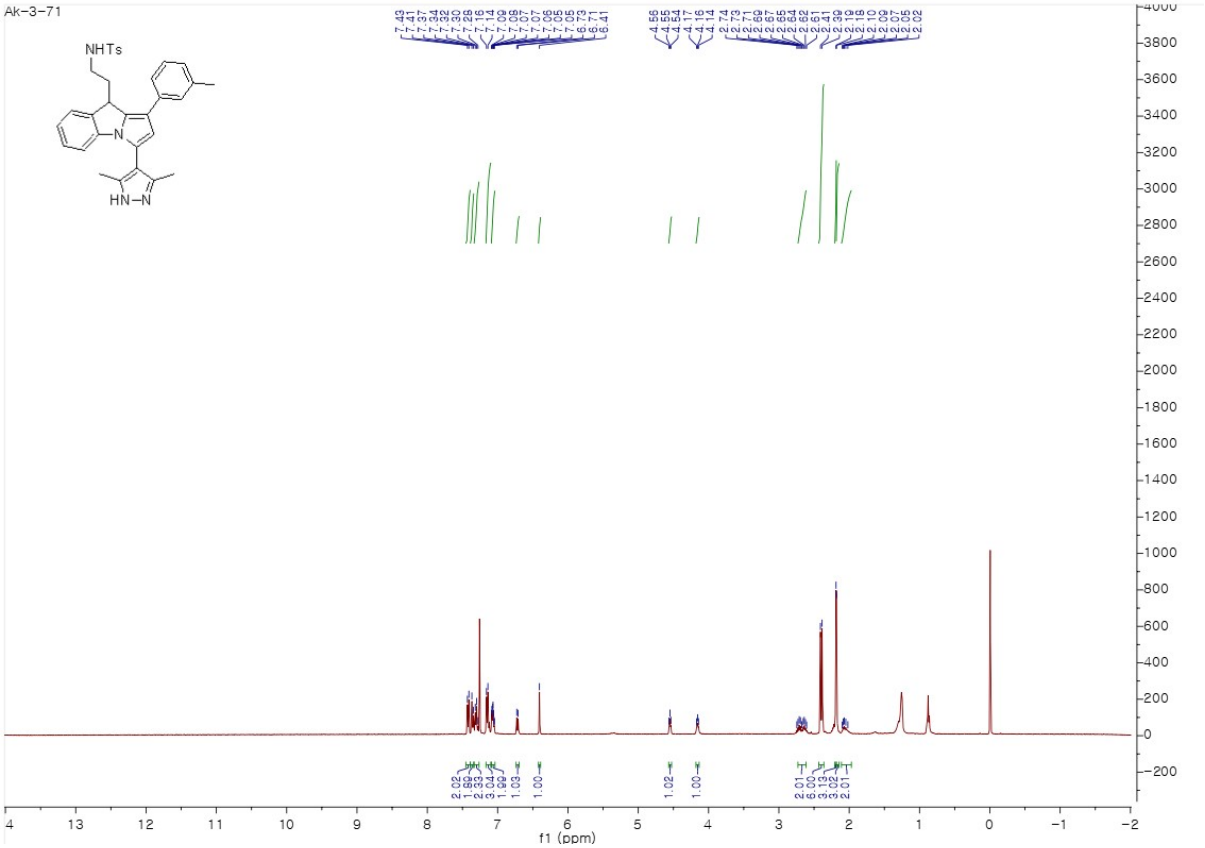


^{1}H NMR spectra of compound 3ad (400MHz, $CDCl_3$)

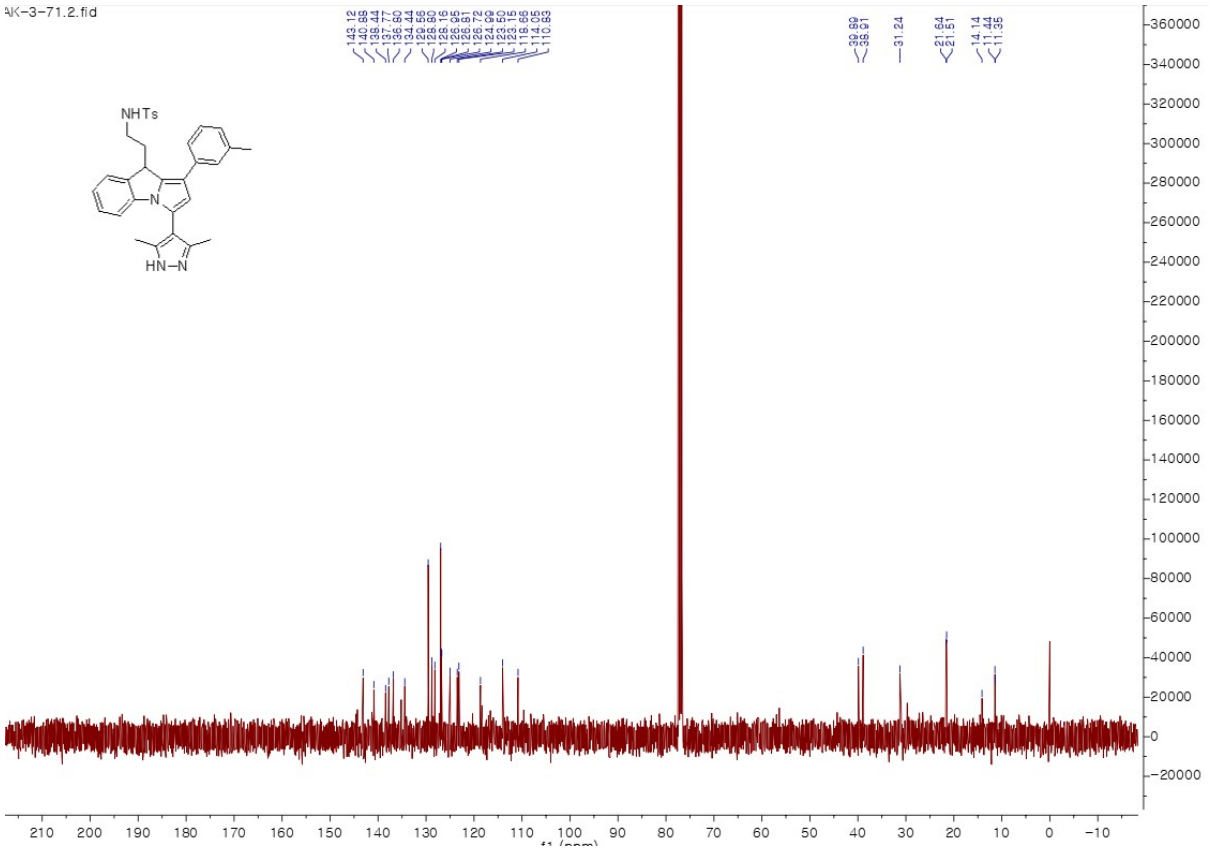


^{13}C NMR spectra of compound 3ad (126MHz, $CDCl_3$)

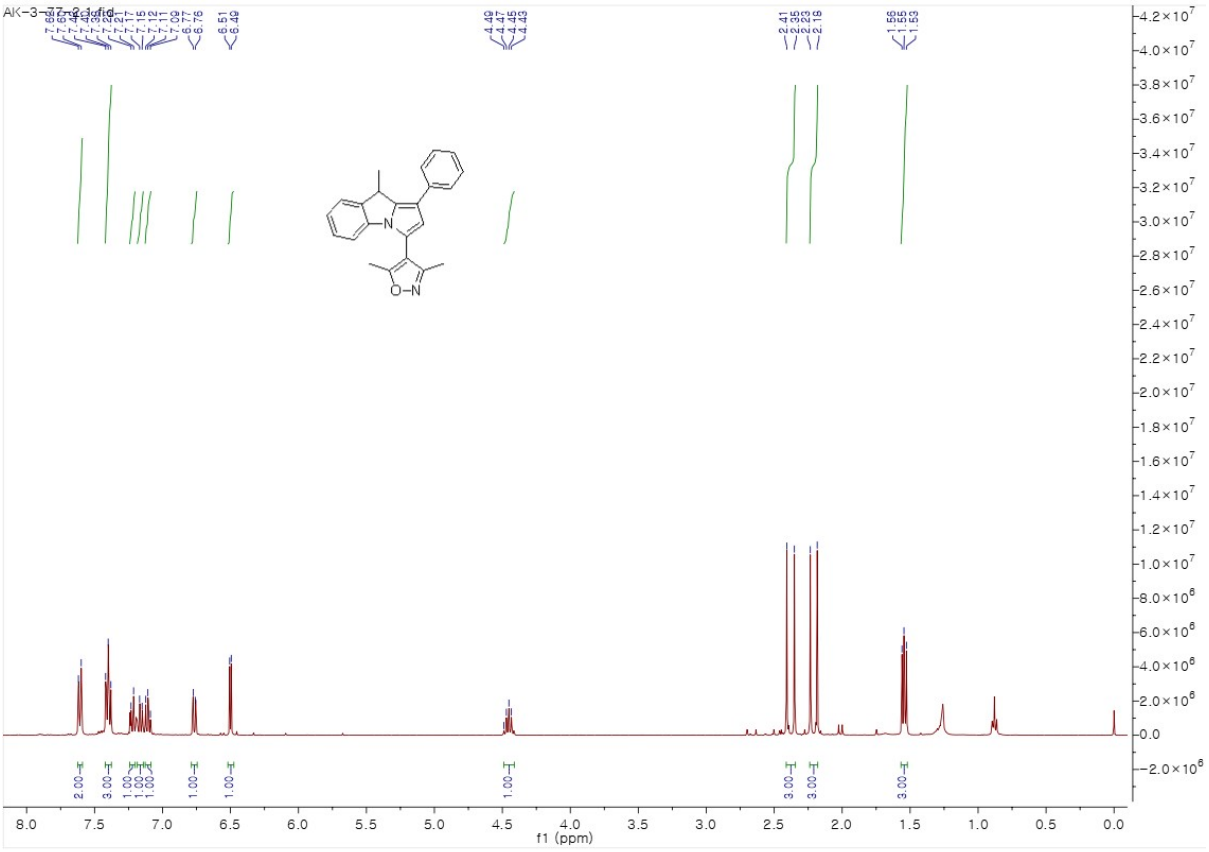
NMR copies of compound 4



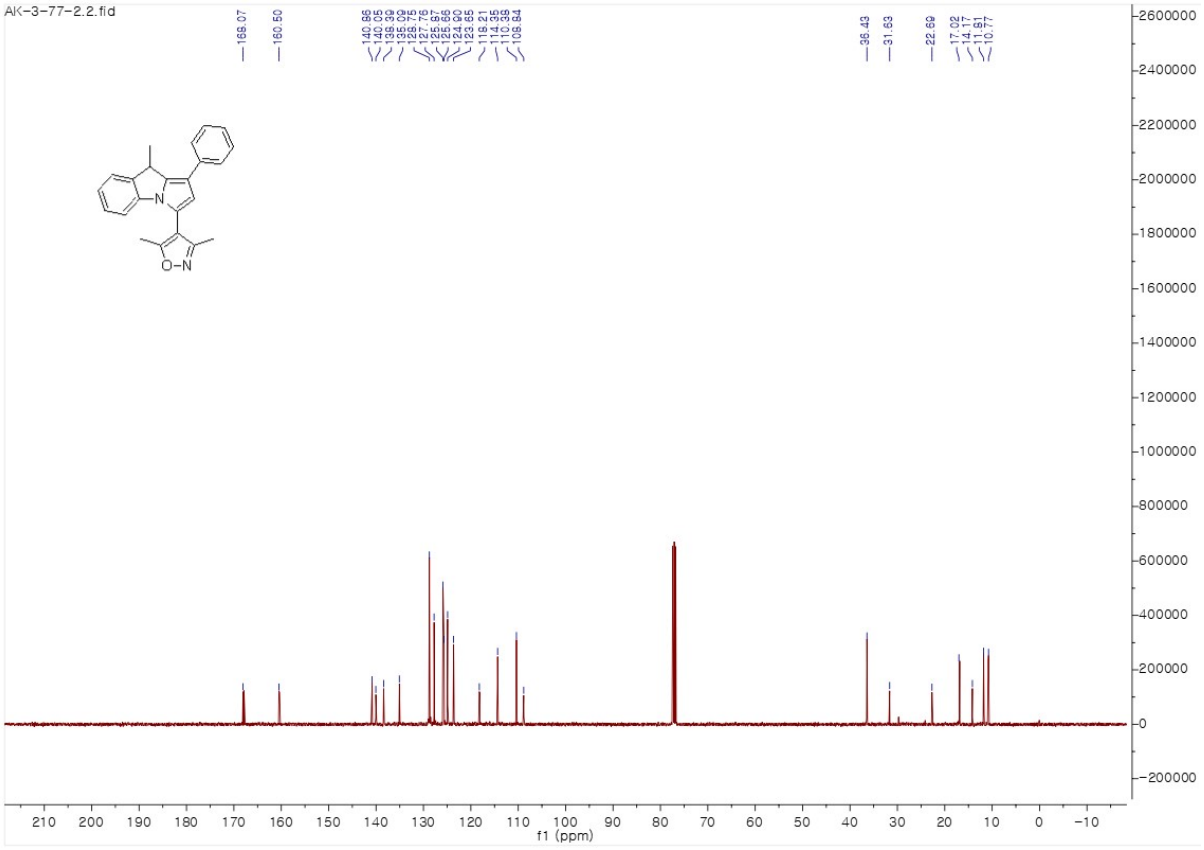
^{1}H NMR spectra of compound 4a (400MHz, $CDCl_3$)



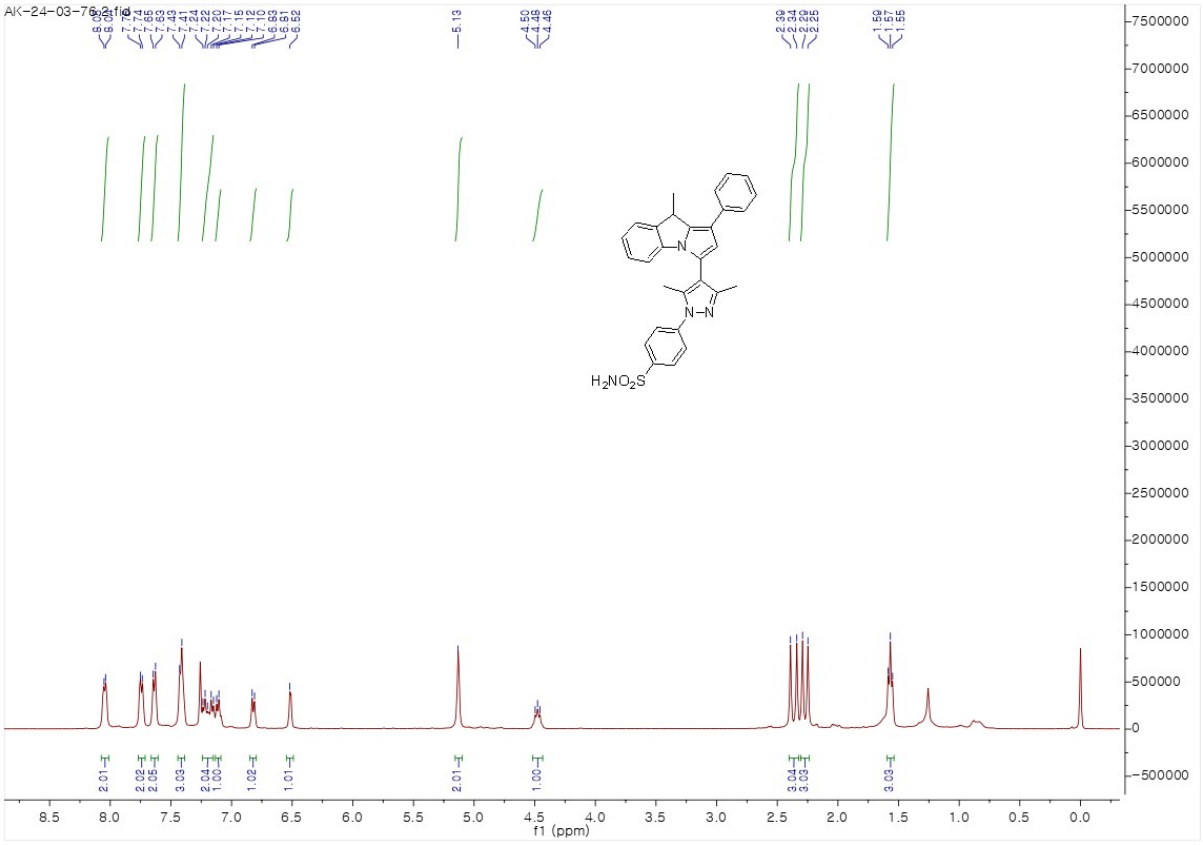
^{13}C NMR spectra of compound 4a (101MHz, $CDCl_3$)



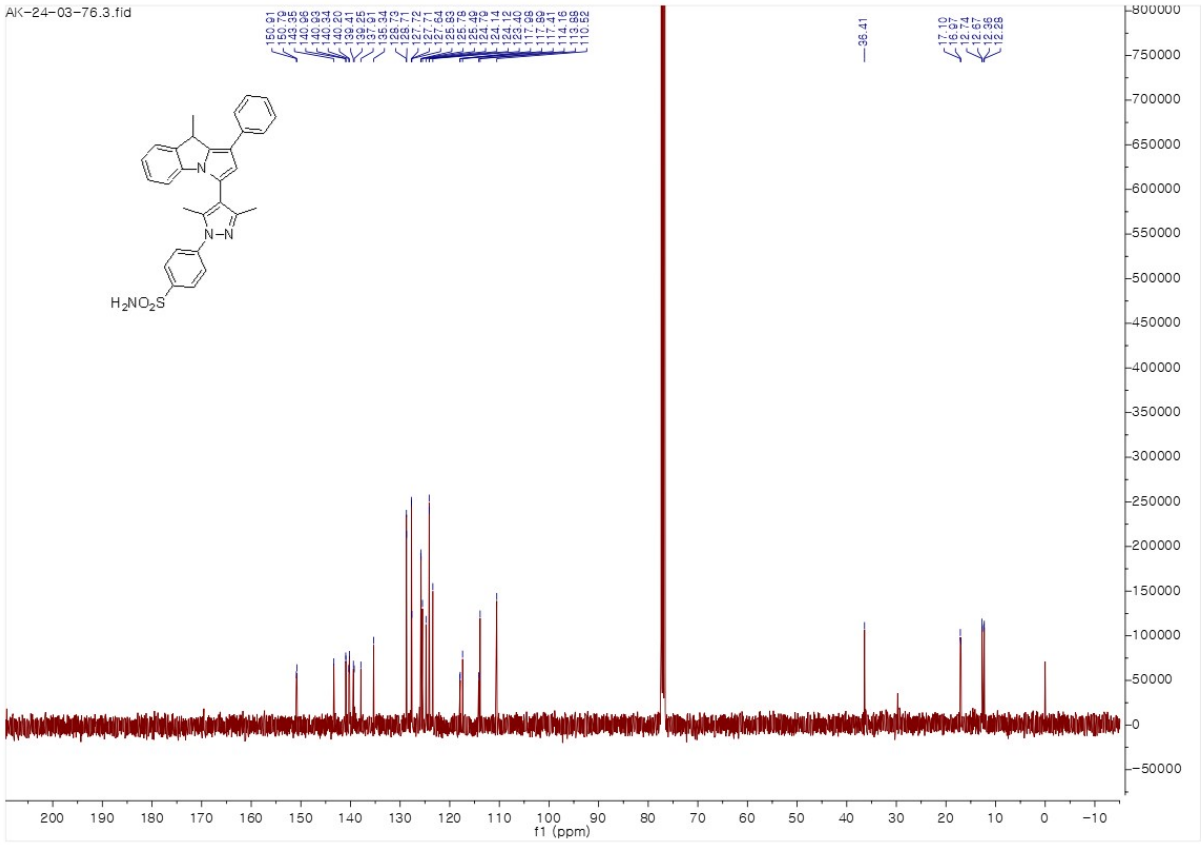
^{1}H NMR spectra of compound 4b (400MHz, $CDCl_3$)



^{13}C NMR spectra of compound 4b (101MHz, $CDCl_3$)



^{1}H NMR spectra of compound 4c (400MHz, $CDCl_3$)



^{13}C NMR spectra of compound 4c (101MHz, $CDCl_3$)