Supplementary Information

Synthesis of spirosuccinimides via annulative cyclization between *N*-aryl indazolols and maleimides under rhodium(III) catalysis

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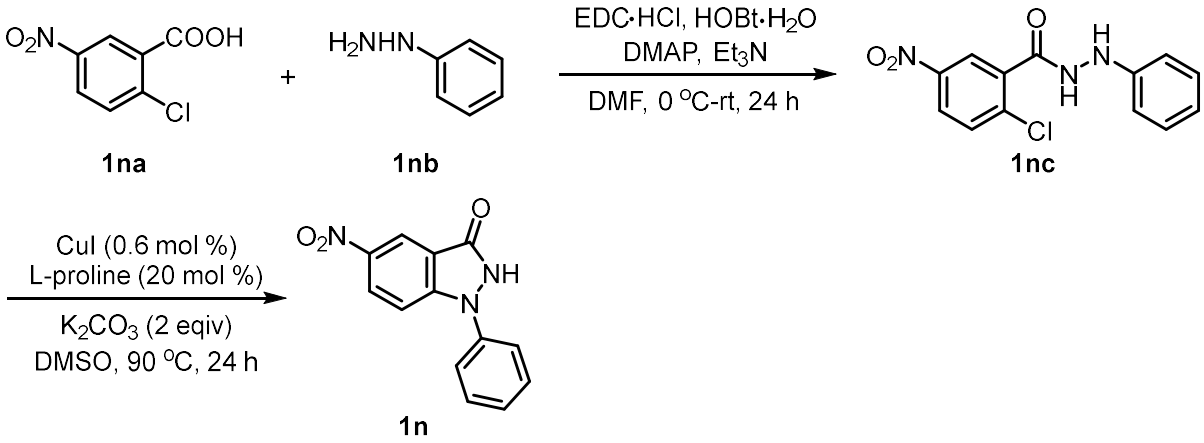
General methods

Commercially available reagents were used without additional purification, unless otherwise stated. *N*-Aryl indazol-3-ols **1a**−**1m** were prepared according to the reported literatures.[1] Maleimides **2b**−**2h**, **2k**, and **2t** were purchased from TCI. Maleates **2o** and **2p** were purchased from TCI. Maleimides **2i**, **2j**, **2l**, and **2n** were prepared according to the reported literatures.[2] 1-Methyl-1,5-dihydro-2*H*-pyrrol-2-one (**5a**) as an α,β-unsaturated γ-lactam was prepared according to the reported literature.[3] All the reactions were performed in an oil bath by using IKA universal hot plate magnetic stirrer. Sealed tubes (13 × 100 mm^2) were purchased from Fischer Scientific and dried in oven for overnight and cooled at room temperature prior to use. Thin layer chromatography was carried out using plates coated with Kieselgel $60F_{254}$ (Merck). For flash column chromatography, E. Merck Kieselgel 60 (230–400 mesh) was used. Nuclear magnetic resonance spectra (^1H, ^{13}C, and ^{19}F NMR) were recorded on a Bruker Unity 300, 400, 500, and 700 MHz spectrometers in $CDCl_3$, CD_3COCD_3, and DMSO-d_6 solution and chemical shifts are reported as parts per million (ppm). Resonance patterns are reported with the notations s (singlet), br (broad), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), ddd (doublet of doublet of doublets), dt (doublet of triplets), doublet of doublet of triplets (ddt), doublet of quartets (dq), td (triplet of doublets), and m (multiplet). In addition, the notation br is used to indicate a broad signal. Coupling constants (*J*) are reported in hertz (Hz). IR spectra were recorded on a Varian 2000 Infrared spectrophotometer and are reported as cm^{-1}. High-resolution mass spectra (HRMS) were recorded on a JEOL JMS-600 spectrometer.

General scheme, procedures, and characterization data for the synthesis of *N*-phenyl indazol-3-ol (1n)



Experimental procedure for the synthesis of 1nc

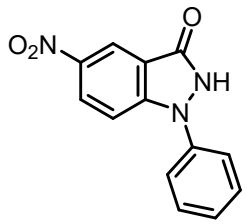
To an oven-dried round bottom flask charged with 2-chloro-5-nitrobenzoic acid (2.0 g, 10.0 mmol, 100 mol %) in DMF (20 mL) were added EDC·HCl (2.1 g, 11.0 mmol, 110 mol %), HOBt·H_2O (1.49 g, 11.0 mmol, 110 mol %), 4-(dimethylamino)pyridine (DMAP, 61.1 mg, 0.5 mmol, 5 mol %), and phenylhydrazine (1.0 mL, 10.0 mmol, 100 mol %) at 0 °C under N_2 atmosphere. The reaction mixture was allowed to stir for 24 h at room temperature. The reaction mixture was diluted with EtOAc (50 mL) and poured into saturated NH_4Cl solution. Extractive workup with EtOAc (2 x 50 mL). The combined organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (*n*-hexanes/EtOAc = 3:1 to 1:1) to afford 1.87 g of **1nc** as a white solid in 64 % yield.

Experimental procedure and characterization data for the synthesis of 1n

To an oven-dried round bottom flask charged with **1nc** (1.31 g, 4.5 mmol, 100 mol %), CuI (5.1 mg, 0.027 mmol, 0.6 mol %), and L-proline (103.6 mg, 0.9 mmol, 20 mol %) were added K_2CO_3 (1.24 g, 9.0 mmol, 200 mol %) and DMSO (15 mL) at room temperature under N_2 atmosphere. The reaction mixture was allowed to stir for 24 h at 90 °C. The reaction mixture was cooled to room temperature, treated with saturated $NaHCO_3$ solution (100 mL), and extracted with EtOAc (8 x 30 mL). The combined organic layer was washed with H_2O (3 x 50 mL) and

brine (50 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The obtained residue was recrystallized with diethyl ether (10 mL) to afford 0.6 g of **1n** as a yellow solid in 52% yield.

5-Nitro-1-phenyl-1,2-dihydro-3*H*-indazol-3-one (**1n**)



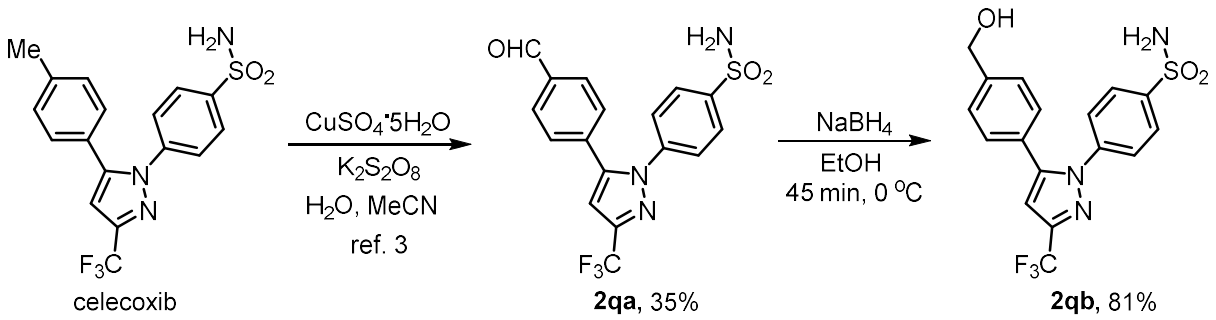
1n

0.6 g (52%); yellow solid; mp = 294.7–297.5 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.9 (s, 1H), 8.74 (d, *J* = 2.0 Hz, 1H), 8.23 (dd, *J* = 9.6, 2.4 Hz, 1H), 7.86 (d, *J* = 9.2 Hz, 1H), 7.71 (d, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 157.9, 140.9, 140.6, 138.9, 129.7, 126.5, 123.0, 121.7, 118.5, 114.1, 111.1; IR (KBr) υ 3056, 2987, 1668, 1602, 1566, 1516, 1342, 1281, 1228, 1140 cm^{-1}; HRMS (quadrupole, EI) m/z: $[M]^+$ Calcd for $C_{13}H_9N_3O_3$ 255.0644; Found 255.0641.

General procedure and characterization data of celecoxib maleimide 2q

Experimental procedure for the synthesis of celecoxib derivative 2qb

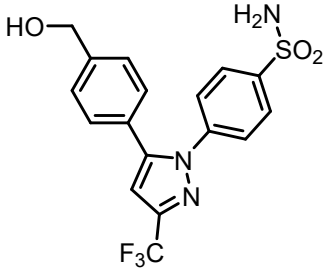
Aldehydic celecoxib **2qa**, 4-(5-(4-formylphenyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)benzenesulfonamide, was synthesized by using the commercially available celecoxib, according to previously reported procedure.[4]



celecoxib **2qa**, 35% **2qb**, 81%

To an oven-dried round bottom flask charged with aldehydic celecoxib **2qa** (520.0 mg, 1.3 mmol, 1.0 equiv.) was added EtOH (6.6 mL, 0.2 M). To the above mixture was added $NaBH_4$ (99.5 mg, 2.6 mmol, 2.0 equiv.) in one portion. The reaction mixture was allowed to stir for 45 min at 0 °C. The reaction mixture was dropwise quenched by *s*-NH_4Cl solution (2 mL), and filtered through Celite pad. The filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (*n*-hexanes/EtOAc = 3:1 to 1:2) to afford 0.42 g of celecoxib derivative **2qb** as a white sticky solid in 81% yield.

4-(5-(4-(Hydroxymethyl)phenyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)benzenesulfonamide (2qb)



2qb

0.42 g (81%); eluent (*n*-hexanes/EtOAc = 3:1 to 1:2); white sticky solid; ^{1}H NMR (500 MHz, CD_3COCD_3) δ 7.95 (dt, *J* = 8.5, 2.5 Hz, 2H), 7.56 (dt, *J* = 8.5, 2.5 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 7.01 (s, 1H), 6.74 (s, 2H), 4.67 (d, *J* = 5.5 Hz, 2H), 4.34 (t,

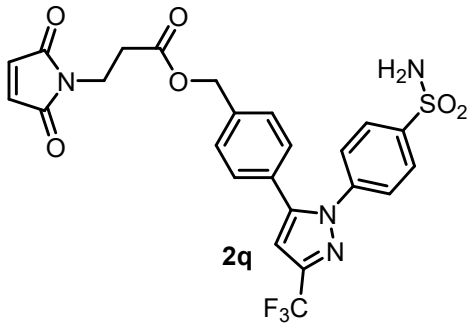
J = 5.5 Hz, 1H); ^{13}C NMR (125 MHz, CD_3COCD_3) δ 146.4, 145.0, 144.9, 143.9 (q, $J_{C\text{-}F}$ = 37.9 Hz), 142.9, 129.8, 128.1, 128.0, 127.6, 126.7, 124.6 (q, $J_{C\text{-}F}$ = 265.1 Hz), 106.9 (q, $J_{C\text{-}F}$ = 2.5 Hz), 64.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.5 (s); IR (KBr) υ 3270, 1498, 1471, 1407, 1338, 1272, 1236, 1159, 1132, 1097, 1024, 975, 942 cm^{-1}; HRMS (quadrupole, EI) m/z: $[M]^+$ Calcd for $C_{17}H_{14}F_3N_3O_3S$ 397.0708; Found 397.0703.

Experimental procedure for the synthesis of celecoxib maleimide 2q from 2qb

To an oven-dried round bottom flask charged with commercially available 3-maleimidopropionic acid (209.0 mg, 1.24 mmol, 1.2 equiv.) and $SOCl_2$ (0.45 mL, 6.2 mmol, 6 equiv.) under N_2 atmosphere. The reaction mixture was allowed to stir for 30 min at 80 °C. The reaction mixture was cooled to room temperature and concentrated in vacuo to obtain the 3-(2,5-dioxo-2,5-dihydro-1*H*-pyrrol-1-yl)propanoyl chloride.

Next, to an oven-dried round bottom flask charged with **2qb** (0.41 g, 1.03 mmol, 1.0 equiv.) and CH_2Cl_2 (5 mL) was added Et_3N (0.27 mL, 1.9 mmol, 1.8 equiv.). The reaction mixture was allowed to stir for 15 min at 0 °C. Then, 3-(2,5-dioxo-2,5-dihydro-1*H*-pyrrol-1-yl)propanoyl chloride and CH_2Cl_2 (3 mL) were added to the above reaction mixture, and the resulting mixture was allowed to stir at room temperature for 4 h. The resulting mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography (*n*-hexanes/EtOAc = 3:1 to 1:1) to afford 140.2 mg of celecoxib maleimide **2q** as a white sticky solid in 25% yield.

4-(1-(4-Sulfamoylphenyl)-3-(trifluoromethyl)-1*H*-pyrazol-5-yl)benzyl 3-(2,5-dioxo-2,5-dihydro-1*H*-pyrrol-1-yl)propanoate (2q)



2q

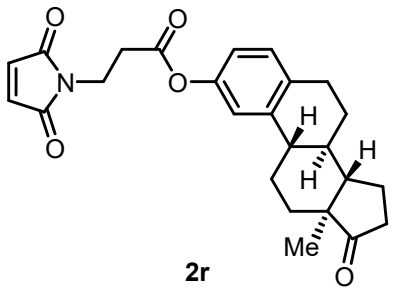
0.14 g (25%); eluent (*n*-hexanes/EtOAc = 3:1 to 1:1); white sticky solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93–7.90 (m, 2H), 7.48–7.44 (m, 2H), 7.35 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.4

Hz, 2H), 6.78 (s, 1H), 6.70 (s, 2H), 5.12 (s, 2H), 5.10 (s, 2H), 3.84 (t, J = 7.2 Hz, 2H), 2.71 (t, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 170.5, 144.7, 144.3 (q, $J_{C\text{-}F}$ = 37.3 Hz), 142.4, 141.8, 137.3, 134.4, 129.2, 128.9, 128.7, 127.7, 125.7, 121.1 (q, $J_{C\text{-}F}$ = 270.4 Hz), 106.8 (q, $J_{C\text{-}F}$ = 2.5 Hz), 65.9, 33.7, 33.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.4 (s); IR (KBr) υ 3268, 3102, 2923, 1704, 1446, 1407, 1373, 1342, 1267, 12324, 1160, 1130, 1097, 973, 898, 827 cm^{-1}; HRMS (quadrupole, EI) m/z: $[M]^+$ Calcd for $C_{24}H_{19}F_3N_4O_6S$ 548.0977; Found 548.0977.

General procedure and characterization data of estrone maleimide 2r

To an oven-dried round bottom flask charged with commercially available 3-maleimidopropionic acid (75.0 mg, 0.44 mmol, 1.2 equiv.) and $SOCl_2$ (0.2 mL, 2.64 mmol, 6 equiv.) under N_2 atmosphere. The reaction mixture was allowed to stir for 30 min at 80 °C. The reaction mixture was cooled to room temperature and concentrated in vacuo to obtain the 3-(2,5-dioxo-2,5-dihydro-1*H*-pyrrol-1-yl)propanoyl chloride. Next, to an oven-dried round bottom flask charged with commercially available estrone (97.2 mg, 0.36 mmol, 1.0 equiv.) and CH_2Cl_2 (1 mL), cooled in an ice bath and was added Et_3N (0.1 mL, 0.65 mmol, 1.8 equiv.). The reaction mixture was allowed to stir for 15 min at 0 °C. Then, 3-(2,5-dioxo-2,5-dihydro-1*H*-pyrrol-1-yl)propanoyl chloride and CH_2Cl_2 (1 mL) were added to the above reaction mixture, and the resulting mixture was allowed to stir at room temperature for 4 h. The resulting mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography (*n*-hexanes/EtOAc = 5:1 to 2:1) to afford 97.0 mg of estrone maleimide **2r** as a white solid in 43% yield.

(8*R*,9*S*,13*S*,14*S*)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-2-yl 3-(2,5-dioxo-2,5-dihydro-1*H*-pyrrol-1-yl)propanoate (2r)



2r

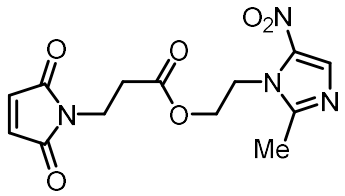
97.0 mg (43%); eluent (*n*-hexanes/EtOAc = 5:1 to 2:1); white solid; mp = 153.8–156.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.8 Hz, 1H), 6.86 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.81 (d, *J* = 2.4 Hz, 1H), 6.72 (s, 2H), 3.95 (t, *J* = 6.8 Hz, 2H), 2.92–2.86 (m, 4H), 2.50 (dd, *J* = 19.2, 8.8 Hz, 1H), 2.42–2.37 (m, 1H), 2.31–2.24 (m, 1H), 2.19–1.94 (m, 4H), 1.68–1.39 (m, 6H), 0.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 169.6, 148.4, 138.2, 137.7, 134.4, 126.6, 121.6, 118.8, 50.6, 48.1, 44.3, 38.1, 36.0, 33.7, 33.2, 31.7, 29.5, 26.5, 25.9, 21.7, 13.9; IR (KBr) υ 2931,

2861, 1733, 1680, 1492, 1444, 1407, 1375, 1315, 1245, 1220, 1159, 1058, 1008, 910, 827 cm^{-1}; HRMS (quadrupole, EI) m/z: $[M]^+$ Calcd for $C_{25}H_{27}NO_5$ 421.1889; Found 421.1886.

General procedure and characterization data of metronidazole maleimide 2s

To an oven-dried round bottom flask charged with commercially available 3-maleimidopropionic acid (209.7 mg, 1.24 mmol, 1.0 equiv.) and $SOCl_2$ (0.54 mL, 7.44 mmol, 6 equiv.) under N_2 atmosphere. The reaction mixture was allowed to stir for 30 min at 80 °C. The reaction mixture was cooled to room temperature and concentrated in vacuo to obtain the 3-(2,5-dioxo-2,5-dihydro-1*H*-pyrrol-1-yl)propanoyl chloride. Next, to an oven-dried round bottom flask charged with commercially available metronidazole (318.3 mg, 1.86 mmol, 1.5 equiv.) and CH_2Cl_2 (5 mL), cooled in an ice bath and was added Et_3N (0.52 mL, 3.72 mmol, 3.0 equiv.). The reaction mixture was allowed to stir for 15 min at 0 °C. Then, 3-(2,5-dioxo-2,5-dihydro-1*H*-pyrrol-1-yl)propanoyl chloride and CH_2Cl_2 (4 mL) were added to the above reaction mixture, and the resulting mixture was allowed to stir at room temperature for 3 h. The resulting mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography (CH_2Cl_2/EtOAc = 2:1 to 1:1) to afford 230.8 mg of metronidazole maleimide **2s** as a white sticky solid in 58% yield.

2-(2-Methyl-5-nitro-1*H*-imidazol-1-yl)ethyl 3-(2,5-dioxo-2,5-dihydro-1*H*-pyrrol-1-yl)propanoate (2s)



2s

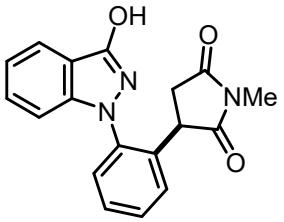
230.8 mg (58%); eluent (CH_2Cl_2/EtOAc = 2:1 to 1:1); white sticky solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (s, 1H), 6.69 (s, 2H), 4.59 (t, *J* = 5.5 Hz, 2H), 4.40 (t, *J* = 5.5 Hz, 2H), 3.78 (t, *J* = 7.0 Hz, 2H), 2.59 (t, *J* = 7.0 Hz, 2H), 2.52 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.3, 170.2, 150.8, 134.4, 132.9, 63.0, 45.0, 33.6, 32.9, 14.4; IR (KBr) υ 3059, 2956, 1739, 1707, 1529, 1465, 1427, 1363, 1263, 1186, 1145, 1076, 1041, 825 cm^{-1}; HRMS (quadrupole, EI) m/z: $[M]^+$ Calcd for $C_{13}H_{14}N_4O_6$ 322.0913; Found 322.0911.

General procedure for the spiroannulation of *N*-aryl indazol-3-ols with maleimides and maleates (3aa, 3a–3n, 4b–4m, and 4o–4t)

To an oven-dried sealed tube charged with 1-phenyl-1*H*-indazol-3-ol (**1a**) (42.1 mg, 0.2 mmol, 100 mol %), $[RhCp^*Cl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol %), $AgSbF_6$ (13.7 mg, 0.04 mmol, 20 mol %), NaOAc (8.2 mg, 0.1 mmol, 50 mol %), and *N*-methyl maleimide (**2a**) (44.4 mg, 0.4 mmol, 200 mol %) was added MeCN (1 mL) under air at room temperature. The reaction mixture was allowed to stir in an oil bath for 20 h at 80 °C. The reaction mixture was cooled to room temperature, diluted with EtOAc (2 mL) and concentrated in vacuo. The residue was purified by flash column chromatography (CH_2Cl_2/EtOAc = 7:1 to 4:1) to afford **3a** (58.2 mg) in 91% yield.

Characterization data for all products (3aa, 3a–3n, 4b–4m, and 4o–4t)

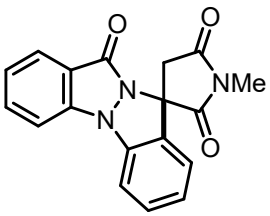
3-(2-(3-Hydroxy-1*H*-indazol-1-yl)phenyl)-1-methylpyrrolidine-2,5-dione (3aa)



3aa

16.2 mg (25%); eluent (CH_2Cl_2/EtOAc = 4:1 to 1:1); light brown solid; mp = 103.4–106.2 °C; ^{1}H NMR (500 MHz, CD_3COCD_3) δ 9.83 (brs, 1H), 7.72 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.51–7.45 (m, 3H), 7.42–7.38 (m, 2H), 7.23 (d, *J* = 8.5 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 4.27 (dd, *J* = 10.0, 5.5 Hz, 1H), 3.06 (dd, *J* = 18.0, 9.5 Hz, 1H), 2.73 (dd, *J* = 18.0, 5.5 Hz, 1H), 2.71 (s, 3H); ^{13}C NMR (125 MHz, CD_3COCD_3) δ 178.2, 176.5, 156.9, 143.3, 139.6, 137.4, 131.4, 129.4, 129.3, 128.8, 128.3, 121.0, 120.8, 114.6, 111.0, 44.1, 38.6, 24.8; IR (KBr) υ 3056, 1776, 1718, 1616, 1540, 1500, 1438, 1380, 1282, 1228, 1118, 954 cm^{-1}; HRMS (quadrupole, EI) m/z: $[M]^+$ Calcd for $C_{18}H_{15}N_3O_3$ 321.1113; Found 321.1114.

1'-Methyl-12*H*-spiro[indazolo[1,2-*a*]indazole-10,3'-pyrrolidine]-2',5',12-trione (3a)

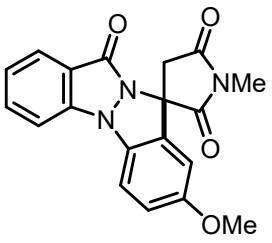


3a

58.2 mg (91%); eluent (CH_2Cl_2/EtOAc = 7:1 to 4:1); white solid; mp = 272.8–275.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.67 (ddd, *J* = 9.6, 7.2, 1.2 Hz, 1H), 7.52 (dt, *J* = 8.4, 0.8 Hz, 1H), 7.49 (ddd, *J* = 9.6, 6.8, 1.6 Hz, 1H), 7.36 (dt, *J* = 8.0, 0.8 Hz, 1H), 7.25 (ddd, *J* = 8.8, 7.2, 0.8 Hz, 1H), 7.19–7.12 (m, 2H), 4.02 (d, *J* = 18.0 Hz, 1H), 3.22 (s, 3H), 3.21 (d, *J* = 18.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 172.4, 161.0, 141.9, 137.4, 133.4, 131.1, 130.6, 125.2, 124.0, 122.6, 122.4, 119.6, 110.8, 109.7, 66.9, 40.3, 26.0; IR (KBr) υ

3054, 2925, 2360, 1714, 1660, 1600, 1496, 1467, 1432, 1375, 1361, 1313, 1267, 1139, 890 cm^{-1}; HRMS (quadrupole, EI) m/z: $[M]^+$ Calcd for $C_{18}H_{13}N_3O_3$ 319.0957; Found 319.0955.

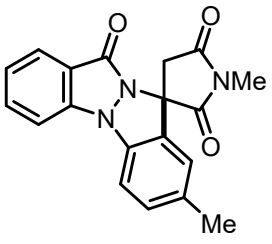
8-Methoxy-1'-methyl-12*H*-spiro[indazolo[1,2-*a*]indazole-10,3'-pyrrolidine]-2',5',12-trione (3b)



3b

55.9 mg (80%); eluent (CH_2Cl_2/EtOAc = 7:1 to 4:1); pale yellow solid; mp = 168.8–171.6 °C; mp = 152.2–155.3 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.62 (ddd, *J* = 9.6, 7.2, 1.2 Hz, 1H), 7.43 (dt, *J* = 8.4, 0.8 Hz, 1H), 7.26 (d, *J* = 8.8 Hz, 1H), 7.19 (ddd, *J* = 8.8, 7.2, 0.8 Hz, 1H), 6.98 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.67 (d, *J* = 2.4 Hz, 1H), 3.96 (d, *J* = 18.4 Hz, 1H), 3.78 (s, 3H), 3.20 (s, 3H), 3.19 (d, *J* = 18.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 172.3, 161.5, 156.9, 142.6, 133.3, 131.6, 131.5, 125.1, 122.2, 119.1, 116.3, 110.6, 110.5, 108.3, 67.1, 56.2, 40.2, 25.9; IR (KBr) υ 3054, 2989, 1791, 1712, 1666, 1617, 1494, 1459, 1432, 1378, 1282, 1267, 1220, 1141, 1078, 1024, 983, 804 cm^{-1}; HRMS (quadrupole, EI) m/z: $[M]^+$ Calcd for $C_{19}H_{15}N_3O_4$ 349.1063; Found 349.1061.

1',8-Dimethyl-12*H*-spiro[indazolo[1,2-*a*]indazole-10,3'-pyrrolidine]-2',5',12-trione (3c)

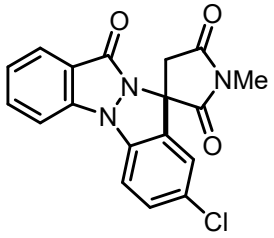


3c

54.7 mg (82%); eluent (CH_2Cl_2/EtOAc = 7:1 to 4:1); pale yellow solid; mp = 224.4–227.2 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (dt, *J* = 8.0, 0.8 Hz, 1H), 7.64 (ddd, *J* = 9.6, 7.2, 1.2 Hz,

1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.28–7.19 (m, 3H), 6.95 (s, 1H), 3.99 (d, *J* = 18.0 Hz, 1H), 3.20 (s, 3H), 3.19 (d, *J* = 18.0 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 172.5, 161.1, 142.1, 135.2, 134.1, 133.3, 131.6, 130.7, 125.1, 122.7, 122.4, 119.4, 110.7, 109.5, 66.9, 40.3, 25.9, 21.1; IR (KBr) υ 3054, 2987, 1791, 1714, 1670, 1614, 1500, 1461, 1434, 1378, 1284, 1267, 1141, 983, 804 cm^{-1}; HRMS (quadrupole, EI) m/z: $[M]^+$ Calcd for $C_{19}H_{15}N_3O_3$ 333.1113; Found 333.1113.

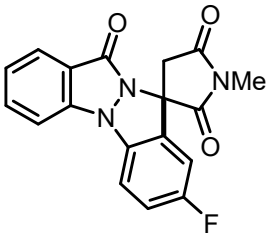
8-Chloro-1'-methyl-12*H*-spiro[indazolo[1,2-*a*]indazole-10,3'-pyrrolidine]-2',5',12-trione (3d)



3d

61.6 mg (87%); eluent (CH_2Cl_2/EtOAc = 6:1 to 4:1); pale orange solid; mp = 236.5–239.2 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.65 (ddd, *J* = 9.6, 7.2, 1.2 Hz, 1H), 7.45 (dt, *J* = 8.4, 0.8 Hz, 1H), 7.42 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.27–7.22 (m, 2H), 7.14 (d, *J* = 2.0 Hz, 1H), 3.97 (d, *J* = 18.4 Hz, 1H), 3.21 (s, 3H), 3.20 (d, *J* = 18.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 171.9, 161.1, 141.9, 136.0, 133.6, 131.9, 131.2, 129.1, 125.2, 122.9, 122.8, 119.6, 110.8, 110.5, 66.8, 40.3, 26.1; IR (KBr) υ 3054, 2987, 1793, 1718, 1679, 1619, 1606, 1494, 1428, 1380, 1346, 1267, 1082, 820 cm^{-1}; HRMS (quadrupole, EI) m/z: $[M]^+$ Calcd for $C_{18}H_{12}ClN_3O_3$ 353.0567; Found 353.0563.

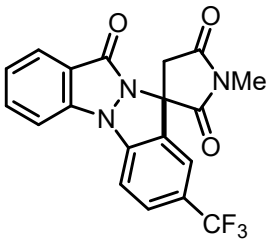
8-Fluoro-1'-methyl-12*H*-spiro[indazolo[1,2-*a*]indazole-10,3'-pyrrolidine]-2',5',12-trione (3e)



3e

54.2 mg (80%); eluent (CH_2Cl_2/EtOAc = 6:1 to 4:1); pale orange solid; mp = 221.2–224.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.66 (ddd, *J* = 9.6, 7.2, 1.2 Hz, 1H), 7.46 (dt, *J* = 8.4, 0.8 Hz, 1H), 7.29 (dd, *J* = 8.8, 4.0 Hz, 1H), 7.24 (ddd, *J* = 8.8, 7.2, 0.8 Hz, 1H), 7.19 (td, *J* = 8.8, 2.4 Hz, 1H), 6.91 (dd, *J* = 7.6, 2.4 Hz, 1H), 3.98 (d, *J* = 18.8 Hz, 1H), 3.21 (s, 3H), 3.20 (d, *J* = 18.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 171.9, 161.6, 159.3 (d, $J_{C\text{-}F}$ = 243.7 Hz), 142.6, 134.1 (d, $J_{C\text{-}F}$ = 2.2 Hz), 133.5, 131.7 (d, $J_{C\text{-}F}$ = 8.1 Hz), 125.2, 122.8, 117.9 (d, $J_{C\text{-}F}$ = 24.0 Hz), 110.7, 110.6, 110.4 (d, $J_{C\text{-}F}$ = 13.4 Hz), 110.2, 67.0 (d, $J_{C\text{-}F}$ = 2.5 Hz), 40.3, 26.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ −117.3 (s); IR (KBr) υ 3070, 3019, 1791, 1718, 1680, 1540, 1490, 1461, 1410, 1378, 1351, 1284, 1209, 1166, 1141, 985, 902, 808 cm^{-1}; HRMS (quadrupole, EI) m/z: $[M]^+$ Calcd for $C_{18}H_{12}FN_3O_3$ 337.0863; Found 337.0864.

1'-Methyl-8-(trifluoromethyl)-12*H*-spiro[indazolo[1,2-*a*]indazole-10,3'-pyrrolidine]-2',5',12-trione (3f)

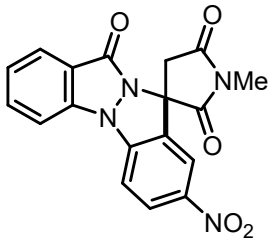


3f

60.4 mg (78%); eluent (CH_2Cl_2/EtOAc = 7:1 to 4:1); yellow solid; mp = 221.9–224.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.73 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.70 (ddd, *J* = 9.6, 7.2, 1.2 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 7.2 Hz, 1H), 7.39 (s, 1H), 7.29 (t, *J* = 7.2 Hz, 1H), 3.98 (d, *J* = 18.4 Hz, 1H), 3.25 (d, *J* = 18.4 Hz, 1H), 3.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 171.8, 160.9, 141.3, 139.6, 133.7, 131.0, 128.9 (q, $J_{C\text{-}F}$ = 3.9 Hz), 126.0 (q, $J_{C\text{-}F}$ = 33.3 Hz), 125.3, 123.6 (q, $J_{C\text{-}F}$ = 270.1 Hz), 123.5, 119.9, 119.8 (q, $J_{C\text{-}F}$ =

3.7 Hz), 110.9, 109.4, 66.8, 40.4, 26.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ −61.6 (s); IR (KBr) υ 3060, 2921, 2852, 2653, 2373, 2254, 1700, 1677, 1604, 1502, 1482, 1459, 1430, 1375, 1319, 1284, 1190, 1168, 1114, 1054, 1020, 981, 946, 908, 815 cm^{-1}; HRMS (quadrupole, EI) m/z: $[M]^+$ Calcd for $C_{19}H_{12}F_3N_3O_3$ 387.0831; Found 387.0832.

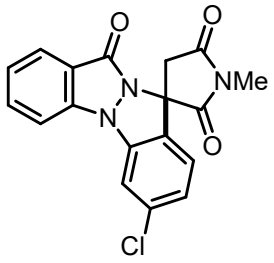
1'-Methyl-8-nitro-12*H*-spiro[indazolo[1,2-*a*]indazole-10,3'-pyrrolidine]-2',5',12-trione (3g)



3g

64.2 mg (88%); eluent (CH_2Cl_2/EtOAc = 6:1 to 4:1); yellow solid; mp = > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (dt, *J* = 8.8, 2.0 Hz, 1H), 8.90 (d, *J* = 2.0 Hz, 1H), 7.93 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.73 (ddd, *J* = 9.6, 7.2, 1.2 Hz, 1H), 7.55 (dt, *J* = 8.4, 0.8 Hz, 1H), 7.37 (d, *J* = 8.8 Hz, 1H), 7.36 (t, *J* = 7.2 Hz, 1H), 3.97 (d, *J* = 18.4 Hz, 1H), 3.29 (d, *J* = 18.8 Hz, 1H), 3.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 171.5, 160.4, 143.3, 140.8, 140.2, 134.0, 131.3, 128.2, 125.5, 124.2, 120.4, 119.1, 110.9, 108.5, 66.6, 40.4, 26.3; IR (KBr) υ 3019, 2925, 1793, 1708, 1673, 1596, 1517, 1494, 1459, 1436, 1378, 1321, 1288, 1214, 1133, 1110, 985, 854 cm^{-1}; HRMS (quadrupole, EI) m/z: $[M]^+$ Calcd for $C_{18}H_{12}N_4O_5$ 364.0808; Found 364.0807.

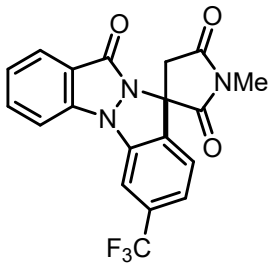
7-Chloro-1'-methyl-12*H*-spiro[indazolo[1,2-*a*]indazole-10,3'-pyrrolidine]-2',5',12-trione (3h)



3h

50.9 mg (72%); eluent (CH_2Cl_2/EtOAc = 7:1 to 4:1); pale yellow solid; mp = 238.4–241.2 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (dt, *J* = 8.0, 0.8 Hz, 1H), 7.69 (ddd, *J* = 9.6, 7.2, 1.2 Hz, 1H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.32 (s, 1H), 7.27 (t, *J* = 8.0 Hz, 1H), 7.11–7.07 (m, 2H), 3.98 (d, *J* = 18.4 Hz, 1H), 3.20 (s, 3H), 3.19 (d, *J* = 18.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 172.0, 161.1, 141.7, 138.3, 137.2, 133.6, 128.9, 125.3, 123.9, 123.3, 123.2, 119.8, 110.9, 110.1, 66.8, 40.3, 26.0; IR (KBr) υ 3054, 2987, 1791, 1716, 1679, 1604, 1494, 1465, 1432, 1380, 1267, 1145, 1053, 810 cm^{-1}; HRMS (quadrupole, EI) m/z: $[M]^+$ Calcd for $C_{18}H_{12}ClN_3O_3$ 353.0567; Found 353.0567.

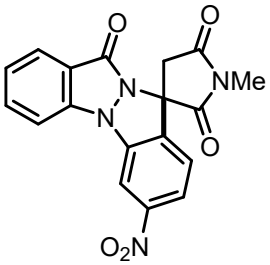
1'-Methyl-7-(trifluoromethyl)-12*H*-spiro[indazolo[1,2-*a*]indazole-10,3'-pyrrolidine]-2',5',12-trione (3i)



3i

39.6 mg (51%); eluent (CH_2Cl_2/EtOAc = 7:1 to 4:1); pale yellow solid; mp = 199.9–202.8 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.69 (ddd, *J* = 9.6, 7.2, 1.2 Hz, 1H), 7.56 (dt, *J* = 8.4, 0.8 Hz, 1H), 7.53 (t, *J* = 0.4 Hz, 1H), 7.39 (dq, *J* = 8.4, 0.8 Hz, 1H), 7.32–7.28 (m, 2H), 3.99 (d, *J* = 18.0 Hz, 1H), 3.23 (d, *J* = 18.4 Hz, 1H), 3.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 171.7, 161.2, 141.9, 137.9, 133.9 (q, J_{C-F} = 1.3 Hz), 133.8, 133.7 (q, J_{C-F} = 30.5 Hz), 125.3, 123.5, 123.4 (q, J_{C-F} = 271.5 Hz), 123.0, 120.8 (q, J_{C-F} = 3.7 Hz), 119.8, 111.1, 106.5 (q, J_{C-F} = 3.8 Hz), 66.9, 40.5, 26.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.7 (s); IR (KBr) υ 2919, 2850, 1791, 1740, 1642, 1612, 1504, 1436, 1378, 1280, 1210, 1168, 1110, 1060, 979, 964, 910, 829 cm^{-1}; HRMS (quadrupole, EI) m/z: $[M]^+$ Calcd for $C_{19}H_{12}F_3N_3O_3$ 387.0831; Found 387.0832.

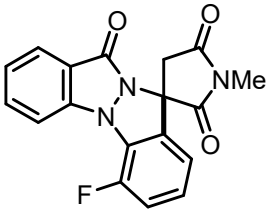
1'-Methyl-7-nitro-12*H*-spiro[indazolo[1,2-*a*]indazole-10,3'-pyrrolidine]-2',5',12-trione (3j)



3j

36.5 mg (50%); eluent (CH_2Cl_2/EtOAc = 6:1 to 4:1); yellow solid; mp = 270.1–273.2 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.48–8.47 (m, 1H), 8.23 (dd, *J* = 8.4, 1.6 Hz, 1H), 8.08–8.03 (m, 2H), 7.85–7.80 (m, 2H), 7.38 (td, *J* = 7.2, 0.8 Hz, 1H), 3.79 (d, *J* = 18.4 Hz, 1H), 3.52 (d, *J* = 18.4 Hz, 1H), 3.04 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.2, 172.0, 159.9, 149.8, 141.2, 137.7, 136.4, 133.8, 125.6, 124.0, 123.5, 119.0, 118.9, 112.4, 104.3, 66.8, 40.0, 25.4; IR (KBr) υ 2256, 1741, 1710, 1652, 1533, 1490, 1461, 1432, 1394, 1351, 1292, 1047, 1010, 823 cm^{-1}; HRMS (quadrupole, EI) m/z: $[M]^+$ Calcd for $C_{18}H_{12}N_4O_5$ 364.0808; Found 364.0804.

6-Fluoro-1'-methyl-12*H*-spiro[indazolo[1,2-*a*]indazole-10,3'-pyrrolidine]-2',5',12-trione (3k)

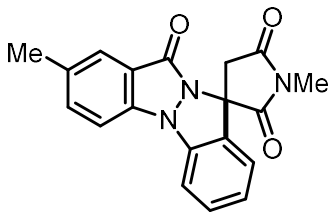


3k

23.7 mg (35%); eluent (CH_2Cl_2/EtOAc = 7:1 to 4:1); pale yellow solid; mp = 266.8–269.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.76 (dq, *J* = 8.4, 0.8 Hz, 1H), 7.65 (ddd, *J* = 10.0, 7.2, 1.2 Hz, 1H), 7.28–7.23 (m, 2H), 7.10 (td, *J* = 7.6, 4.0 Hz, 1H), 6.95 (dd, *J* = 7.6, 0.8 Hz, 1H), 3.95 (d, *J* = 18.4 Hz, 1H), 3.22 (d, *J* = 18.4 Hz, 1H), 3.21 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 172.7, 172.1, 161.5, 147.4 (d, $J_{C\text{-}F}$ = 245.7 Hz), 142.5, 133.7 (d, $J_{C\text{-}F}$ = 2.2 Hz), 133.5 (d, $J_{C\text{-}F}$ = 3.3 Hz), 125.6, 125.5, 125.2 (d, $J_{C\text{-}F}$ = 6.4 Hz), 123.0 (d, $J_{C\text{-}F}$ = 0.8 Hz), 119.6, 118.5 (d, $J_{C\text{-}F}$ = 19.1 Hz), 118.1 (d, $J_{C\text{-}F}$ = 3.5 Hz), 112.9 (d, $J_{C\text{-}F}$ = 14.6 Hz), 66.9, 40.8, 26.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ −125.1 (s); IR (KBr) υ 3054, 1793, 1716, 1679, 1614, 1494,

1434, 1380, 1348, 1282, 1140, 1012, 820 cm^{-1}; HRMS (quadrupole, EI) m/z: $[M]^+$ Calcd for $C_{18}H_{12}FN_3O_3$ 337.0863; Found 337.0865.

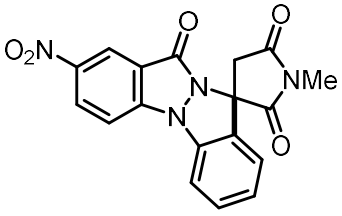
1',2-Dimethyl-12*H*-spiro[indazolo[1,2-*a*]indazole-10,3'-pyrrolidine]-2',5',12-trione (3m)



3m

60.8 mg (91%); eluent (CH_2Cl_2/EtOAc = 6:1 to 4:1); light orange solid; mp = 205.2–208.1 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.64 (s, 1H), 7.46–7.42 (m, 2H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 7.08 (t, *J* = 7.0 Hz, 1H), 3.98 (d, *J* = 18.2 Hz, 1H), 3.18 (d, *J* = 18.9 Hz, 1H), 3.17 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.9, 172.4, 161.2, 140.7, 137.6, 134.8, 132.5, 131.0, 130.4, 124.4, 123.6, 122.2, 119.7, 110.6, 109.5, 66.9, 40.3, 25.9, 21.1; IR (KBr) υ 3059, 2987, 1714, 1668, 1504, 1471, 1433, 1379, 1282, 1144, 987 cm^{-1}; HRMS (quadrupole, EI) m/z: $[M]^+$ Calcd for $C_{19}H_{15}N_3O_3$ 333.1113; Found 333.1116.

1'-Methyl-2-nitro-12*H*-spiro[indazolo[1,2-*a*]indazole-10,3'-pyrrolidine]-2',5',12-trione (3n)

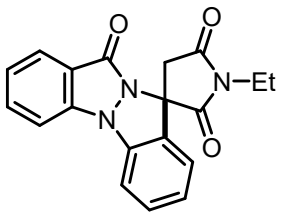


3n

53.2 mg (73%); eluent (CH_2Cl_2/EtOAc = 7:1 to 1:1); orange solid; mp = 284.3–286.9 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.57 (d, *J* = 2.4 Hz, 1H), 8.52 (dd, *J* = 9.2, 2.4 Hz, 1H), 8.21 (d, *J* = 8.8 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.63 (td, *J* = 7.6, 1.2 Hz, 1H), 7.32 (td, *J* = 7.6, 0.8 Hz, 1H), 3.78 (d, *J* = 18.8 Hz, 1H), 3.48 (d, *J* = 18.4 Hz, 1H), 3.05 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.2, 172.3, 157.1, 141.5, 140.0, 134.5, 131.1, 130.4,

128.0, 125.2, 124.5, 121.0, 117.8, 111.5, 110.3, 66.8, 40.1, 25.4; IR (KBr) υ 3057, 2927, 1720, 1685, 1622, 1601, 1520, 1495, 1468, 1431, 1371, 1335, 1317, 1269, 1151, 1117 cm^{-1}; HRMS (ion trap, FAB) m/z: $[M + H]^+$ Calcd for $C_{18}H_{13}N_4O_5$ 365.0886; Found 365.0886.

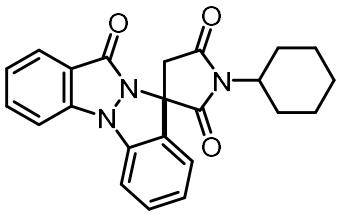
1'-Ethyl-12*H*-spiro[indazolo[1,2-*a*]indazole-10,3'-pyrrolidine]-2',5',12-trione (4b)



4b

58.2 mg (87%); eluent (CH_2Cl_2/EtOAc = 7:1 to 4:1); pale yellow solid; mp = 196.5–199.6 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.65 (ddd, *J* = 9.6, 7.2, 1.2 Hz, 1H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.47 (ddd, *J* = 8.0, 6.0, 2.8 Hz, 1H), 7.34 (dt, *J* = 8.4, 0.8 Hz, 1H), 7.23 (ddd, *J* = 8.8, 7.2, 0.8 Hz, 1H), 7.15–7.10 (m, 2H), 3.98 (d, *J* = 18.4 Hz, 1H), 3.77 (q, *J* = 7.2 Hz, 2H), 3.18 (d, *J* = 18.4 Hz, 1H), 1.30 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 172.0, 160.9, 141.8, 137.2, 133.3, 131.1, 130.7, 125.1, 123.9, 122.5, 122.2, 119.6, 110.7, 109.6, 66.8, 40.4, 35.1, 13.1; IR (KBr) υ 3653, 3622, 3572, 3531, 3485, 2979, 2937, 1788, 1740, 1692, 1580, 1460, 1411, 1323, 1379, 1243, 1110, 1033, 893 cm^{-1}; HRMS (quadrupole, EI) m/z: $[M]^+$ Calcd for $C_{19}H_{15}N_3O_3$ 333.1113; Found 333.1112.

1'-Cyclohexyl-12*H*-spiro[indazolo[1,2-*a*]indazole-10,3'-pyrrolidine]-2',5',12-trione (4c)

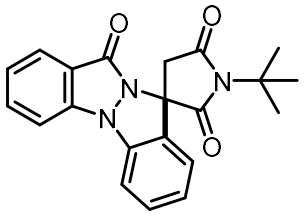


4c

60.5 mg (78%); eluent (CH_2Cl_2/EtOAc = 7:1 to 4:1); pale yellow solid; mp = 203.0–205.2 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (dt, *J* = 8.0, 0.8 Hz, 1H), 7.65 (ddd, *J* = 9.6, 7.2, 1.2 Hz, 1H), 7.49 (dt, *J* = 8.4, 0.8 Hz, 1H), 7.49–7.45 (m, 1H), 7.33 (dt, *J* = 8.0, 0.8 Hz, 1H), 7.23 (ddd,

J = 9.2, 7.6, 1.2 Hz, 1H), 7.13–7.12 (m, 2H), 4.18–4.11 (m, 1H), 3.93 (d, *J* = 18.0 Hz, 1H), 3.15 (d, *J* = 18.0 Hz, 1H), 2.29–2.11 (m, 2H), 1.87–1.75 (m, 4H), 1.68–1.62 (m, 2H), 1.36–1.32 (m, 1H), 1.31–1.18 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 172.2, 161.1, 141.9, 137.3, 133.3, 131.0, 130.9, 125.2, 123.9, 122.5, 122.0, 119.7, 110.8, 109.6, 66.5, 53.2, 40.4, 29.1, 28.9, 25.9, 25.8, 25.1; IR (KBr) υ 3059, 2931, 2856, 1756, 1711, 1670, 1920, 1600, 1491, 1468, 1396, 1365, 1344, 1306, 1259, 1196, 1149, 1120, 1036, 945 cm^{-1}; HRMS (quadrupole, EI) m/z: $[M]^+$ Calcd for $C_{23}H_{21}N_3O_3$ 387.1583; Found 387.1580.

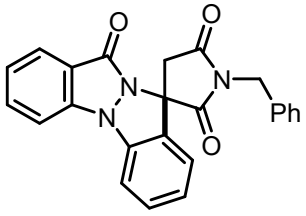
1'-(*tert*-Butyl)-12*H*-spiro[indazolo[1,2-*a*]indazole-10,3'-pyrrolidine]-2',5',12-trione (4d)



4d

44.8 mg (62%); eluent (CH_2Cl_2/EtOAc = 6:1 to 4:1); pale orange solid; mp = 191.1–194.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dt, *J* = 8.0, 0.8 Hz, 1H), 7.65 (ddd, *J* = 9.6, 7.2, 1.2 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.50–7.45 (m, 2H), 7.23 (ddd, *J* = 9.2, 7.2, 0.8 Hz, 1H), 7.17–7.11 (m, 2H), 3.95 (d, *J* = 18.0 Hz, 1H), 3.09 (d, *J* = 18.0 Hz, 1H), 1.67 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 173.1, 161.0, 141.5, 137.1, 133.2, 131.1, 130.9, 125.2, 123.8, 122.4, 121.8, 119.8, 110.6, 109.6, 66.9, 60.3, 40.3, 28.5; IR (KBr) υ 1714, 1671, 1621, 1602, 1490, 1463, 1396, 1338, 1303, 1253, 1174, 1027, 1000 cm^{-1}; HRMS (quadrupole, EI) m/z: $[M]^+$ Calcd for $C_{21}H_{19}N_3O_3$ 361.1426; Found 361.1421.

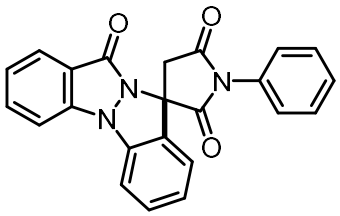
1'-Benzyl-12*H*-spiro[indazolo[1,2-*a*]indazole-10,3'-pyrrolidine]-2',5',12-trione (4e)



4e

57.1 mg (72%); eluent (CH_2Cl_2/EtOAc = 7:1 to 4:1); pale yellow solid; mp = 196.7–199.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.66 (ddd, *J* = 9.6, 7.2, 1.2 Hz, 1H), 7.49 (dt, *J* = 8.4, 0.8 Hz, 1H), 7.45–7.40 (m, 3H), 7.36–7.30 (m, 4H), 7.24 (ddd, *J* = 8.8, 7.2, 0.8 Hz, 1H), 7.03 (td, *J* = 7.6, 1.2 Hz, 1H), 6.88 (dt, *J* = 8.0, 0.8 Hz, 1H), 4.86 (q, *J* = 14.0 Hz, 2H), 4.05 (d, *J* = 18.0 Hz, 1H), 3.17 (d, *J* = 18.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 171.9, 161.0, 141.9, 137.2, 135.3, 133.4, 131.1, 130.7, 128.9, 128.6, 128.3, 125.2, 123.9, 122.6, 122.1, 119.7, 110.7, 109.6, 66.9, 43.5, 40.3; IR (KBr) υ 3060, 2927, 1792, 1771, 1720, 1622, 1603, 1493, 1468, 1431, 1392, 1344, 1309, 1250, 1176, 1119, 943 cm^{-1}; HRMS (quadrupole, EI) m/z: $[M]^+$ Calcd for $C_{24}H_{17}N_3O_3$ 395.1270; Found 395.1270.

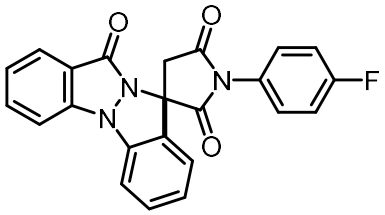
1'-Phenyl-12*H*-spiro[indazolo[1,2-*a*]indazole-10,3'-pyrrolidine]-2',5',12-trione (4f)



4f

49.6 mg (65%); eluent (CH_2Cl_2/EtOAc = 6:1 to 4:1); orange solid; mp = 239.5–242.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dt, *J* = 8.0, 0.8 Hz, 1H), 7.67 (ddd, *J* = 9.6, 7.2, 1.2 Hz, 1H), 7.53–7.40 (m, 7H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.25 (ddd, *J* = 9.2, 7.2, 1.2 Hz, 1H), 7.18 (td, *J* = 7.6, 0.8 Hz, 1H), 4.16 (d, *J* = 18.4 Hz, 1H), 3.39 (d, *J* = 18.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 171.4, 161.4, 142.1, 137.5, 133.4, 131.7, 131.2, 130.5, 129.4, 129.3, 126.7, 125.2, 124.0, 122.7, 122.4, 119.6, 110.9, 109.8, 66.9, 40.6; IR (KBr) υ 2924, 2852, 1792, 1780, 1719, 1642, 1580, 1532, 1410, 1380, 1278, 1028, 980, 820 cm^{-1}; HRMS (quadrupole, EI) m/z: $[M]^+$ Calcd for $C_{23}H_{15}N_3O_3$ 381.1113; Found 381.1114.

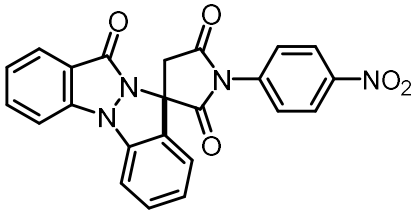
1'-(4-Fluorophenyl)-12*H*-spiro[indazolo[1,2-*a*]indazole-10,3'-pyrrolidine]-2',5',12-trione (4g)



4g

57.6 mg (72%); eluent (CH_2Cl_2/EtOAc = 7:1 to 4:1); pale yellow solid; mp = 207.4–210.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dt, *J* = 8.0, 0.8 Hz, 1H), 7.60 (ddd, *J* = 9.6, 7.2, 1.2 Hz, 1H), 7.46–7.41 (m, 2H), 7.37 (dq, *J* = 9.2, 2.0 Hz, 2H), 7.29 (dt, *J* = 8.0, 0.8 Hz, 1H), 7.22 (d, *J* = 7.2 Hz, 1H), 7.16 (ddd, *J* = 8.8, 6.0, 0.8 Hz, 1H), 7.14–7.08 (m, 3H), 4.04 (d, *J* = 18.4 Hz, 1H), 3.32 (d, *J* = 18.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 171.4, 162.7 (d, $J_{C\text{-}F}$ = 247.8 Hz), 161.5, 142.3, 137.6, 133.5, 131.3, 130.3, 128.6 (d, $J_{C\text{-}F}$ = 8.8 Hz), 127.6, 127.5 (d, $J_{C\text{-}F}$ = 3.3 Hz), 125.2, 124.1, 122.5 (d, $J_{C\text{-}F}$ = 35.5 Hz), 119.6, 116.4 (d, $J_{C\text{-}F}$ = 22.9 Hz), 110.9, 109.8, 66.9, 40.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ −111.4 (s); IR (KBr) υ 3057, 2991, 1793, 1726, 1674, 1622, 1603, 1508, 1495, 1467, 1383, 1350, 1265, 1196, 1155, 1080, 835 cm^{-1}; HRMS (quadrupole, EI) m/z: $[M]^+$ Calcd for $C_{23}H_{14}FN_3O_3$ 399.1019; Found 399.1017.

1'-(4-Nitrophenyl)-12*H*-spiro[indazolo[1,2-*a*]indazole-10,3'-pyrrolidine]-2',5',12-trione (4h)

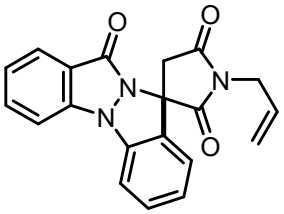


4h

41.9 mg (49%); eluent (CH_2Cl_2/EtOAc = 6:1 to 4:1); yellow solid; mp = 187.2–190.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (dt, *J* = 9.2, 2.8 Hz, 2H), 7.91 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.72 (dt, *J* = 9.2, 2.8 Hz, 2H), 7.69 (ddd, *J* = 8.4, 6.0, 0.8 Hz, 1H), 7.56–7.51 (m, 2H), 7.39 (dt, *J* = 8.4, 0.8 Hz, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.27 (ddd, *J* = 8.8, 7.2, 0.8 Hz, 1H), 7.19 (td, *J* = 7.6, 1.2 Hz, 1H), 4.13 (d, *J* = 18.8 Hz, 1H), 3.45 (d, *J* = 18.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 170.9, 161.8, 147.6, 142.5, 137.7, 137.1, 133.7, 131.5, 129.8, 127.4, 125.2, 124.7, 124.2, 122.9, 122.5, 119.5, 111.0, 109.9, 66.9, 40.8; IR (KBr) υ 3055, 2989, 1795, 1728, 1672, 1601, 1523, 1493, 1468, 1375, 1344, 1306, 1267, 1186, 1050, 845 cm^{-1}; HRMS (quadrupole, EI) m/z:

[M]$^+$ Calcd for $C_{23}H_{14}N_4O_5$ 426.0964; Found 426.0966.

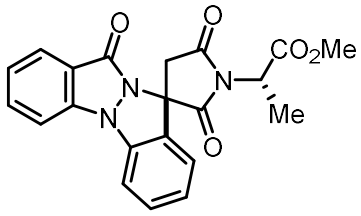
1'-Allyl-12*H*-spiro[indazolo[1,2-*a*]indazole-10,3'-pyrrolidine]-2',5',12-trione (4i)



4i

40.1 mg (58%); eluent (CH_2Cl_2/EtOAc = 6:1 to 4:1); pale orange solid; mp = 167.1–170.0 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 (ddd, *J* = 9.6, 7.2, 1.2 Hz, 1H), 7.89 (dt, *J* = 8.0, 0.8 Hz, 1H), 7.50 (dt, *J* = 8.4, 1.2 Hz, 1H), 7.47 (ddd, *J* = 9.6, 6.8, 0.8 Hz, 1H), 7.34 (dt, *J* = 8.0, 0.8 Hz, 1H), 7.23 (ddd, *J* = 8.8, 7.2, 0.8 Hz, 1H), 7.17–7.11 (m, 2H), 5.88 (ddt, *J* = 17.2, 10.2, 5.6 Hz, 1H), 5.39 (dq, *J* = 16.8, 1.2 Hz, 1H), 5.28 (dq, *J* = 10.2, 1.2 Hz, 1H), 4.30 (dt, *J* = 5.6, 1.6 Hz, 2H), 4.03 (d, *J* = 18.4 Hz, 1H), 3.22 (d, *J* = 18.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 171.8, 160.9, 141.7, 137.2, 133.3, 131.1, 130.6, 129.9, 125.2, 123.9, 122.5, 122.2, 119.6, 119.1, 110.7, 109.6, 66.8, 41.9, 40.3; IR (KBr) υ 3057, 2927, 1788, 1712, 1657, 1620, 1599, 1401, 1466, 1429, 1367, 1356, 1329, 1265, 1180, 1151, 1120, 995, 943, 862 cm^{-1}; HRMS (quadrupole, EI) m/z: [M]$^+$ Calcd for $C_{20}H_{15}N_3O_3$ 345.1113; Found 345.1114.

Methyl (2*S*)-2-(2',5',12-trioxo-12*H*-spiro[indazolo[1,2-a]indazole-10,3'-pyrrolidin]-1'-yl)propanoate (4j)

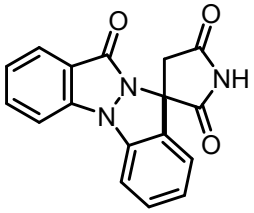


4j

49.4 mg (63%, dr = 1:1); eluent (CH_2Cl_2/EtOAc = 6:1 to 4:1); pale yellow solid; mp = 102.9–105.6 ^oC; ^1H NMR (400 MHz, $CDCl_3$) **diastereomer A**: δ 7.90–7.87 (m, 1H), 7.67–7.62 (m, 1H), 7.51–7.48 (m, 1H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.37–7.31 (m, 2H), 7.26–7.20 (m, 1H),

7.17–7.12 (m, 1H), 5.05 (q, *J* = 7.2 Hz, 1H), 4.03 (d, *J* = 18.4 Hz, 1H), 3.82 (s, 3H), 3.25 (d, *J* = 18.4 Hz, 1H), 1.75 (d, *J* = 5.6 Hz, 3H); **diastereomer B**: δ 7.90–7.87 (m, 1H), 7.67–7.62 (m, 1H), 7.51–7.48 (m, 1H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.37–7.31 (m, 2H), 7.26–7.20 (m, 1H), 7.17–7.12 (m, 1H), 4.92 (q, *J* = 7.2 Hz, 1H), 4.02 (d, *J* = 18.4 Hz, 1H), 3.71 (s, 3H), 3.20 (d, *J* = 18.0 Hz, 1H), 1.73 (d, *J* = 5.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) **diastereomer A**: δ 172.0, 171.4, 169.4, 161.1, 142.1, 137.2, 133.4, 131.1, 130.7, 125.1, 124.1, 122.8, 122.6, 119.5, 110.8, 109.5, 66.9, 53.1, 49.6, 40.4, 14.5; **diastereomer B**: δ 171.8, 171.3, 169.3, 161.0, 142.0, 137.1, 133.3, 131.0, 130.6, 125.0, 124.0, 122.7, 122.5, 119.5, 110.7, 109.5, 66.4, 53.0, 49.1, 40.3, 14.4; IR (KBr) υ 2829, 1791, 1747, 1722, 1673, 1621, 1602, 1490, 1463, 1434, 1390, 1359, 1309, 1251, 1209, 1060, 1027, 1002, 946, 871 cm^{-1}; HRMS (quadrupole, EI) m/z: $[M]^+$ Calcd for $C_{21}H_{17}N_3O_5$ 391.1168; Found 391.1169.

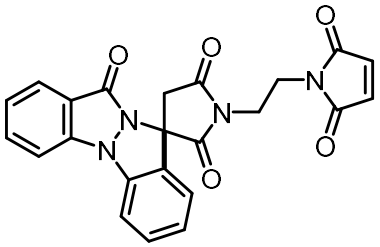
12*H*-Spiro[indazolo[1,2-*a*]indazole-10,3'-pyrrolidine]-2',5',12-trione (4k)



4k

31.8 mg (52%); eluent (CH_2Cl_2/EtOAc = 8:1 to 3:1); white solid; mp = 267.0–270.2 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.1 (brs, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.81–7.45 (m, 3H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.53 (t, *J* = 8.0 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 3.65 (d, *J* = 18.5 Hz, 1H), 3.36 (d, *J* = 18.5 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 174.6, 173.9, 159.7, 104.9, 136.4, 133.4, 1130.7, 130.3, 124.0, 123.8, 123.6, 122.4, 118.6, 111.5, 109.6, 67.9, 41.0; IR (KBr) υ 2954, 2919, 1791, 1739, 1710, 1639, 1606, 1506, 1459, 1390, 1309, 1251, 1187, 1114, 1074, 1035, 997, 889 cm^{-1}; HRMS (quadrupole, EI) m/z: $[M]^+$ Calcd for $C_{17}H_{11}N_3O_3$ 305.0800; Found 305.0800.

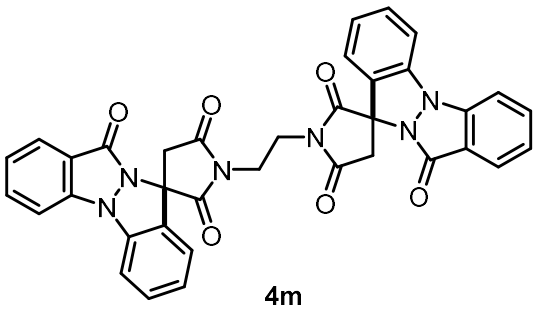
1'-(2-(2,5-Dioxo-2,5-dihydro-1*H*-pyrrol-1-yl)ethyl)-12*H*-spiro[indazolo[1,2-*a*]indazole-10,3'-pyrrolidine]-2',5',12-trione (4l)



4l

27.5 mg (32%); eluent (CH_2Cl_2/EtOAc = 8:1 to 3:1); light yellow solid; mp = 237.6–240.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dt, *J* = 8.0, 0.8 Hz, 1H), 7.65 (ddd, *J* = 9.6, 7.2, 1.2 Hz, 1H), 7.59 (dt, *J* = 7.6, 0.8 Hz, 1H), 7.51–7.46 (m, 2H), 7.33 (dt, *J* = 8.0, 0.8 Hz, 1H), 7.24–7.18 (m, 2H), 6.69 (s, 2H), 4.01–3.95 (m, 1H), 3.92–3.78 (m, 4H), 3.20 (d, *J* = 18.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 172.4, 170.9, 160.8, 141.9, 137.5, 134.4, 133.3, 131.0, 130.2, 125.1, 124.1, 123.8, 122.6, 119.5, 110.8, 109.4, 66.7, 40.6, 38.9, 36.3; IR (KBr) υ 2925, 2854, 1789, 1740, 1780, 1600, 1490, 1467, 1434, 1390, 1355, 1334, 1247, 1201, 1151, 1118, 1031, 975, 939, 896, 827 cm^{-1}; HRMS (quadrupole, EI) m/z: $[M]^+$ Calcd for $C_{23}H_{16}N_4O_5$ 428.1121; Found 428.1121.

1',1'''-(Ethane-1,2-diyl)bis(12*H*-spiro[indazolo[1,2-*a*]indazole-10,3'-pyrrolidine]-2',5',12-trione) (4m)

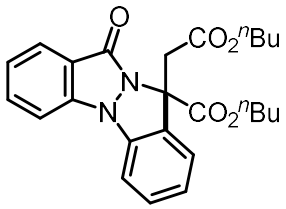


4m

85.5 mg (67%); eluent (CH_2Cl_2/EtOAc = 6:1 to 2:1); yellow solid; mp = 278.0–281.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.85 (m, 2H), 7.70–7.65 (m, 2H), 7.54–7.50 (m, 3H), 7.49 (d, *J* = 8.8 Hz, 1H), 7.46–7.40 (m, 2H), 7.32 (dd, *J* = 8.4, 2.4 Hz, 2H), 7.26–7.22 (m, 2H), 7.07 (td, *J* = 7.6, 1.2 Hz, 1H), 6.96 (td, *J* = 7.6, 1.2 Hz, 1H), 4.18–4.12 (m, 2H), 4.00–3.93 (m, 2H), 3.85 (d, *J* = 18.4 Hz, 2H), 3.44 (d, *J* = 18.4 Hz, 1H), 3.17 (d, *J* = 18.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 172.1, 161.1, 142.0, 137.3, 133.4, 130.9, 130.2, 125.1, 124.2, 123.9,

122.5, 119.5, 110.9, 109.2, 67.3, 41.8, 38.4; IR (KBr) υ 3480, 2927, 1789, 1716, 1668, 1621, 1600, 1490, 1465, 1392, 1353, 1305, 1261, 1214, 1168, 1116, 1085, 1031, 943, 910, 860 cm^{-1}; HRMS (quadrupole, EI) m/z: $[M]^+$ Calcd for $C_{36}H_{24}N_6O_6$ 636.1757; Found 636.1753.

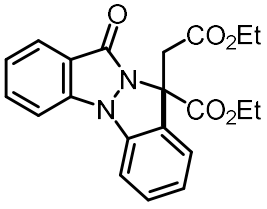
Butyl 10-(2-butoxy-2-oxoethyl)-12-oxo-10*H*,12*H*-indazolo[1,2-*a*]indazole-10-carboxylate (4o)



4o

44.8 mg (51%); eluent (CH_2Cl_2/EtOAc = 7:1 to 4:1); yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.63 (ddd, *J* = 9.6, 7.2, 1.2 Hz, 1H), 7.49 (dt, *J* = 8.4, 0.8 Hz, 1H), 7.45–7.35 (m, 2H), 7.29 (dt, *J* = 8.0, 0.8 Hz, 1H), 7.19 (ddd, *J* = 8.8, 7.2, 0.8 Hz, 1H), 7.07 (td, *J* = 7.6, 0.8 Hz, 1H), 4.21–4.10 (m, 3H), 3.75 (t, *J* = 6.8 Hz, 2H), 3.59 (d, *J* = 16.8 Hz, 1H), 1.56–1.49 (m, 2H), 1.25–1.14 (m, 4H), 1.09–1.00 (m, 2H), 0.79 (t, *J* = 7.2 Hz, 3H), 0.71 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 167.9, 160.3, 140.3, 137.0, 132.6, 130.5, 130.4, 125.0, 123.5, 123.0, 121.8, 119.9, 110.2, 108.6, 68.0, 67.0, 64.8, 36.9, 30.4, 30.3, 19.0, 18.9, 13.7, 13.6; IR (KBr) υ 2958, 2933, 2871, 1735, 1671, 1619, 1600, 1492, 1465, 1394, 1353, 1305, 1245, 1226, 1189, 1058, 1024, 946 cm^{-1}; HRMS (quadrupole, EI) m/z: $[M]^+$ Calcd for $C_{25}H_{28}N_2O_5$ 436.1998; Found 436.1993.

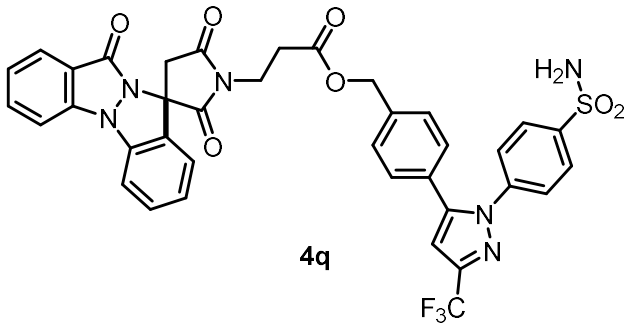
Ethyl 10-(2-ethoxy-2-oxoethyl)-12-oxo-10*H*,12*H*-indazolo[1,2-*a*]indazole-10-carboxylate (4p)



4p

36.3 mg (48%); eluent (CH_2Cl_2/EtOAc = 7:1 to 5:1); orange sticky solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.62 (ddd, *J* = 10.0, 7.5, 1.5 Hz, 1H), 7.48 (dt, *J* = 8.5, 1.0 Hz, 1H), 7.42–7.40 (m, 2H), 7.28 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.20 (ddd, *J* = 9.0, 7.0, 1.0 Hz, 1H), 7.07 (td, *J* = 7.5, 1.0 Hz, 1H), 4.28–4.18 (m, 2H), 4.17 (d, *J* = 17.0 Hz, 1H), 3.82–3.76 (m, 2H), 3.57 (d, *J* = 17.0 Hz, 1H), 1.20 (t, *J* = 7.5 Hz, 3H), 0.82 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.3, 167.8, 160.2, 140.3, 137.1, 132.7, 130.6, 130.3, 124.9, 123.6, 123.0, 121.8, 119.9, 110.2, 108.6, 67.9, 63.2, 60.8, 36.9, 14.0, 13.7; IR (KBr) υ 3066, 2981, 1736, 1672, 1619, 1600, 1493, 1468, 1367, 1351, 1303, 1240, 1193, 1095, 1026, 944, 860 cm^{-1}; HRMS (quadrupole, EI) m/z: $[M]^+$ Calcd for $C_{21}H_{20}N_2O_5$ 380.1372; Found 380.1372.

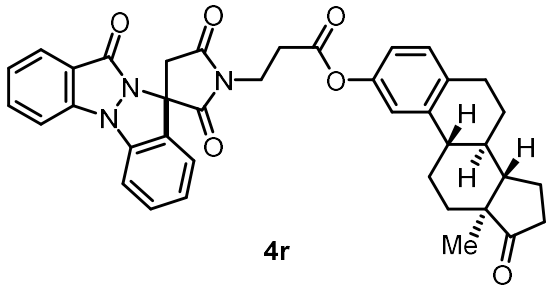
4-(1-(4-Sulfamoylphenyl)-3-(trifluoromethyl)-1*H*-pyrazol-5-yl)benzyl 3-(2',5',12-trioxo-12*H*-spiro[indazolo[1,2-*a*]indazole-10,3'-pyrrolidin]-1'-yl)propanoate (4q)



4q

83.2 mg (55%); eluent (CH_2Cl_2/EtOAc = 5:1 to 1:1); light yellow solid; mp = 104.5–107.6 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82–7.78 (m, 3H), 7.62 (ddd, *J* = 9.5, 7.0, 1.0 Hz, 1H), 7.47–7.44 (m, 2H), 7.35–7.30 (m, 5H), 7.23 (d, *J* = 8.0 Hz, 1H), 6.73 (s, 1H), 7.19–7.14 (m, 3H), 7.11 (t, *J* = 7.5 Hz, 1H), 5.49 (s, 2H), 5.09 (s, 2H), 4.02–3.93 (m, 2H), 3.88 (d, *J* = 18.5 Hz, 1H), 3.20 (d, *J* = 18.5 Hz, 1H), 2.78 (td, *J* = 6.5, 1.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 171.9, 170.5, 160.9, 144.7, 144.1 (q, $J_{C\text{-}F}$ = 38.0 Hz), 142.1, 142.0, 141.6, 137.1 (d, $J_{C\text{-}F}$ = 7.2 Hz), 133.5, 131.2, 130.2, 129.2, 129.1, 128.7, 127.5, 125.5, 124.9, 124.1, 122.8, 122.7, 122.2 (q, $J_{C\text{-}F}$ = 267.7 Hz), 119.2, 110.7, 109.6, 106.7, 106.6, 66.7, 66.1, 40.5, 35.7, 32.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.3 (s); IR (KBr) υ 3062, 1791, 1716, 1658, 1600, 1494, 1469, 1446, 1346, 1315, 1267, 1234, 1160, 1132, 1097, 973, 842 cm^{-1}; HRMS (quadrupole, EI) m/z: $[M]^+$ Calcd for $C_{37}H_{27}F_3N_6O_7S$ 756.1614; Found 756.1685.

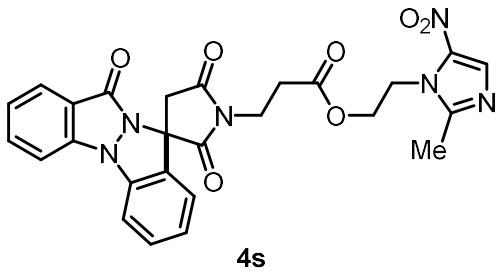
(8*R*,9*S*,13*S*,14*S*)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-2-yl 3-(2',5',12-trioxo-12*H*-spiro[indazolo[1,2-a]indazole-10,3'-pyrrolidin]-1'-yl)propanoate (4r)



4r

85.8 mg (68%, dr = 1:1); eluent (CH_2Cl_2/EtOAc = 7:1 to 3:1); pale yellow solid; mp = 125.0–128.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.6 Hz, 1H), 7.66 (ddd, *J* = 9.6, 7.2, 1.2 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.48–7.43 (m, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.27–7.22 (m, 3H), 7.06 (td, *J* = 8.4, 2.8 Hz, 1H), 6.84 (dd, *J* = 8.4, 2.8 Hz, 1H), 6.80 (t, *J* = 3.2 Hz, 1H), 4.22–4.15 (m, 1H), 4.12–4.06 (m, 1H), 3.96 (d, *J* = 18.4 Hz, 1H), 3.23 (d, *J* = 18.4 Hz, 1H), 2.99 (t, *J* = 6.8 Hz, 2H), 2.90–2.86 (m, 2H), 2.53–2.47 (m, 1H), 2.42–2.36 (m, 1H), 2.30–2.24 (m, 1H), 2.18–2.07 (m, 1H), 2.05–1.93 (m, 3H), 1.67–1.58 (m, 2H), 1.55–1.37 (m, 4H), 0.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 171.9, 169.7, 161.1, 148.4, 142.0, 138.2, 137.7, 137.3, 133.4, 131.0 (two carbons overlap), 130.4, 126.5, 125.1, 124.0, 122.9, 122.6, 121.6, 119.5, 118.8, 110.8, 109.5, 66.7, 50.5, 48.0, 44.3, 40.6, 38.1, 35.9, 35.6, 32.2, 31.7, 29.5, 26.4, 25.8, 21.7, 13.9; IR (KBr) υ 3018, 2933, 1792, 1716, 1668, 1622, 1603, 1491, 1468, 1394, 1371, 1352, 1308, 1250, 1217, 1153, 1088, 1009, 972, 908 cm^{-1}; HRMS (quadrupole, EI) m/z: $[M]^+$ Calcd for $C_{38}H_{35}N_3O_6$ 629.2526; Found 629.2520.

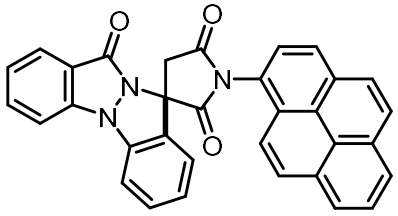
2-(2-Methyl-5-nitro-1*H*-imidazol-1-yl)ethyl 3-(2',5',12-trioxo-12*H*-spiro[indazolo[1,2-*a*]indazole-10,3'-pyrrolidin]-1'-yl)propanoate (4s)



4s

76.5 mg (72%); eluent (CH_2Cl_2/EtOAc = 1:1 to only EtOAc); pale yellow solid; mp = 106.4–108.9 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.86 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.66 (ddd, *J* = 9.5, 7.0, 1.0 Hz, 1H), 7.52–7.47 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.26–7.22 (m, 2H), 7.15 (t, *J* = 6.5 Hz, 1H), 4.57 (td, *J* = 5.5, 2.0 Hz, 2H), 4.45–7.35 (m, 2H), 3.97 (td, *J* = 6.5, 1.5 Hz, 2H), 3.92 (d, *J* = 18.5 Hz, 1H), 3.22 (d, *J* = 18.5 Hz, 1H), 2.75–2.72 (m, 2H), 2.49 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.5, 171.9, 170.2, 161.0, 141.9, 137.3, 133.4, 133.2, 131.2, 130.3, 125.1, 124.1, 122.8, 122.7, 119.5, 110.8, 109.6, 66.6, 63.1, 44.9, 40.6, 35.6, 31.9, 14.4; IR (KBr) υ 3060, 2979, 1716, 1674, 1529, 1488, 1468, 1430, 1363, 1313, 1263, 1187, 1120, 1033, 946, 825 cm^{-1}; HRMS (quadrupole, EI) m/z: $[M]^+$ Calcd for $C_{26}H_{22}N_6O_7$ 530.1550; Found 530.1548.

1'-(Pyren-1-yl)-12*H*-spiro[indazolo[1,2-*a*]indazole-10,3'-pyrrolidine]-2',5',12-trione (4t)

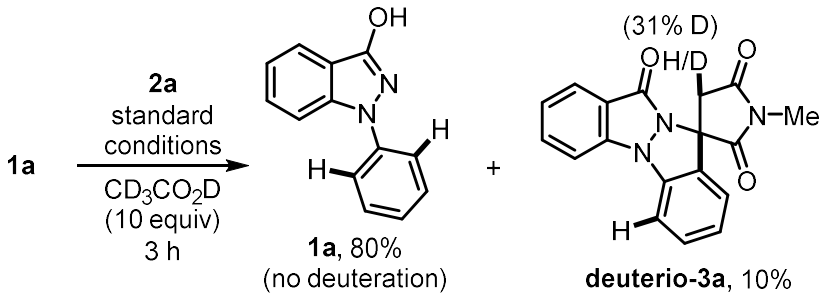


4t

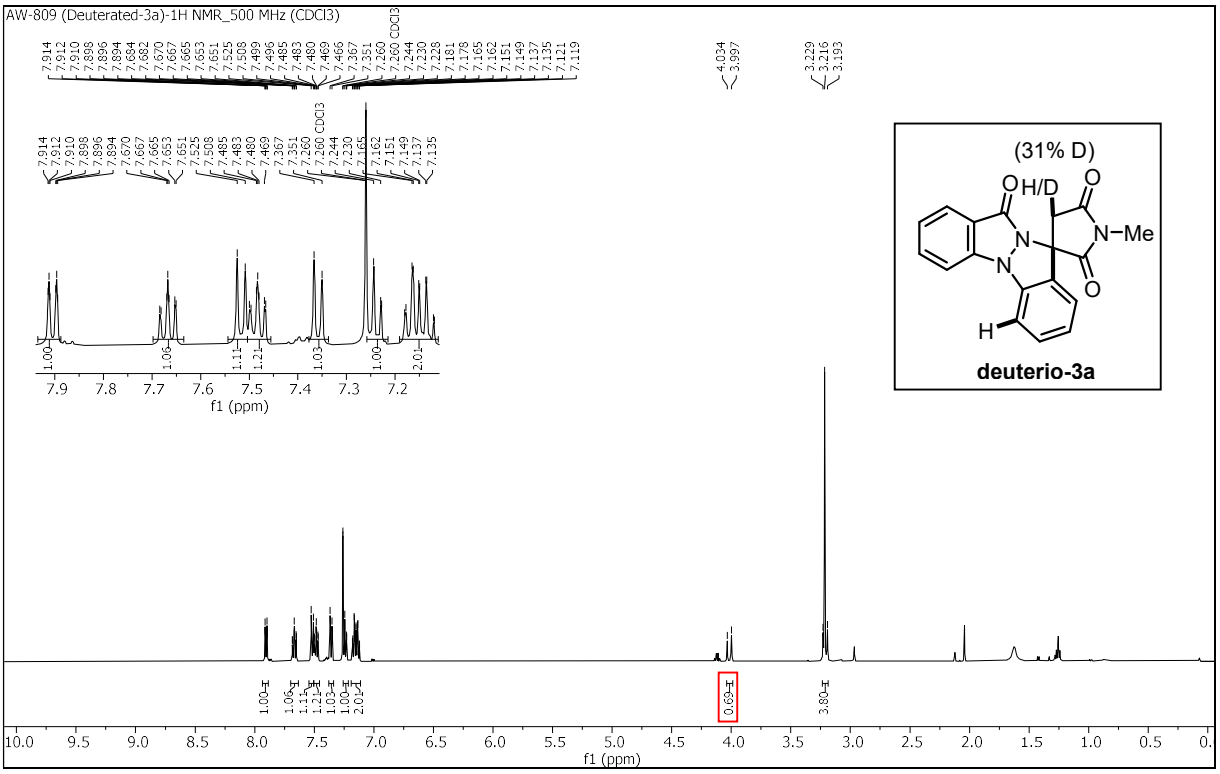
88.2 mg (87%, rotomers ratio = 2:1); eluent (CH_2Cl_2/EtOAc = 10:1 to 5:1); pale yellow solid; mp = 288.3–291.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) **rotomer A**: δ 8.41–8.31 (m, 1H), 8.28–8.21 (m, 3H), 8.19–8.11 (m, 3H), 8.09–8.03 (m, 1H), 8.01 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.70–7.63 (m, 1H), 7.59–7.50 (m, 2H), 7.41 (t, *J* = 8.4 Hz, 1H), 7.28–7.23 (m, 3H), 4.42 (d, *J* = 18.8 Hz, 1H), 3.66 (d, *J* = 18.8 Hz, 1H); **rotomer B**: δ 8.41–8.31 (m, 1H), 8.28–8.21 (m, 3H), 8.19–8.11 (m, 3H), 8.09–8.03 (m, 1H), 7.96 (dt, *J* = 8.0, 0.8 Hz, 1H), 7.79 (d, *J* = 9.2 Hz, 1H), 7.70–7.63 (m, 1H), 7.59–7.50 (m, 2H), 7.32 (td, *J* = 7.6, 0.8 Hz, 1H), 7.28–7.23

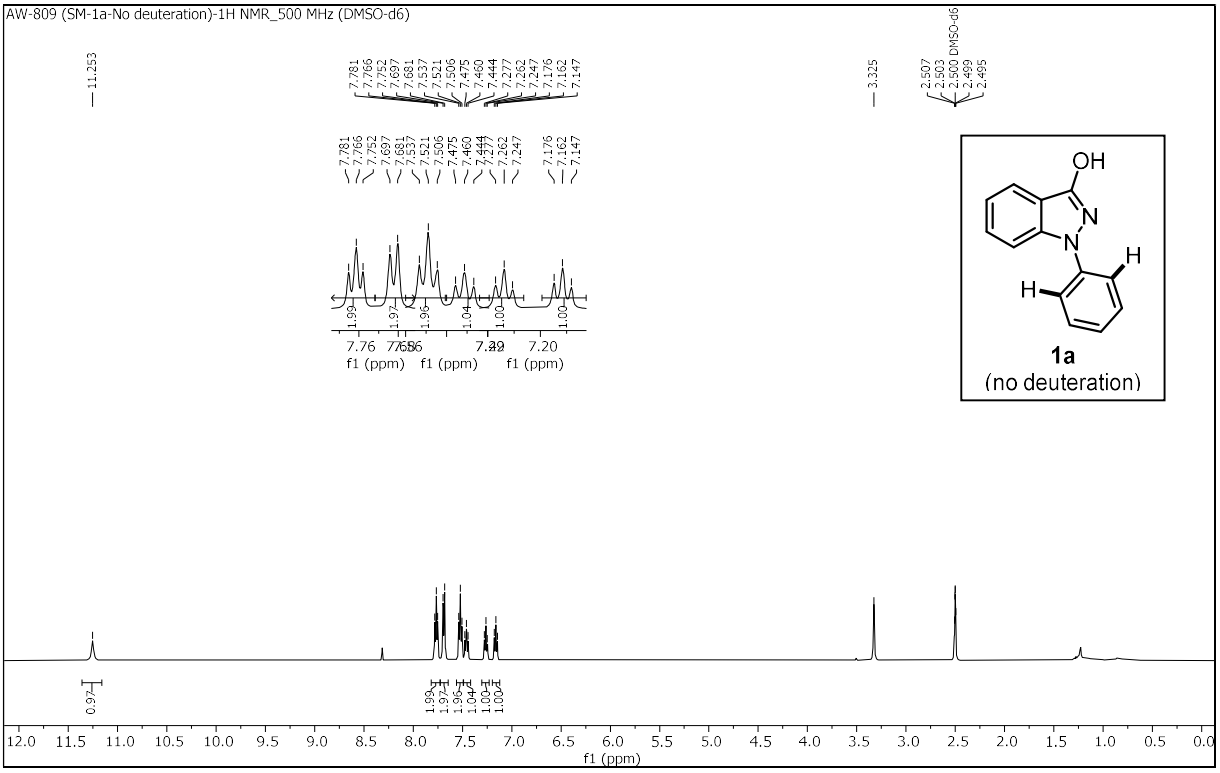
(m, 3H), 4.30 (d, J = 18.4 Hz, 1H), 3.59 (d, J = 18.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) **rotomer A**: δ 172.7, 161.7, 142.2, 137.7, 133.7, 132.6, 131.4, 131.1, 131.0, 130.7, 130.0, 129.4, 128.7, 127.4, 126.6, 126.4, 126.1, 125.7, 125.4, 125.3, 125.2, 125.0, 124.6, 124.2, 122.7, 122.5, 122.0, 119.7, 110.9, 110.0, 67.5, 41.4; **rotomer B**: δ 172.0, 160.9, 141.6, 137.2, 133.4, 132.5, 131.3, 131.1, 131.0, 130.5, 130.0, 128.9, 128.3, 127.1, 126.5, 126.3, 126.0, 125.6, 125.4, 125.3, 125.2, 124.9, 124.4, 124.1, 122.6, 122.4, 120.7, 119.6, 110.7, 109.8, 67.1, 41.0; IR (KBr) υ 3496, 3424, 3052, 2925, 2854, 1793, 1720, 1650, 1600, 1510, 1460, 1346, 1307, 1263, 1180, 1118, 946, 844 cm^{-1}; HRMS (quadrupole, EI) m/z: $[M]^+$ Calcd for $C_{33}H_{19}N_3O_3$ 505.1426; Found 505.1430.

General procedure and ^{1}H NMR copy for deuterium-labeling experiment



To an oven-dried sealed tube charged with 1-phenyl-1*H*-indazol-3-ol (**1a**) (42.1 mg, 0.2 mmol, 100 mol %), $[RhCp^*Cl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol %), $AgSbF_6$ (13.7 mg, 0.04 mmol, 20 mol %), NaOAc (8.2 mg, 0.1 mmol, 50 mol %), and *N*-methylmaleimide (**2a**) (44.4 mg, 0.4 mmol, 200 mol %) was added CD_3CO_2D (10 equiv.) and MeCN (1 mL) under air at room temperature. The reaction mixture was allowed to stir in an oil bath for 3 h at 80 °C. The reaction mixture was cooled to room temperature, diluted with EtOAc (2 mL), and concentrated in vacuo. The residue was purified by flash column chromatography (CH_2Cl_2/EtOAc = 7:1 to 4:1) to afford **1a** (33.6 mg, 80% recovered yield) and **deuterio-3a** (6.5 mg, 10% yield), respectively.

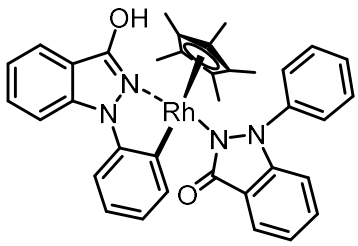



AW-809 (SM-1a-No deuteration)-1H NMR_500 MHz (DMSO-d6)
11.253
7.781
7.766
7.752
7.697
7.681
7.537
7.521
7.506
7.475
7.460
7.444
7.277
7.262
7.247
7.176
7.162
7.147
3.325
2.507
2.503
2.500 DMSO-d6
2.499
2.495
OH
N
N
H
H
1a
(no deuteration)
f1 (ppm)
f1 (ppm)
f1 (ppm)

General procedure and characterization data for the synthesis of rhodacycle-1a

To an oven-dried sealed tube charged with 1-phenyl-1*H*-indazol-3-ol (**1a**) (42.1 mg, 0.2 mmol, 100 mol %), $[RhCp^*Cl_2]_2$ (61.8 mg, 0.1 mmol, 50 mol %), and NaOAc (32.8 mg, 0.4 mmol, 200 mol %) was added DCE (3.5 mL) under air atmosphere at room temperature. The reaction mixture was allowed to stir at room temperature for 2 h. The reaction mixture was diluted with EtOAc (5 mL) and concentrated in vacuo. The residue was purified by flash column chromatography (CH_2Cl_2/MeOH = 100:1) to afford 63.2 mg of **rhodacycle-1a** in 48% yield as a dark brown solid, which was further recrystallized by CH_2Cl_2/pentane (1:5) to give **rhodacycle-1a** as a red solid.

Rhodacycle-1a



rhodacycle-1a

63.2 mg (48%); eluent (CH_2Cl_2/MeOH = 100:1); red solid; mp = > 300 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.82–7.84 (m, 1H), 7.77–7.74 (m, 2H), 7.70–7.67 (m, 2H), 7.58–7.48 (m, 4H), 7.46–7.41 (m, 2H), 7.37 (ddd, *J* = 9.6, 6.9, 1.2 Hz, 1H), 7.28–7.23 (m, 1H), 7.18–7.10 (m, 2H), 6.98 (ddd, *J* = 8.7, 7.2, 0.9 Hz, 1H), 6.89 (td, *J* = 7.5, 1.2 Hz, 1H), 1.72 (s, 15H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9, 153.5, 153.0, 143.6, 138.9, 138.2, 128.9 (two carbons overlap), 128.8, 128.4, 126.7, 126.6, 123.2, 122.4, 121.8, 121.5, 120.6, 119.6, 116.9, 110.2, 110.1, 108.5, 97.1, 97.0, 9.68; HRMS (ion trap, FAB) m/z: $[M + H]^+$ Calcd for $C_{36}H_{34}N_4O_2Rh$ 657.1737; Found 657.1731.

Experimental procedure for the reaction of 1a and 2a using rhodacycle-1a

To an oven-dried sealed tube charged with 1-phenyl-1*H*-indazol-3-ol (**1a**) (42.1 mg, 0.2 mmol, 100 mol %), **rhodacycle-1a** (6.6 mg, 0.01 mmol, 5 mol %), NaOAc (8.2 mg, 0.1 mmol, 50 mol %), and *N*-methyl maleimide (**2a**) (44.4 mg, 0.4 mmol, 200 mol %) was added MeCN (1 mL) under air at room temperature. The reaction mixture was allowed to stir in an oil bath for 20 h at 80 °C. The reaction mixture was cooled to room temperature, diluted with EtOAc (2 mL), and concentrated in vacuo. The residue was purified by flash column chromatography (CH_2Cl_2/EtOAc = 7:1 to 4:1) to afford **3a** (45.5 mg) in 71% yield.

Experimental procedure for the reaction of 1a and 2a using [RhCp*(OAc)$_2$]

To an oven-dried sealed tube charged with 1-phenyl-1*H*-indazol-3-ol (**1a**) (42.1 mg, 0.2 mmol, 100 mol %), RhCp*(OAc)$_2$ (7.2 mg, 0.01 mmol, 5 mol %), NaOAc (8.2 mg, 0.1 mmol, 50 mol %), and *N*-methyl maleimide (**2a**) (44.4 mg, 0.4 mmol, 200 mol %) was added MeCN (1 mL) under air at room temperature. The reaction mixture was allowed to stir in an oil bath for 20 h at 80 ^{o}C. The reaction mixture was cooled to room temperature, diluted with EtOAc (2 mL), and concentrated in vacuo. The residue was purified by flash column chromatography (CH_2Cl_2/EtOAc = 7:1 to 4:1) to afford **3a** (36.4 mg) in 57% yield.

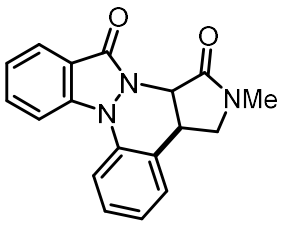
General procedure for the spiroannulation of rhodacycle-1a with maleimide for the formation of 3a

To an oven-dried sealed tube charged with **rhodacycle-1a** (32.8 mg, 0.05 mmol, 100 mol %), NaOAc (2.1 mg, 0.025 mmol, 50 mol %), and *N*-methyl maleimide (**2a**) (11.1 mg, 0.1 mmol, 200 mol %) was added MeCN (0.5 mL) under air at room temperature. The reaction mixture was allowed to stir in an oil bath for 20 h at 80 °C. The reaction mixture was cooled to room temperature, diluted with EtOAc (1 mL) and concentrated in vacuo. The residue was purified by flash column chromatography (CH_2Cl_2/EtOAc = 6:1 to 3:1) to afford **3a** (14.4 mg) in 90% yield.

General procedure and characterization data for the reaction of 1-phenyl-1*H*-indazol-3-ol (1a) with 1-methyl-1,5-dihydro-2*H*-pyrrol-2-one (5a)

To an oven-dried sealed tube charged with 1-phenyl-1*H*-indazol-3-ol (**1a**) (42.1 mg, 0.2 mmol, 100 mol %), $[RhCp^*Cl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol %), $AgSbF_6$ (13.7 mg, 0.04 mmol, 20 mol %), NaOAc (8.2 mg, 0.1 mmol, 50 mol %), and 1-methyl-1,5-dihydro-2*H*-pyrrol-2-one (**5a**) (38.8 mg, 0.4 mmol, 200 mol %) was added MeCN (1 mL) under air at room temperature. The reaction mixture was allowed to stir in an oil bath for 20 h at 80 °C. The reaction mixture was cooled to room temperature, diluted with EtOAc (2 mL) and concentrated in vacuo. The residue was purified by flash column chromatography (CH_2Cl_2/EtOAc = 1:1 to 1:4) to afford **6a** (21.6 mg) in 35% yield.

2-Methyl-2,3,3*a*,14*a*-tetrahydro-1*H*,13*H*-indazolo[1,2-*a*]pyrrolo[3,4-*c*]cinnoline-1,13-dione (6a)



6a

21.6 mg (35%); eluent (CH_2Cl_2/EtOAc = 1:1 to 1:4); pale yellow sticky solid; ^{1}H NMR (500 MHz, $CD_3COCD_3/CDCl_3$ = 10:1) δ 7.84 (dt, *J* = 8.5, 0.5 Hz, 1H), 7.79 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.73 (ddd, *J* = 8.5, 7.0, 1.5 Hz, 1H), 7.67 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.58 (ddd, *J* = 8.5, 7.5, 0.5 Hz, 2H), 7.25 (tdd, *J* = 15.5, 3.0, 1.0 Hz, 2H), 3.07 (dt, *J* = 16.5, 9.5 Hz, 1H), 2.92 (ddd, *J* = 14.0, 9.5, 2.0 Hz, 1H), 2.75 (dt, *J* = 14.0, 9.5 Hz, 1H), 2.56 (ddd, *J* = 16.5, 9.5, 2.9 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (125 MHz, $CD_3COCD_3/CDCl_3$ = 10:1) δ 175.0, 159.9, 142.0, 138.3, 133.9, 132.0, 131.4, 125.5, 125.1, 124.5, 122.9, 120.9, 111.9, 110.3, 85.2, 32.6, 30.8, 25.1; IR (KBr) υ 3469, 2925, 1672, 1584, 1481, 1445, 1380, 1349, 1297, 1245, 1149, 1114, 995, 904 cm^{-1}; HRMS (quadrupole, EI) m/z: $[M]^+$ Calcd for $C_{18}H_{15}N_3O_2$ 305.1164; Found 305.1161.

General procedure for the gram scale experiment of 3a

To an oven-dried sealed tube charged with 1-phenyl-1*H*-indazol-3-ol (**1a**) (1.0 g, 4.8 mmol, 100 mol %), $[RhCp^*Cl_2]_2$ (74.2 mg, 0.12 mmol, 2.5 mol %), $AgSbF_6$ (329.9 mg, 0.96 mmol, 20 mol %), NaOAc (196.9 mg, 2.4 mmol, 50 mol %), and *N*-methyl maleimide (**2a**) (1.07 g, 9.6 mmol, 200 mol %) was added MeCN (24 mL) under air at room temperature. The reaction mixture was allowed to stir in an oil bath for 20 h at 80 °C. The reaction mixture was cooled to room temperature, diluted with EtOAc (20 mL), and concentrated in vacuo. The residue was purified by flash column chromatography (CH_2Cl_2/EtOAc = 7:1 to 4:1) to afford **3a** (1.38 g) in 90% yield.

X-ray crystallographic data of 1-phenyl-1*H*-indazol-3-ol (1a) (CCDC 2096892)

Sample preparation (solvent evaporation)

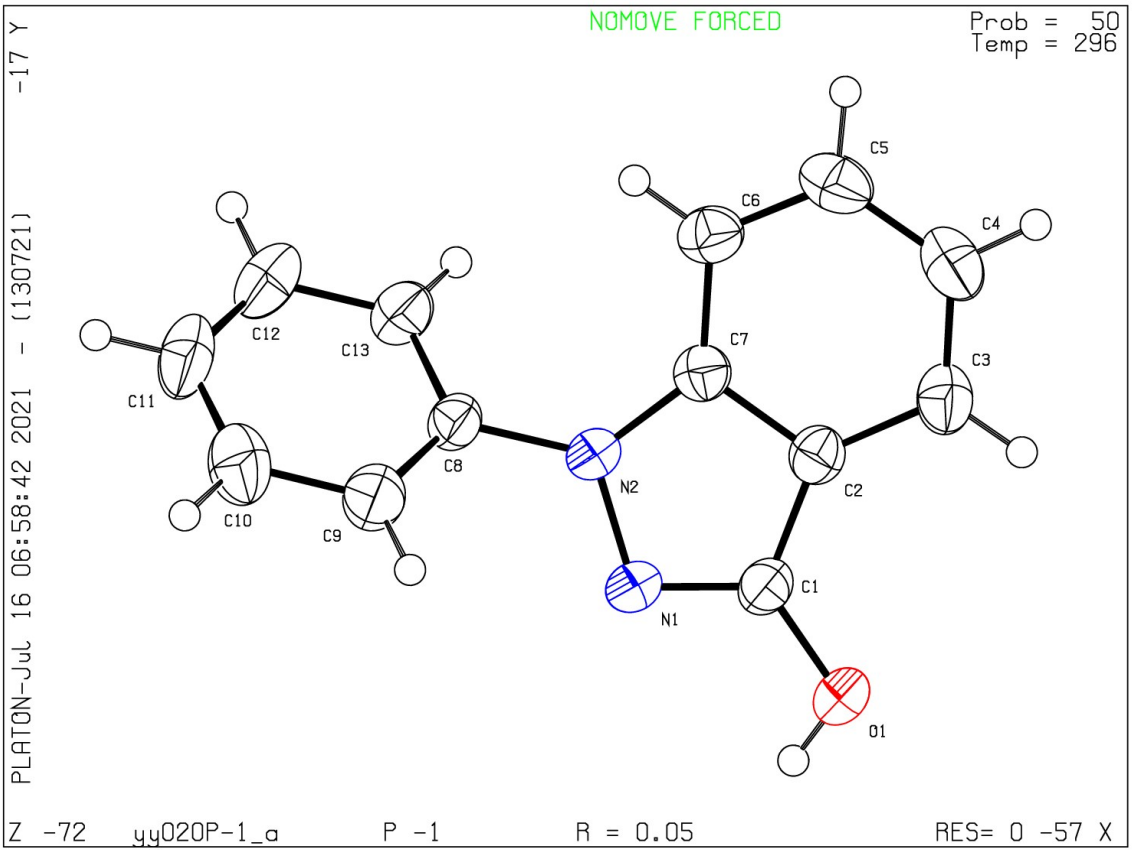
Compound **1a** (25 mg) was dissolved with 1 mL of CH_2Cl_2 in opened inner vessel, and *n*-pentane (5 mL) as an anti-solvent has been employed in closed outer vessel. After vapor diffusion for 2 days, the single crystals of compound **1a** were obtained.

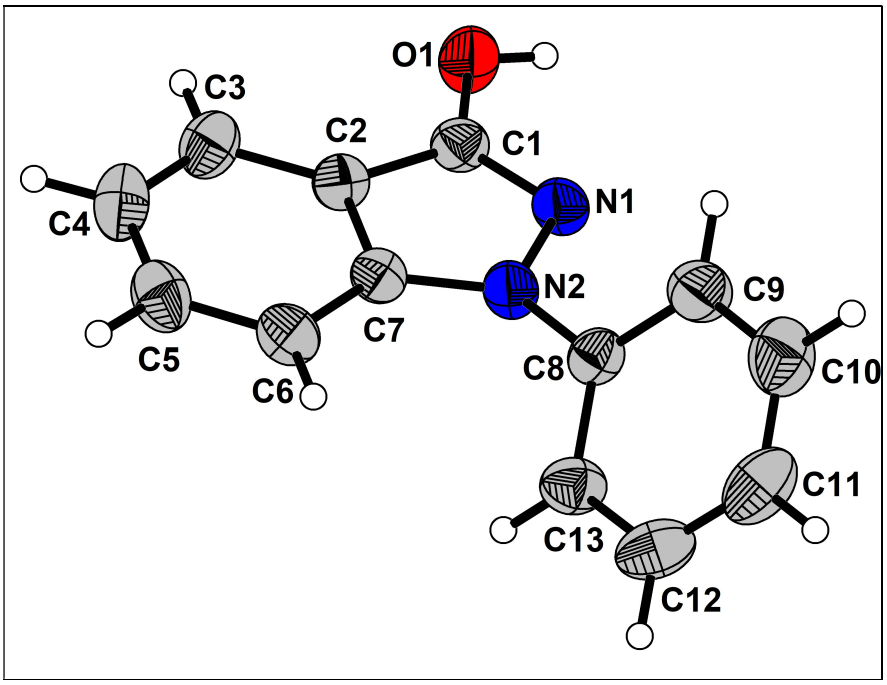
Detailed experimental description for the crystal measurement of 1-phenyl-1*H*-indazol-3-ol (1a)

Crystals grew as colorless plate-like in CH_2Cl_2 by slow evaporation from *n*-pentane. The crystal structures of compound **1a** were determined by standard crystallographic methods. A colorless crystal of $C_{13}H_{10}N_2O$ with approximate dimensions 0.020 x 0.150 x 0.200 mm^3 was used for single-crystal X-ray diffraction. The data were collected at 223(2) K using a Bruker D8 Venture equipped with a graphite monochromator with CuK_α radiation (λ = 0.71073 Å) and a PHOTON III M14 detector in Western Seoul Center of Korea Basic Science Institute. Data collection and integration were performed with SMART APEX3 software package (SAINT).[4] Absorption correction was performed by multi-scan method implemented in SADABS.[5] The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL program package (version 6.14).[6] All the non-hydrogen atoms were refined anisotropically, and hydrogen atoms were added to their geometrically ideal positions.

Details of crystal data, data collection and structure refinement are listed in Table S2. Further details of the individual structures can be obtained from the Cambridge Crystallographic Data Centre by quoting **CCDC 2096892**.

ORTEP diagram of 1a (CCDC 2096892)





A colorless plate-like specimen of $C_{13}H_{10}N_2O$, approximate dimensions 0.020 mm x 0.150 mm x 0.200 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured (λ = 0.71073 Å).

Table S1: Data collection details for 1a.

Axis	dx/mm	2θ/°	ω/°	φ/°	χ/°	Width/°	Frames	Time/s	Wavelength/Å	Voltage/kV	Current/mA	Temperature/K
Phi	60.663	0.00	0.00	0.00	54.74	1.00	180	1.20	0.71073	50	30.0	n/a
Phi	60.663	0.00	0.00	180.00	54.74	1.00	180	1.20	0.71073	50	30.0	n/a
Omega	60.663	18.54	-174.46	-105.00	54.74	1.00	206	10.00	0.71073	50	30.0	n/a
Omega	60.663	18.54	-174.46	102.00	54.74	1.00	206	10.00	0.71073	50	30.0	n/a
Omega	60.663	18.54	-174.46	0.00	54.74	1.00	206	10.00	0.71073	50	30.0	n/a
Phi	60.663	18.54	31.54	0.00	54.74	1.00	360	10.00	0.71073	50	30.0	n/a
Omega	60.663	18.54	-174.46	-156.00	54.74	1.00	206	10.00	0.71073	50	30.0	n/a
Phi	60.663	0.00	0.00	0.00	54.74	360.00	1	108.00	0.71073	50	30.0	n/a

A total of 1545 frames were collected. The total exposure time was 3.44 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 16137 reflections to a maximum θ angle of 28.42° (0.75 Å resolution), of which 2588 were independent (average redundancy 6.235, completeness = 99.5%, R_{int} = 4.00%, R_{sig} = 3.02%) and 2051 (79.25%) were greater than $2\sigma(F^2)$. The final cell constants of a = 6.772(2) Å, b = 9.153(2) Å, c = 9.331(2) Å, α = 70.250(7)°, β = 87.119(8)°, γ = 72.184(8)°, volume = 517.3(2) $Å^3$, are based upon the refinement of the XYZ-centroids of 5540 reflections above 20 σ(I) with 4.646° < 2θ < 55.07°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.914. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9830 and 0.9980.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P -1, with Z = 2 for the formula unit, $C_{13}H_{10}N_2O$. The final anisotropic full-matrix least-squares refinement on F^2 with 146 variables converged at R1 = 4.91%, for the observed data and wR2 = 12.09% for all data. The goodness-of-fit was 1.060. The largest peak in the final difference electron density synthesis was 0.221 $e^-/Å^3$ and the largest hole was -0.220 $e^-/Å^3$ with an RMS deviation of 0.037 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.350 g/cm^3 and F(000), 220 e^-.

Table S2. Sample and crystal data for 1a.

Chemical formula	$C_{13}H_{10}N_2O$	
Formula weight	210.23 g/mol	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal size	0.020 x 0.150 x 0.200 mm	
Crystal habit	colorless plate	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 6.772(2) Å	α = 70.250(7)°
	b = 9.153(2) Å	β = 87.119(8)°
	c = 9.331(2) Å	γ = 72.184(8)°
Volume	517.3(2) $Å^3$	
Z	2	
Density (calculated)	1.350 g/cm^3	
Absorption coefficient	0.088 mm^{-1}	
F(000)	220	

Table S3. Data collection and structure refinement for 1a.

Theta range for data collection	2.32 to 28.42°	
Index ranges	-9≤h≤9, -12≤k≤12, -12≤l≤12	
Reflections collected	16137	
Independent reflections	2588 [R(int) = 0.0400]	
Coverage of independent reflections	99.5%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.9980 and 0.9830	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	2588 / 0 / 146	
Goodness-of-fit on F^2	1.060	
Final R indices	2051 data; I>2σ(I)	R_1 = 0.0491, wR_2 = 0.1134
	all data	R_1 = 0.0640, wR_2 = 0.1209
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0515P)^2+0.1255P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.221 and -0.220 eÅ^{-3}	
R.M.S. deviation from mean	0.037 eÅ^{-3}	

Table S4. Atomic coordinates and equivalent isotropic atomic displacement parameters ($Å^2$) for 1a.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
C1	0.2204(2)	0.02157(16)	0.61760(15)	0.0349(3)
C2	0.3879(2)	0.06146(16)	0.66562(16)	0.0339(3)
C3	0.5245(2)	0.99798(18)	0.79570(17)	0.0434(4)
C4	0.6646(2)	0.0772(2)	0.80102(19)	0.0490(4)
C5	0.6728(2)	0.2166(2)	0.6802(2)	0.0468(4)
C6	0.5418(2)	0.28130(18)	0.55217(18)	0.0405(3)
C7	0.3974(2)	0.20133(16)	0.54635(15)	0.0331(3)
C8	0.1710(2)	0.38125(16)	0.30941(15)	0.0340(3)
C9	0.9629(2)	0.47121(19)	0.29050(18)	0.0465(4)
C10	0.8930(3)	0.6122(2)	0.1654(2)	0.0574(5)
C11	0.0298(3)	0.6635(2)	0.06100(19)	0.0564(5)
C12	0.2368(3)	0.5747(2)	0.08195(18)	0.0527(4)
C13	0.3093(2)	0.43257(18)	0.20520(17)	0.0420(3)
N1	0.13324(17)	0.12638(14)	0.48492(13)	0.0363(3)
N2	0.24482(17)	0.23690(14)	0.43820(13)	0.0358(3)
O1	0.16032(17)	0.89214(13)	0.69579(12)	0.0467(3)

Table S5. Bond lengths (Å) for 1a.

C1-N1	1.3136(18)	C1-O1	1.3349(16)
C1-C2	1.427(2)	C2-C7	1.4008(19)
C2-C3	1.405(2)	C3-C4	1.371(2)
C3-H3	0.93	C4-C5	1.402(2)
C4-H4	0.93	C5-C6	1.368(2)
C5-H5	0.93	C6-C7	1.401(2)
C6-H6	0.93	C7-N2	1.3673(18)
C8-C13	1.383(2)	C8-C9	1.383(2)
C8-N2	1.4222(17)	C9-C10	1.384(2)
C9-H9	0.93	C10-C11	1.376(3)
C10-H10	0.93	C11-C12	1.373(3)
C11-H11	0.93	C12-C13	1.382(2)
C12-H12	0.93	C13-H13	0.93
N1-N2	1.3859(16)	O1-H1	0.82

Table S6. Bond angles (°) for 1a.

N1-C1-O1	123.56(13)	N1-C1-C2	111.87(12)
O1-C1-C2	124.56(12)	C7-C2-C3	120.14(13)
C7-C2-C1	104.14(12)	C3-C2-C1	135.69(13)
C4-C3-C2	117.90(14)	C4-C3-H3	121.1
C2-C3-H3	121.1	C3-C4-C5	121.20(14)
C3-C4-H4	119.4	C5-C4-H4	119.4
C6-C5-C4	122.24(14)	C6-C5-H5	118.9
C4-C5-H5	118.9	C5-C6-C7	116.84(14)
C5-C6-H6	121.6	C7-C6-H6	121.6
N2-C7-C2	107.32(12)	N2-C7-C6	130.99(13)
C2-C7-C6	121.67(13)	C13-C8-C9	120.35(14)
C13-C8-N2	119.58(13)	C9-C8-N2	120.05(13)
C8-C9-C10	119.57(15)	C8-C9-H9	120.2
C10-C9-H9	120.2	C11-C10-C9	120.31(16)
C11-C10-H10	119.8	C9-C10-H10	119.8
C12-C11-C10	119.72(15)	C12-C11-H11	120.1
C10-C11-H11	120.1	C11-C12-C13	120.89(16)
C11-C12-H12	119.6	C13-C12-H12	119.6
C12-C13-C8	119.15(15)	C12-C13-H13	120.4
C8-C13-H13	120.4	C1-N1-N2	106.10(11)
C7-N2-N1	110.54(11)	C7-N2-C8	127.98(12)
N1-N2-C8	120.27(11)	C1-O1-H1	109.5

Table S7. Anisotropic atomic displacement parameters (Å^2) for 1a.

The anisotropic atomic displacement factor exponent takes the form:
$-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.0357(7)	0.0310(7)	0.0341(7)	-0.0054(6)	0.0035(5)	-0.0114(5)
C2	0.0350(7)	0.0299(6)	0.0349(7)	-0.0102(5)	0.0020(5)	-0.0081(5)
C3	0.0486(8)	0.0354(8)	0.0390(8)	-0.0079(6)	-0.0053(6)	-0.0068(6)
C4	0.0459(8)	0.0476(9)	0.0507(9)	-0.0194(8)	-0.0130(7)	-0.0050(7)
C5	0.0396(8)	0.0494(9)	0.0599(10)	-0.0268(8)	-0.0016(7)	-0.0154(7)
C6	0.0397(7)	0.0362(7)	0.0480(8)	-0.0148(6)	0.0049(6)	-0.0148(6)
C7	0.0323(6)	0.0308(7)	0.0356(7)	-0.0117(5)	0.0028(5)	-0.0087(5)
C8	0.0400(7)	0.0288(6)	0.0319(7)	-0.0067(5)	0.0004(5)	-0.0126(6)
C9	0.0420(8)	0.0447(9)	0.0453(8)	-0.0077(7)	0.0034(6)	-0.0113(7)
C10	0.0522(10)	0.0449(9)	0.0589(11)	-0.0089(8)	-0.0096(8)	0.0000(8)
C11	0.0817(13)	0.0341(8)	0.0408(9)	-0.0008(7)	-0.0071(8)	-0.0120(8)
C12	0.0723(11)	0.0428(9)	0.0392(8)	-0.0061(7)	0.0129(8)	-0.0227(8)
C13	0.0441(8)	0.0377(8)	0.0408(8)	-0.0089(6)	0.0078(6)	-0.0137(6)
N1	0.0355(6)	0.0335(6)	0.0378(6)	-0.0039(5)	0.0011(5)	-0.0166(5)
N2	0.0359(6)	0.0321(6)	0.0368(6)	-0.0030(5)	-0.0010(5)	-0.0160(5)
O1	0.0515(6)	0.0421(6)	0.0413(6)	0.0033(5)	-0.0052(5)	-0.0253(5)

Table S8. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for 1a.

	x/a	y/b	z/c	U(eq)
H3	0.5200	-0.0949	0.8757	0.052
H4	0.7559	0.0378	0.8863	0.059
H5	0.7706	0.2667	0.6874	0.056
H6	0.5482	0.3740	0.4728	0.049
H9	-0.1296	0.4372	0.3614	0.056
H10	-0.2470	0.6726	0.1518	0.069
H11	-0.0176	0.7578	-0.0234	0.068
H12	0.3294	0.6107	0.0123	0.063
H13	0.4494	0.3722	0.2179	0.05
H1	0.0676	-0.1128	0.6461	0.07

X-ray crystallographic data of rhodacycle-1a (CCDC 2095228)

Sample preparation (solvent evaporation)

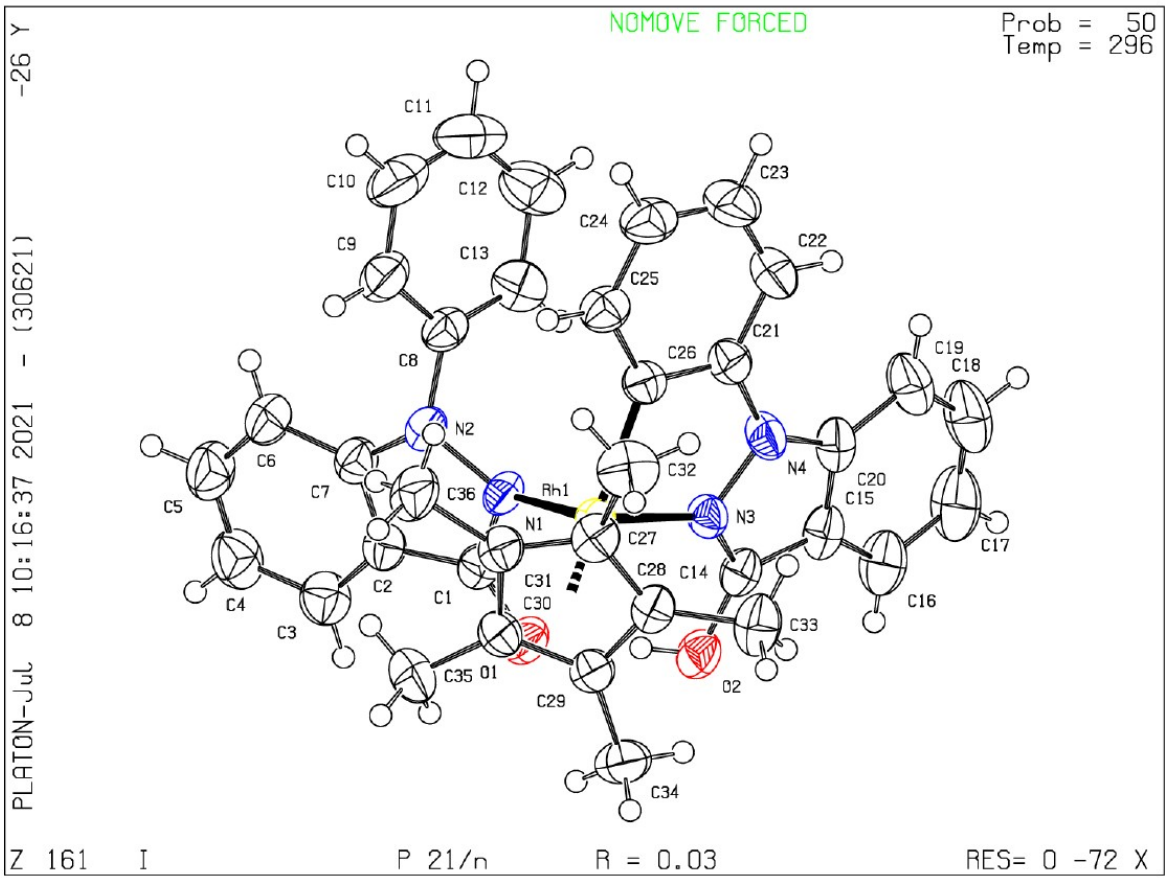
Isolated **rhodacycle-1a** (50 mg) was dissolved with CH_2Cl_2 (1 mL) and *n*-pentane (5 mL) in a sample vial that has a perforated cap. With slow solvent evaporation for 2 days, the single crystals of **rhodacycle-1a** were obtained.

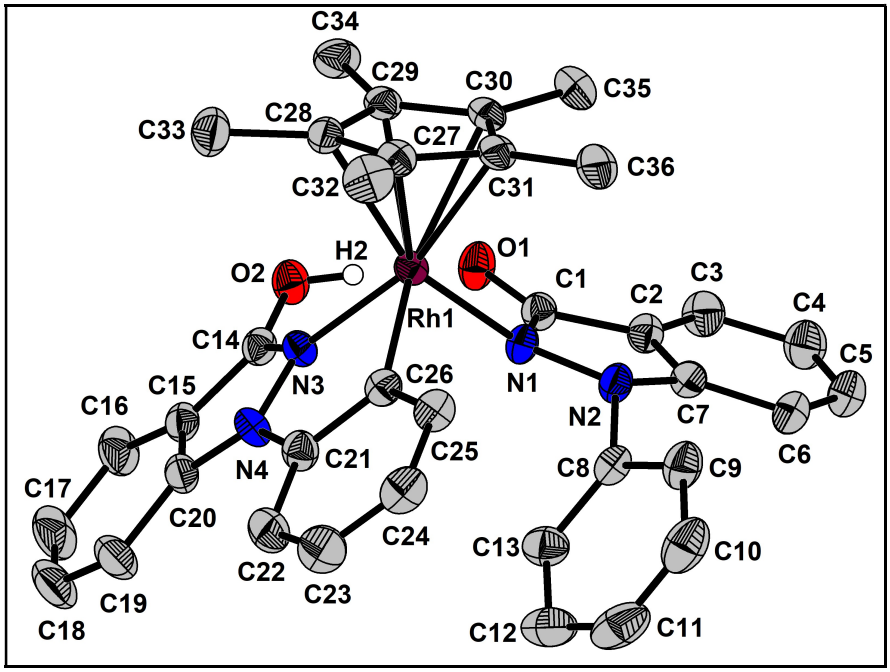
Detailed experimental description for the crystal measurement of rhodacycle-1a

Crystals grew as red color in CH_2Cl_2 by slow evaporation from *n*-pentane. The crystal structures of **rhodacycle-1a** were determined by standard crystallographic methods. A red block-like crystal of $C_{36}H_{33}N_4O_2Rh$ with approximate dimensions 0.080 x 0.190 x 0.200 mm^3 was used for single-crystal X-ray diffraction. The data were collected at 223(2) K using a Bruker D8 Venture equipped with a graphite monochromator with CuK_α radiation (λ = 0.71073 Å) and a PHOTON III M14 detector in Western Seoul Center of Korea Basic Science Institute. Data collection and integration were performed with SMART APEX3 software package (SAINT).[5] Absorption correction was performed by multi-scan method implemented in SADABS.[6] The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL program package (version 6.14).[7] All the non-hydrogen atoms were refined anisotropically, and hydrogen atoms were added to their geometrically ideal positions.

Details of crystal data, data collection and structure refinement are listed in Table S10. Further details of the individual structures can be obtained from the Cambridge Crystallographic Data Centre by quoting **CCDC 2095228**.

ORTEP diagram of rhodacycle-1a (CCDC 2095228)





A red block-like specimen of $C_{36}H_{33}N_4O_2Rh$, approximate dimensions 0.080 mm x 0.190 mm x 0.200 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured (λ = 0.71073 Å).

Table S9: Data collection details for rhodacycle-1a (CCDC 2095228).

Axis	dx/mm	2θ/°	ω/°	φ/°	χ/°	Width/°	Frames	Time/s	Wavelength/Å	Voltage/kV	Current/mA	Temperature/K
Phi	60.558	0.00	0.00	0.00	54.74	1.00	180	1.20	0.71073	50	30.0	n/a
Phi	60.558	0.00	0.00	180.00	54.74	1.00	180	1.20	0.71073	50	30.0	n/a
Omega	60.558	18.54	-174.46	153.00	54.74	1.00	206	10.00	0.71073	50	30.0	n/a
Omega	60.558	27.81	-165.19	0.00	54.74	1.00	206	10.00	0.71073	50	30.0	n/a
Omega	60.558	18.54	-174.46	-105.00	54.74	1.00	206	10.00	0.71073	50	30.0	n/a
Omega	60.558	18.54	-174.46	102.00	54.74	1.00	206	10.00	0.71073	50	30.0	n/a
Omega	60.558	18.54	-174.46	-54.00	54.74	1.00	206	10.00	0.71073	50	30.0	n/a
Omega	60.558	18.54	-174.46	51.00	54.74	1.00	206	10.00	0.71073	50	30.0	n/a
Omega	60.558	18.54	-174.46	-156.00	54.74	1.00	206	10.00	0.71073	50	30.0	n/a
Omega	60.558	18.54	-174.46	0.00	54.74	1.00	206	10.00	0.71073	50	30.0	n/a
Phi	60.558	0.00	0.00	0.00	54.74	360.00	1	108.00	0.71073	50	30.0	n/a

A total of 2009 frames were collected. The total exposure time was 4.73 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 112285 reflections to a maximum θ angle of 25.05° (0.84 Å resolution), of which 5304 were independent (average redundancy 21.170, completeness = 99.9%, R_{int} = 4.55%, R_{sig} = 1.41%) and 4740 (89.37%) were greater than $2\sigma(F^2)$. The final cell constants of a = 12.8432(6) Å, b = 14.0502(6) Å, c = 16.6156(7) Å, β = 93.340(2)°, volume = 2993.2(2) $Å^3$, are based upon the refinement of the XYZ-centroids of 9908 reflections above 20 σ(I) with 5.043° < 2θ < 56.48°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.912. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8880 and 0.9530.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/n 1, with Z = 4 for the formula unit, $C_{36}H_{33}N_4O_2Rh$. The final anisotropic full-matrix least-squares refinement on F^2 with 394 variables converged at R1 = 3.13%, for the observed data and wR2 = 8.68% for all data. The goodness-of-fit was 1.060. The largest peak in the final difference electron density synthesis was 1.850 $e^-/Å^3$ and the largest hole was -0.604 $e^-/Å^3$ with an RMS deviation of 0.058 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.457 g/cm^3 and F(000), 1352 e^-.

Table S10. Sample and crystal data for rhodacycle-1a.

Chemical formula	$C_{36}H_{33}N_4O_2Rh$	
Formula weight	656.57 g/mol	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal size	0.080 x 0.190 x 0.200 mm	
Crystal habit	red block	
Crystal system	monoclinic	
Space group	P 2_1/n	
Unit cell dimensions	a = 12.8432(6) Å	α = 90°
	b = 14.0502(6) Å	β = 93.340(2)°
	c = 16.6156(7) Å	γ = 90°
Volume	2993.2(2) $Å^3$	
Z	4	
Density (calculated)	1.457 g/cm^3	
Absorption coefficient	0.610 mm^{-1}	
F(000)	1352	

Table S11. Data collection and structure refinement for rhodacycle-1a.

Theta range for data collection	1.90 to 25.05°	
Index ranges	-15≤h≤15, -16≤k≤16, -19≤l≤19	
Reflections collected	112285	
Independent reflections	5304 [R(int) = 0.0455]	
Coverage of independent reflections	99.9%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.9530 and 0.8880	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	5304 / 2 / 394	
Goodness-of-fit on F^2	1.060	
Δ/σ_{max}	0.001	
Final R indices	4740 data; I>2σ(I)	R_1 = 0.0313, wR_2 = 0.0814
	all data	R_1 = 0.0369, wR_2 = 0.0868
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0409P)^2+3.7289P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	1.850 and -0.604 eÅ^{-3}	
R.M.S. deviation from mean	0.058 eÅ^{-3}	

Table S12. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for rhodacycle-1a.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
C1	0.8071(2)	0.7509(2)	0.26002(11)	0.0406(6)
C2	0.9102(2)	0.7381(2)	0.29989(18)	0.0423(6)
C3	0.0082(3)	0.7260(2)	0.2703(2)	0.0552(8)
C4	0.0921(3)	0.7162(3)	0.3258(3)	0.0638(9)
C5	0.0776(3)	0.7181(3)	0.4081(2)	0.0636(10)
C6	0.9820(3)	0.7309(2)	0.4385(2)	0.0540(8)
C7	0.8972(2)	0.7426(2)	0.38187(18)	0.0426(7)
C8	0.7439(2)	0.7238(2)	0.46171(17)	0.0425(7)
C9	0.7621(3)	0.7679(3)	0.53563(19)	0.0574(9)
C10	0.7201(3)	0.7314(4)	0.6026(2)	0.0735(12)
C11	0.6609(4)	0.6512(4)	0.5977(3)	0.0797(14)
C12	0.6409(3)	0.6062(3)	0.5242(3)	0.0728(11)
C13	0.6832(3)	0.6426(2)	0.4556(2)	0.0549(8)
C14	0.54997(18)	0.6894(2)	0.16374(15)	0.0394(6)
C15	0.4793(2)	0.6124(2)	0.15312(19)	0.0441(7)
C16	0.4636(3)	0.5454(2)	0.0923(2)	0.0614(9)
C17	0.3911(3)	0.4753(3)	0.1025(3)	0.0764(12)
C18	0.3366(3)	0.4724(3)	0.1716(3)	0.0763(12)
C19	0.3499(3)	0.5376(3)	0.2328(3)	0.0639(10)
C20	0.4243(2)	0.6095(2)	0.2224(2)	0.0449(7)
C21	0.4476(2)	0.7111(2)	0.35009(18)	0.0435(7)
C22	0.3781(3)	0.6683(3)	0.4003(2)	0.0605(9)
C23	0.3747(3)	0.6984(3)	0.4790(2)	0.0652(10)
C24	0.4378(3)	0.7701(3)	0.5074(2)	0.0569(9)
C25	0.5069(2)	0.8130(2)	0.45714(18)	0.0465(7)
C26	0.5131(2)	0.7858(2)	0.37690(17)	0.0388(6)
C27	0.5358(2)	0.9862(2)	0.31377(18)	0.0435(7)
C28	0.5196(2)	0.9607(2)	0.23070(18)	0.0419(6)
C29	0.6196(2)	0.9580(2)	0.19536(17)	0.0403(6)
C30	0.6959(2)	0.9745(2)	0.25723(18)	0.0423(7)
C31	0.6459(2)	0.98847(19)	0.33204(17)	0.0420(7)
C32	0.4523(3)	0.0113(3)	0.3687(2)	0.0630(9)
C33	0.4161(3)	0.9500(3)	0.1846(2)	0.0629(9)

	x/a	y/b	z/c	U(eq)
C34	0.6352(3)	0.9473(3)	0.10701(19)	0.0565(8)
C35	0.8112(3)	0.9805(3)	0.2487(2)	0.0599(9)
C36	0.7011(3)	0.0153(3)	0.4108(2)	0.0591(9)
N1	0.73788(18)	0.76225(17)	0.31744(13)	0.0387(5)
N2	0.79342(19)	0.76121(18)	0.39391(14)	0.0423(6)
N3	0.53676(18)	0.73200(16)	0.23163(14)	0.0374(5)
N4	0.45830(19)	0.68386(18)	0.27000(15)	0.0434(6)
O1	0.78865(16)	0.75462(17)	0.18516(10)	0.0510(5)
O2	0.62258(16)	0.71603(16)	0.11391(11)	0.0476(5)
Rh1	0.60155(2)	0.84694(2)	0.29261(2)	0.03282(9)

Table S13. Bond lengths (Å) for rhodacycle-1a.

C1-O1	1.2538(10)	C1-N1	1.351(3)
C1-C2	1.456(4)	C2-C7	1.383(4)
C2-C3	1.388(4)	C3-C4	1.384(5)
C3-H3	0.93	C4-C5	1.391(5)
C4-H4	0.93	C5-C6	1.366(5)
C5-H5	0.93	C6-C7	1.407(4)
C6-H6	0.93	C7-N2	1.384(4)
C8-C13	1.382(5)	C8-C9	1.383(4)
C8-N2	1.426(4)	C9-C10	1.365(5)
C9-H9	0.93	C10-C11	1.359(6)
C10-H10	0.93	C11-C12	1.385(6)
C11-H11	0.93	C12-C13	1.388(5)
C12-H12	0.93	C13-H13	0.93
C14-N3	1.297(3)	C14-O2	1.3362(10)
C14-C15	1.416(4)	C15-C20	1.386(5)
C15-C16	1.387(4)	C16-C17	1.372(6)
C16-H16	0.93	C17-C18	1.380(6)
C17-H17	0.93	C18-C19	1.371(6)
C18-H18	0.93	C19-C20	1.408(4)
C19-H19	0.93	C20-N4	1.367(4)
C21-C22	1.394(4)	C21-N4	1.399(4)
C21-C26	1.401(4)	C22-C23	1.378(5)
C22-H22	0.93	C23-C24	1.360(5)
C23-H23	0.93	C24-C25	1.391(5)
C24-H24	0.93	C25-C26	1.394(4)
C25-H25	0.93	C26-Rh1	2.043(3)
C27-C28	1.429(4)	C27-C31	1.429(4)
C27-C32	1.491(4)	C27-Rh1	2.168(3)
C28-C29	1.444(4)	C28-C33	1.502(4)
C28-Rh1	2.143(3)	C29-C30	1.398(4)
C29-C34	1.501(4)	C29-Rh1	2.268(3)
C30-C31	1.445(4)	C30-C35	1.498(4)
C30-Rh1	2.260(3)	C31-C36	1.501(4)
C31-Rh1	2.160(3)	C32-H32A	0.96
C32-H32B	0.96	C32-H32C	0.96
C33-H33A	0.96	C33-H33B	0.96

C33-H33C	0.96	C34-H34A	0.96
C34-H34B	0.96	C34-H34C	0.96
C35-H35A	0.96	C35-H35B	0.96
C35-H35C	0.96	C36-H36A	0.96
C36-H36B	0.96	C36-H36C	0.96
N1-N2	1.420(3)	N1-Rh1	2.137(2)
N3-N4	1.398(3)	N3-Rh1	2.056(2)
O2-H2	0.82		

Table S14. Bond angles (°) for rhodacycle-1a.

O1-C1-N1	127.0(3)	O1-C1-C2	124.8(3)
N1-C1-C2	108.15(19)	C7-C2-C3	121.2(3)
C7-C2-C1	106.5(2)	C3-C2-C1	132.3(3)
C4-C3-C2	117.6(3)	C4-C3-H3	121.2
C2-C3-H3	121.2	C3-C4-C5	120.6(3)
C3-C4-H4	119.7	C5-C4-H4	119.7
C6-C5-C4	122.7(3)	C6-C5-H5	118.7
C4-C5-H5	118.7	C5-C6-C7	116.5(3)
C5-C6-H6	121.7	C7-C6-H6	121.7
C2-C7-N2	108.9(2)	C2-C7-C6	121.3(3)
N2-C7-C6	129.8(3)	C13-C8-C9	120.0(3)
C13-C8-N2	121.5(3)	C9-C8-N2	118.4(3)
C10-C9-C8	120.1(4)	C10-C9-H9	120.0
C8-C9-H9	120.0	C11-C10-C9	120.6(4)
C11-C10-H10	119.7	C9-C10-H10	119.7
C10-C11-C12	120.4(4)	C10-C11-H11	119.8
C12-C11-H11	119.8	C11-C12-C13	119.6(4)
C11-C12-H12	120.2	C13-C12-H12	120.2
C8-C13-C12	119.3(4)	C8-C13-H13	120.3
C12-C13-H13	120.3	N3-C14-O2	122.7(2)
N3-C14-C15	110.2(2)	O2-C14-C15	127.0(3)
C20-C15-C16	121.7(3)	C20-C15-C14	105.8(2)
C16-C15-C14	132.4(3)	C17-C16-C15	117.9(4)
C17-C16-H16	121.0	C15-C16-H16	121.0
C16-C17-C18	120.3(4)	C16-C17-H17	119.8
C18-C17-H17	119.8	C19-C18-C17	123.4(4)
C19-C18-H18	118.3	C17-C18-H18	118.3
C18-C19-C20	116.3(4)	C18-C19-H19	121.8
C20-C19-H19	121.8	N4-C20-C15	107.3(3)
N4-C20-C19	132.3(3)	C15-C20-C19	120.4(3)
C22-C21-N4	123.5(3)	C22-C21-C26	121.8(3)
N4-C21-C26	114.7(3)	C23-C22-C21	119.4(3)
C23-C22-H22	120.3	C21-C22-H22	120.3
C24-C23-C22	120.4(3)	C24-C23-H23	119.8
C22-C23-H23	119.8	C23-C24-C25	120.0(3)
C23-C24-H24	120.0	C25-C24-H24	120.0
C24-C25-C26	122.0(3)	C24-C25-H25	119.0

C26-C25-H25	119.0	C25-C26-C21	116.3(3)
C25-C26-Rh1	127.3(2)	C21-C26-Rh1	116.4(2)
C28-C27-C31	107.3(3)	C28-C27-C32	125.5(3)
C31-C27-C32	127.1(3)	C28-C27-Rh1	69.72(16)
C31-C27-Rh1	70.41(16)	C32-C27-Rh1	127.9(2)
C27-C28-C29	108.4(3)	C27-C28-C33	126.3(3)
C29-C28-C33	124.9(3)	C27-C28-Rh1	71.56(16)
C29-C28-Rh1	75.63(16)	C33-C28-Rh1	124.4(2)
C30-C29-C28	107.4(3)	C30-C29-C34	127.5(3)
C28-C29-C34	125.0(3)	C30-C29-Rh1	71.73(16)
C28-C29-Rh1	66.28(16)	C34-C29-Rh1	130.8(2)
C29-C30-C31	109.1(3)	C29-C30-C35	126.5(3)
C31-C30-C35	124.4(3)	C29-C30-Rh1	72.32(16)
C31-C30-Rh1	67.18(15)	C35-C30-Rh1	128.1(2)
C27-C31-C30	107.3(2)	C27-C31-C36	127.0(3)
C30-C31-C36	125.0(3)	C27-C31-Rh1	71.02(16)
C30-C31-Rh1	74.74(16)	C36-C31-Rh1	126.8(2)
C27-C32-H32A	109.5	C27-C32-H32B	109.5
H32A-C32-H32B	109.5	C27-C32-H32C	109.5
H32A-C32-H32C	109.5	H32B-C32-H32C	109.5
C28-C33-H33A	109.5	C28-C33-H33B	109.5
H33A-C33-H33B	109.5	C28-C33-H33C	109.5
H33A-C33-H33C	109.5	H33B-C33-H33C	109.5
C29-C34-H34A	109.5	C29-C34-H34B	109.5
H34A-C34-H34B	109.5	C29-C34-H34C	109.5
H34A-C34-H34C	109.5	H34B-C34-H34C	109.5
C30-C35-H35A	109.5	C30-C35-H35B	109.5
H35A-C35-H35B	109.5	C30-C35-H35C	109.5
H35A-C35-H35C	109.5	H35B-C35-H35C	109.5
C31-C36-H36A	109.5	C31-C36-H36B	109.5
H36A-C36-H36B	109.5	C31-C36-H36C	109.5
H36A-C36-H36C	109.5	H36B-C36-H36C	109.5
C1-N1-N2	108.3(2)	C1-N1-Rh1	119.67(17)
N2-N1-Rh1	122.78(17)	C7-N2-N1	108.1(2)
C7-N2-C8	121.4(2)	N1-N2-C8	119.1(2)
C14-N3-N4	107.9(2)	C14-N3-Rh1	136.18(18)
N4-N3-Rh1	115.92(17)	C20-N4-N3	108.7(2)
C20-N4-C21	135.6(3)	N3-N4-C21	114.5(2)

C14-O2-H2	109.5	C26-Rh1-N3	77.44(10)
C26-Rh1-N1	96.64(10)	N3-Rh1-N1	87.78(9)
C26-Rh1-C28	111.41(11)	N3-Rh1-C28	100.12(10)
N1-Rh1-C28	151.86(11)	C26-Rh1-C31	109.05(11)
N3-Rh1-C31	164.69(10)	N1-Rh1-C31	104.80(10)
C28-Rh1-C31	64.70(11)	C26-Rh1-C27	91.76(11)
N3-Rh1-C27	129.67(10)	N1-Rh1-C27	142.54(10)
C28-Rh1-C27	38.72(11)	C31-Rh1-C27	38.58(11)
C26-Rh1-C30	147.08(11)	N3-Rh1-C30	134.61(10)
N1-Rh1-C30	92.65(10)	C28-Rh1-C30	62.60(11)
C31-Rh1-C30	38.08(11)	C27-Rh1-C30	63.02(11)
C26-Rh1-C29	149.50(11)	N3-Rh1-C29	104.15(9)
N1-Rh1-C29	113.82(10)	C28-Rh1-C29	38.09(11)
C31-Rh1-C29	63.03(10)	C27-Rh1-C29	63.36(11)
C30-Rh1-C29	35.95(10)		

Table S15. Anisotropic atomic displacement parameters (Å^2) for rhodacycle-1a.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.0415(15)	0.0410(15)	0.0388(15)	-0.0025(12)	-0.0022(12)	-0.0012(12)
C2	0.0389(15)	0.0438(16)	0.0438(16)	-0.0015(13)	-0.0004(12)	0.0016(12)
C3	0.0503(19)	0.058(2)	0.058(2)	-0.0034(16)	0.0042(15)	0.0034(15)
C4	0.0403(18)	0.071(2)	0.080(3)	0.003(2)	0.0024(17)	0.0062(16)
C5	0.049(2)	0.068(2)	0.072(2)	0.0094(19)	-0.0147(17)	0.0036(17)
C6	0.0482(18)	0.061(2)	0.0517(19)	0.0082(15)	-0.0098(15)	0.0024(15)
C7	0.0443(16)	0.0395(15)	0.0433(16)	0.0016(12)	-0.0037(13)	-0.0005(13)
C8	0.0419(16)	0.0485(17)	0.0367(15)	0.0027(12)	-0.0011(12)	0.0087(13)
C9	0.057(2)	0.073(2)	0.0408(17)	-0.0019(16)	-0.0054(15)	0.0016(17)
C10	0.074(3)	0.105(3)	0.0407(19)	0.003(2)	0.0003(17)	0.017(2)
C11	0.078(3)	0.099(4)	0.064(3)	0.036(2)	0.025(2)	0.026(3)
C12	0.072(3)	0.057(2)	0.091(3)	0.023(2)	0.019(2)	0.0059(19)
C13	0.060(2)	0.0435(18)	0.062(2)	0.0020(15)	0.0080(17)	0.0047(15)
C14	0.0414(15)	0.0362(14)	0.0397(15)	-0.0051(12)	-0.0054(12)	0.0034(12)
C15	0.0435(16)	0.0334(14)	0.0534(18)	-0.0057(13)	-0.0132(14)	0.0048(12)
C16	0.063(2)	0.0500(19)	0.069(2)	-0.0204(17)	-0.0110(18)	-0.0024(17)
C17	0.079(3)	0.053(2)	0.095(3)	-0.030(2)	-0.017(2)	-0.012(2)
C18	0.064(2)	0.051(2)	0.113(4)	-0.013(2)	-0.007(2)	-0.0219(18)
C19	0.052(2)	0.050(2)	0.089(3)	-0.0025(19)	0.0002(19)	-0.0161(16)
C20	0.0376(15)	0.0360(15)	0.0598(19)	-0.0042(14)	-0.0095(14)	-0.0003(12)
C21	0.0352(15)	0.0510(17)	0.0443(16)	0.0000(13)	0.0038(12)	-0.0007(13)
C22	0.0424(18)	0.072(2)	0.067(2)	0.0089(18)	0.0064(16)	-0.0131(16)
C23	0.052(2)	0.087(3)	0.059(2)	0.011(2)	0.0208(17)	-0.0031(19)
C24	0.055(2)	0.074(2)	0.0435(17)	0.0034(16)	0.0147(15)	0.0126(18)
C25	0.0496(17)	0.0517(17)	0.0386(16)	-0.0046(13)	0.0065(13)	0.0061(14)
C26	0.0356(14)	0.0419(15)	0.0392(15)	0.0007(12)	0.0046(12)	0.0046(12)
C27	0.0514(17)	0.0338(15)	0.0454(16)	-0.0063(12)	0.0023(13)	0.0027(13)
C28	0.0453(16)	0.0345(14)	0.0449(16)	-0.0014(12)	-0.0056(13)	0.0015(12)
C29	0.0496(17)	0.0320(14)	0.0389(15)	-0.0006(11)	-0.0003(12)	-0.0052(12)
C30	0.0475(16)	0.0317(14)	0.0473(16)	-0.0001(12)	0.0004(13)	-0.0086(12)
C31	0.0548(18)	0.0303(14)	0.0404(15)	-0.0060(12)	-0.0021(13)	-0.0065(12)
C32	0.069(2)	0.058(2)	0.064(2)	-0.0117(17)	0.0160(18)	0.0154(18)
C33	0.0501(19)	0.065(2)	0.072(2)	-0.0035(18)	-0.0134(17)	0.0046(17)
C34	0.077(2)	0.0533(19)	0.0396(17)	0.0035(14)	0.0044(16)	-0.0077(17)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C35	0.0505(19)	0.059(2)	0.070(2)	0.0015(17)	0.0024(17)	-0.0167(16)
C36	0.075(2)	0.0516(19)	0.0489(19)	-0.0118(15)	-0.0110(17)	-0.0141(17)
N1	0.0385(12)	0.0473(14)	0.0295(11)	-0.0030(10)	-0.0045(9)	0.0021(10)
N2	0.0398(13)	0.0511(14)	0.0352(12)	0.0017(11)	-0.0049(10)	0.0003(11)
N3	0.0380(12)	0.0361(12)	0.0381(12)	-0.0046(10)	0.0018(10)	-0.0056(10)
N4	0.0386(13)	0.0413(13)	0.0504(15)	-0.0053(11)	0.0036(11)	-0.0113(11)
O1	0.0452(12)	0.0744(15)	0.0331(11)	-0.0061(10)	-0.0002(9)	-0.0003(11)
O2	0.0503(12)	0.0552(13)	0.0368(11)	-0.0106(9)	-0.0017(9)	-0.0050(10)
Rh1	0.03704(14)	0.03171(13)	0.02981(13)	-0.00489(8)	0.00278(9)	-0.00193(8)

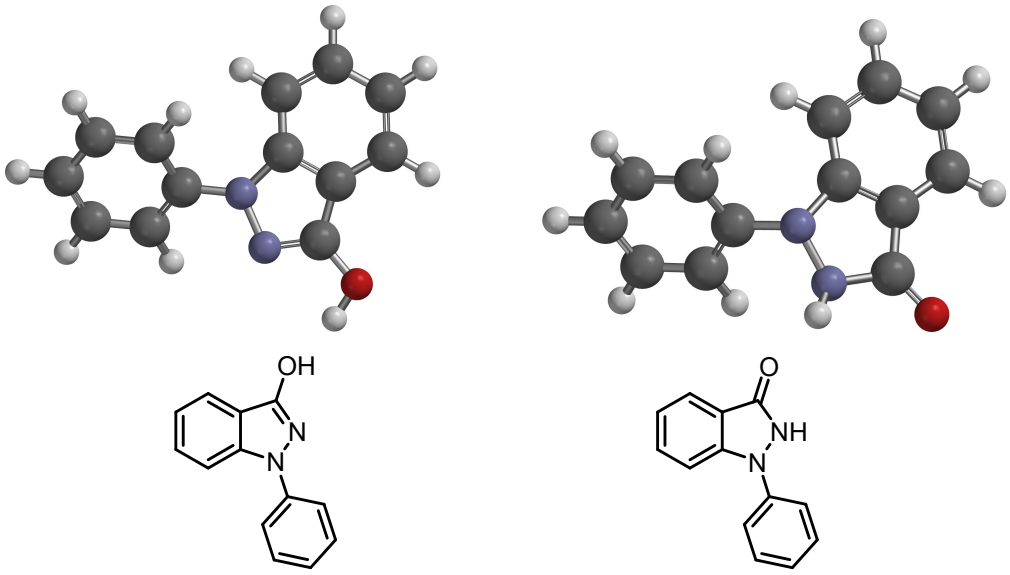
Table S16. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for rhodacycle-1a.

	x/a	y/b	z/c	U(eq)
H3	1.0171	0.7245	0.2152	0.066
H4	1.1588	0.7083	0.3079	0.077
H5	1.1354	0.7103	0.4440	0.076
H6	0.9734	0.7318	0.4937	0.065
H9	0.8031	0.8224	0.5397	0.069
H10	0.7321	0.7616	0.6521	0.088
H11	0.6336	0.6264	0.6439	0.096
H12	0.5994	0.5520	0.5208	0.087
H13	0.6707	0.6127	0.4061	0.066
H16	0.5010	0.5479	0.0461	0.074
H17	0.3786	0.4296	0.0626	0.092
H18	0.2884	0.4238	0.1770	0.092
H19	0.3119	0.5344	0.2787	0.077
H22	0.3343	0.6197	0.3808	0.073
H23	0.3290	0.6696	0.5129	0.078
H24	0.4347	0.7905	0.5604	0.068
H25	0.5502	0.8613	0.4777	0.056
H32A	0.4800	1.0090	0.4236	0.095
H32B	0.3958	0.9669	0.3614	0.095
H32C	0.4273	1.0744	0.3565	0.095
H33A	0.3644	0.9303	0.2207	0.094
H33B	0.4217	0.9030	0.1432	0.094
H33C	0.3960	1.0098	0.1605	0.094
H34A	0.6192	1.0063	0.0800	0.085
H34B	0.5900	0.8982	0.0849	0.085
H34C	0.7065	0.9304	0.0996	0.085
H35A	0.8294	0.9442	0.2027	0.09
H35B	0.8472	0.9553	0.2963	0.09
H35C	0.8309	1.0457	0.2418	0.09
H36A	0.7242	1.0802	0.4084	0.089
H36B	0.7603	0.9744	0.4211	0.089
H36C	0.6542	1.0086	0.4534	0.089
H2	0.6753	0.7330	0.1403	0.071

Computational studies for the stability of tautomers

Experimental details for B3LYP/6-31G* density functional model

Spartan'14 parallel suite (12 threads, 6-core Intel i7-based processor) running on a Windows platform (Wavefunction, Inc., 18401 Von Karman Ave., Suite 370, Irvine, CA 92612, http://www.wavefun.com) was used to search possible tautomers and calculate their relative stability. The DFT-B3LYP with 6-31G* basis set was used for estimating the tautomer stability. In the gas phase, the optimized structures of two tautomeric forms were displayed as below and their calculated properties listed in Table S17.



1a tautomer of **1a**

Table S17. Tautomer stability calculation by B3LYP/6-31G* density functional model.

entry	E HOMO (kJ/mol)	E LUMO (kJ/mol)	Boltzmann Dist	rel. E (kJ/mol)	Dipole
1a	-519.25	-76.32	0.751	0	1.02
tautomer of **1a**	-538.32	-101.96	0.249	2.74	4.30

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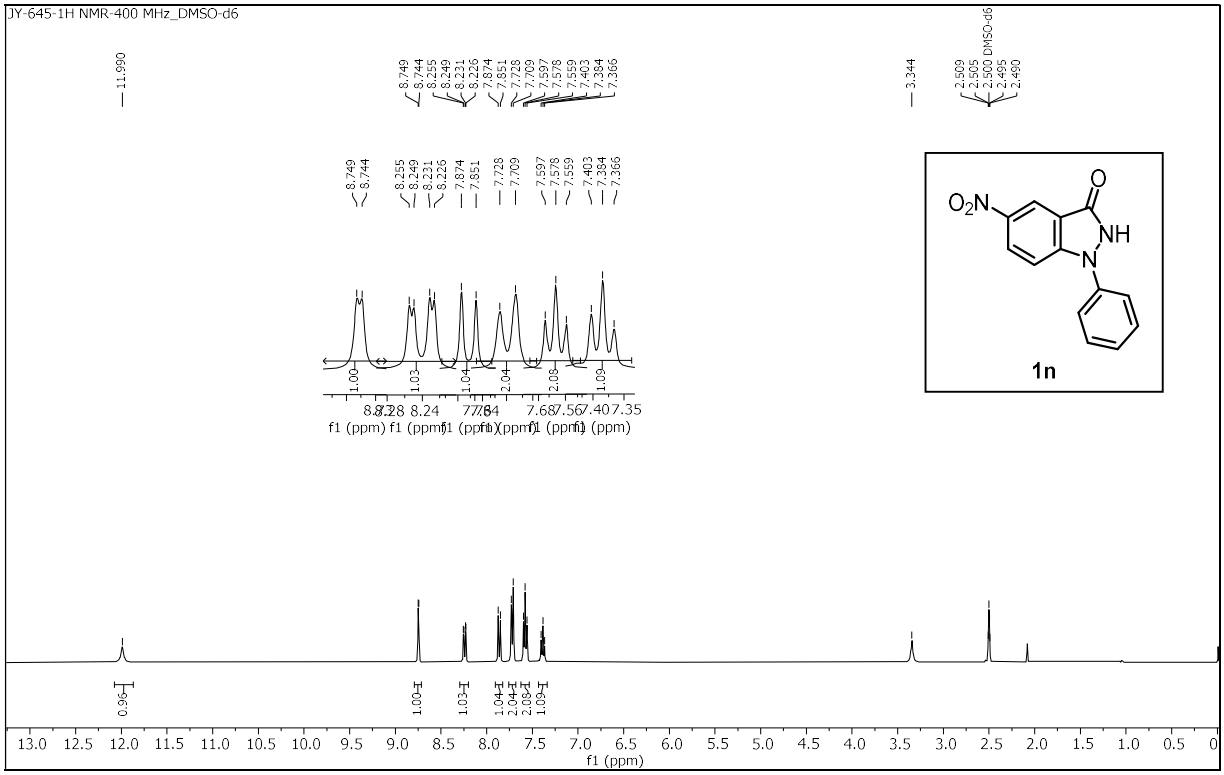
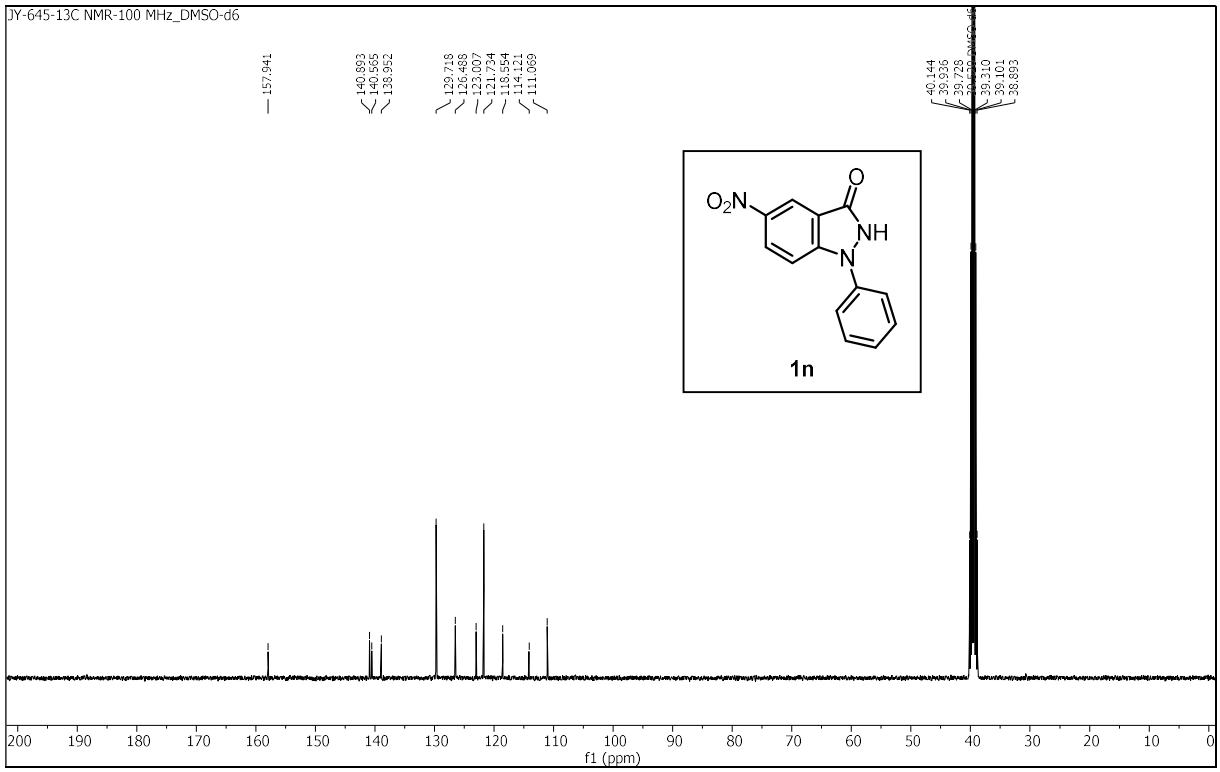
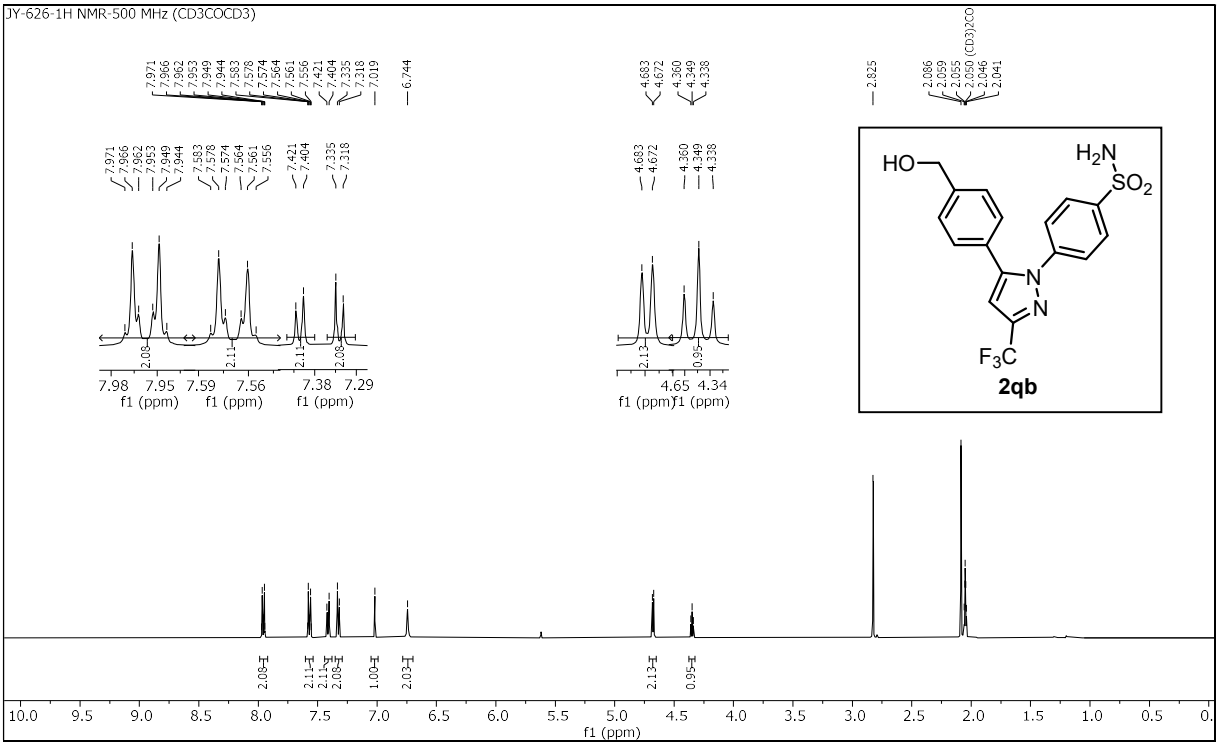
^{1}H and ^{13}C NMR spectra of all compounds



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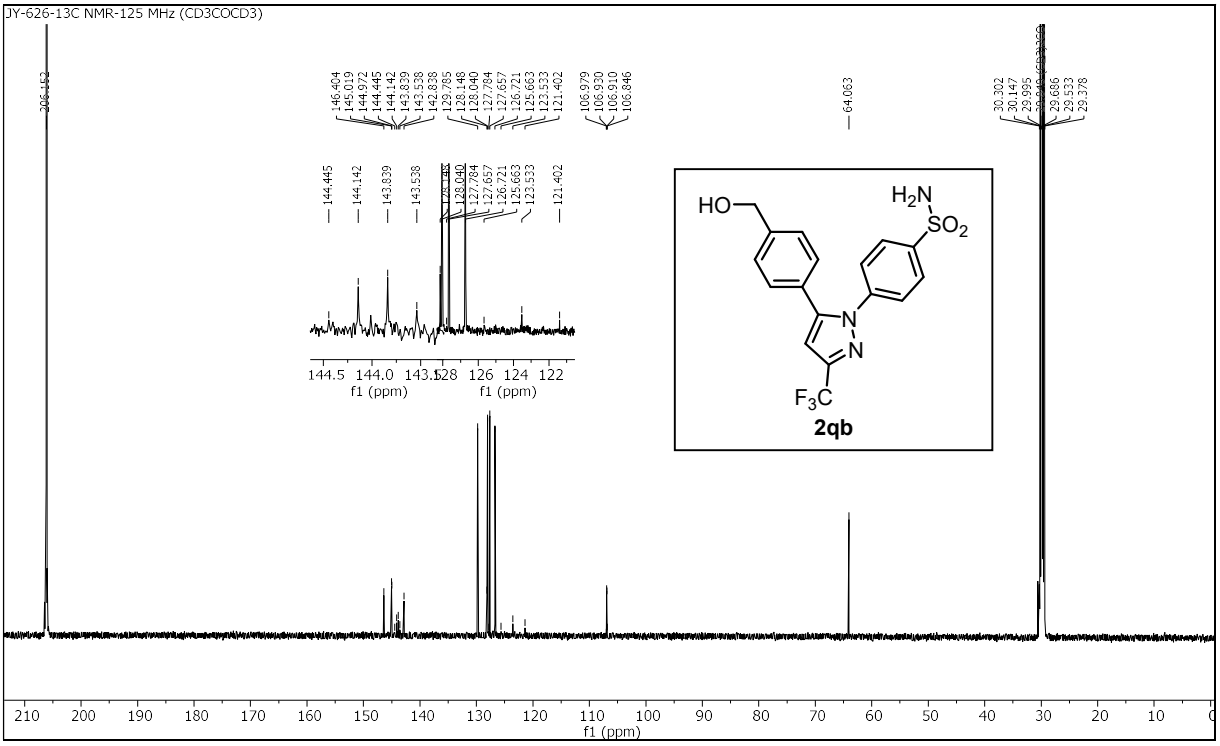
HO
H_2N
SO_2
N
N
F_3C
2qb
f1 (ppm)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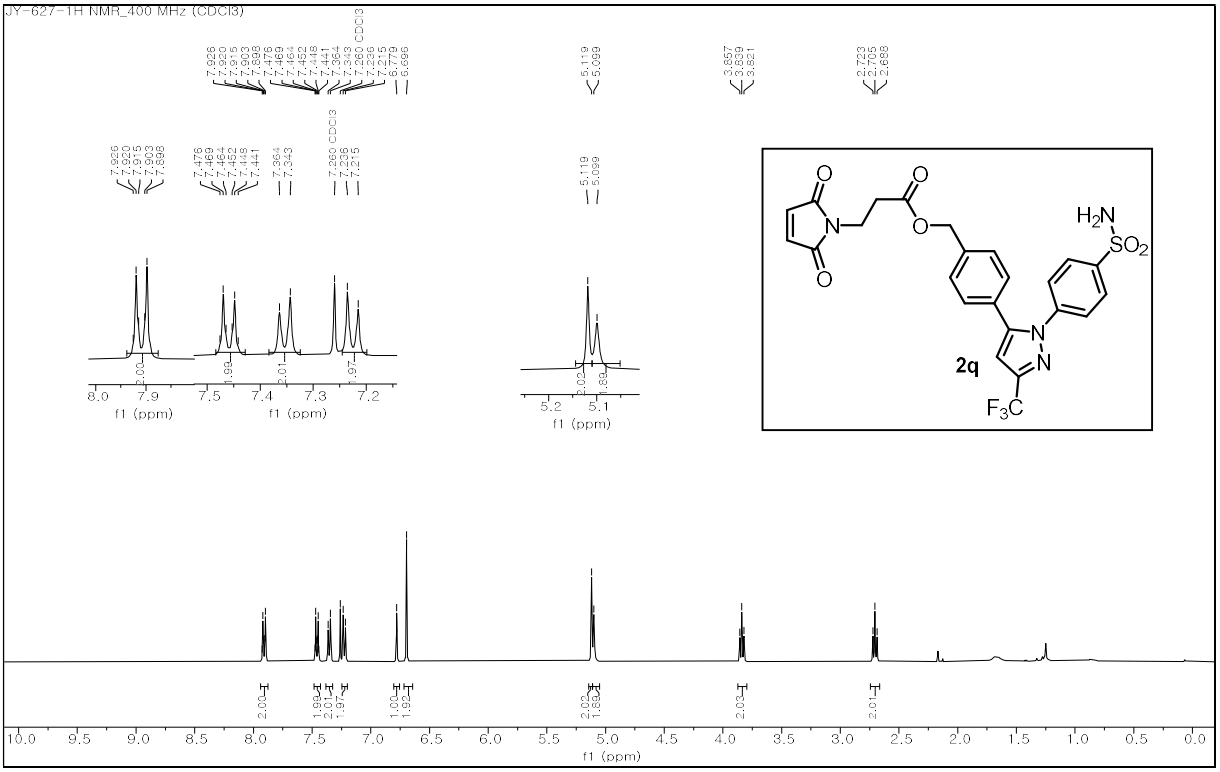
H_2N
SO_2
N
N
F_3C
2qb
f1 (ppm)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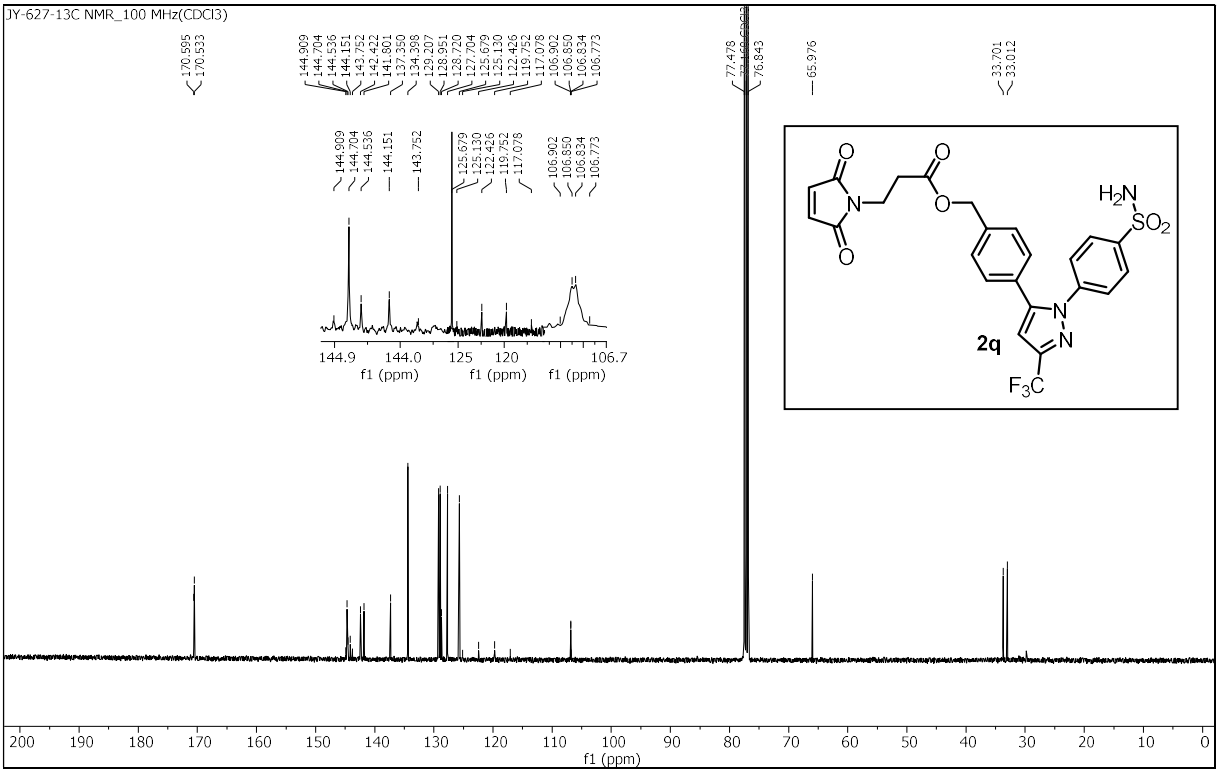
2q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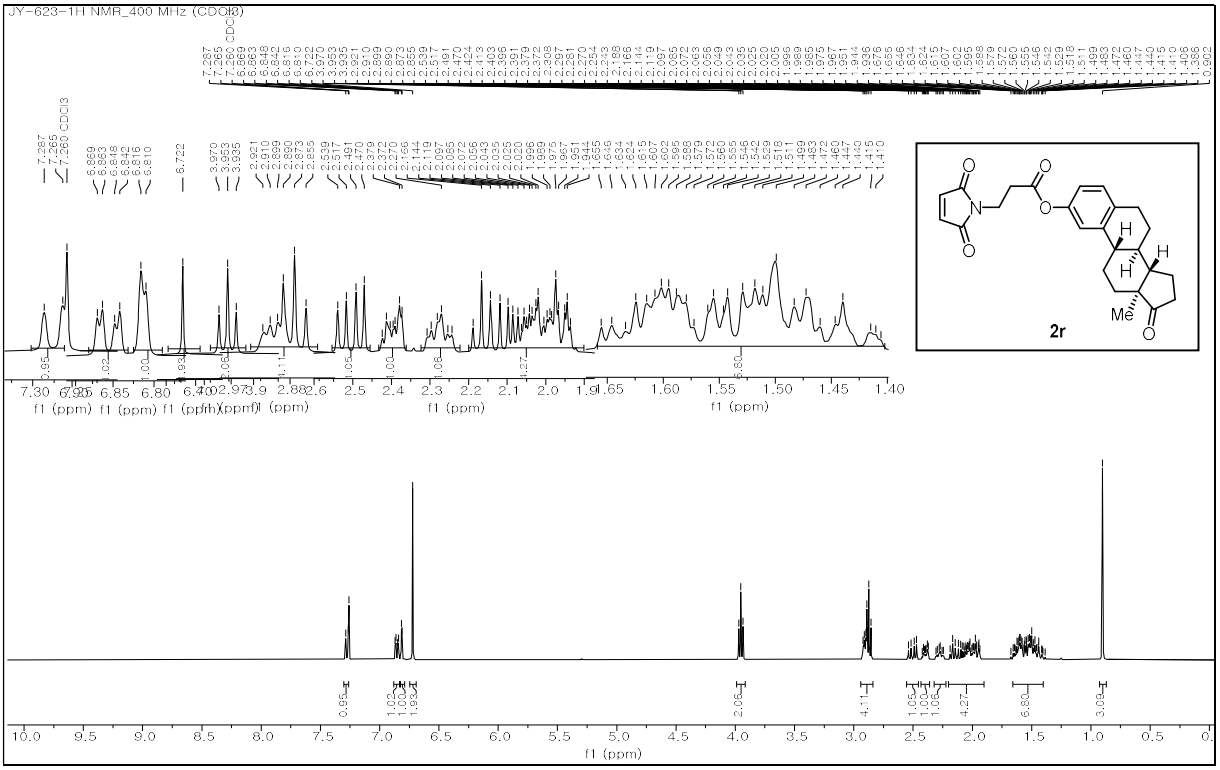
2q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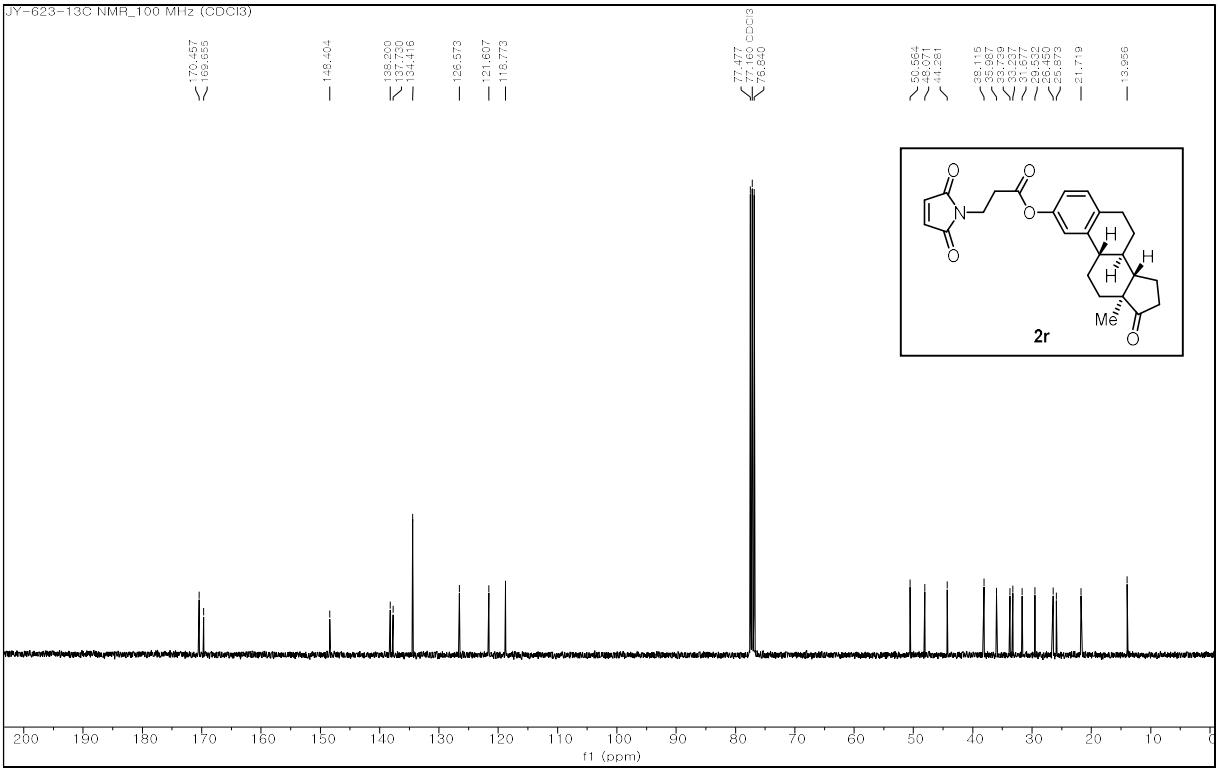
f1 (ppm)
2r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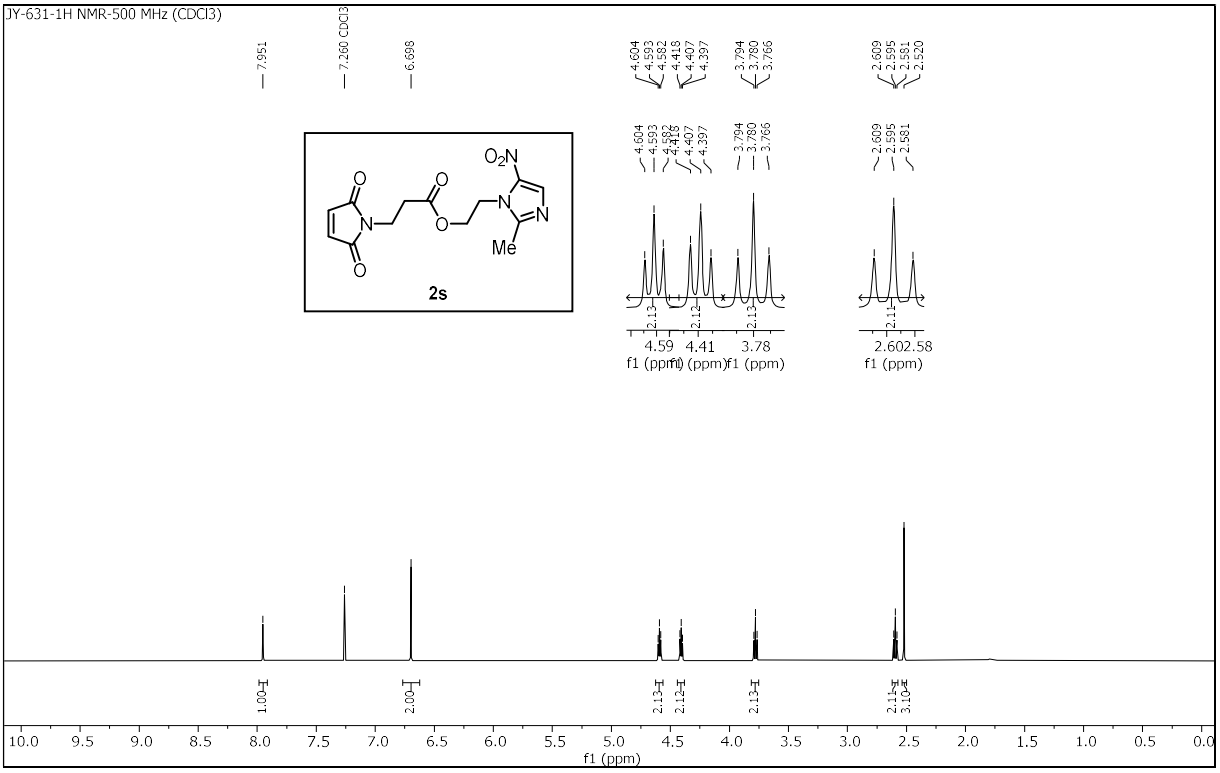
f1 (ppm)
2r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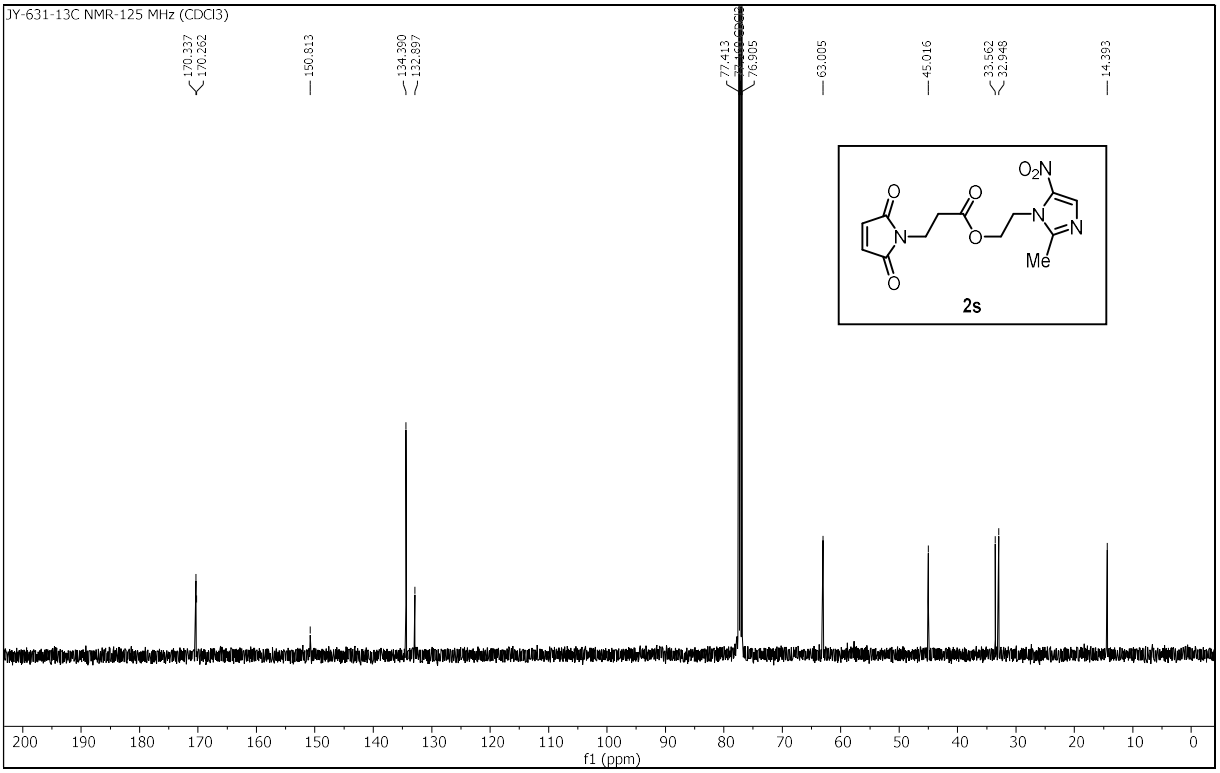
7.260 CDCl3
6.698
4.604
4.593
4.582
4.418
4.407
4.397
3.794
3.780
3.766
2.609
2.595
2.581
2.520
2s
1.00
2.00
2.13
2.12
2.13
2.11
3.10
f1 (ppm)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170.262
150.813
134.390
132.897
77.413
76.905
63.005
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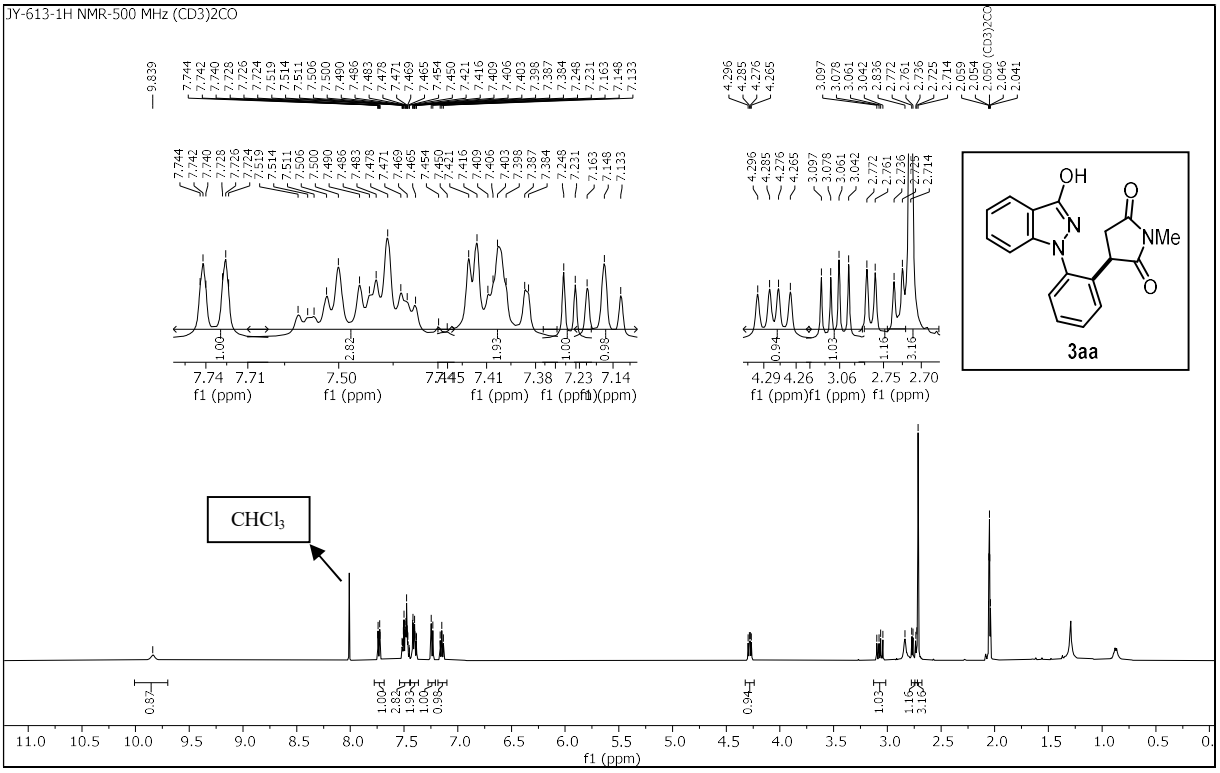
33.562
32.946
14.393
2s
f1 (ppm)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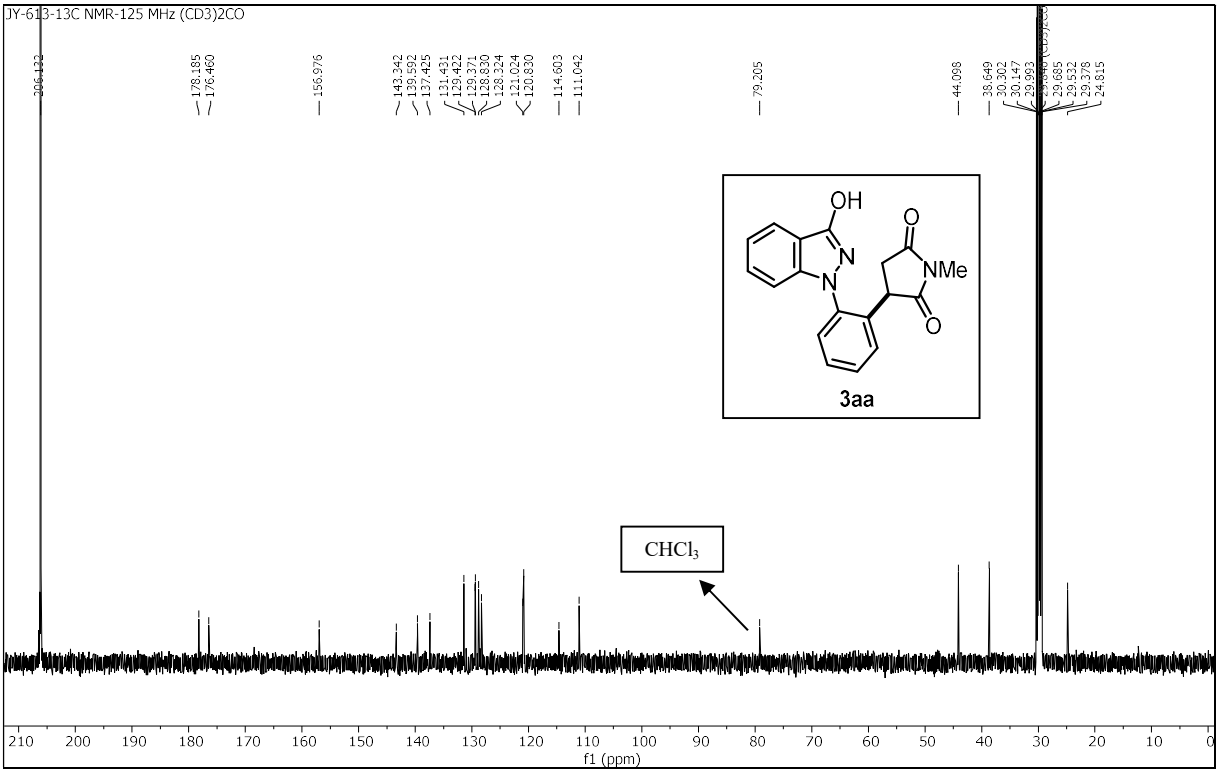
CHCl3
3aa
f1 (ppm)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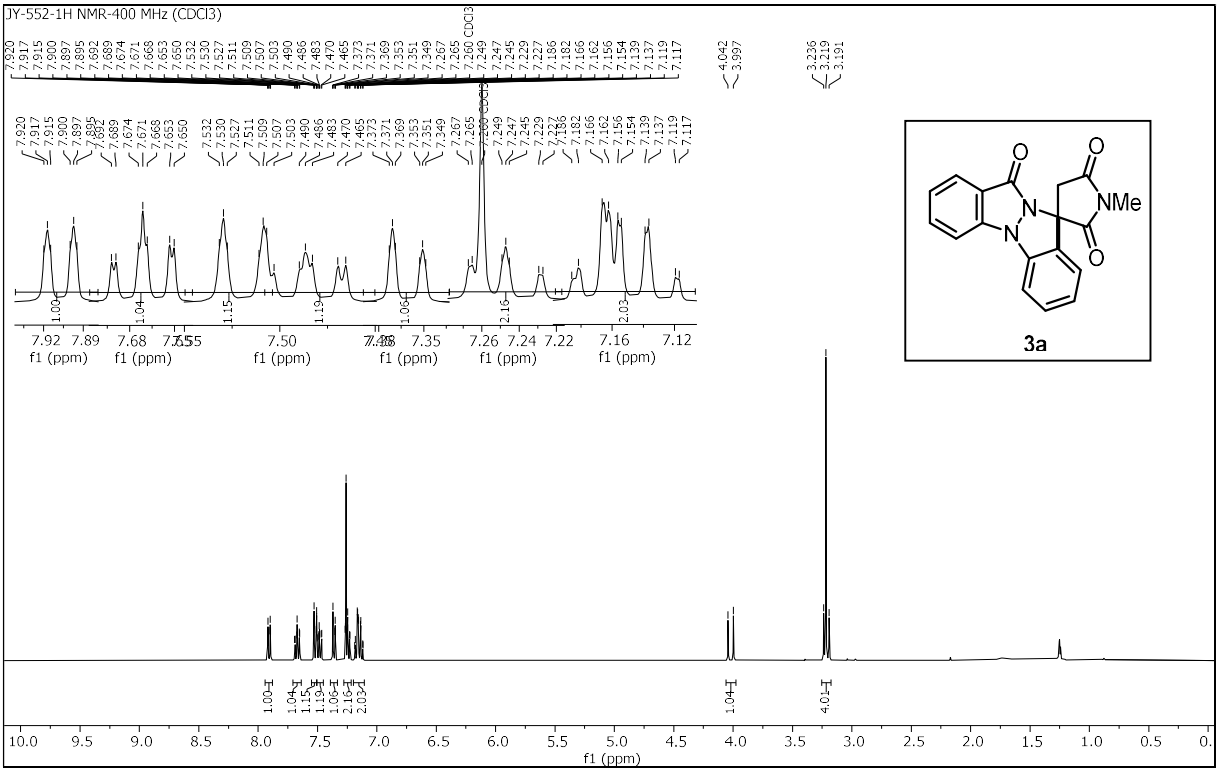
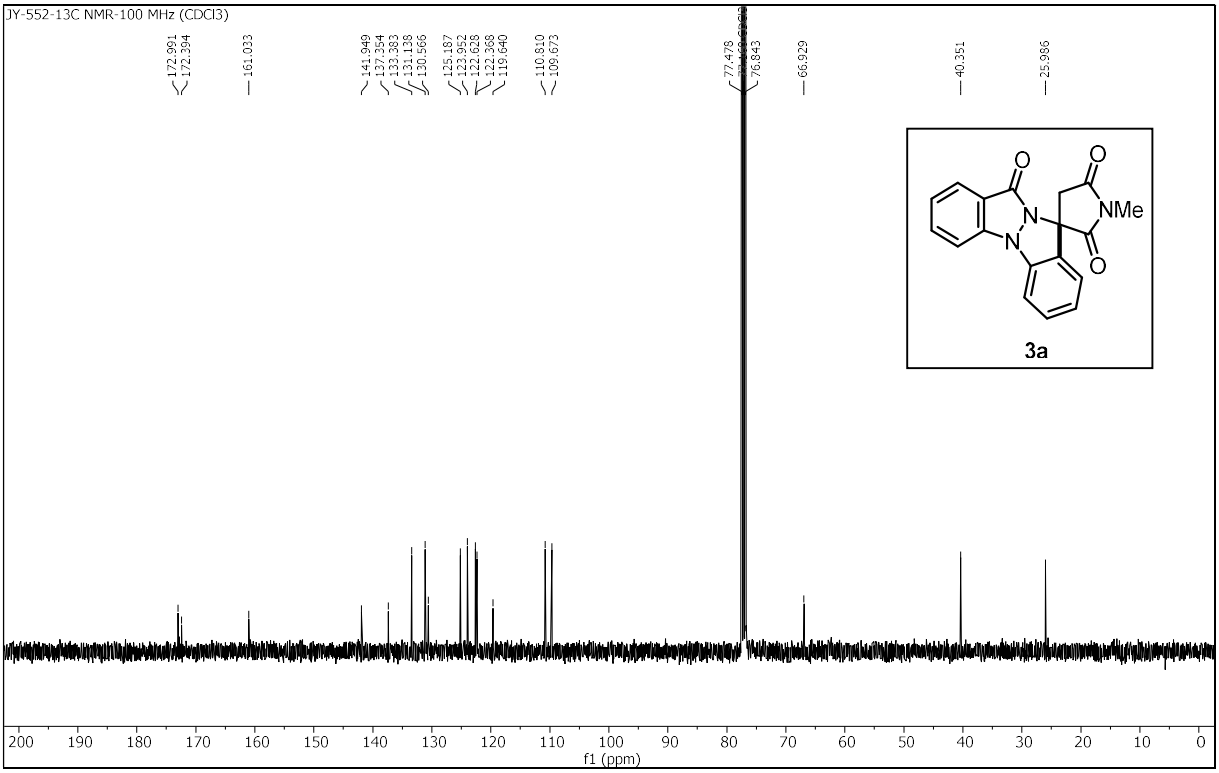
CHCl3
3aa
f1 (ppm)


JY-552-1H NMR-400 MHz (CDCl3)
3a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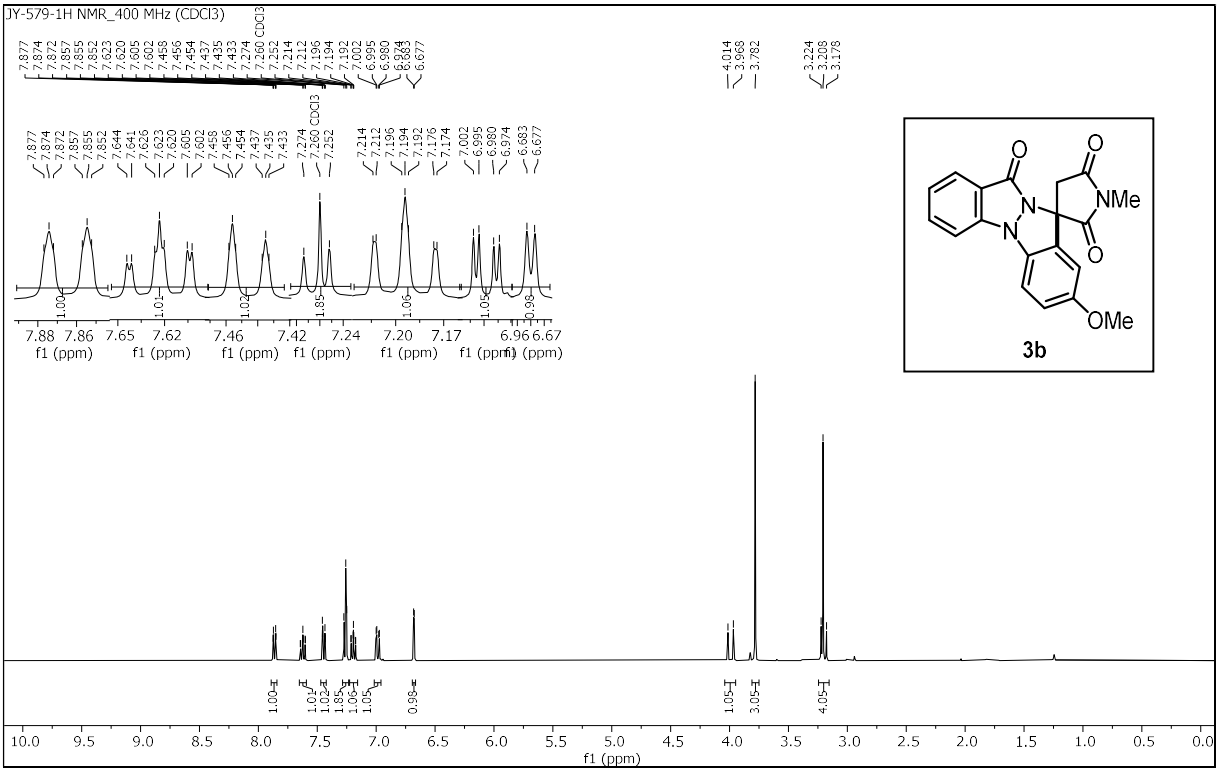
3a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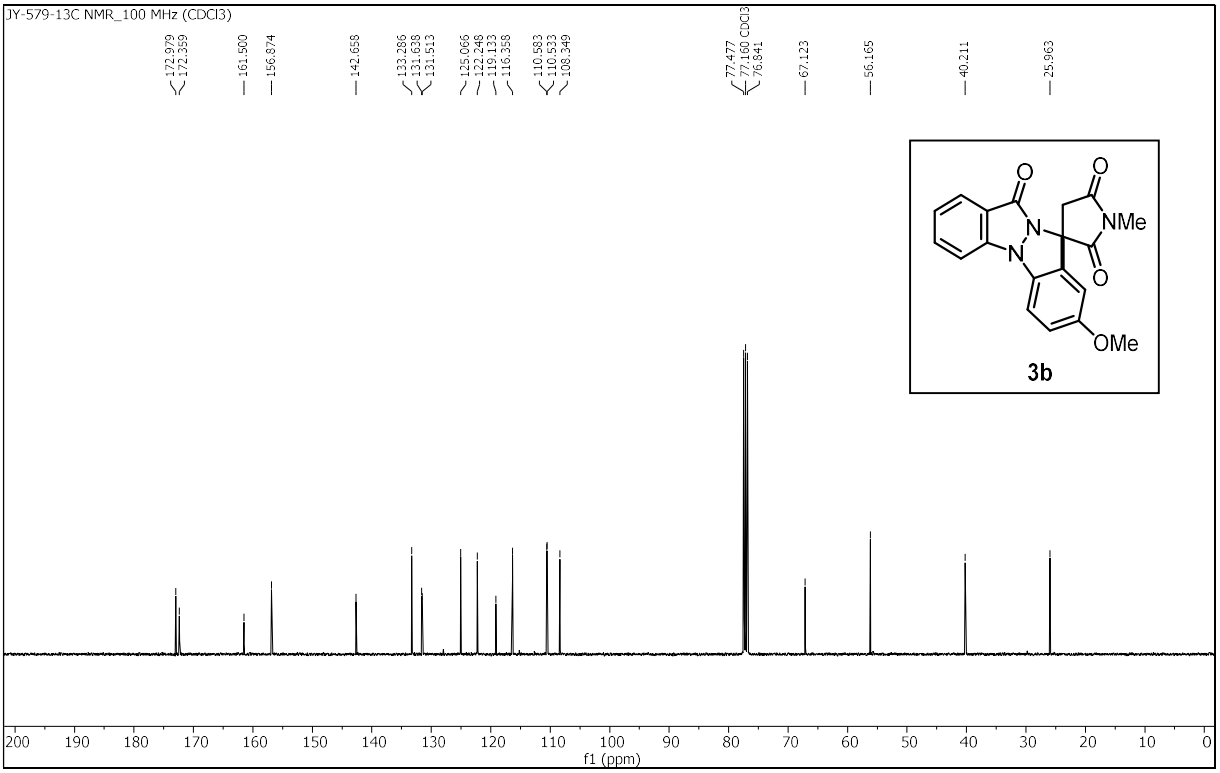
3b
f1 (ppm)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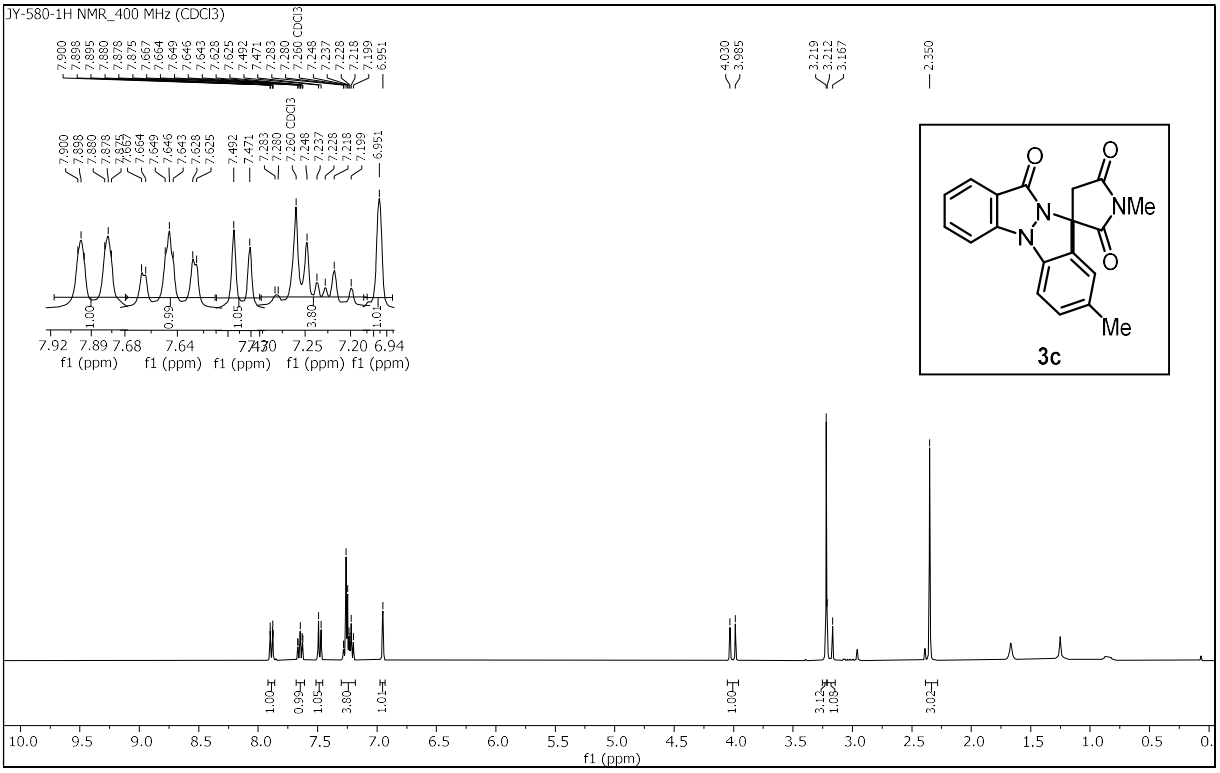
3b
f1 (ppm)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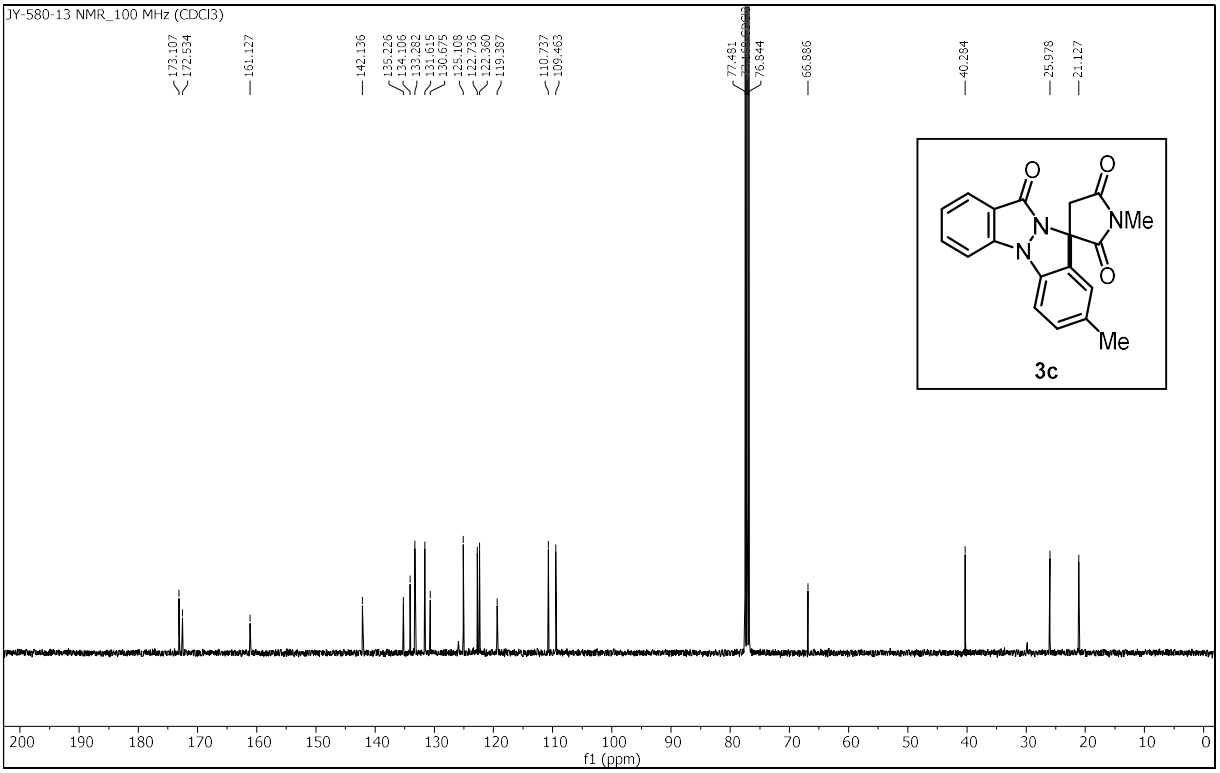
7.898
7.895
7.880
7.878
7.875
7.667
7.664
7.649
7.646
7.643
7.628
7.625
7.492
7.471
7.283
7.280
7.260 CDCl3
7.248
7.237
7.228
7.218
7.199
6.951
4.030
3.985
3.219
3.212
3.167
2.350
1.00
0.99
1.05
3.80
1.01
7.92 7.89 7.68 7.64 7.43 7.30 7.25 7.20 6.94
f1 (ppm)
NMe
Me
3c
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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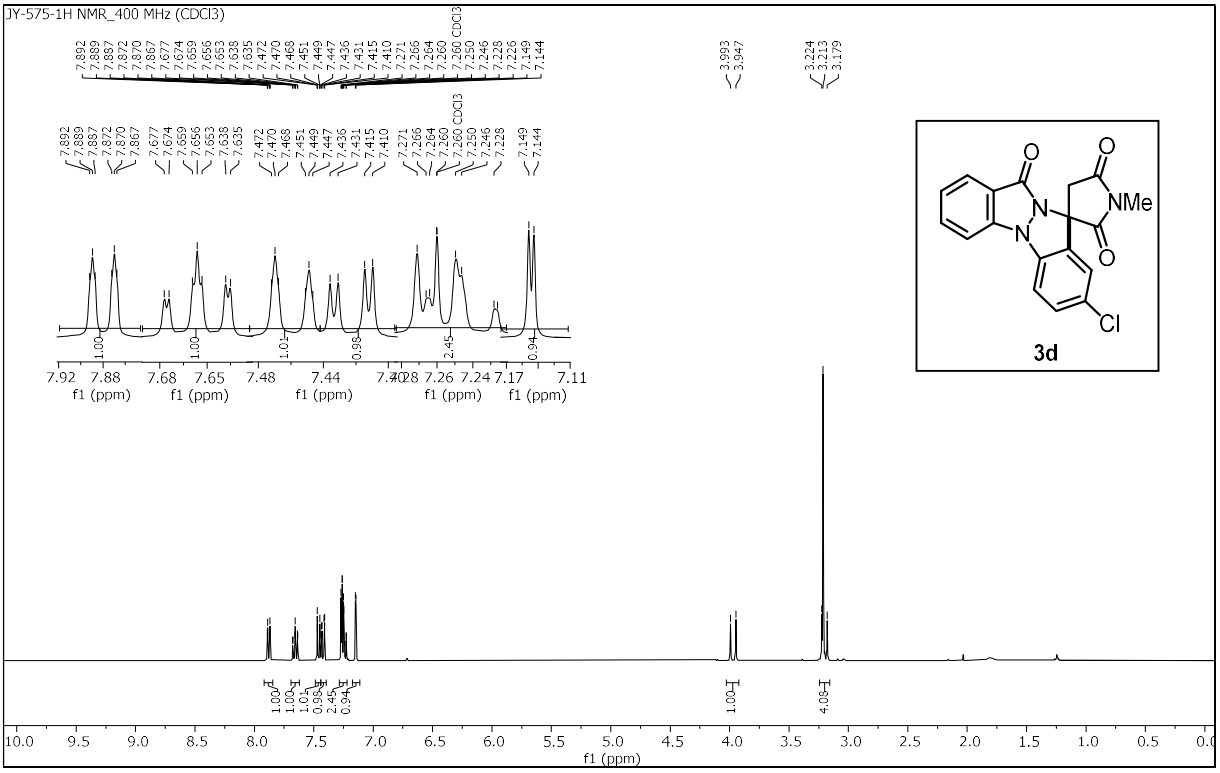
173.107
172.534
161.127
142.136
135.226
134.106
133.282
131.615
130.675
125.108
122.736
122.360
119.387
110.737
109.463
77.481
76.844
66.886
40.284
25.978
21.127
NMe
Me
3c
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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3d
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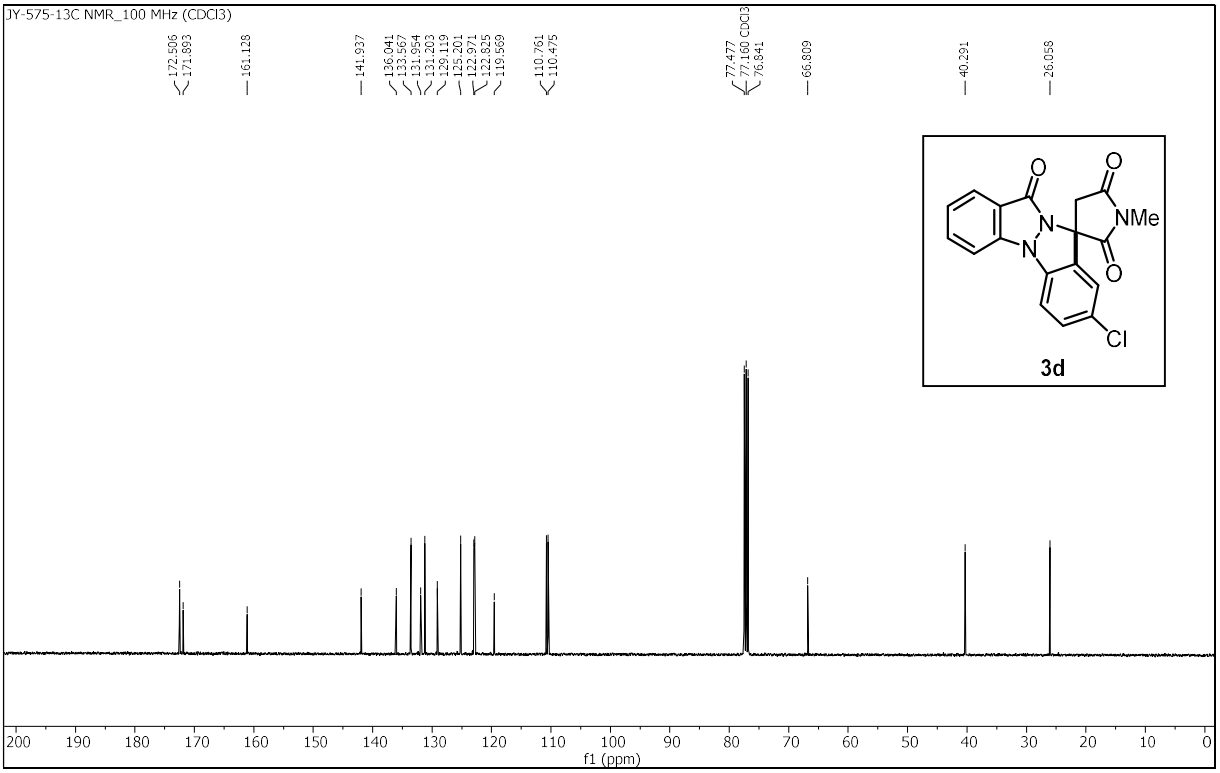
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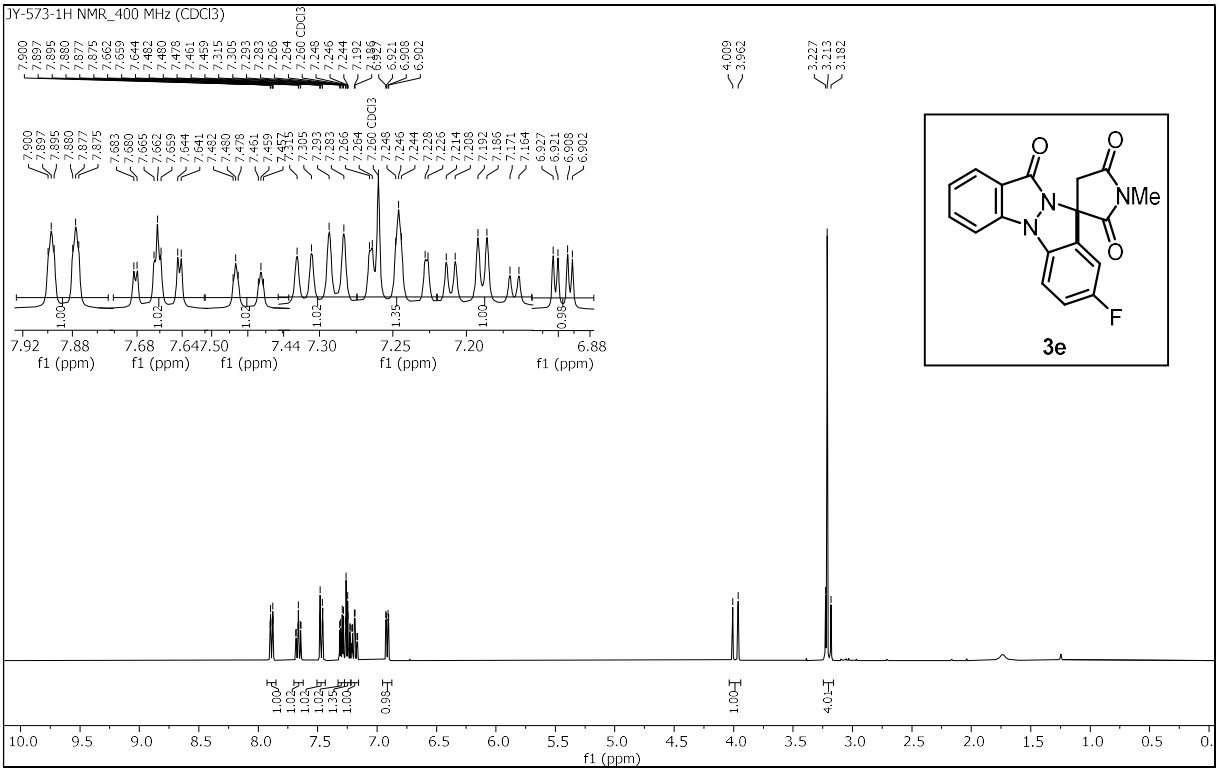
3d
f1 (ppm)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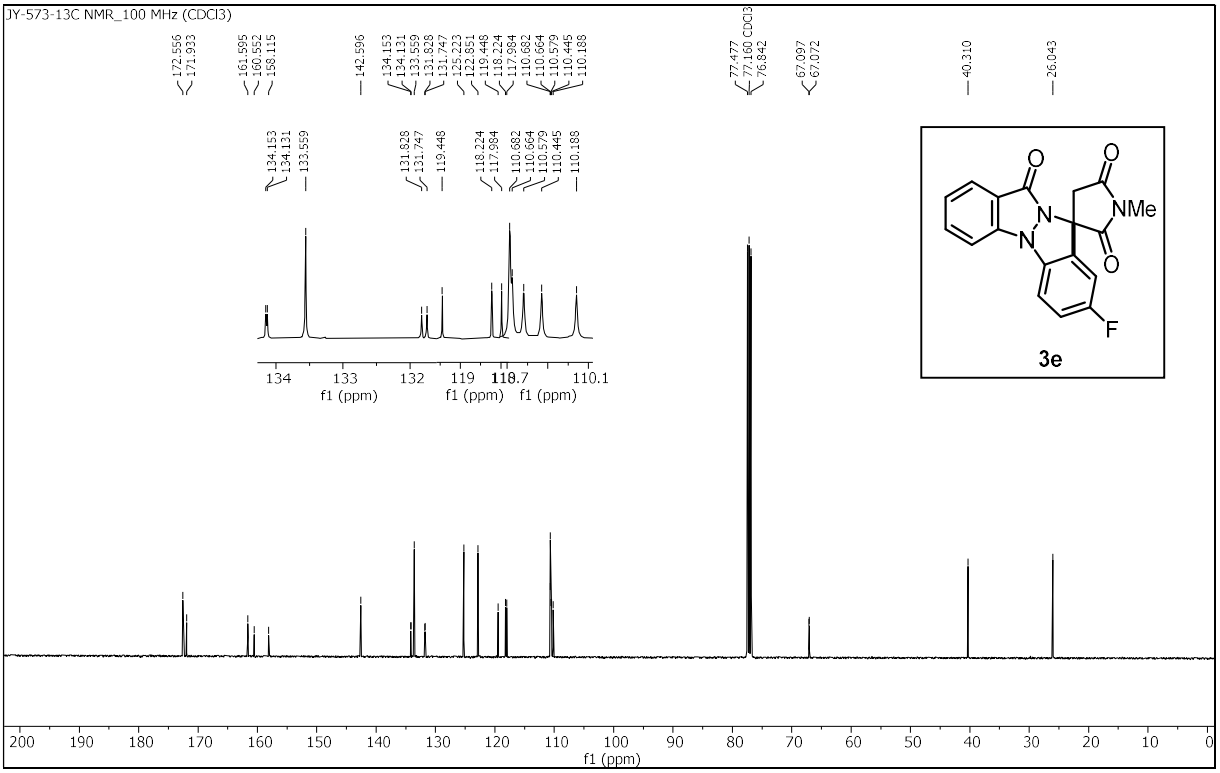
3e
f1 (ppm)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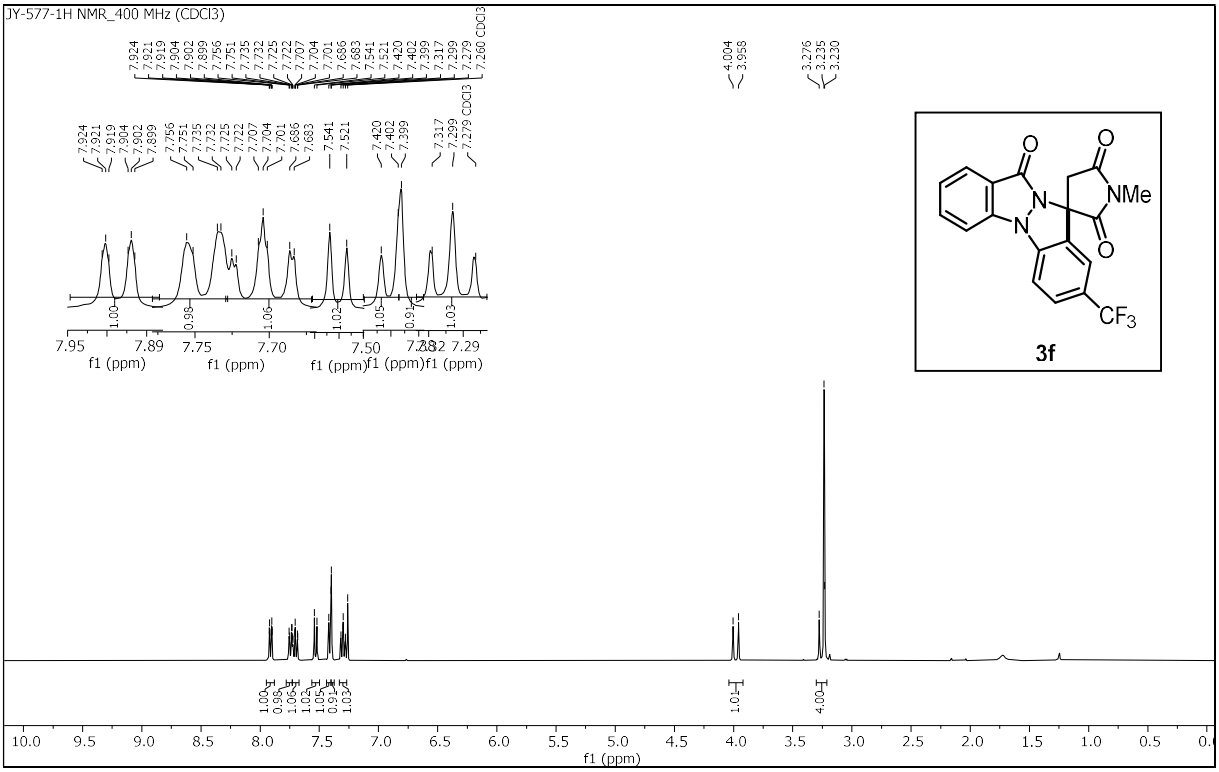
f1 (ppm)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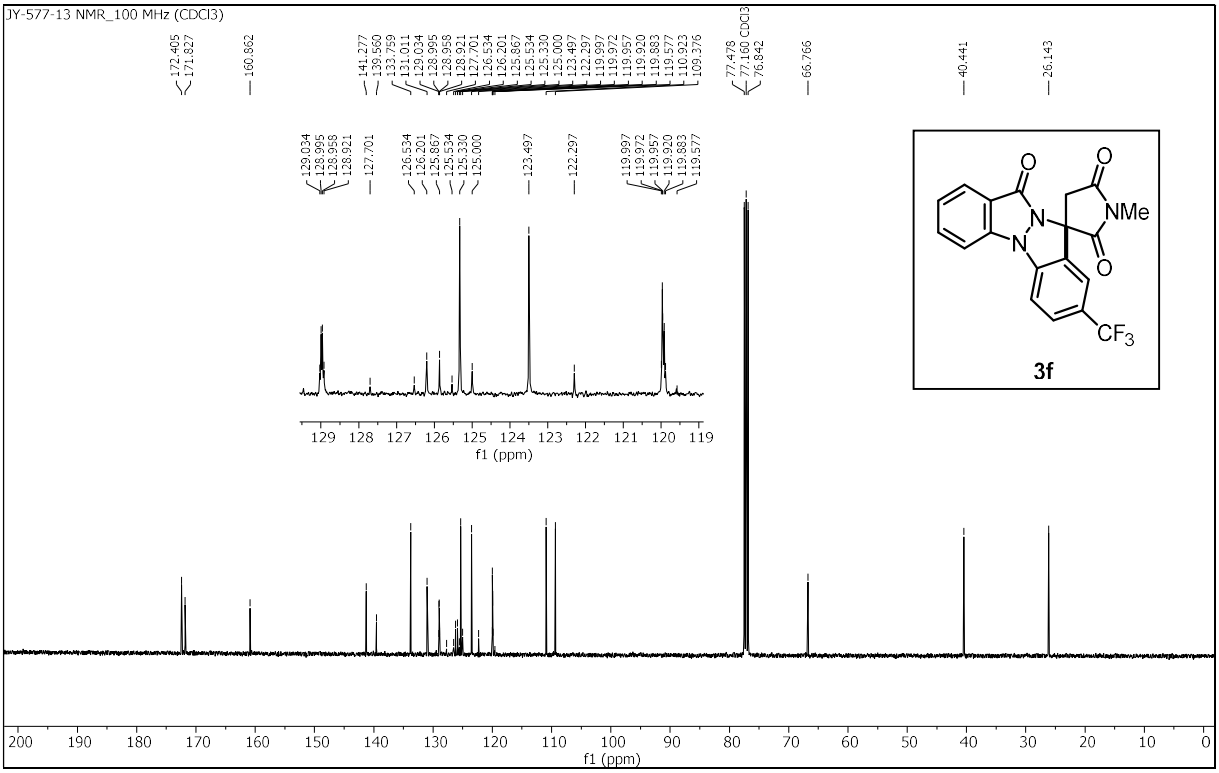
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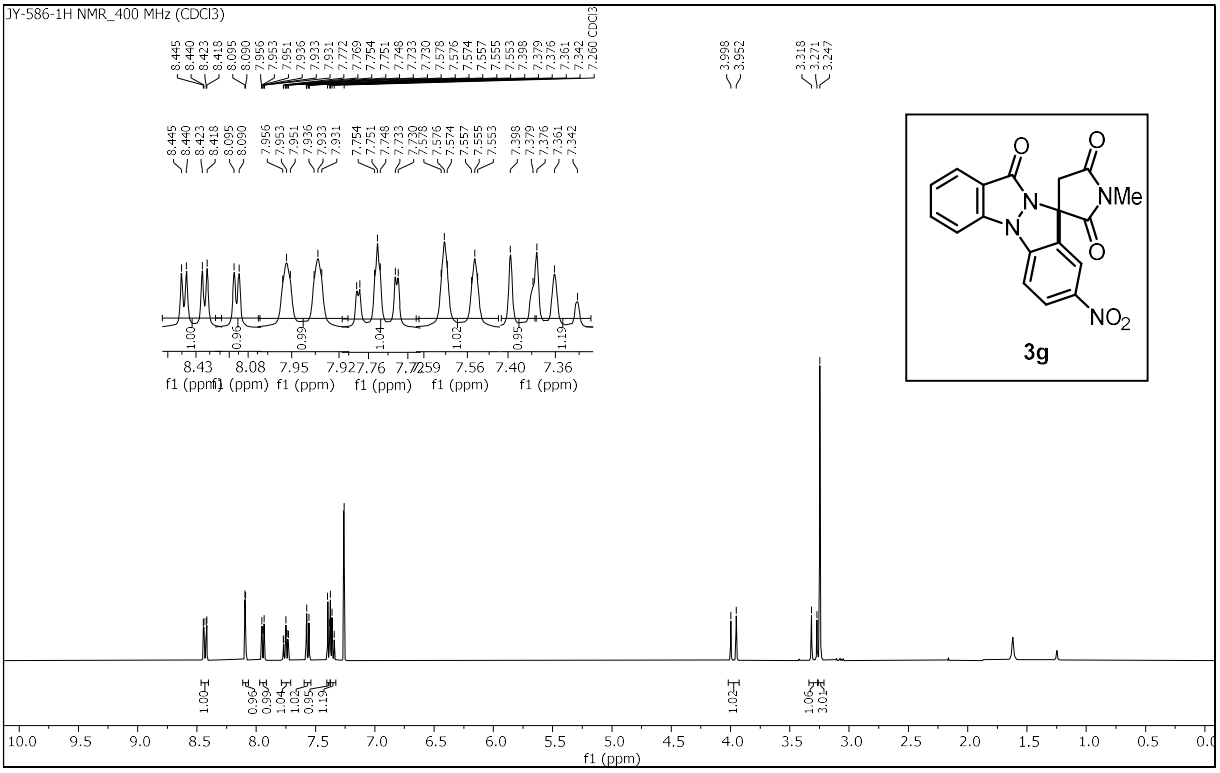
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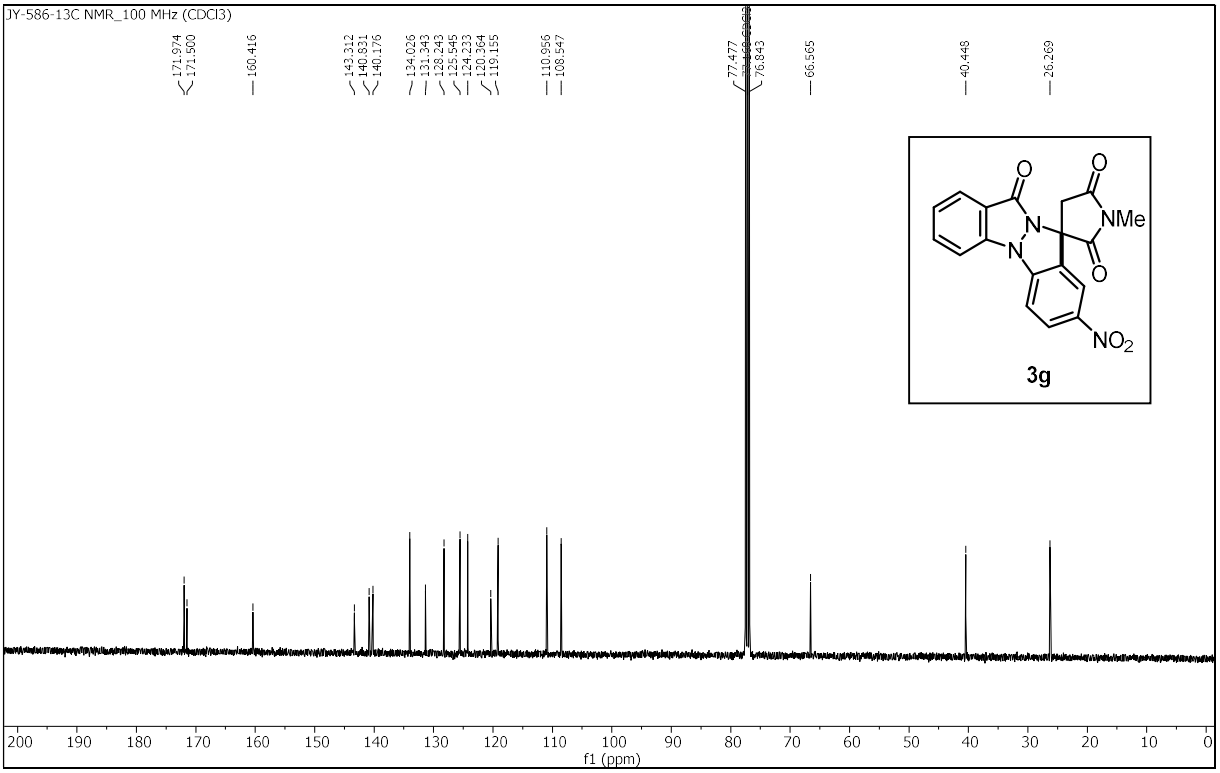
3g
f1 (ppm)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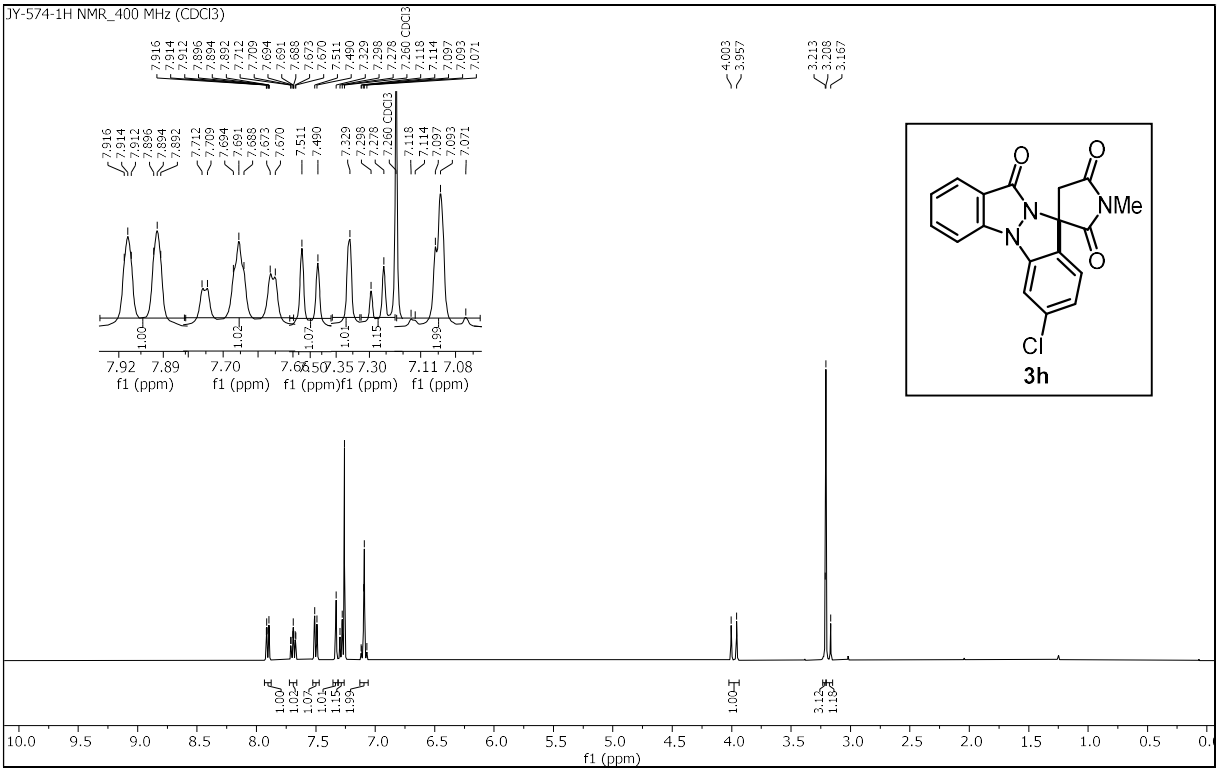
3g
f1 (ppm)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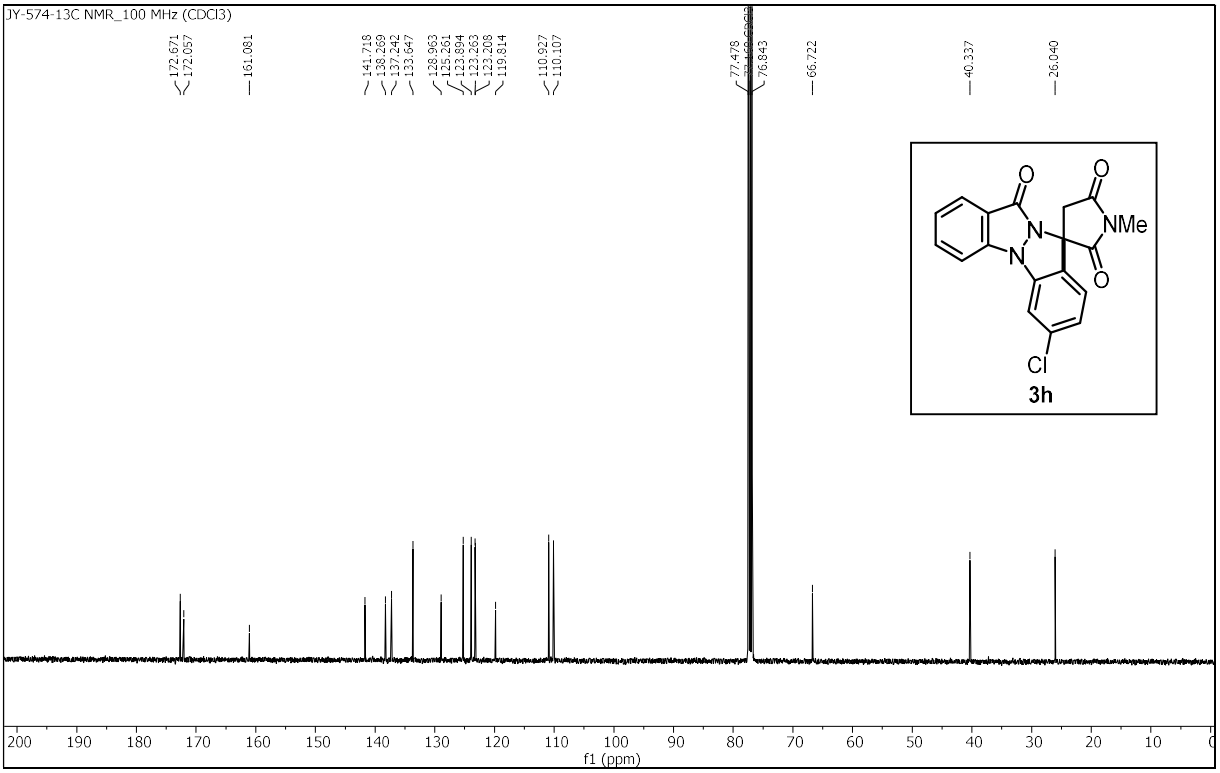
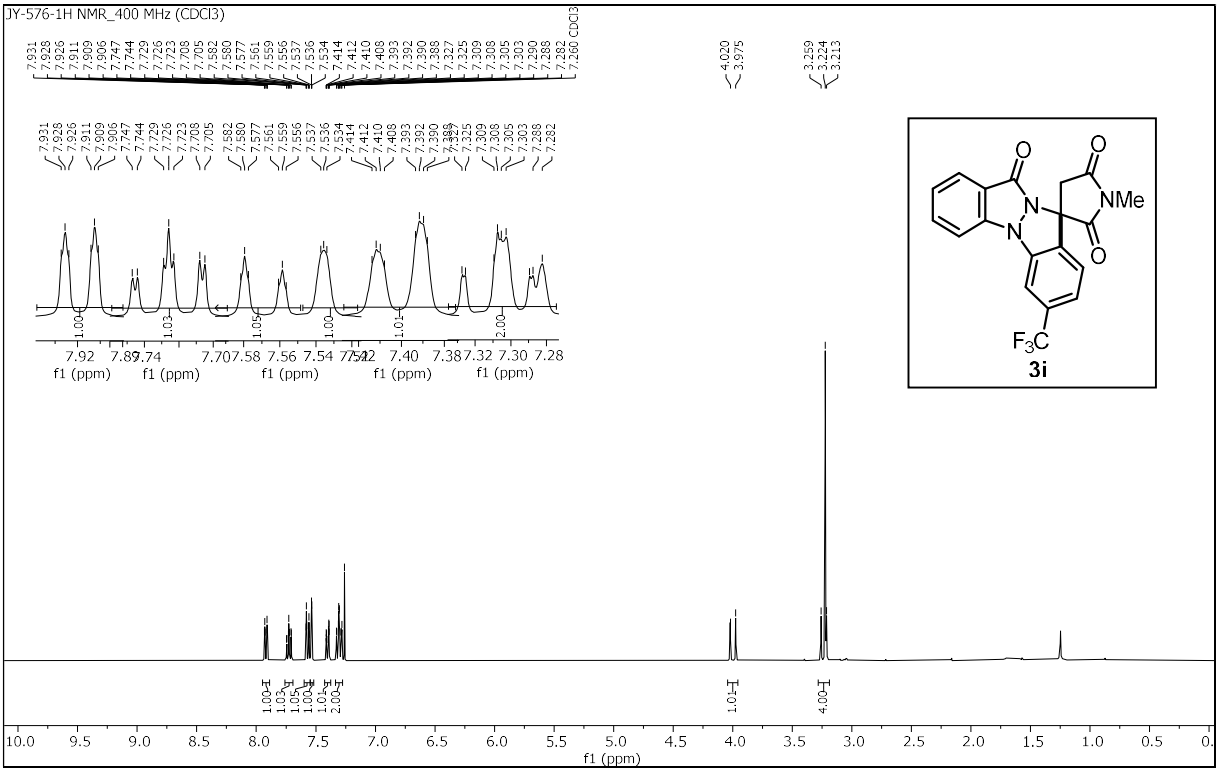
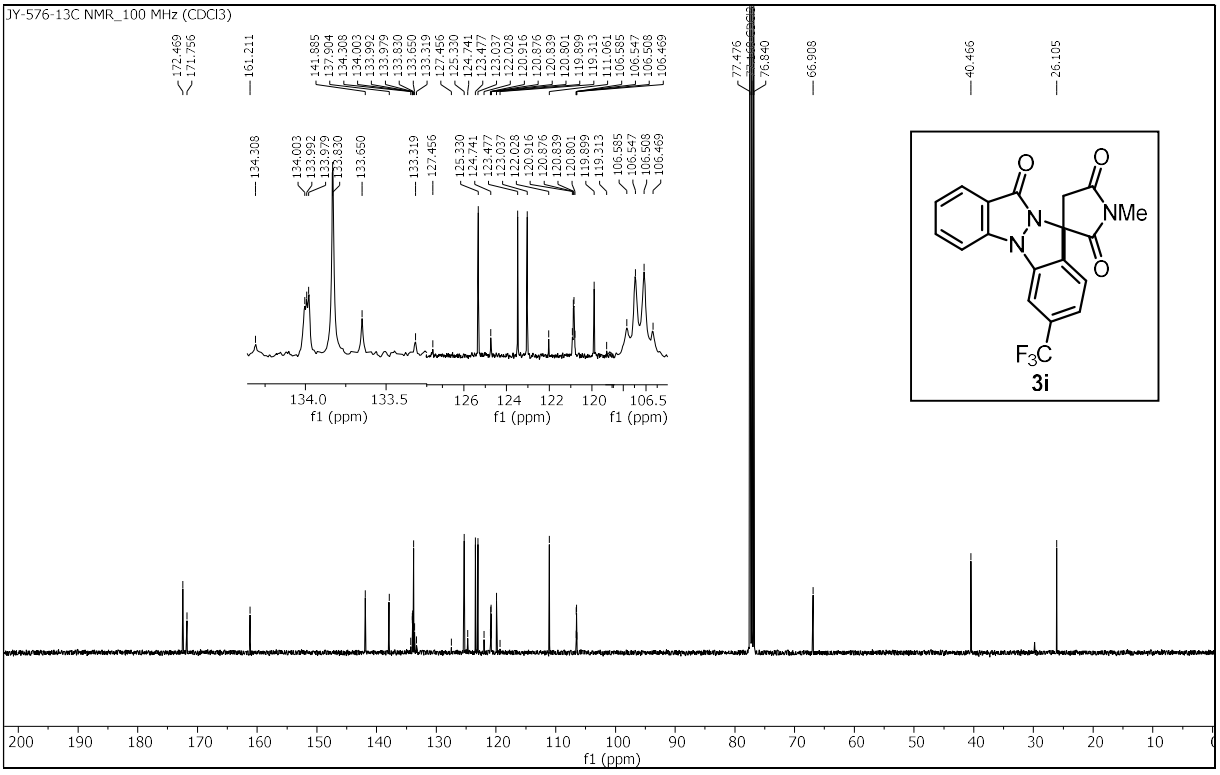
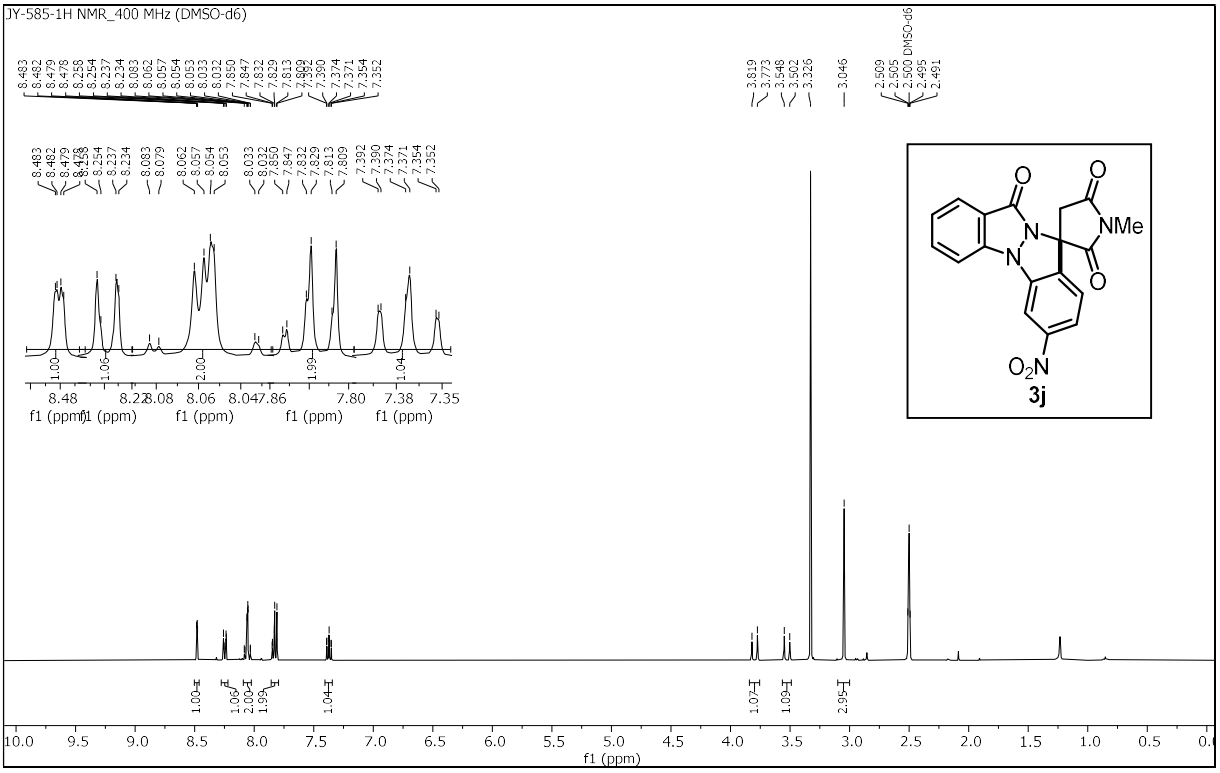
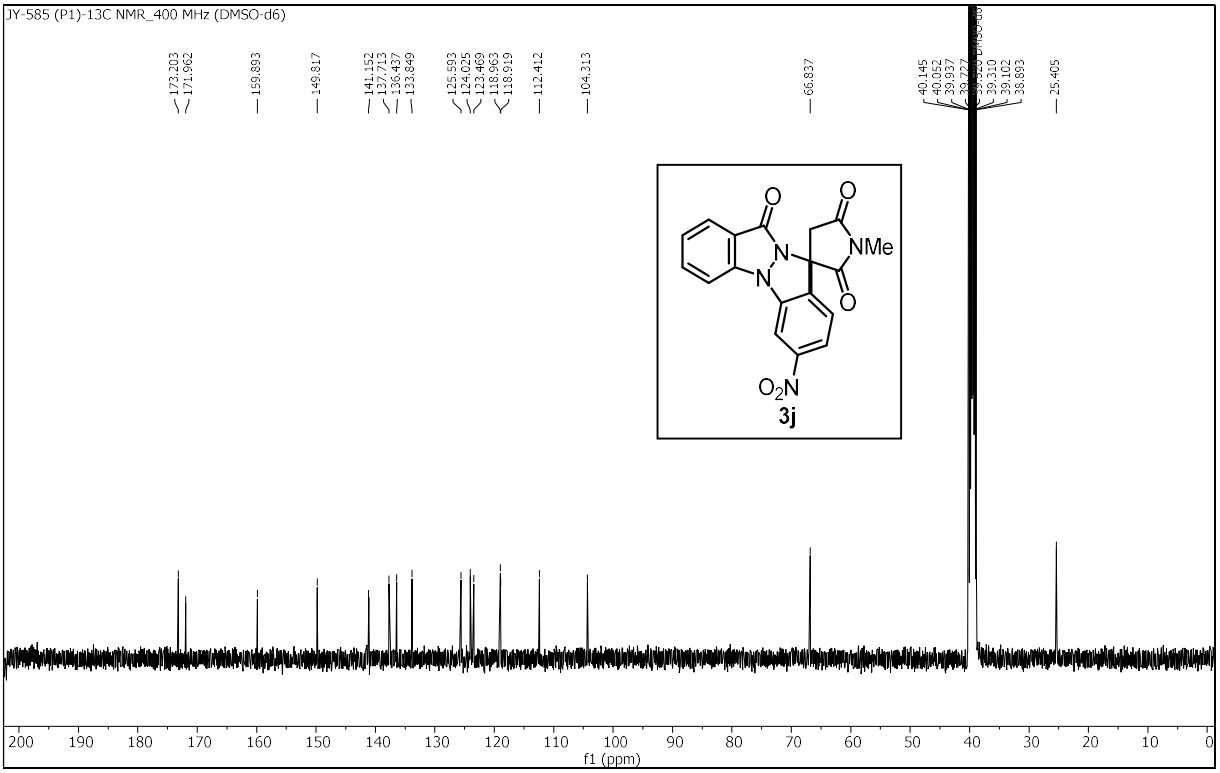
7.916
7.914
7.912
7.896
7.894
7.892
7.712
7.709
7.694
7.691
7.688
7.673
7.670
7.511
7.490
7.329
7.298
7.278
7.260 CDCl3
7.118
7.114
7.097
7.093
7.071
4.003
3.957
3.213
3.208
3.167
1.00
1.02
1.02
1.07
1.01
1.15
1.99
7.92 7.89
7.70
7.65 7.50 7.35 7.30
7.11 7.08
f1 (ppm)
1.00
3.12
1.19
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
O
O
N
N
NMe
O
Cl
3h

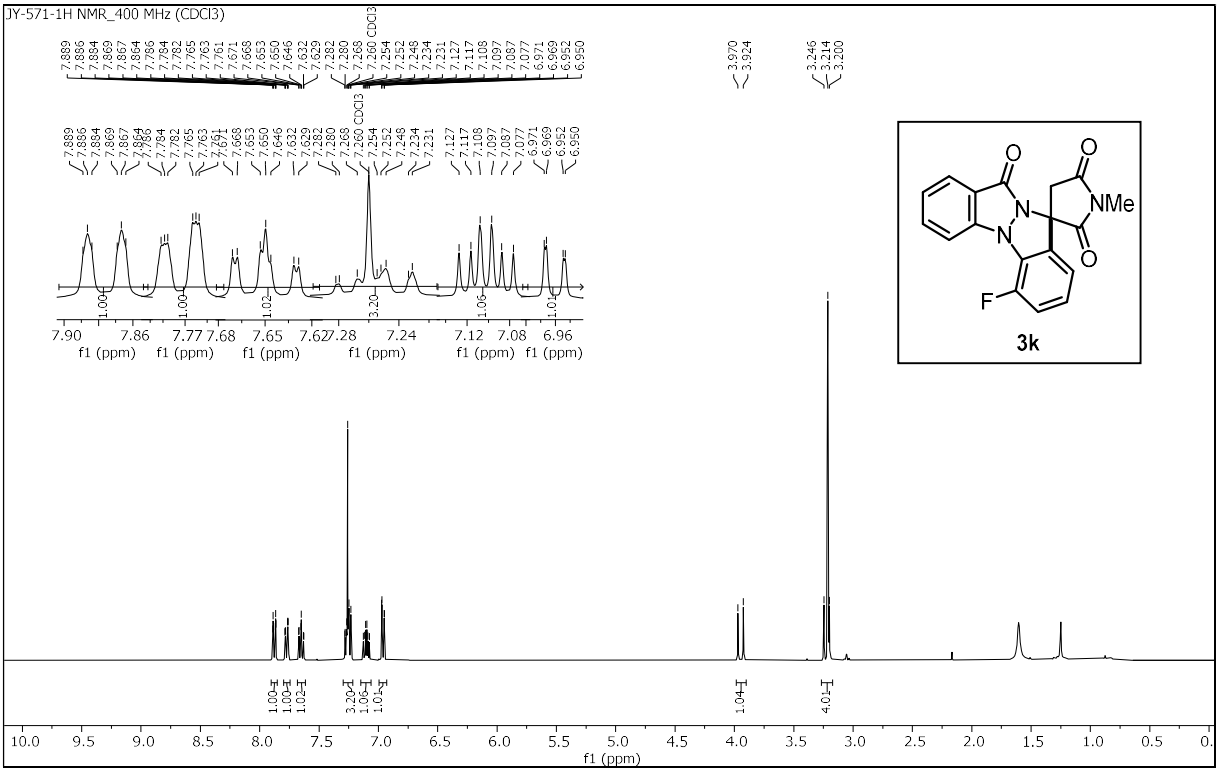

JY-574-13C NMR_100 MHz (CDCl3)
172.671
172.057
161.081
141.718
138.269
137.242
133.647
128.963
125.861
123.994
123.263
123.208
119.814
110.927
110.107
77.478
76.843
66.722
40.337
26.040
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)
O
O
N
N
NMe
O
Cl
3h

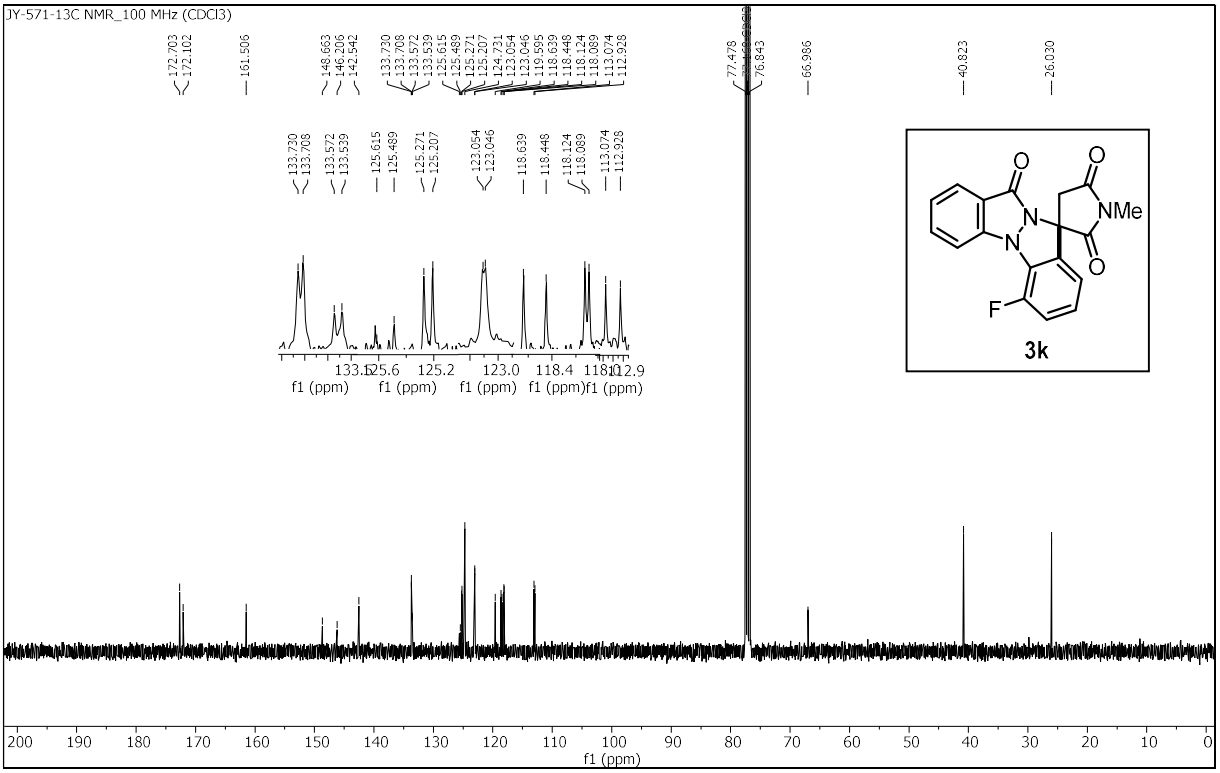

JY-576-1H NMR_400 MHz (CDCl3)
3i

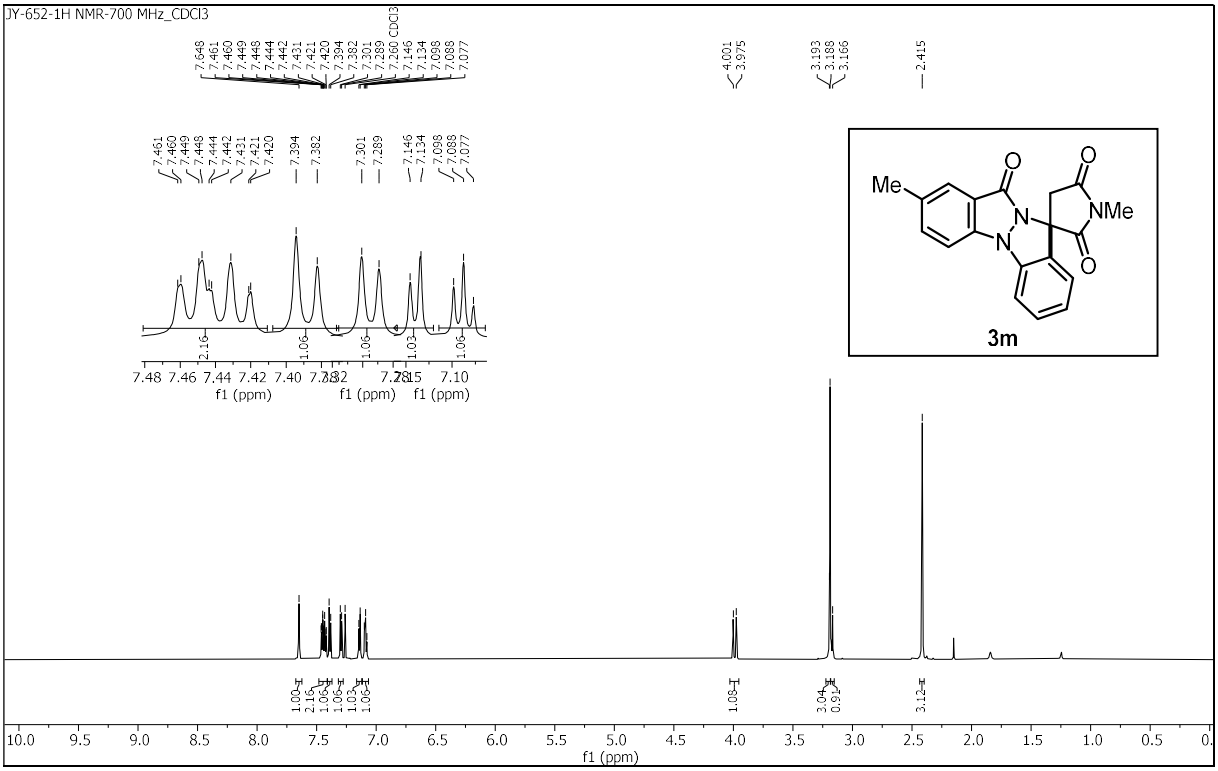

JY-576-13C NMR_100 MHz (CDCl3)
3i

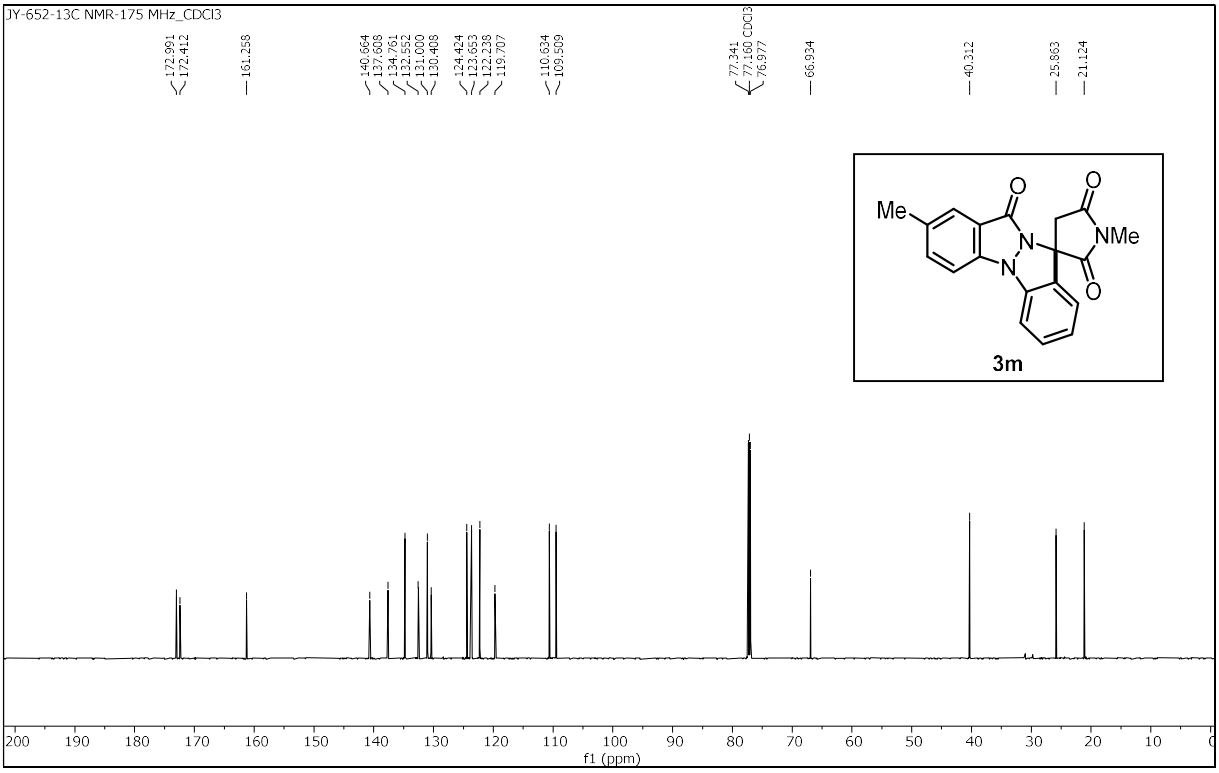

JY-585-1H NMR_400 MHz (DMSO-d6)
3j
f1 (ppm)

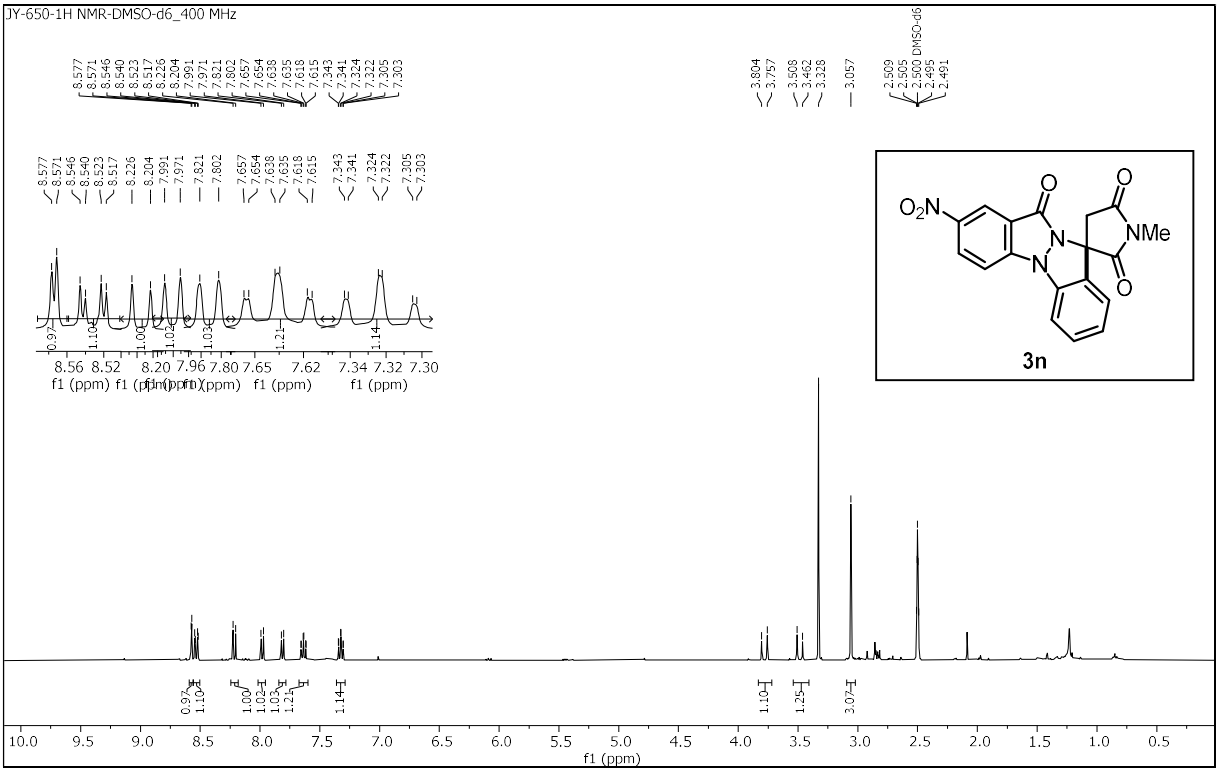

JY-585 (P1)-13C NMR_400 MHz (DMSO-d6)
3j
f1 (ppm)

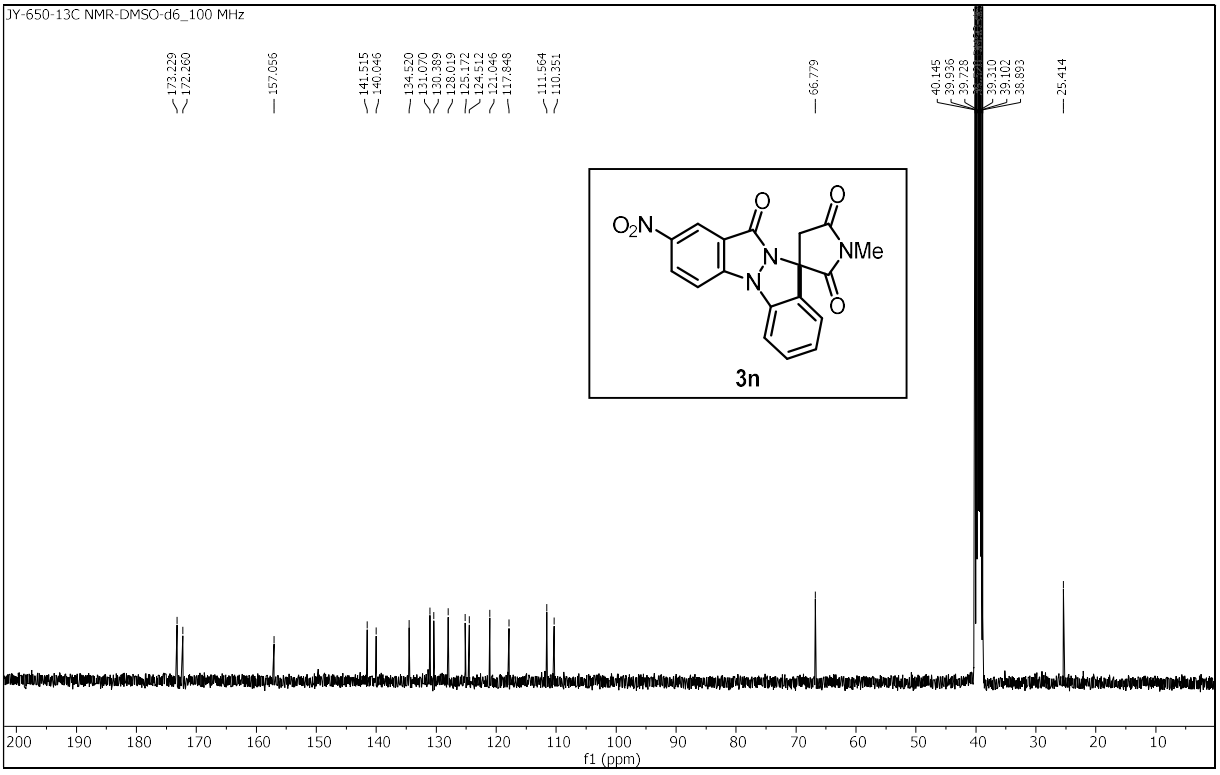

JY-571-1H NMR_400 MHz (CDCl3)
3k

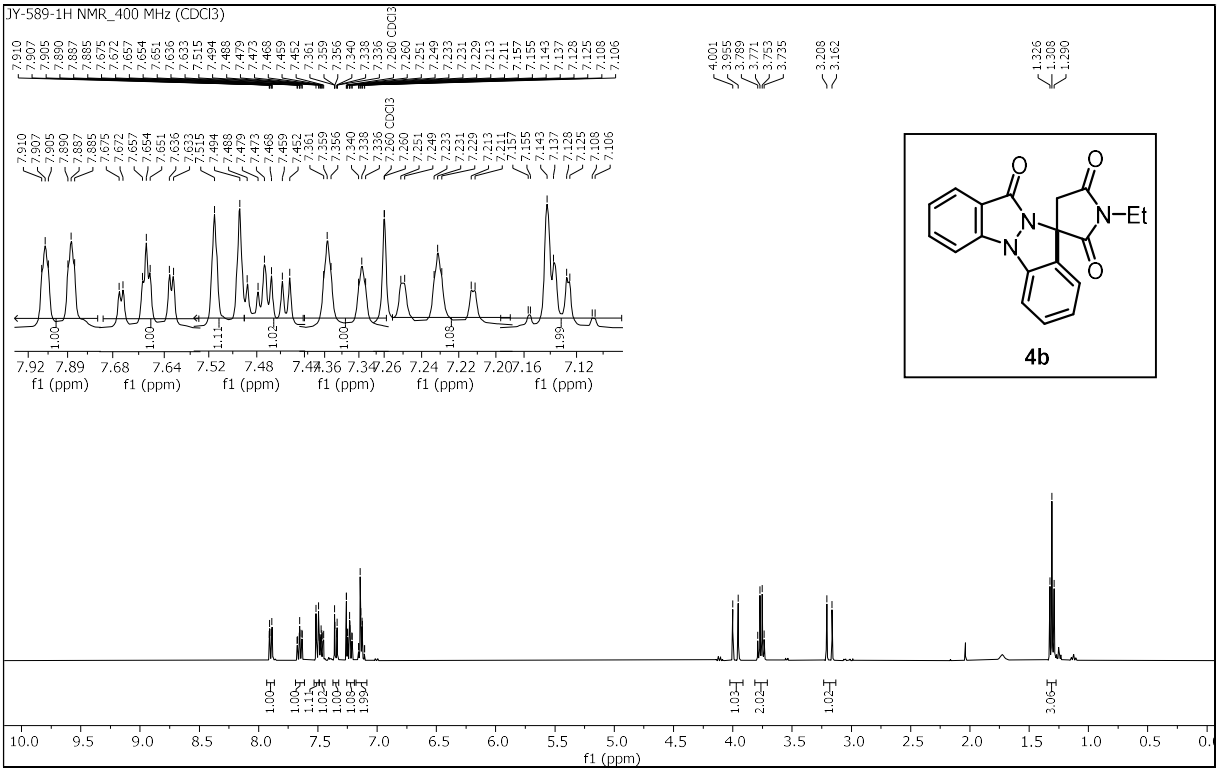

JY-571-13C NMR_100 MHz (CDCl3)
3k

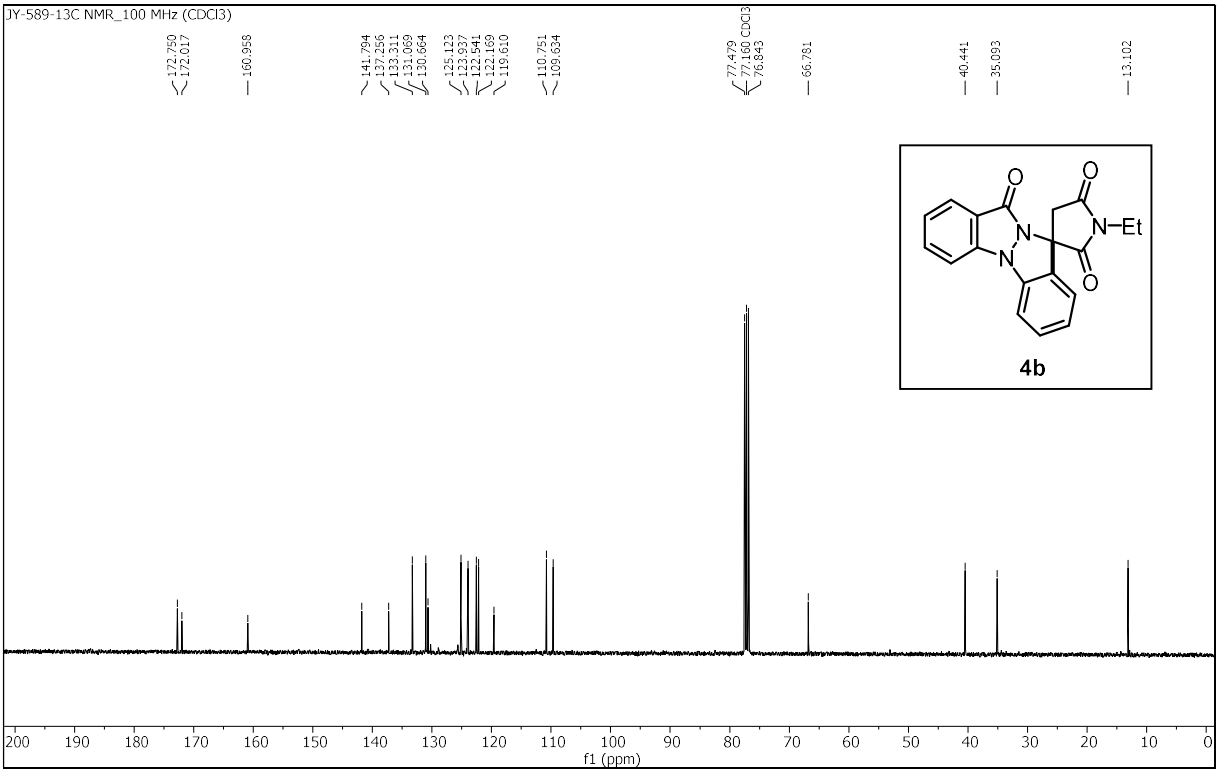

JY-652-1H NMR-700 MHz_CDCl3
7.648
7.461
7.460
7.449
7.448
7.444
7.442
7.431
7.421
7.420
7.394
7.382
7.301
7.289
7.260 CDCl3
7.146
7.134
7.098
7.088
7.077
4.001
3.975
3.193
3.188
3.166
2.415
Me
O
N
N
O
NMe
O
3m
f1 (ppm)

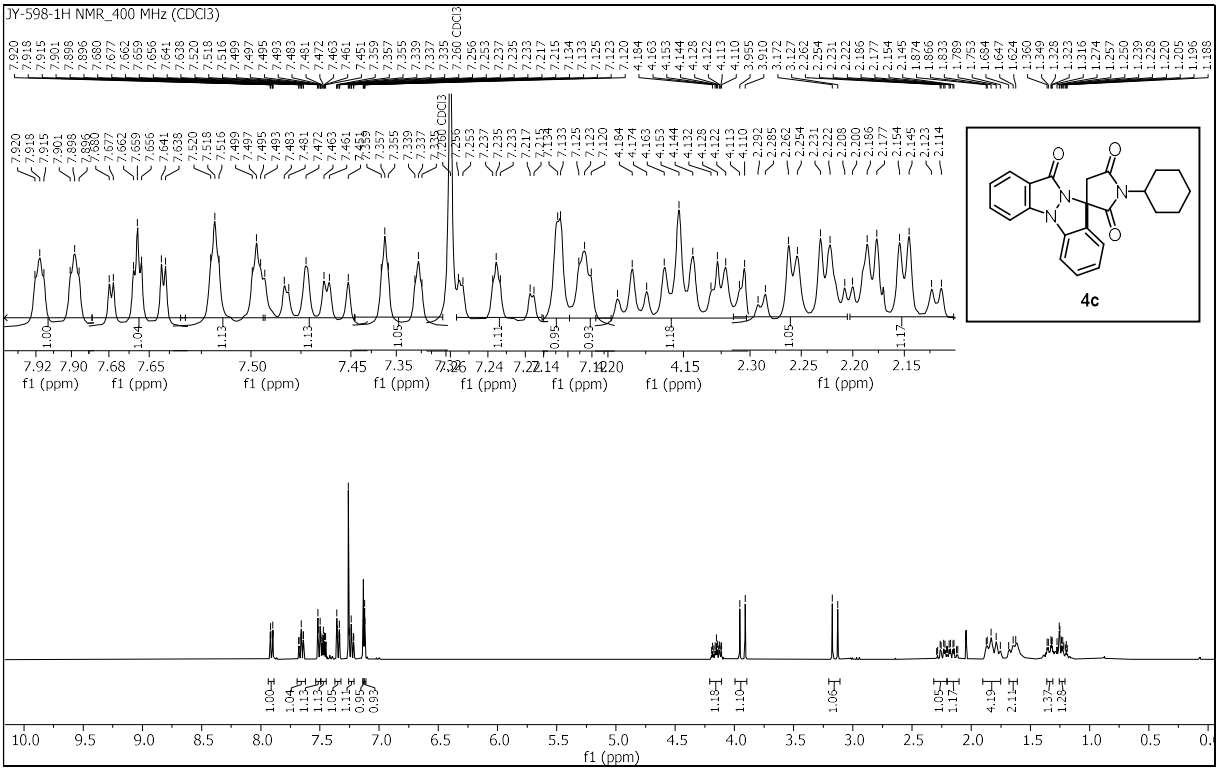

JY-652-13C NMR-175 MHz_CDCl3
172.991
172.412
161.258
140.664
137.608
134.761
132.552
131.000
130.408
124.424
123.653
122.238
115.707
110.634
109.589
77.341
77.160 CDCl3
76.977
66.934
40.312
25.863
21.124
Me
O
N
N
O
NMe
O
3m
f1 (ppm)

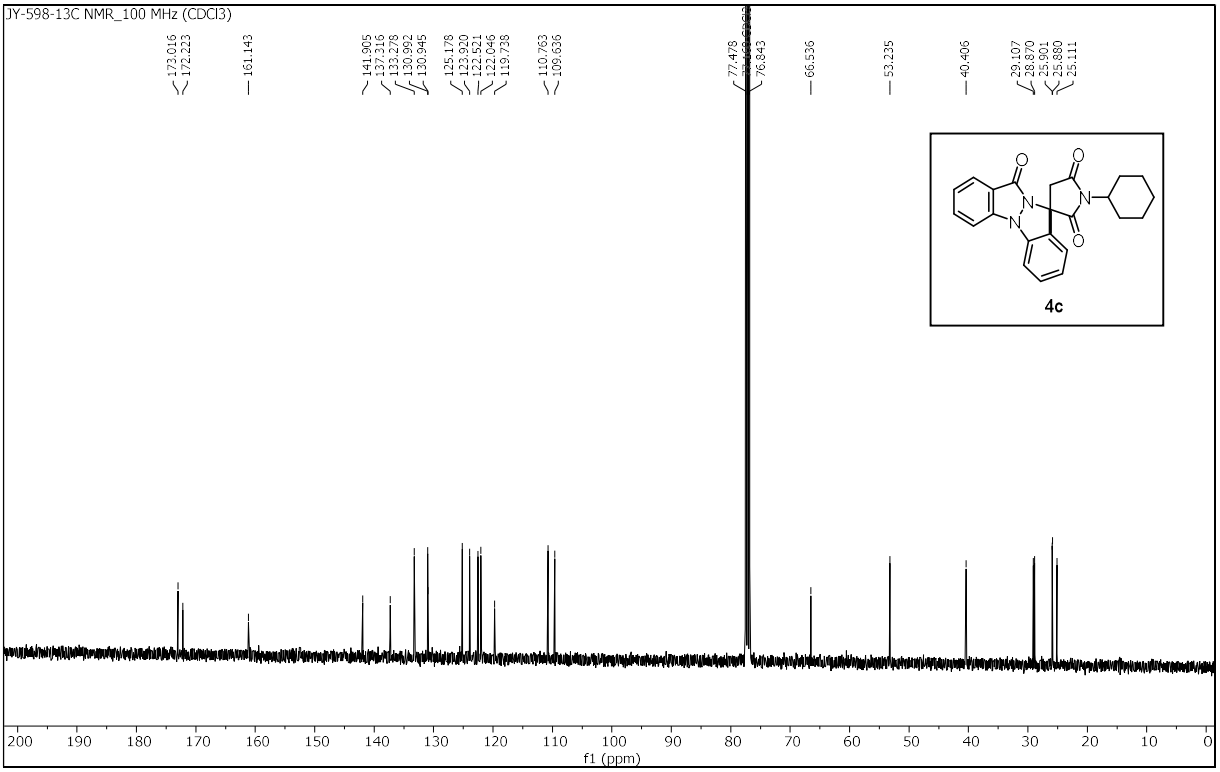

JY-650-1H NMR-DMSO-d6_400 MHz
3n
f1 (ppm)

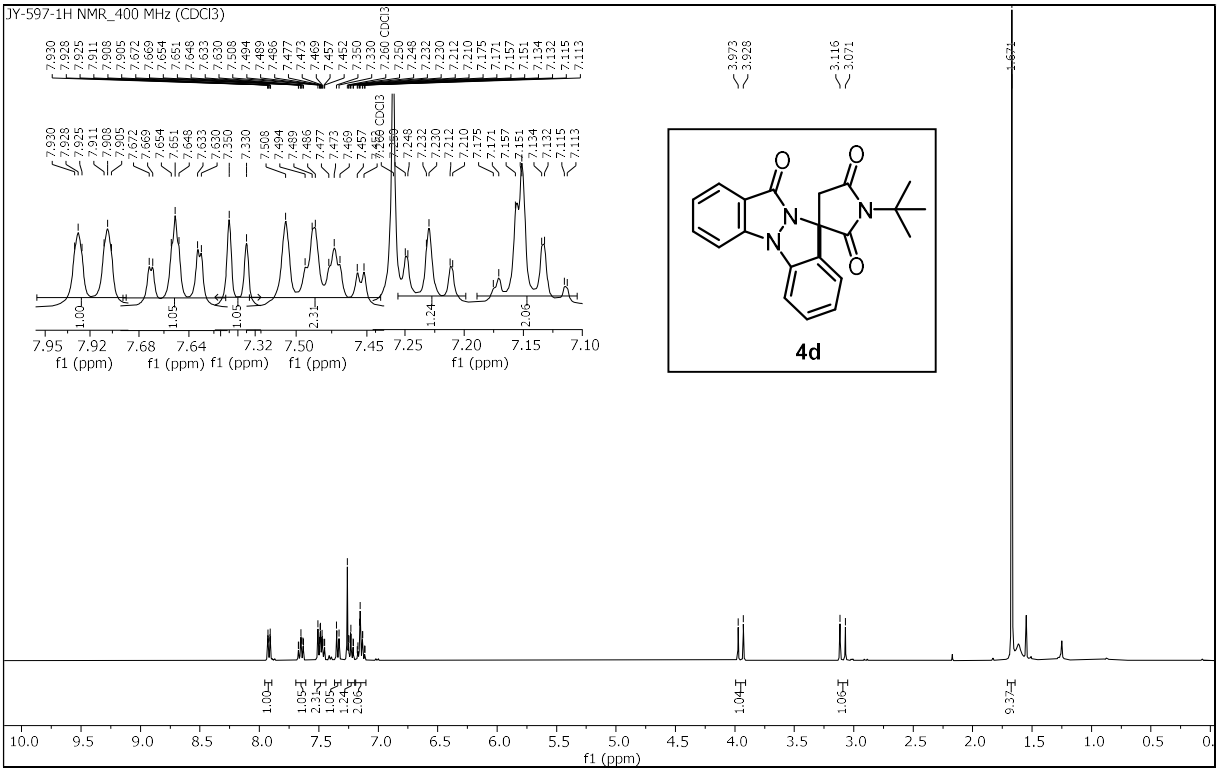

JY-650-13C NMR-DMSO-d6_100 MHz
3n
f1 (ppm)

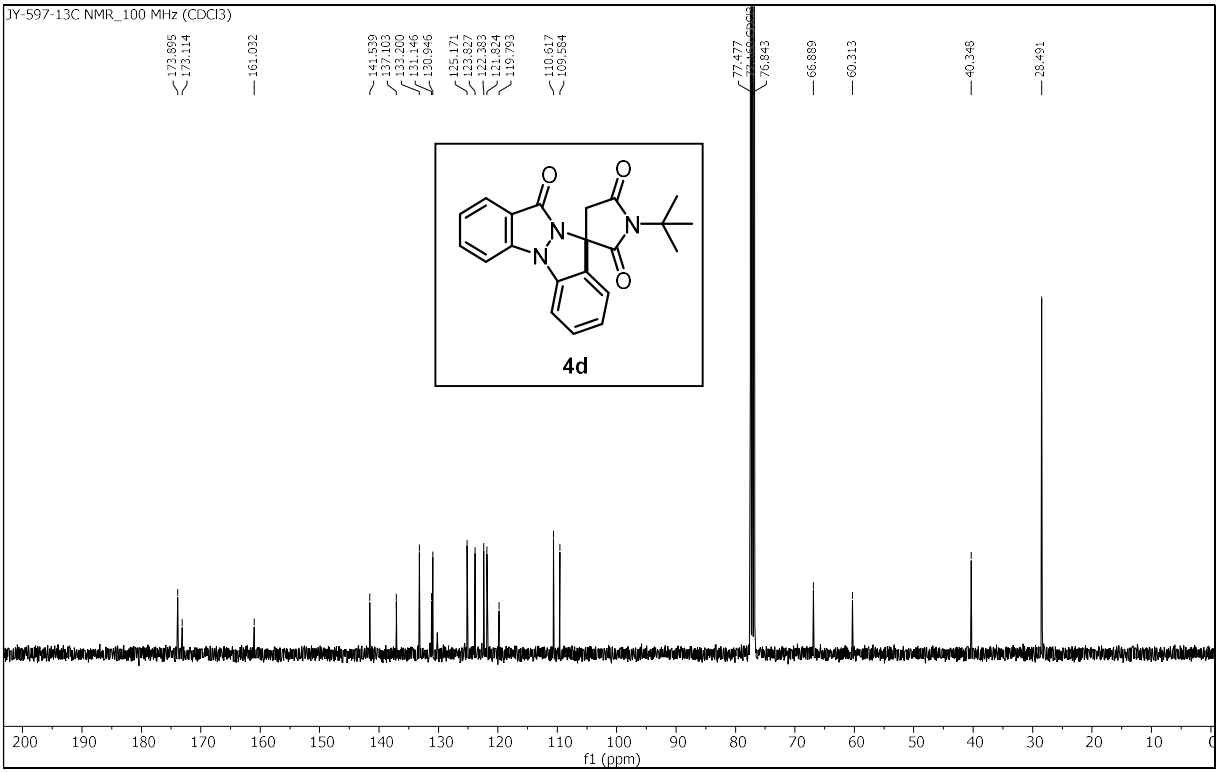

JY-589-1H NMR_400 MHz (CDCl3)
4b

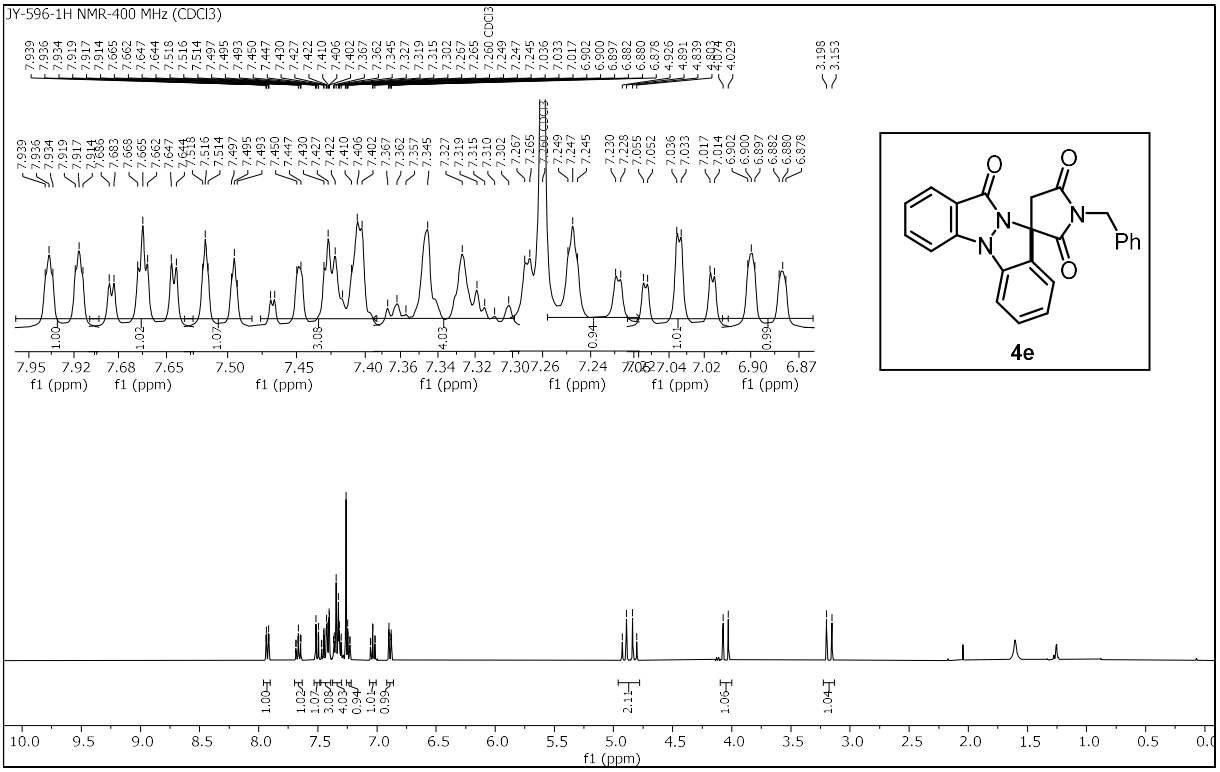

JY-589-13C NMR_100 MHz (CDCl3)
4b

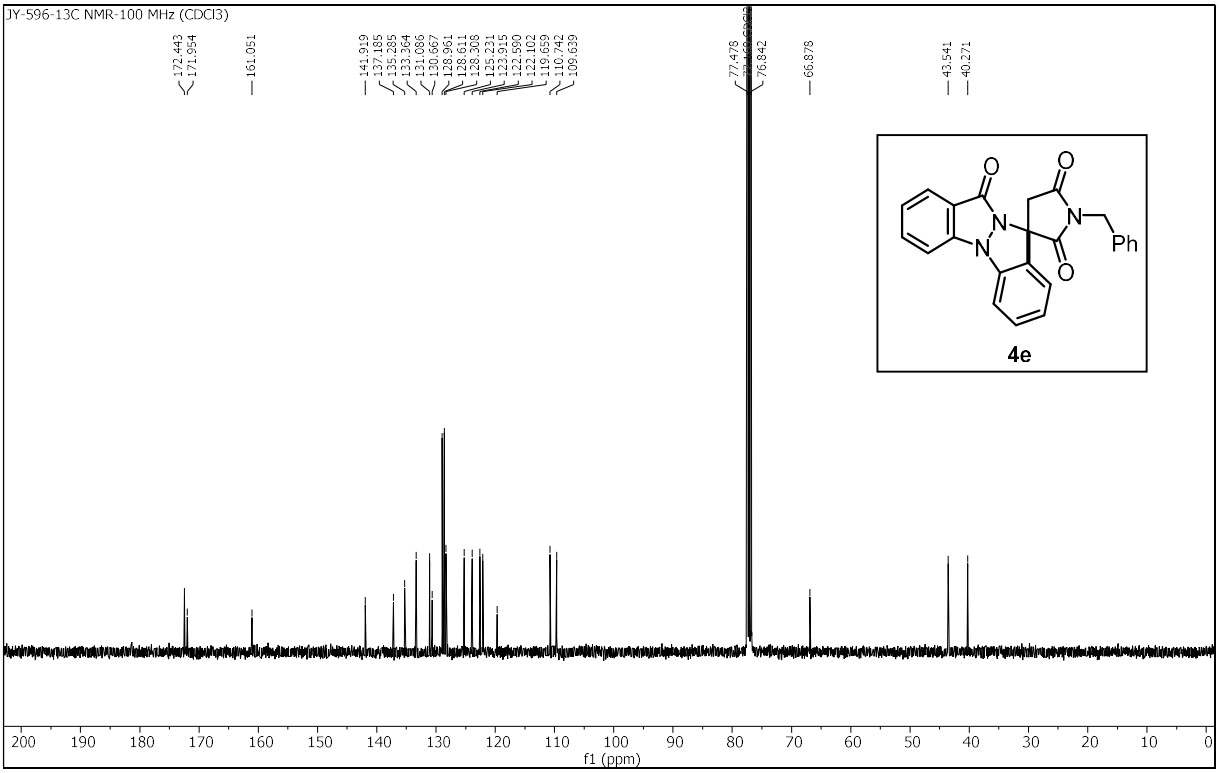

JY-598-1H NMR_400 MHz (CDCl3)
4c
f1 (ppm)

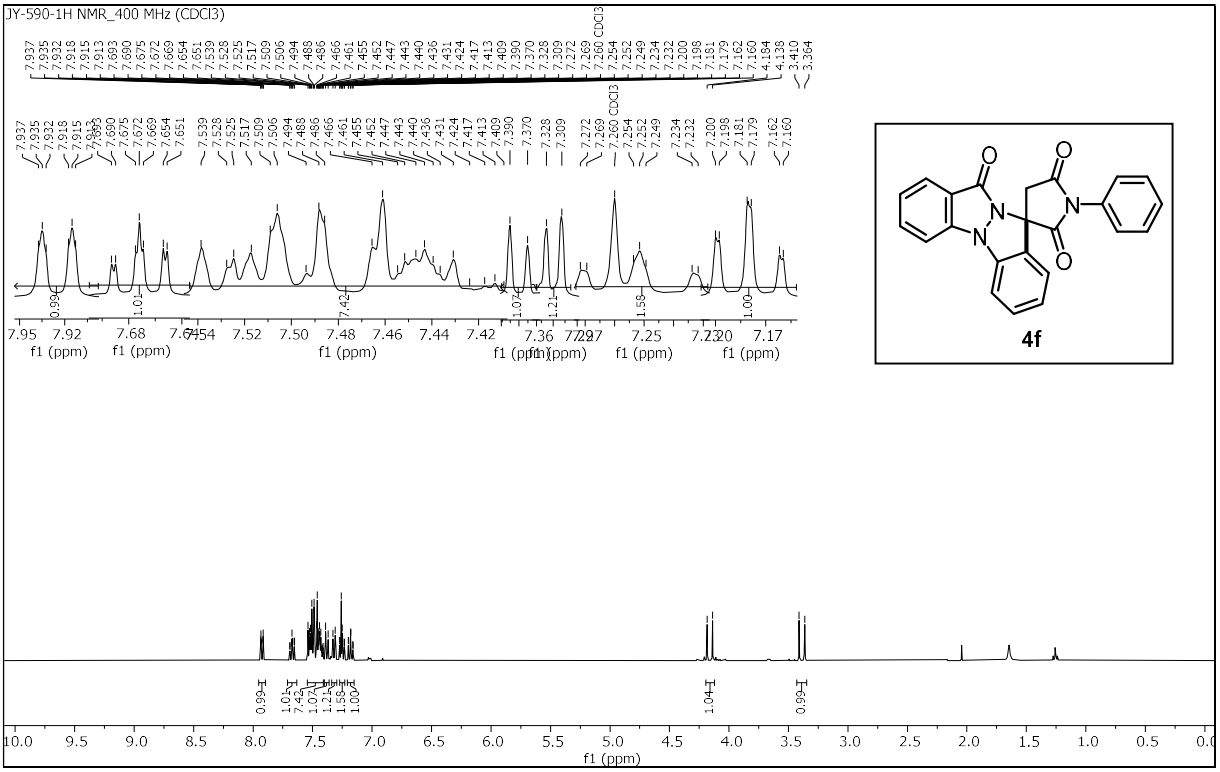

JY-598-13C NMR_100 MHz (CDCl3)
4c
f1 (ppm)

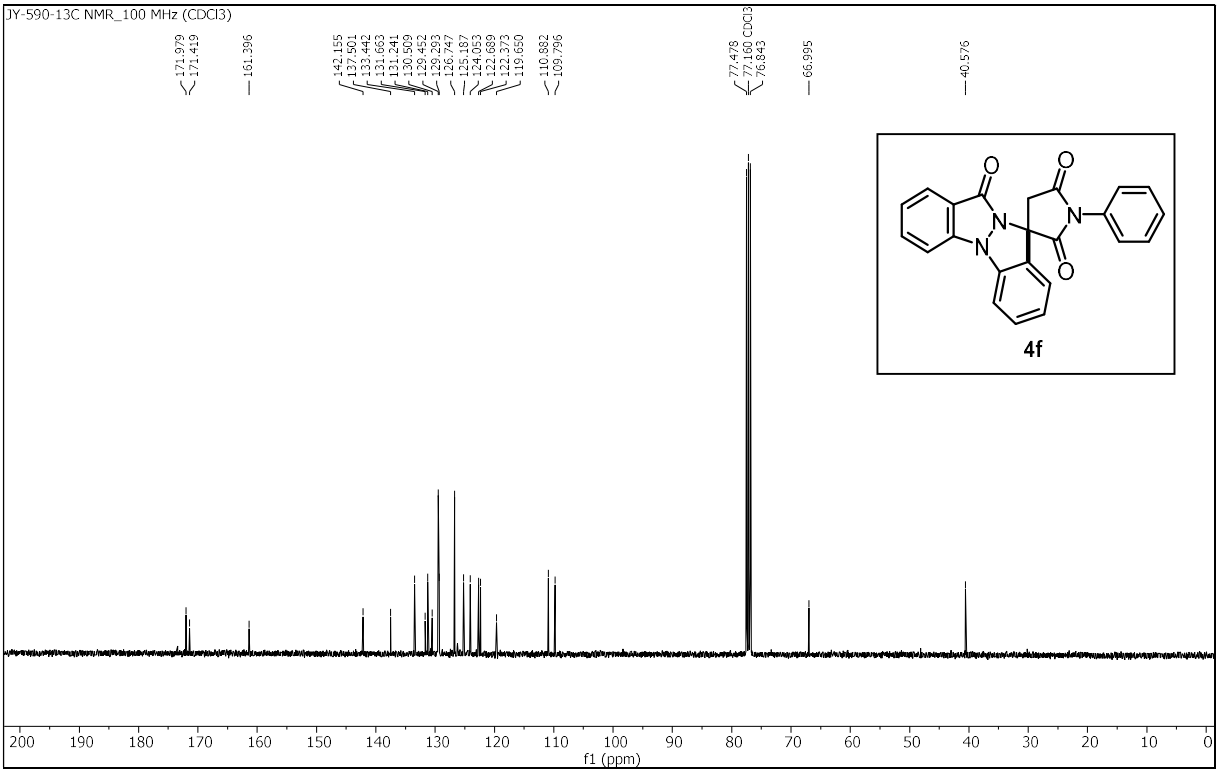

JY-597-1H NMR_400 MHz (CDCl3)
4d
f1 (ppm)

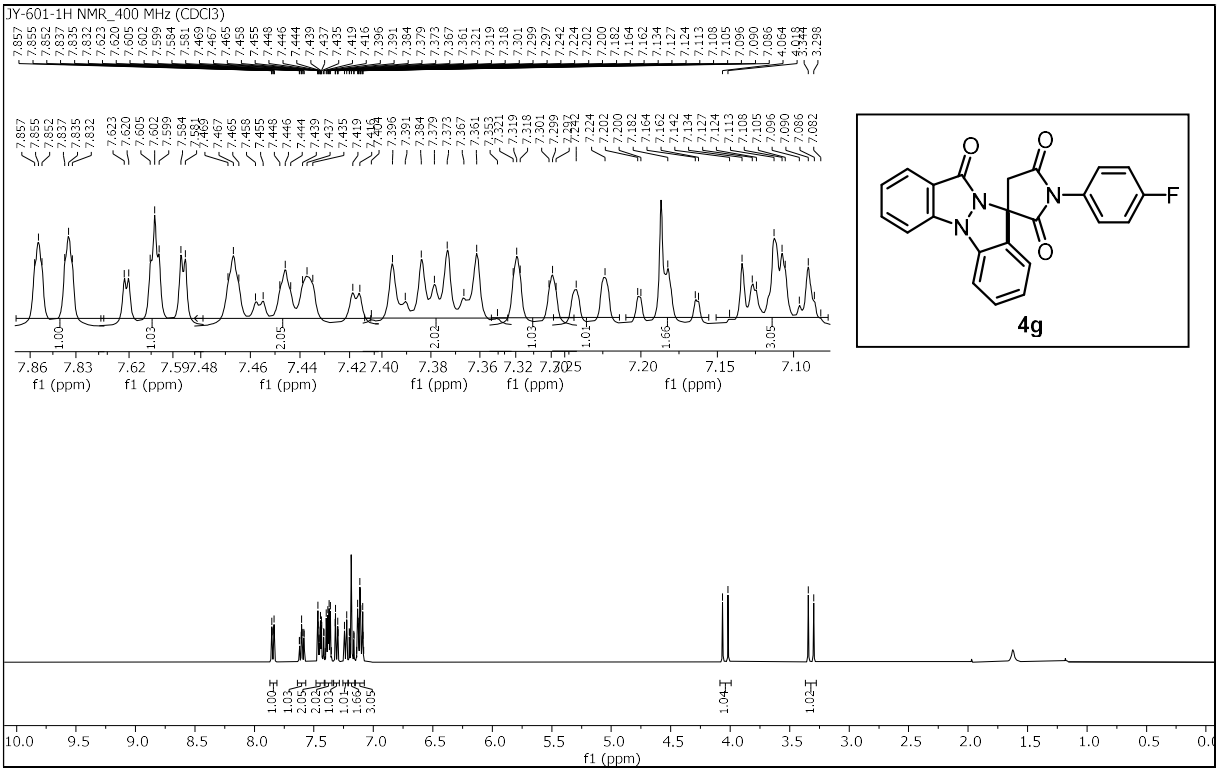

JY-597-13C NMR_100 MHz (CDCl3)
4d
f1 (ppm)

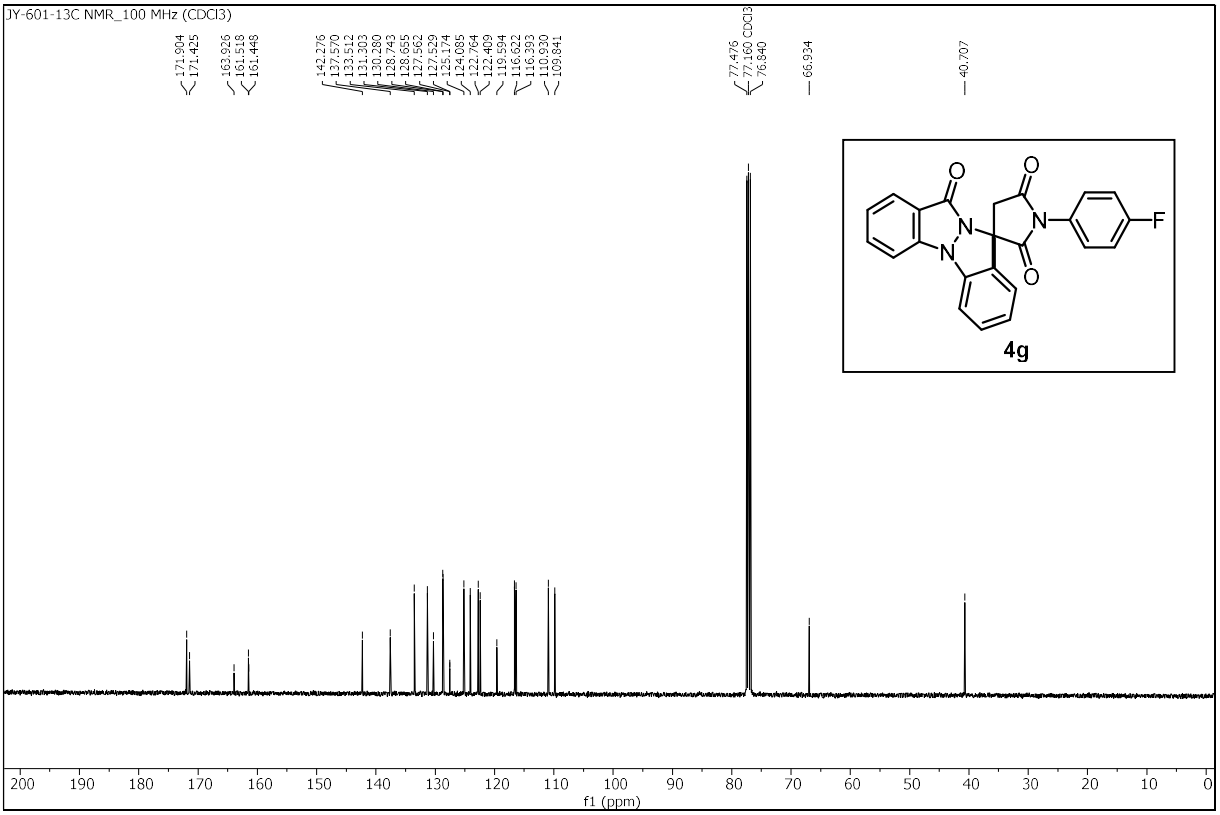

JY-596-1H NMR-400 MHz (CDCl3)
4e

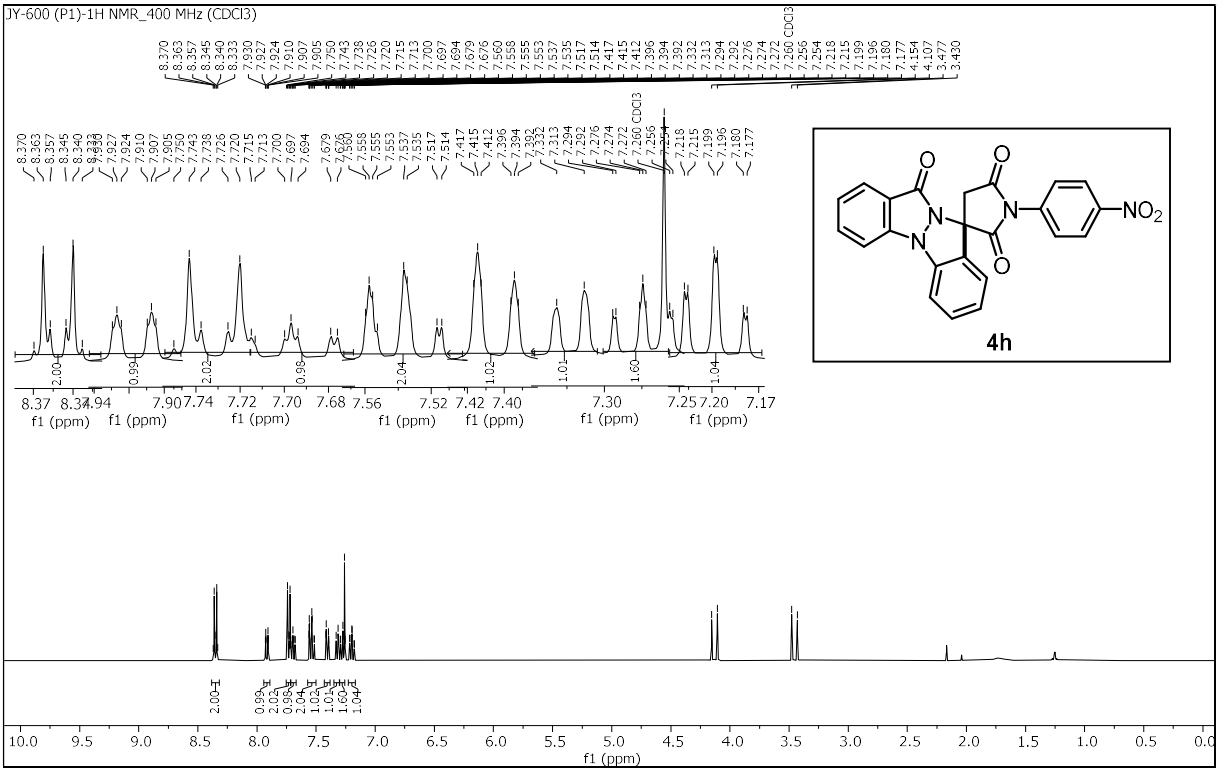

JY-596-13C NMR-100 MHz (CDCl3)
4e

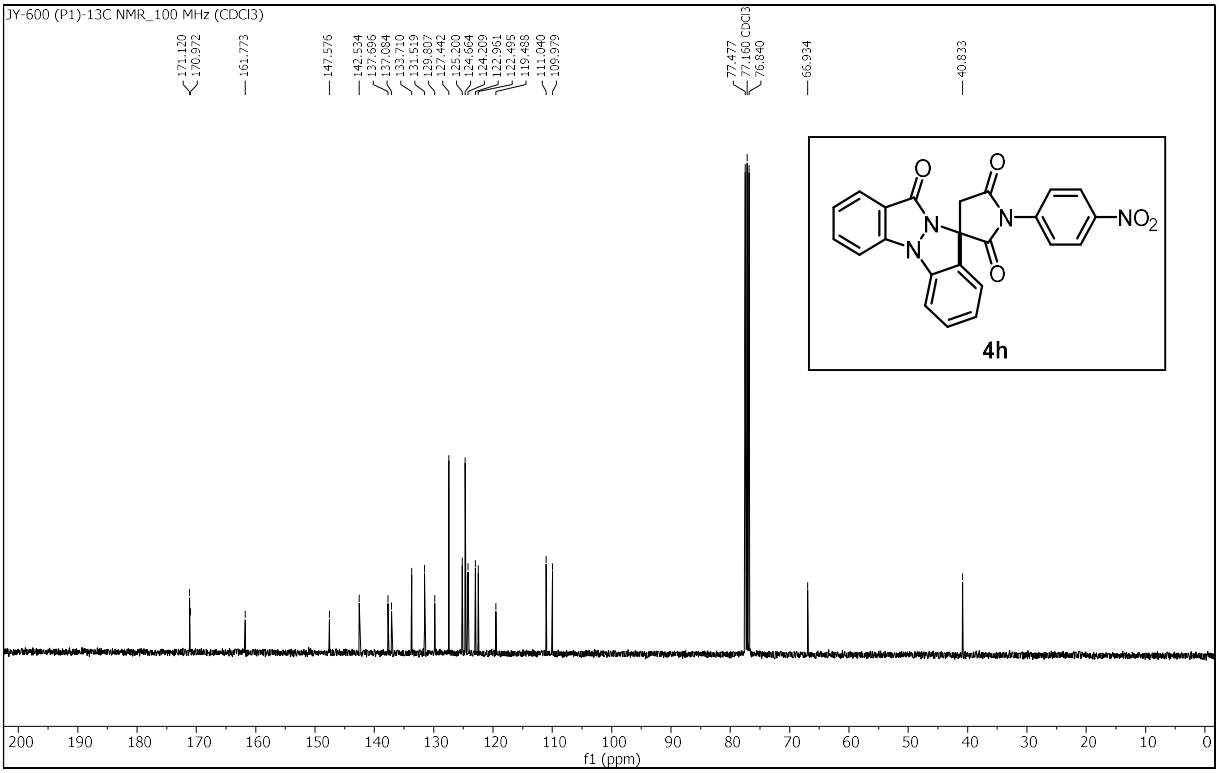

JY-590-1H NMR_400 MHz (CDCl3)
4f

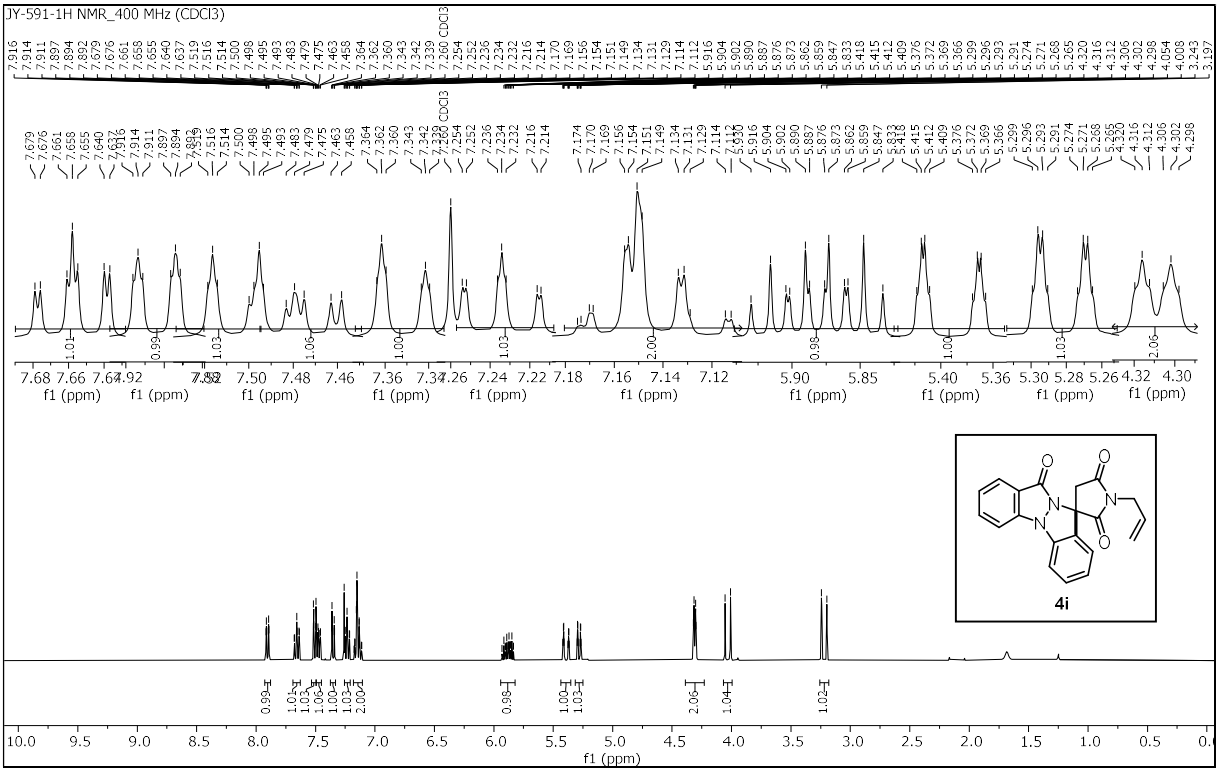

JY-590-13C NMR_100 MHz (CDCl3)
4f

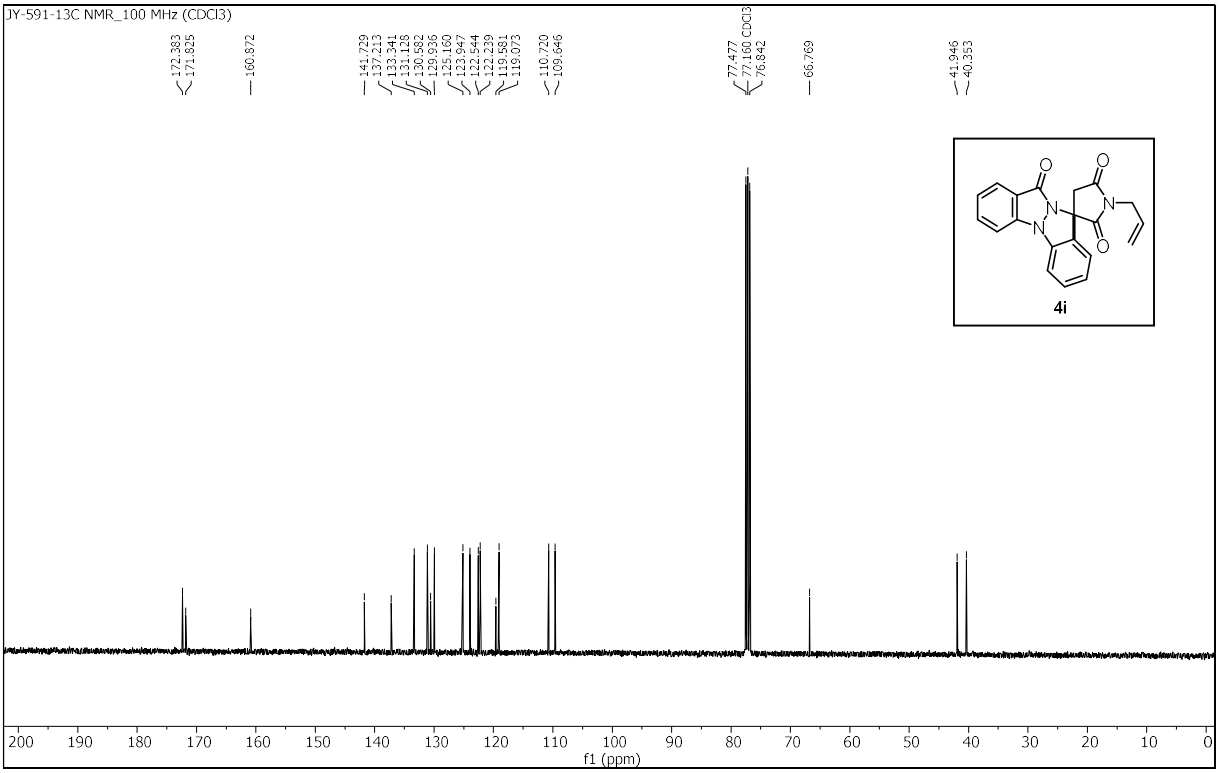

JY-601-1H NMR_400 MHz (CDCl3)
4g
f1 (ppm)

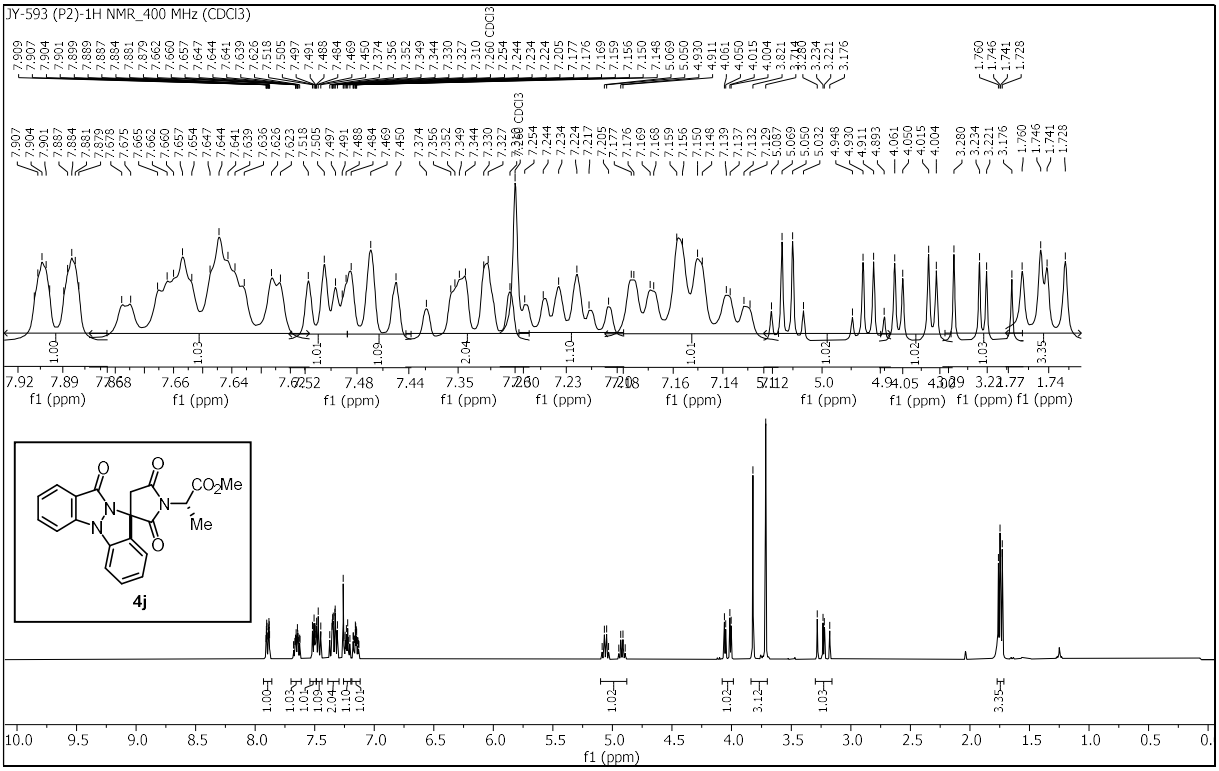

JY-601-13C NMR_100 MHz (CDCl3)
4g
f1 (ppm)

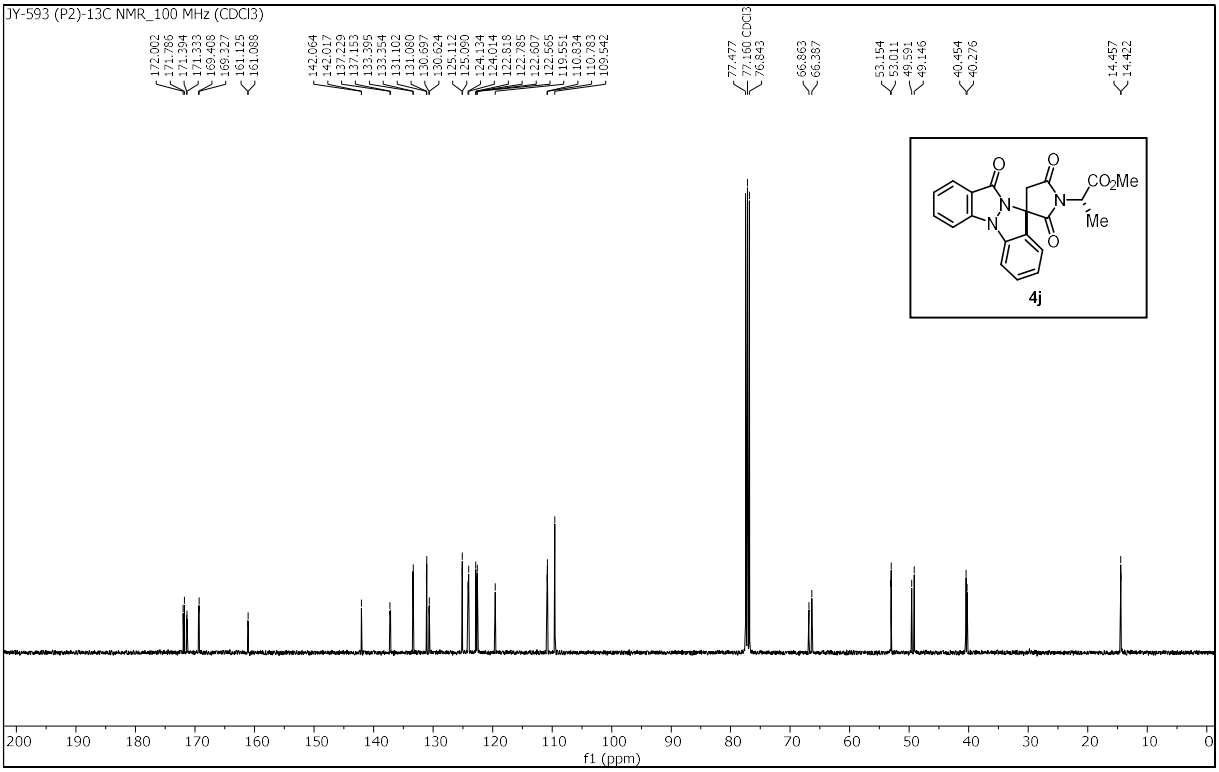

JY-600 (P1)-1H NMR_400 MHz (CDCl3)
4h
f1 (ppm)


JY-600 (P1)-13C NMR_100 MHz (CDCl3)
4h
f1 (ppm)


JY-591-1H NMR_400 MHz (CDCl3)
4i
f1 (ppm)


JY-591-13C NMR_100 MHz (CDCl3)
4i
f1 (ppm)


JY-593 (P2)-1H NMR_400 MHz (CDCl3)
f1 (ppm)
4j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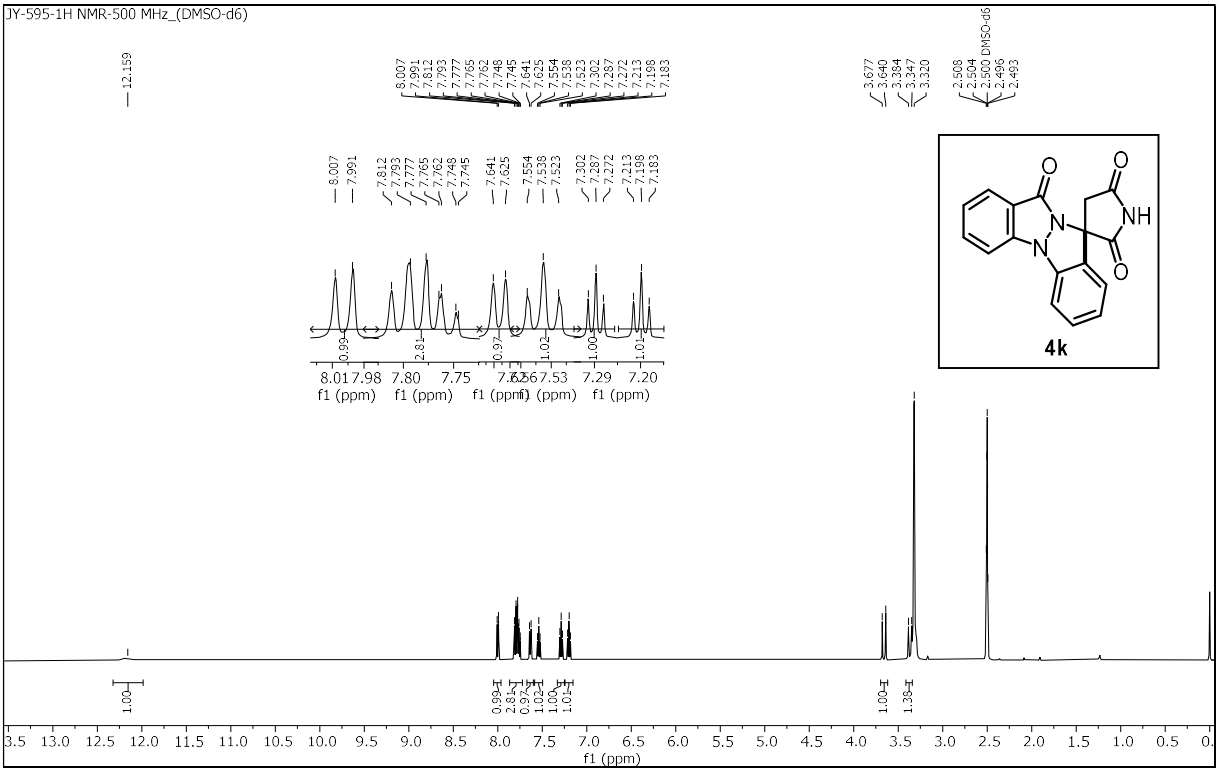
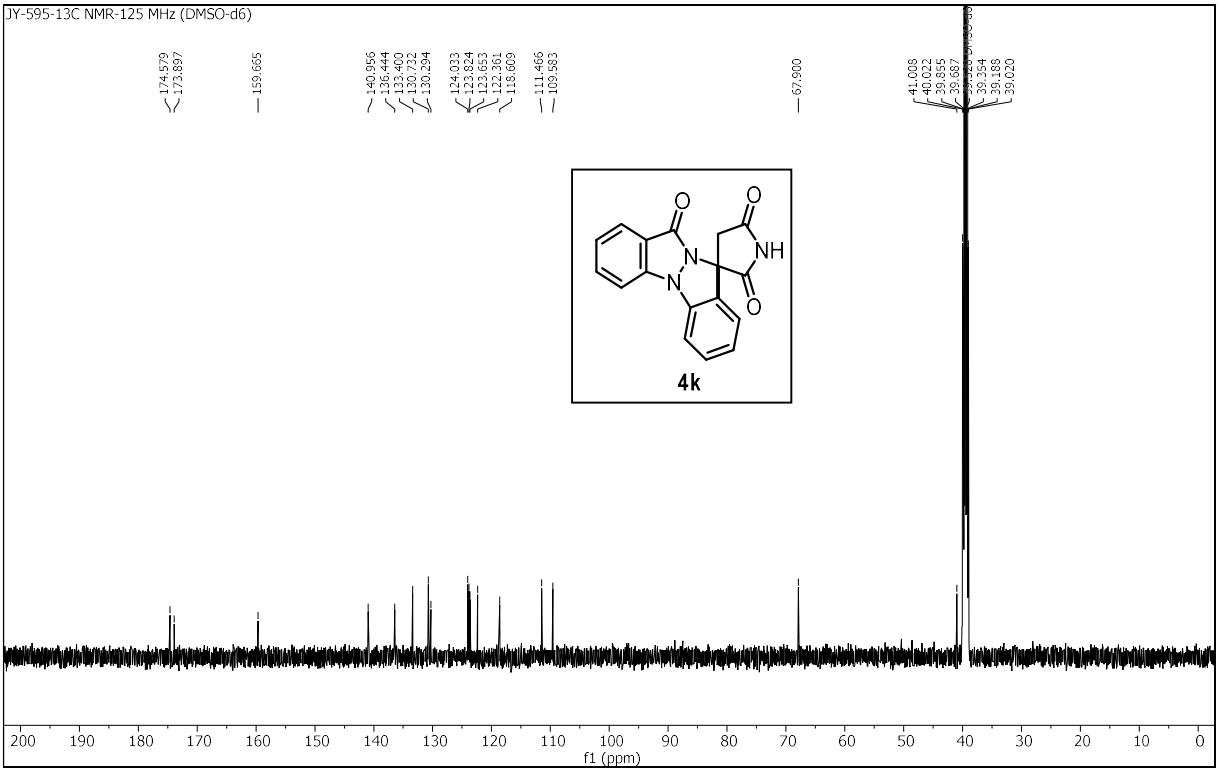
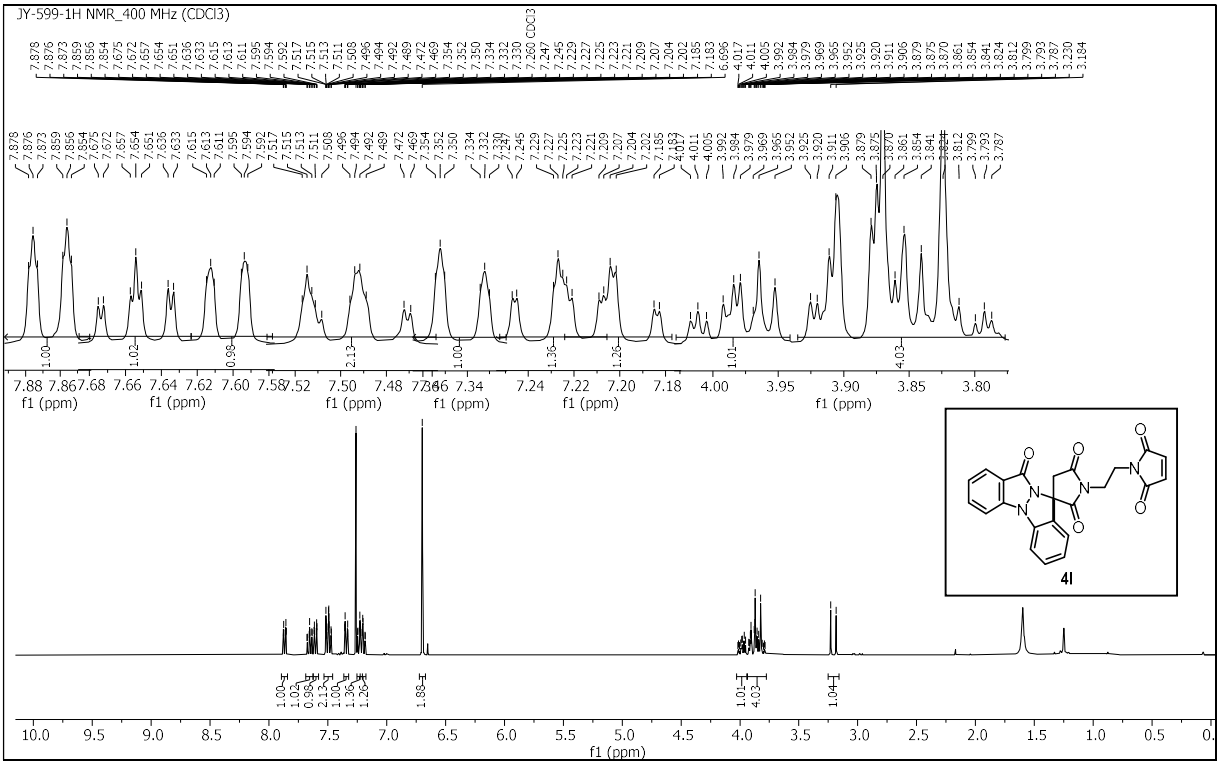
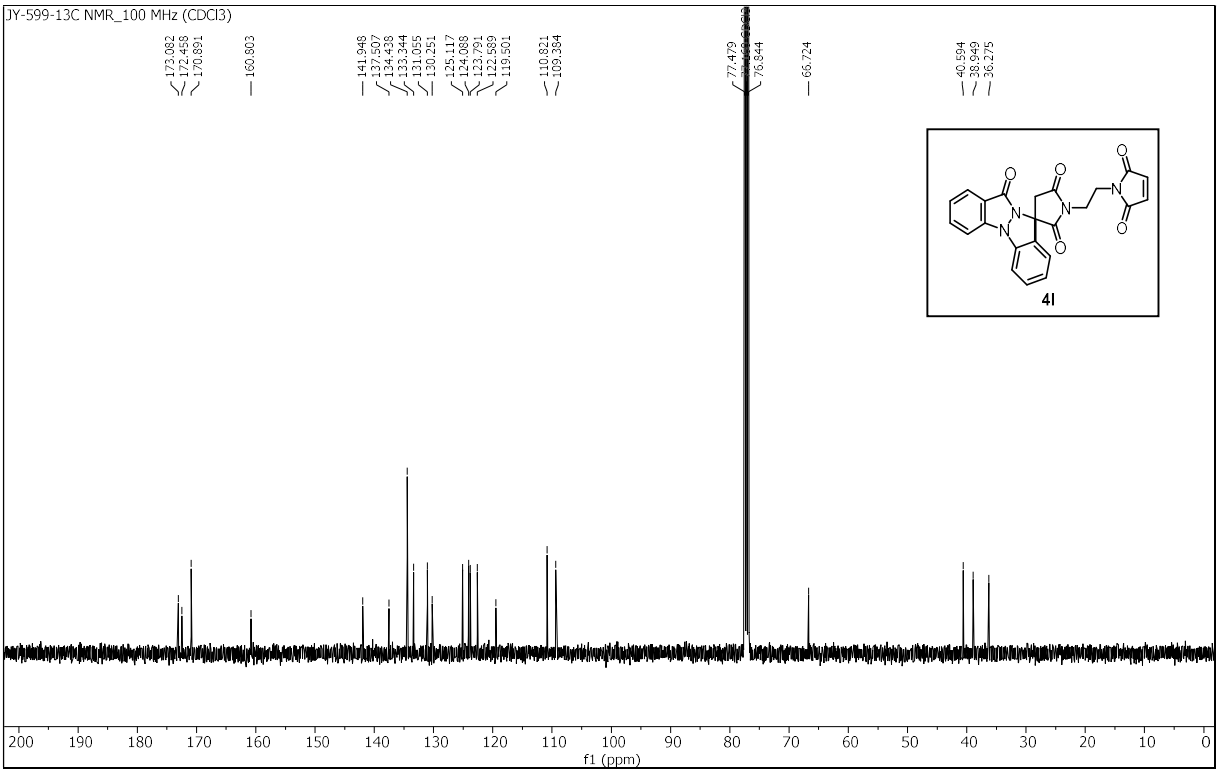
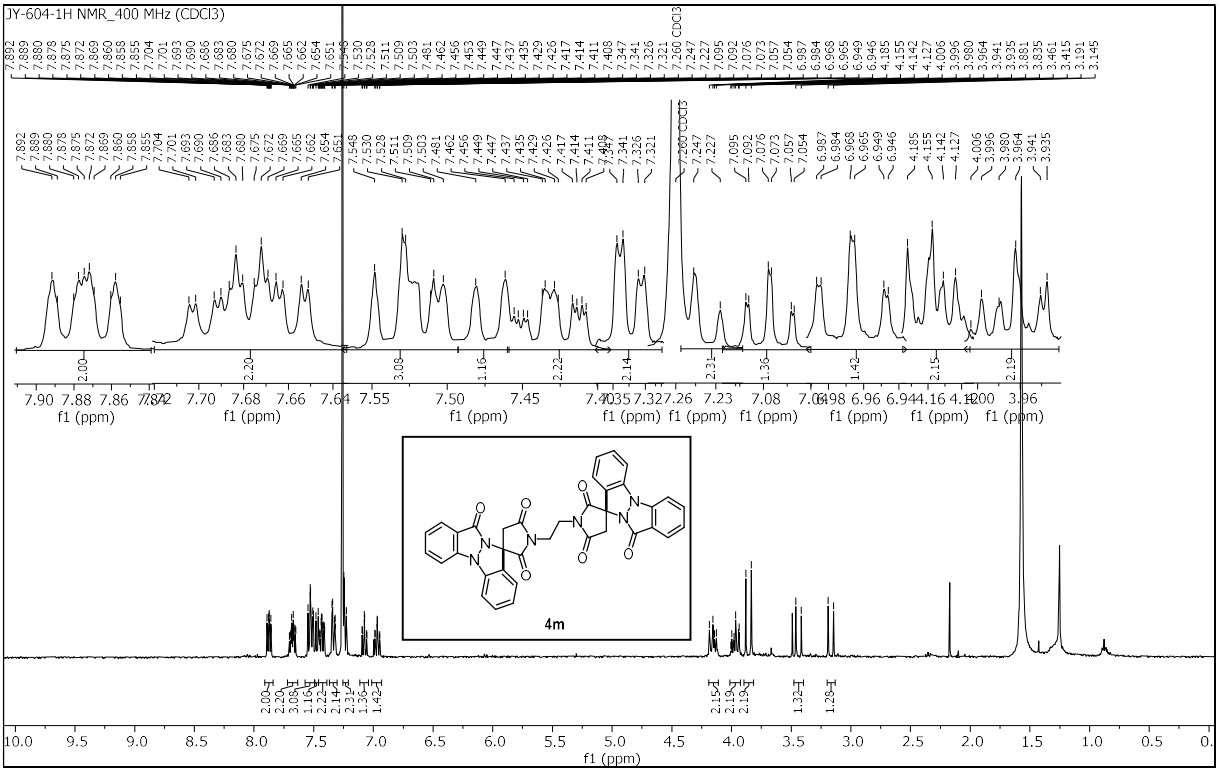
f1 (ppm)
4j

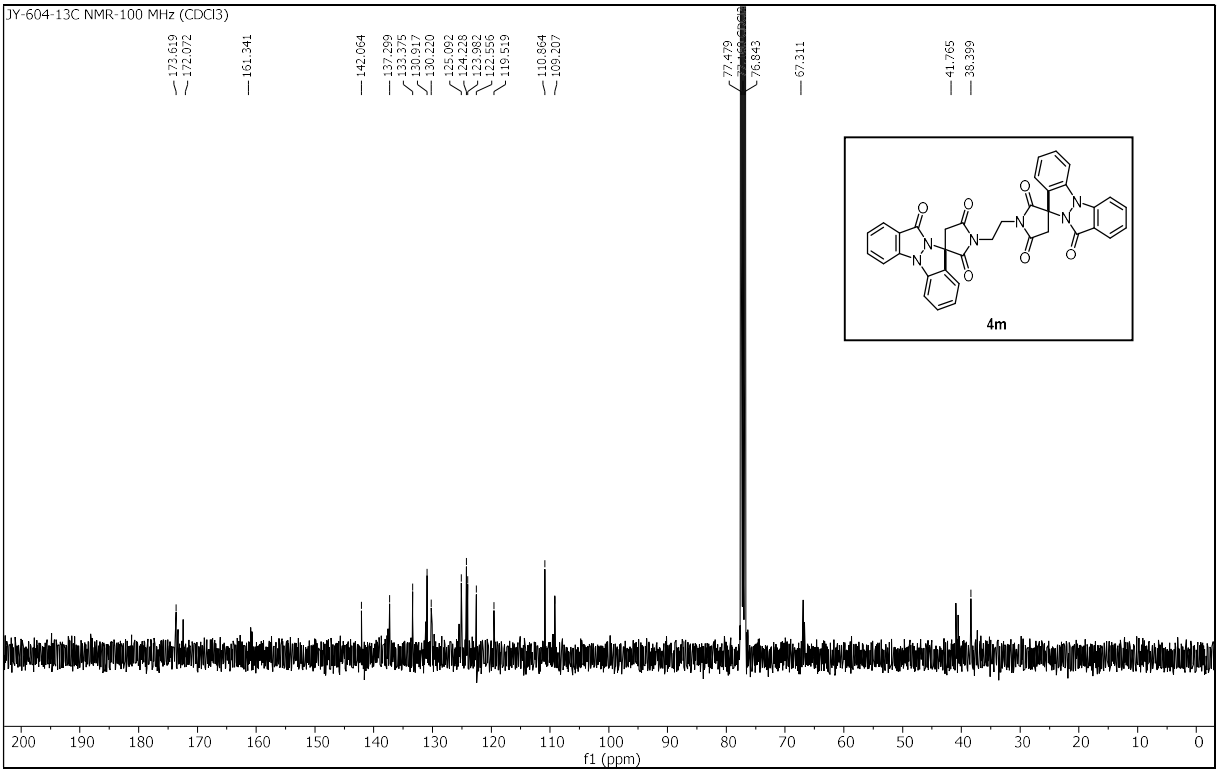

JY-595-1H NMR-500 MHz_(DMSO-d6)
4k
f1 (ppm)

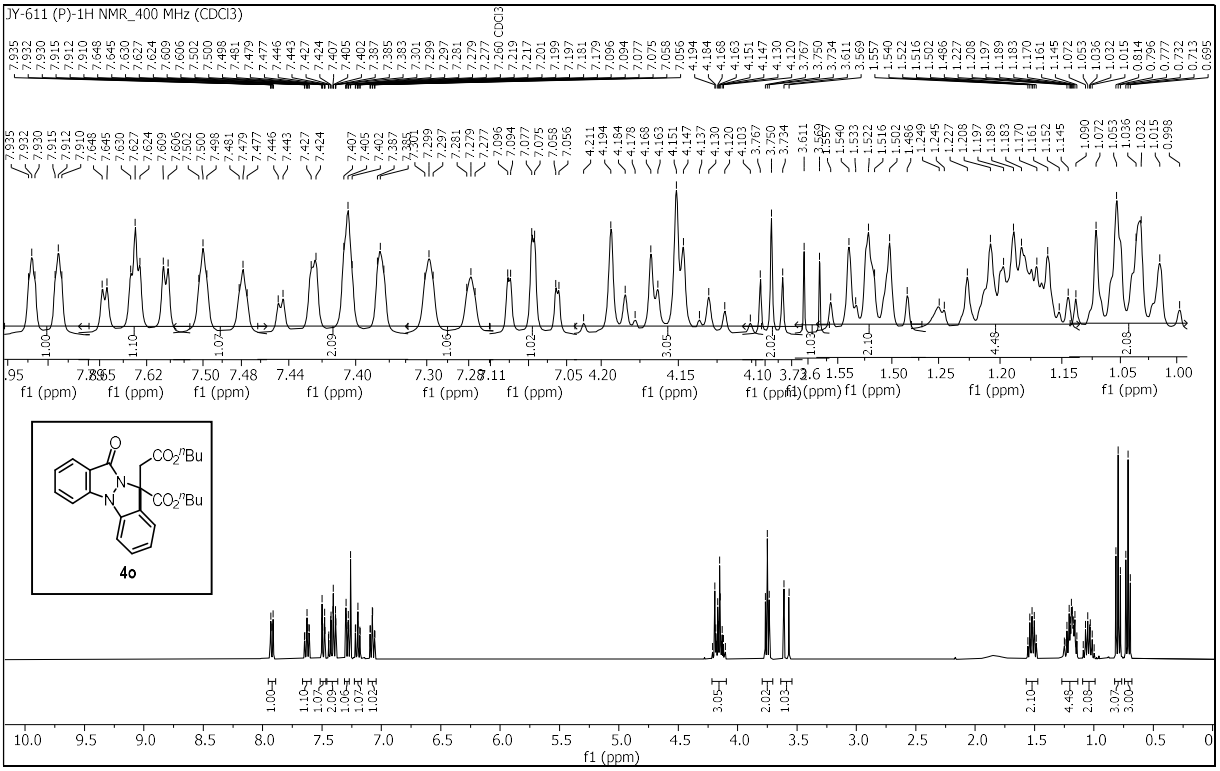

JY-595-13C NMR-125 MHz (DMSO-d6)
4k
f1 (ppm)

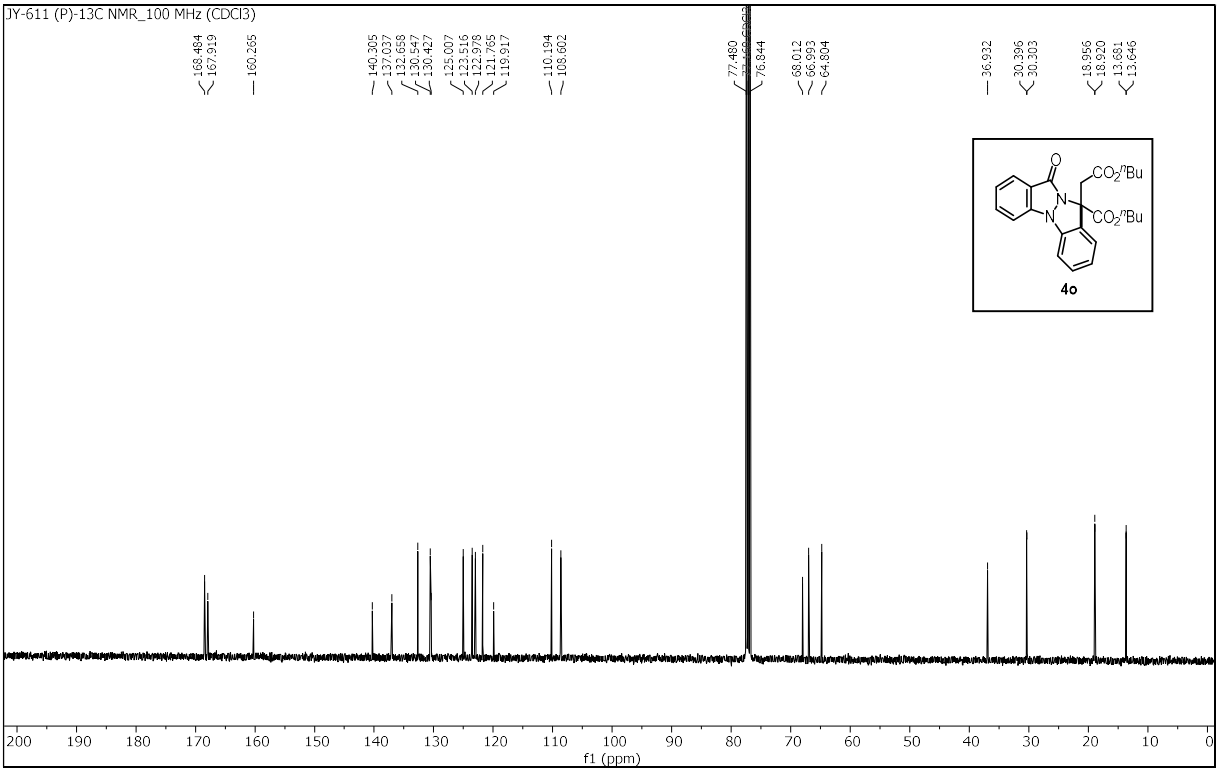

JY-599-1H NMR_400 MHz (CDCl3)
4I

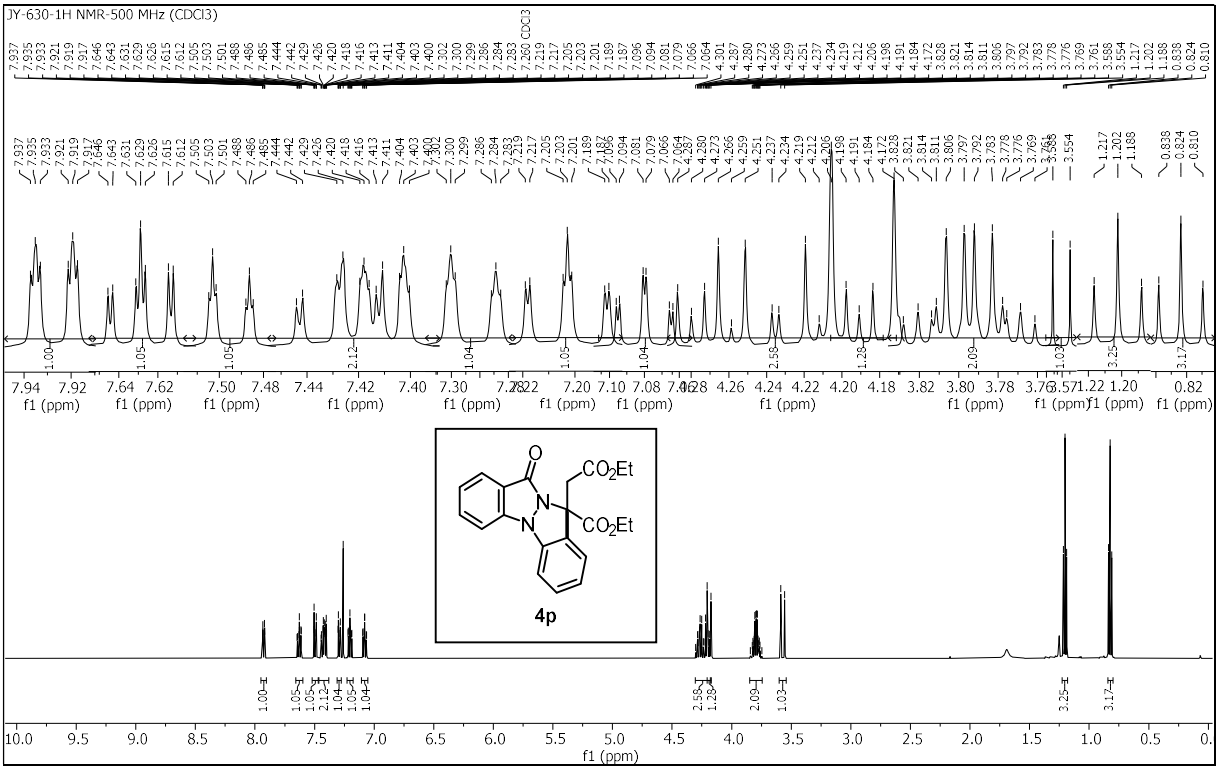

JY-599-13C NMR_100 MHz (CDCl3)
4I

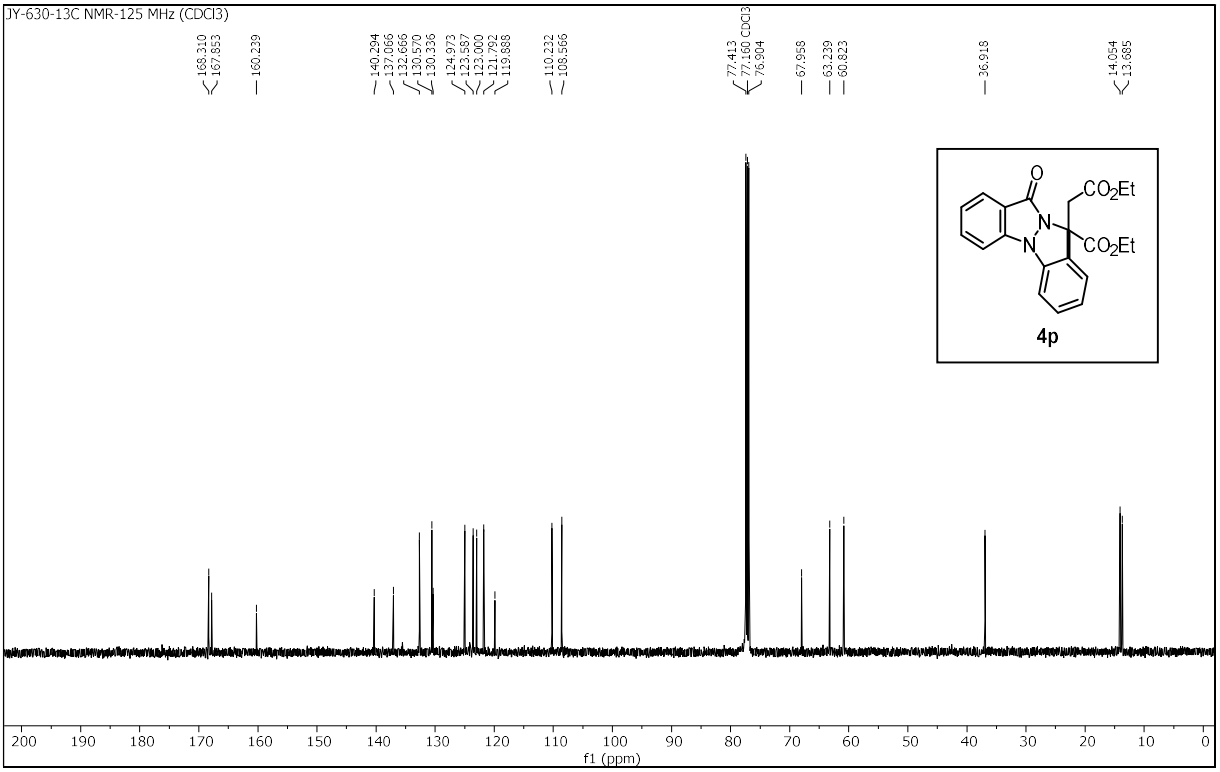

JY-604-1H NMR_400 MHz (CDCl3)
4m
f1 (ppm)

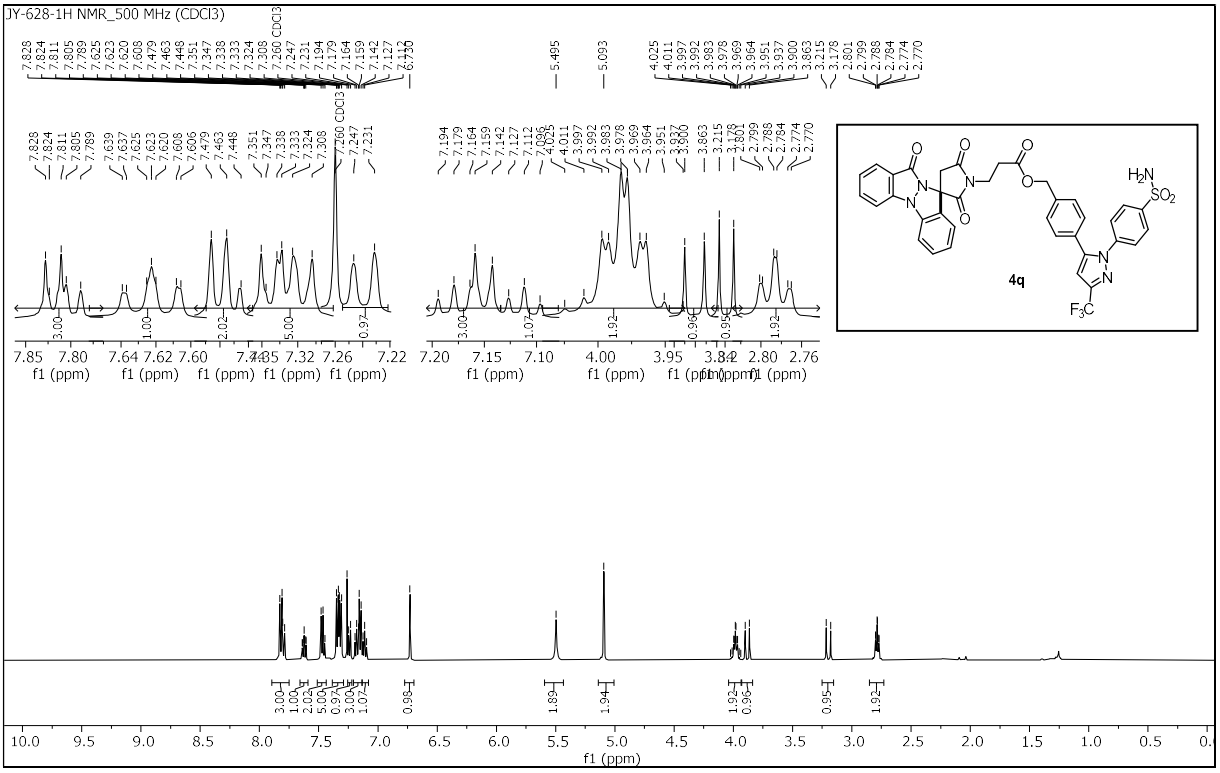

JY-604-13C NMR-100 MHz (CDCl3)
4m
f1 (ppm)

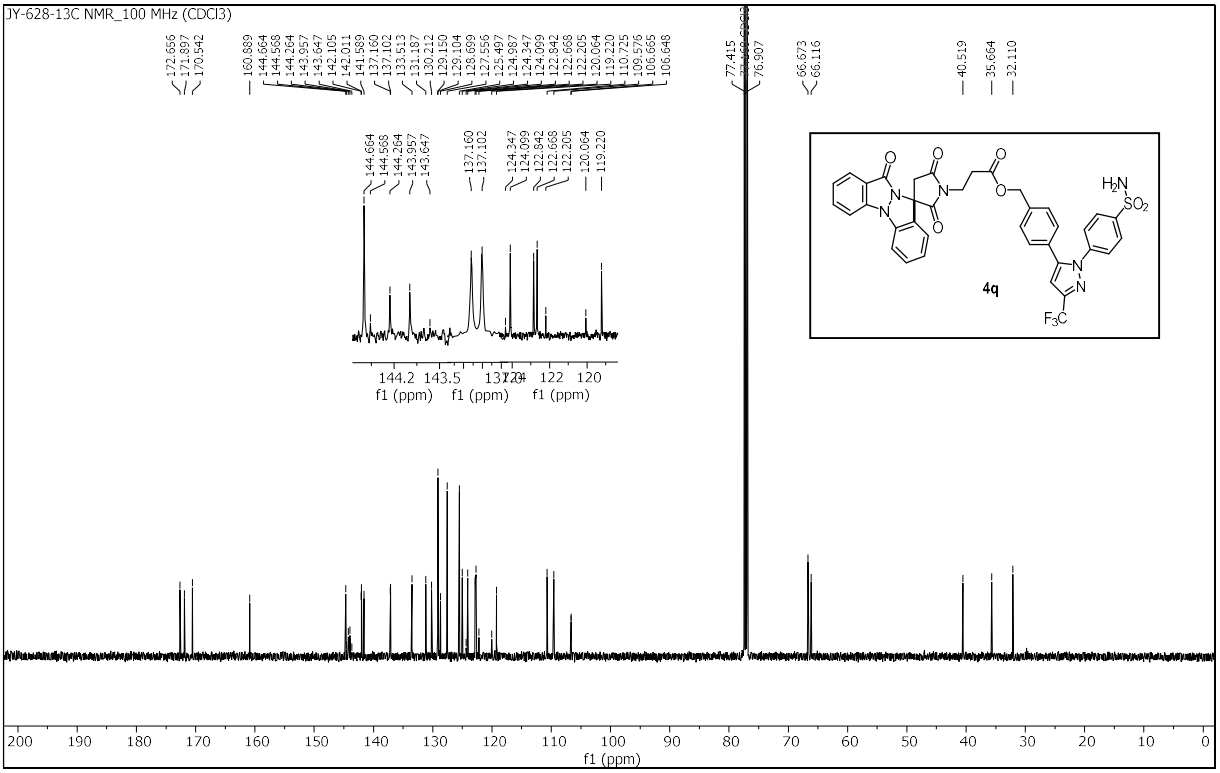

JY-611 (P)-1H NMR_400 MHz (CDCl3)
4o
f1 (ppm)

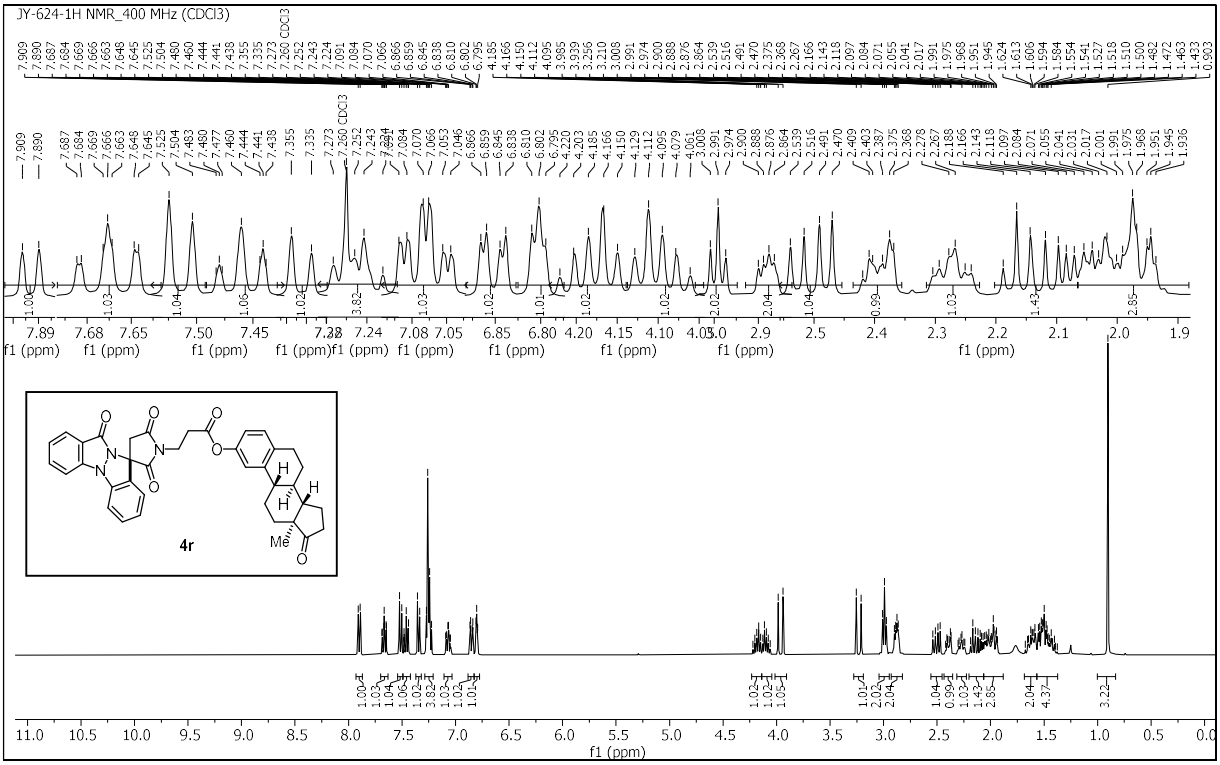

JY-611 (P)-13C NMR_100 MHz (CDCl3)
4o
f1 (ppm)

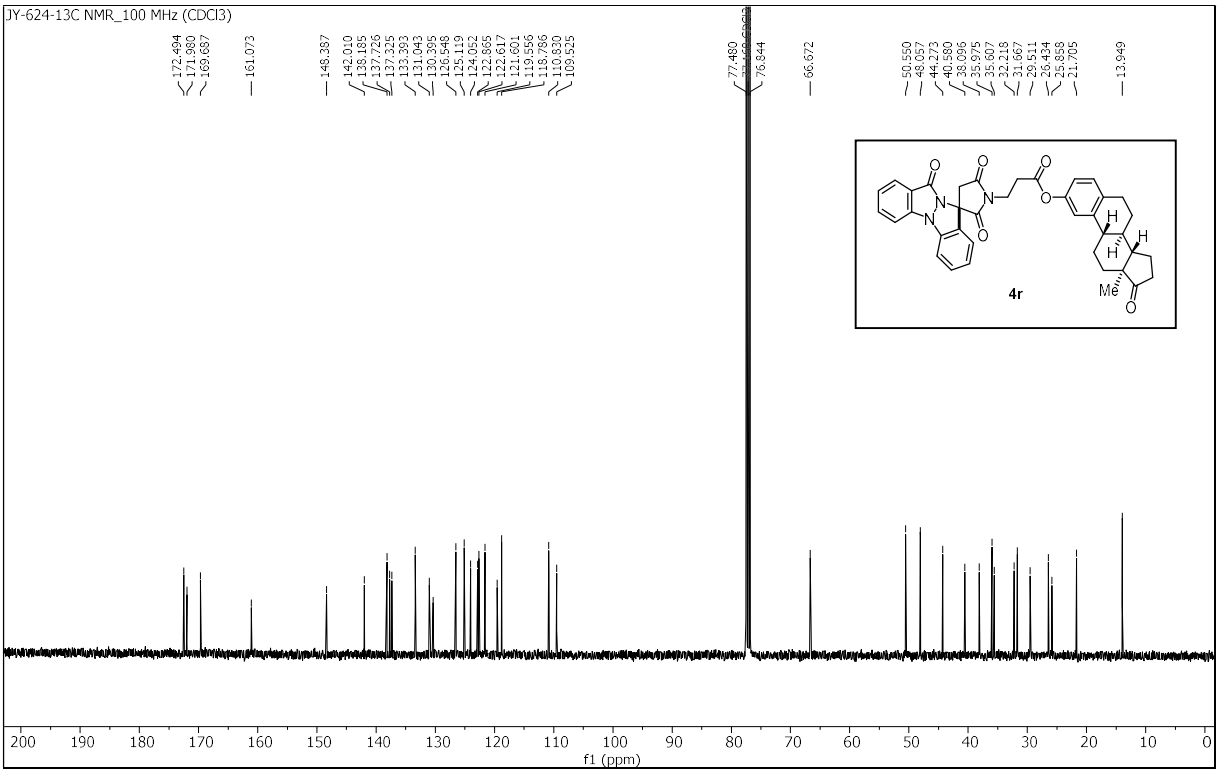

JY-630-1H NMR-500 MHz (CDCl3)
4p

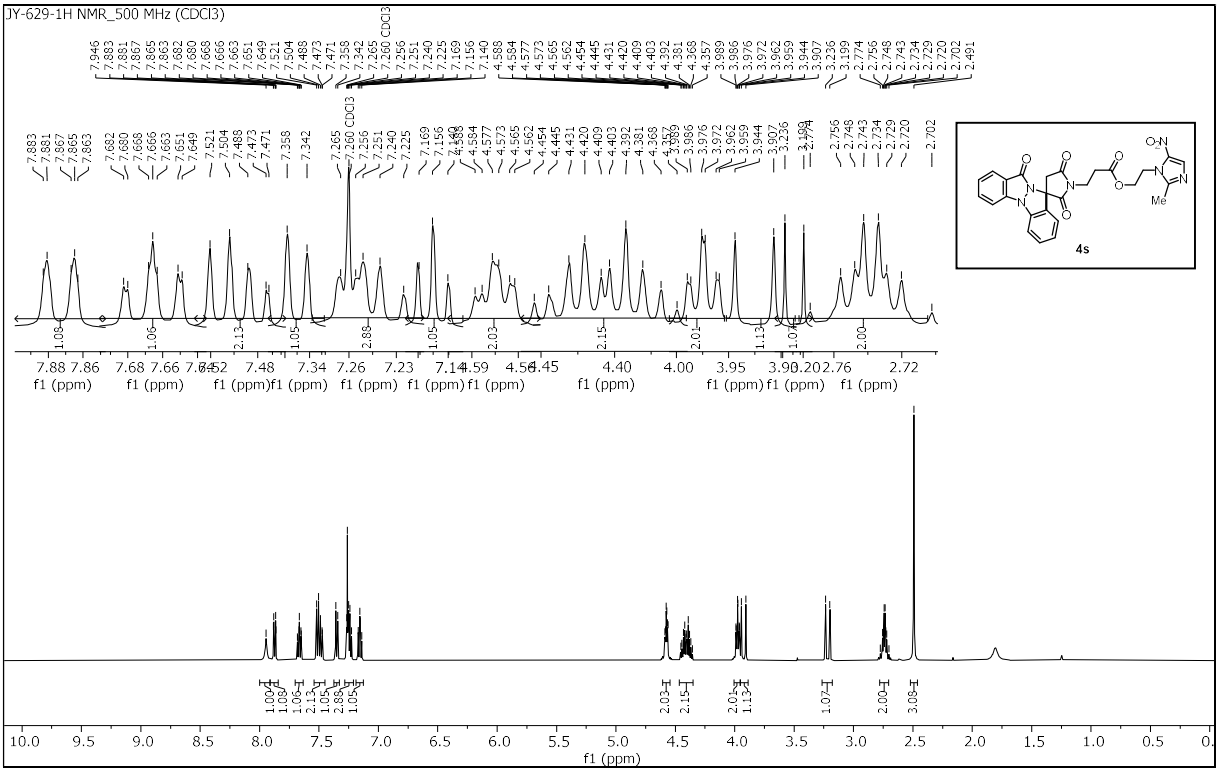

JY-630-13C NMR-125 MHz (CDCl3)
4p

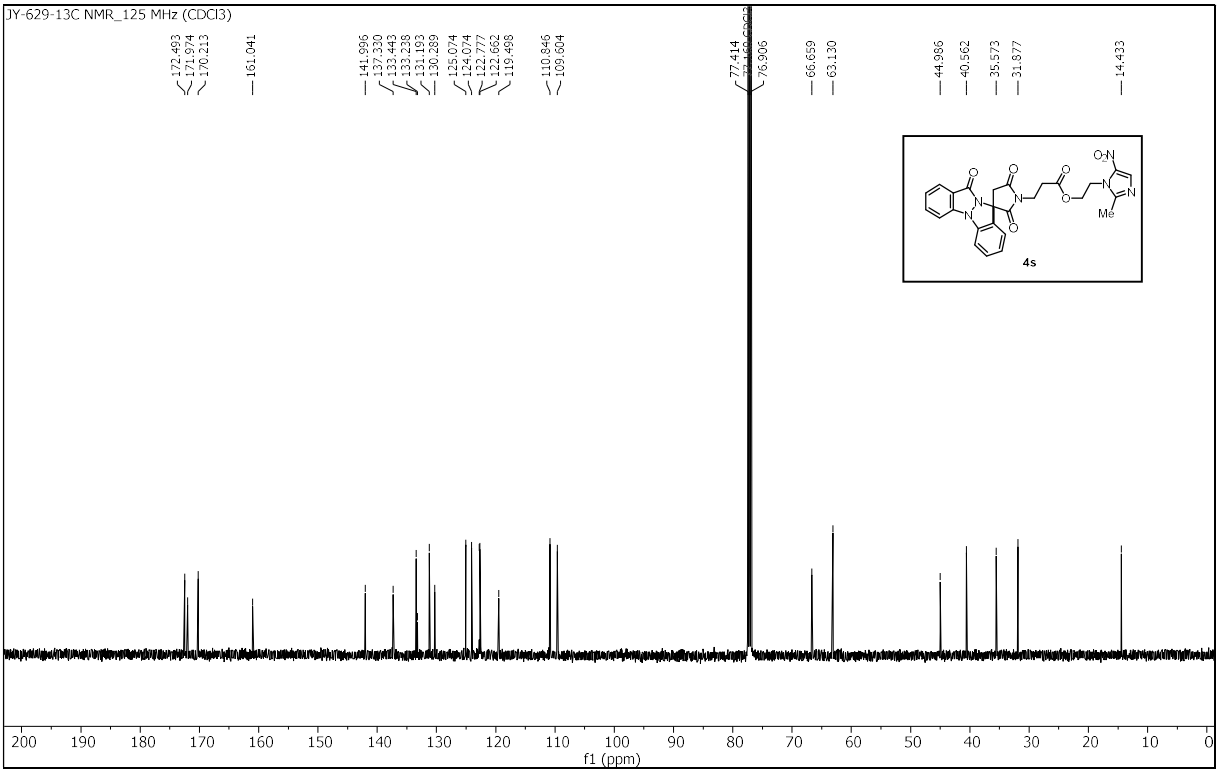

JY-628-1H NMR_500 MHz (CDCl3)
4q
f1 (ppm)

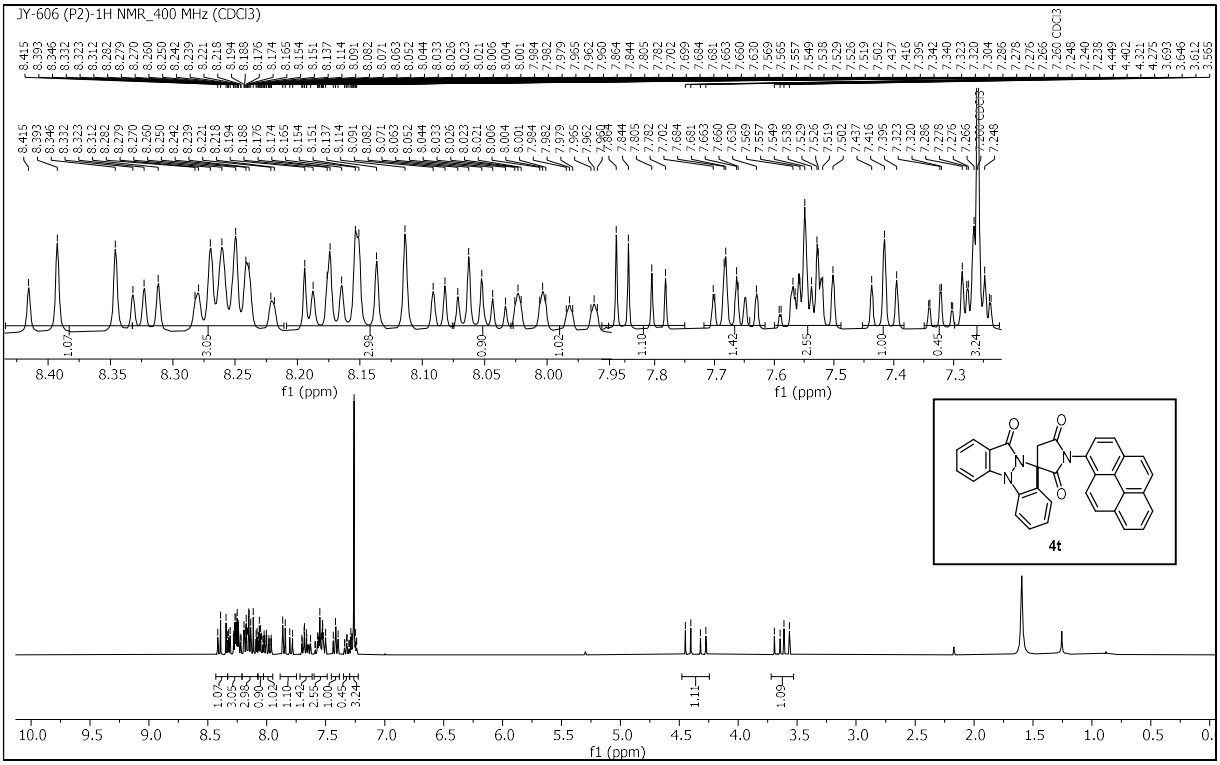

JY-628-13C NMR_100 MHz (CDCl3)
4q
f1 (ppm)

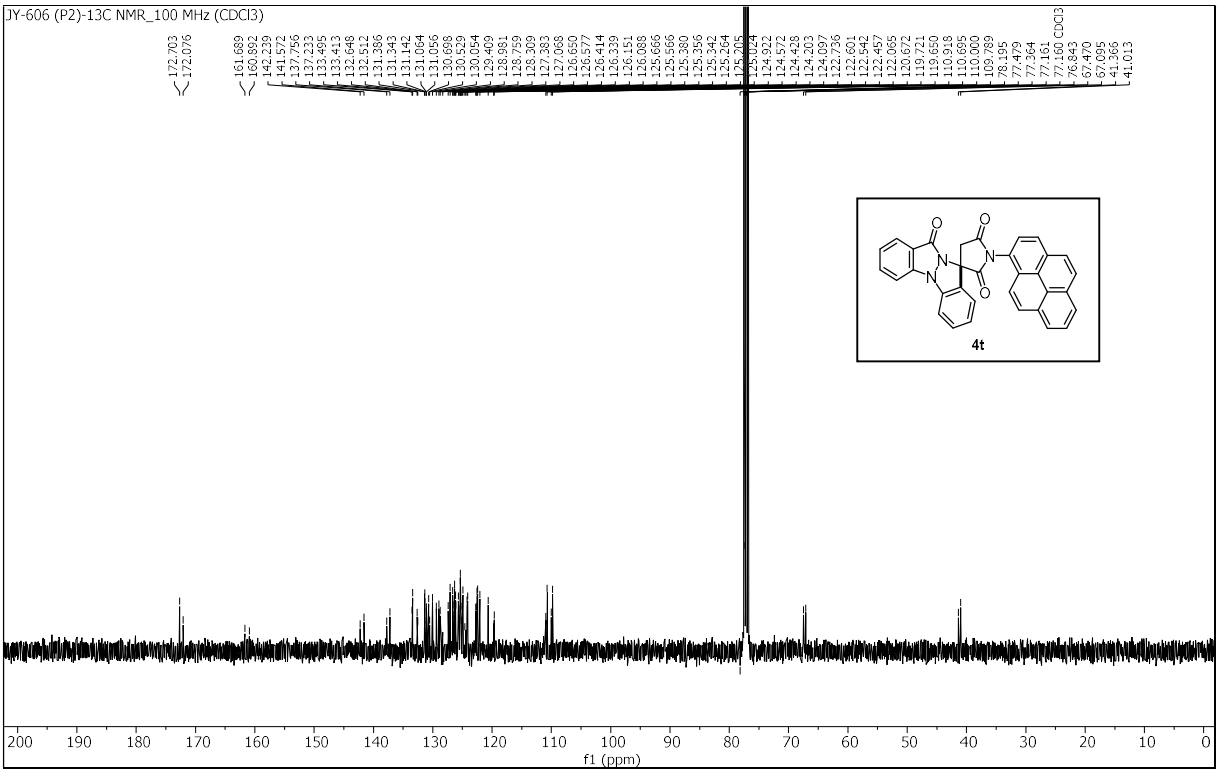

JY-624-1H NMR_400 MHz (CDCl3)
4r
f1 (ppm)

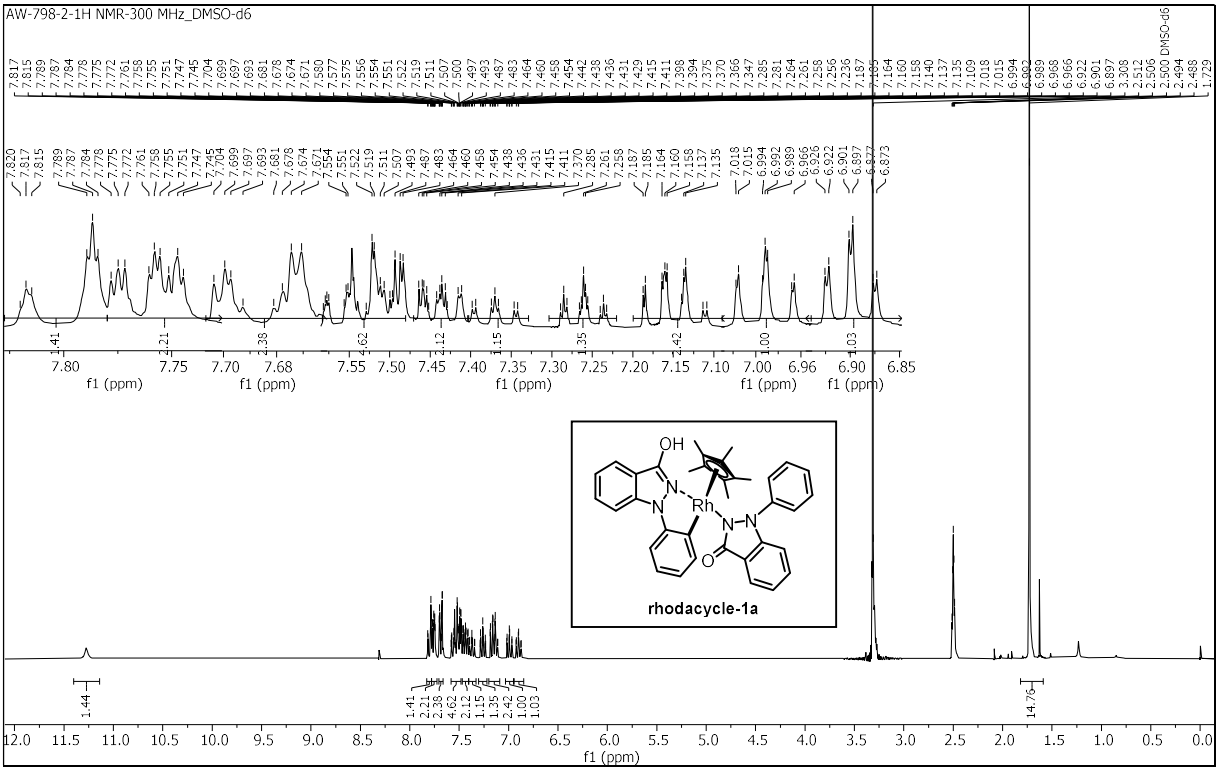

JY-624-13C NMR_100 MHz (CDCl3)
4r
f1 (ppm)

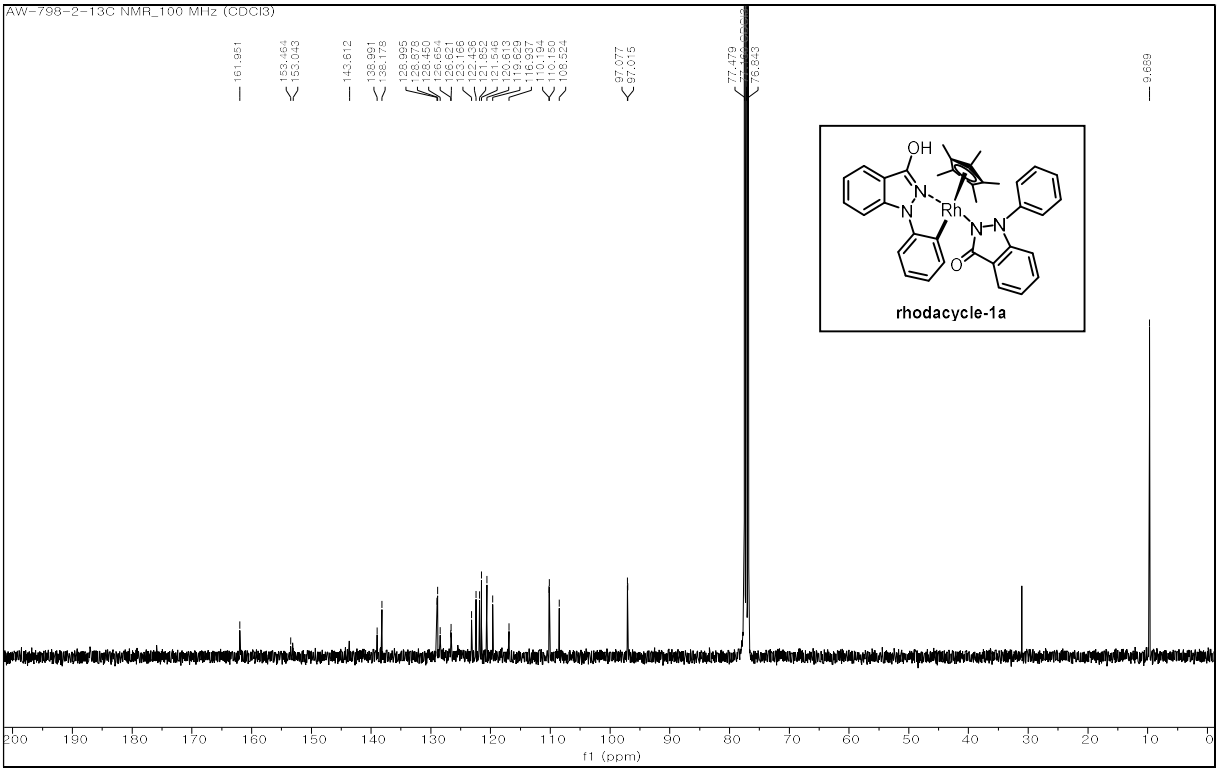

JY-629-1H NMR_500 MHz (CDCl3)
4s
f1 (ppm)

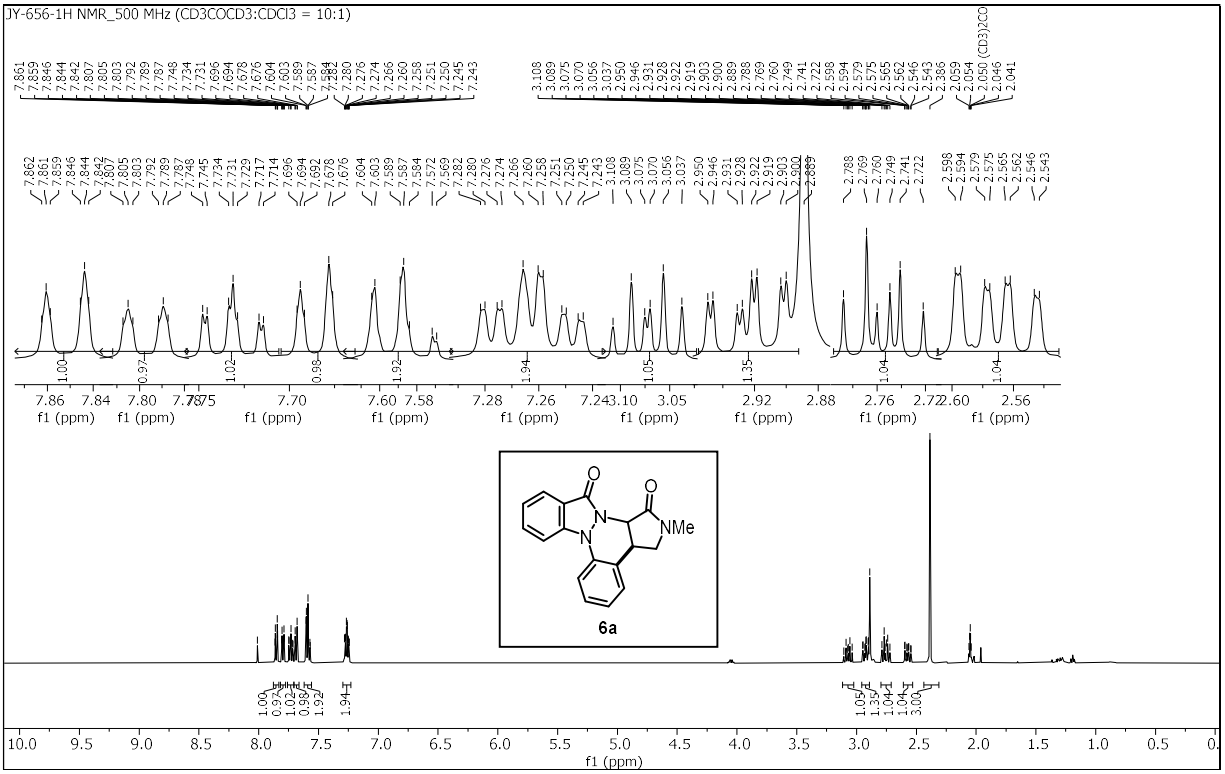

JY-629-13C NMR_125 MHz (CDCl3)
4s
f1 (ppm)

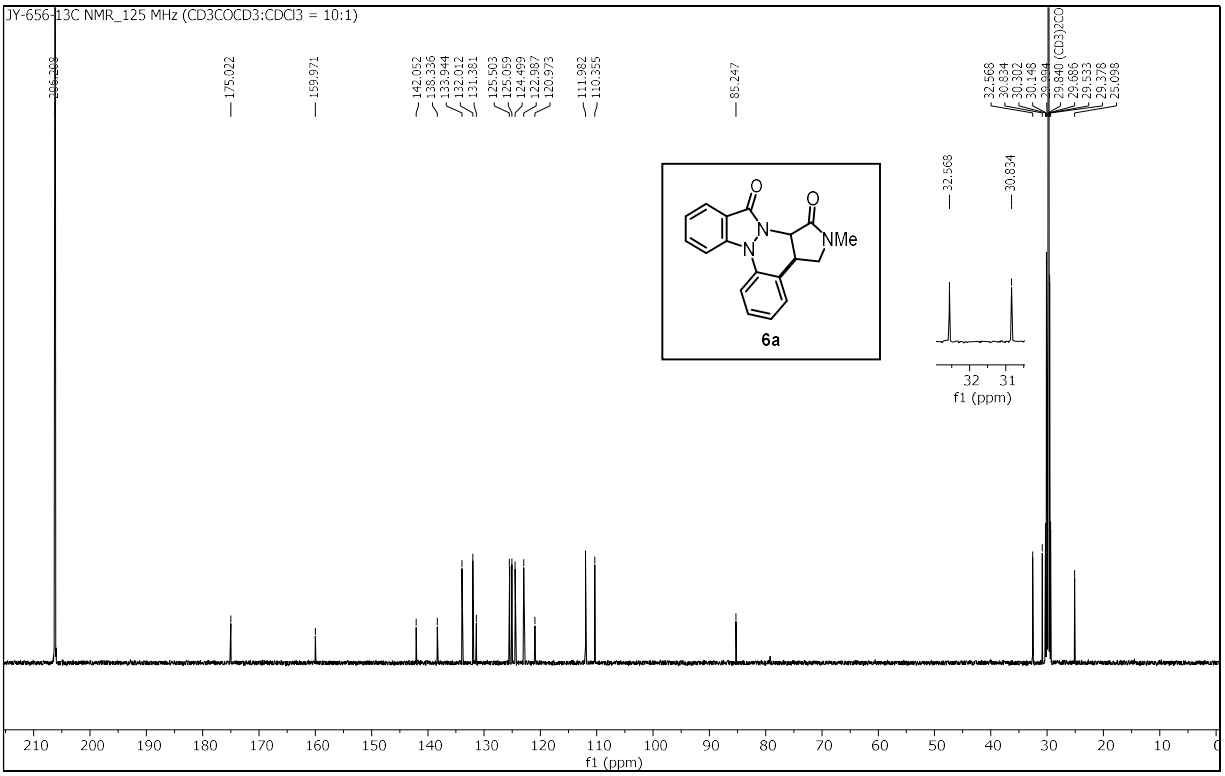

JY-606 (P2)-1H NMR_400 MHz (CDCl3)
f1 (ppm)
4t

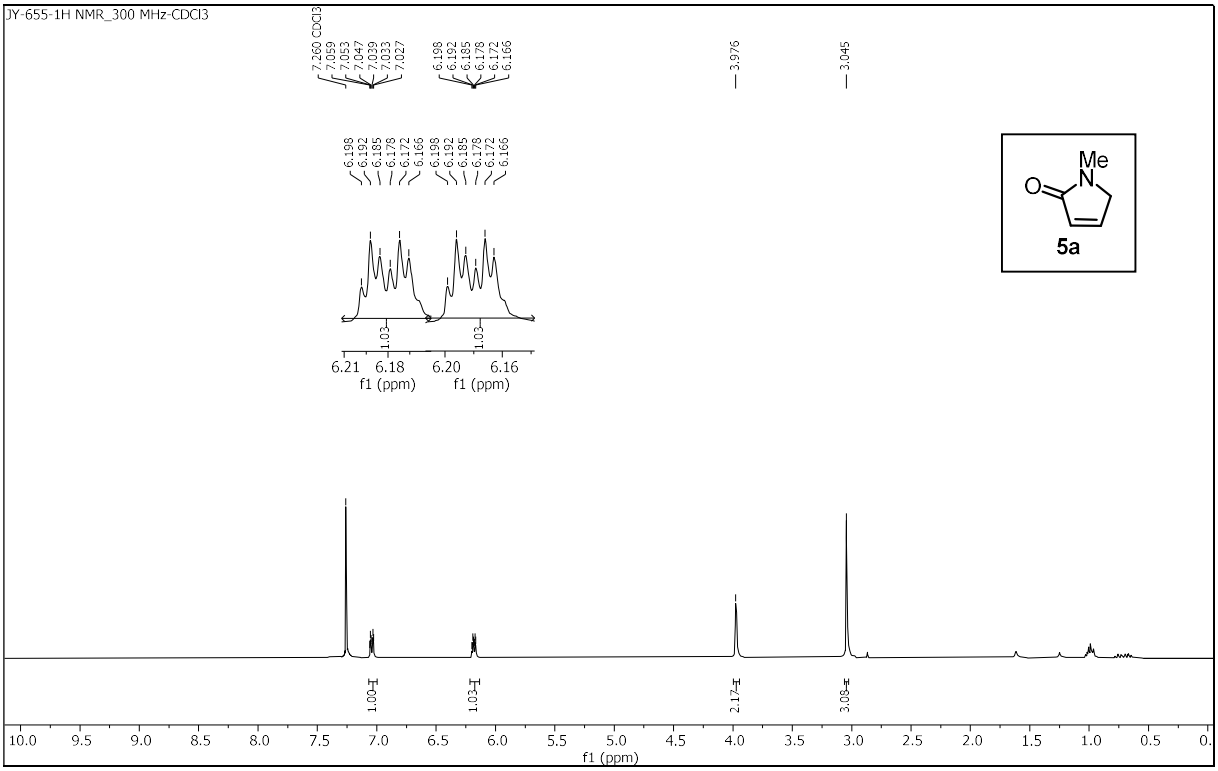

JY-606 (P2)-13C NMR_100 MHz (CDCl3)
f1 (ppm)
4t


AW-798-2-1H NMR-300 MHz_DMSO-d6
rhodacycle-1a
f1 (ppm)

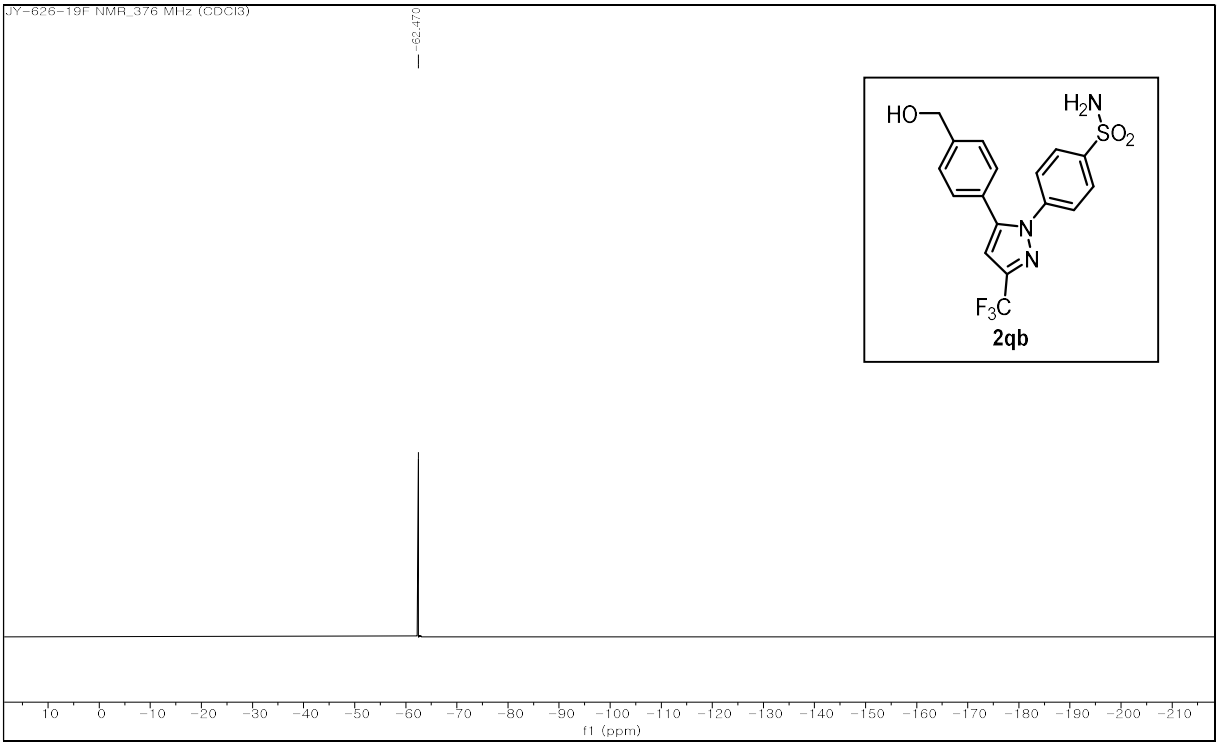

AW-798-2-13C NMR_100 MHz (CDCl3)
rhodacycle-1a
f1 (ppm)

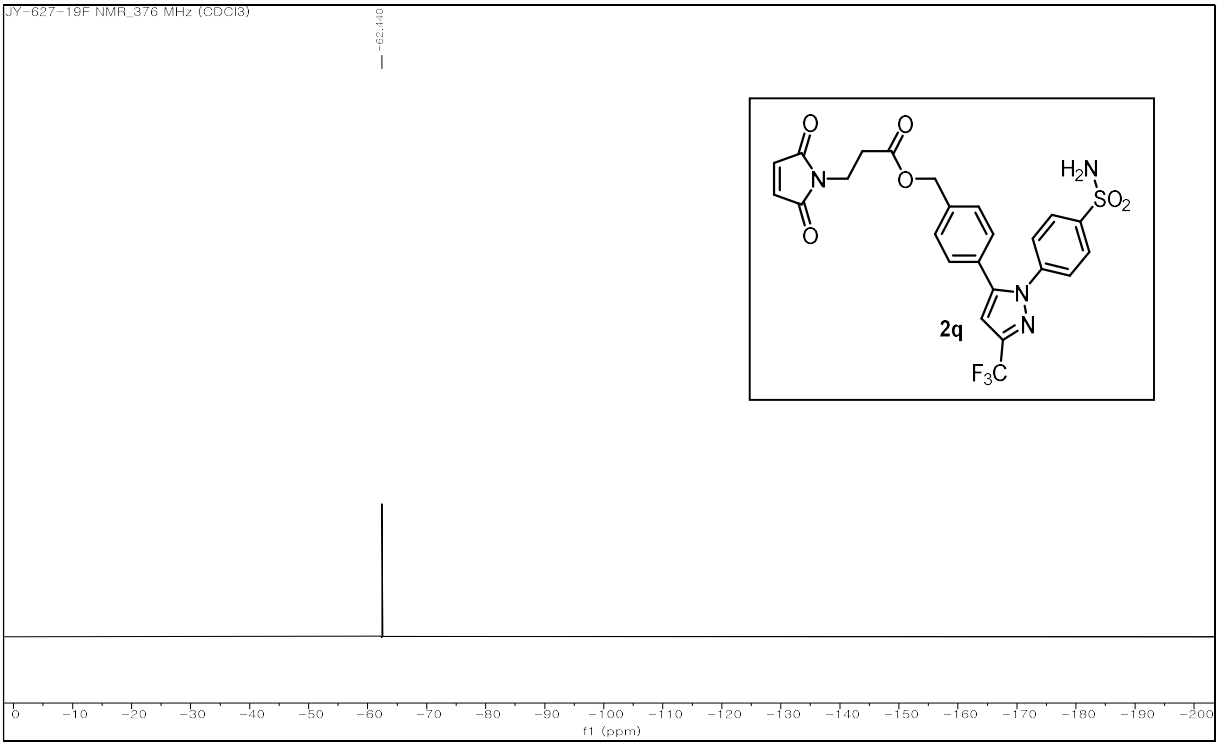

JY-656-1H NMR_500 MHz (CD3COCD3:CDCl3 = 10:1)
6a
f1 (ppm)


JY-656-13C NMR_125 MHz (CD3COCD3:CDCl3 = 10:1)
6a
f1 (ppm)

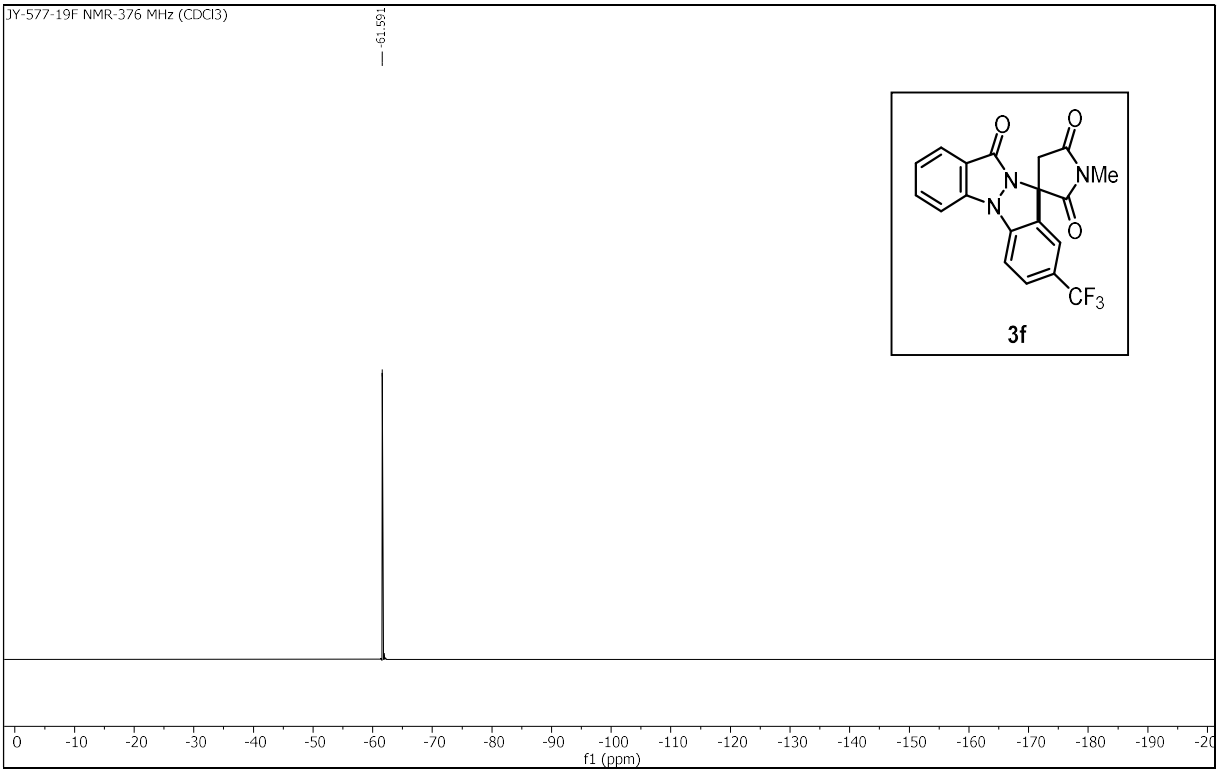

JY-655-1H NMR_300 MHz-CDCl3
7.260 CDCl3
7.059
7.053
7.047
7.039
7.033
7.027
6.198
6.192
6.185
6.178
6.172
6.166
3.976
3.045
Me
N
O
5a
1.03
1.03
6.21 6.18
f1 (ppm)
6.20 6.16
f1 (ppm)
1.00
1.03
2.17
3.08
f1 (ppm)

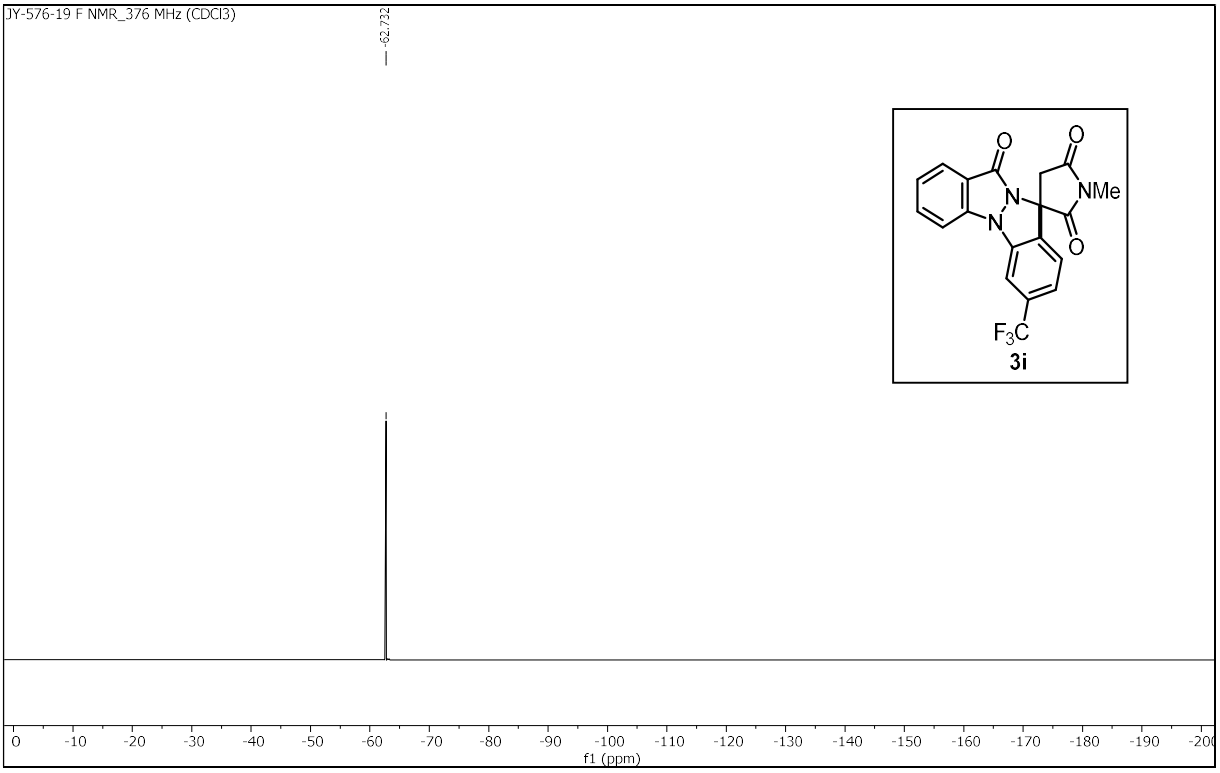
^{19}F NMR spectra of F-containing compounds



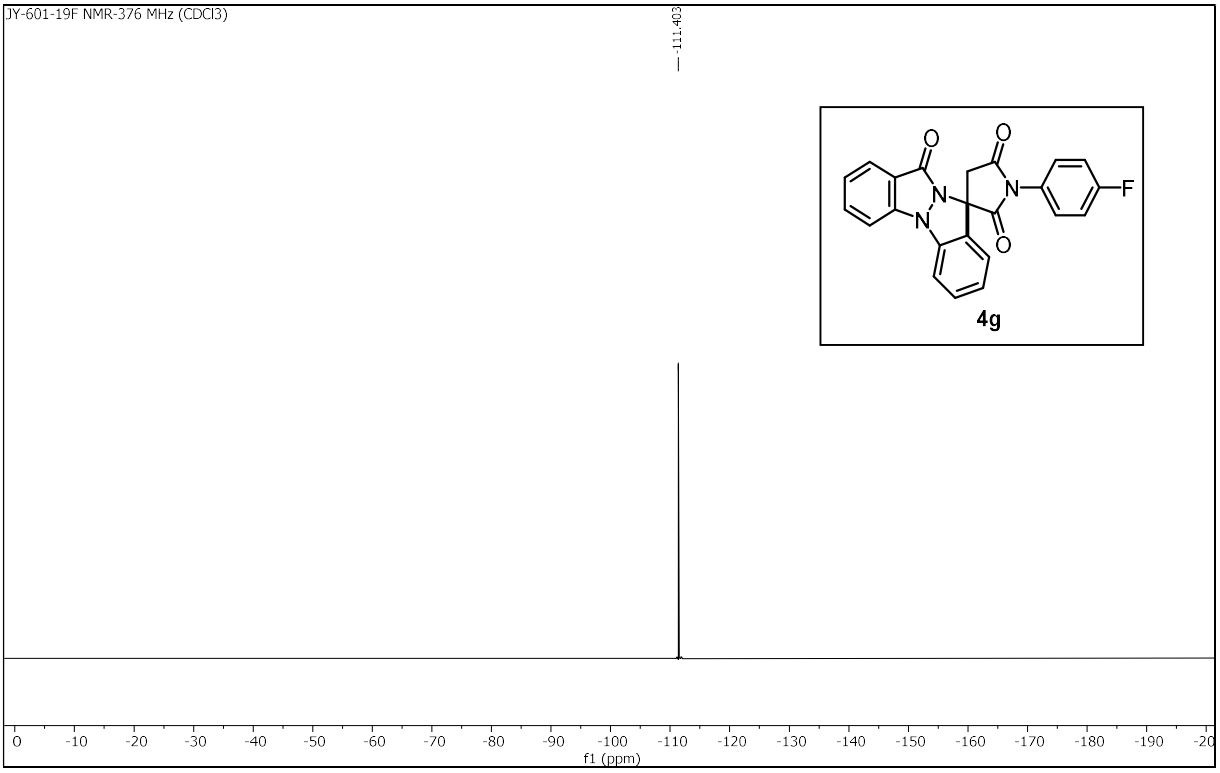


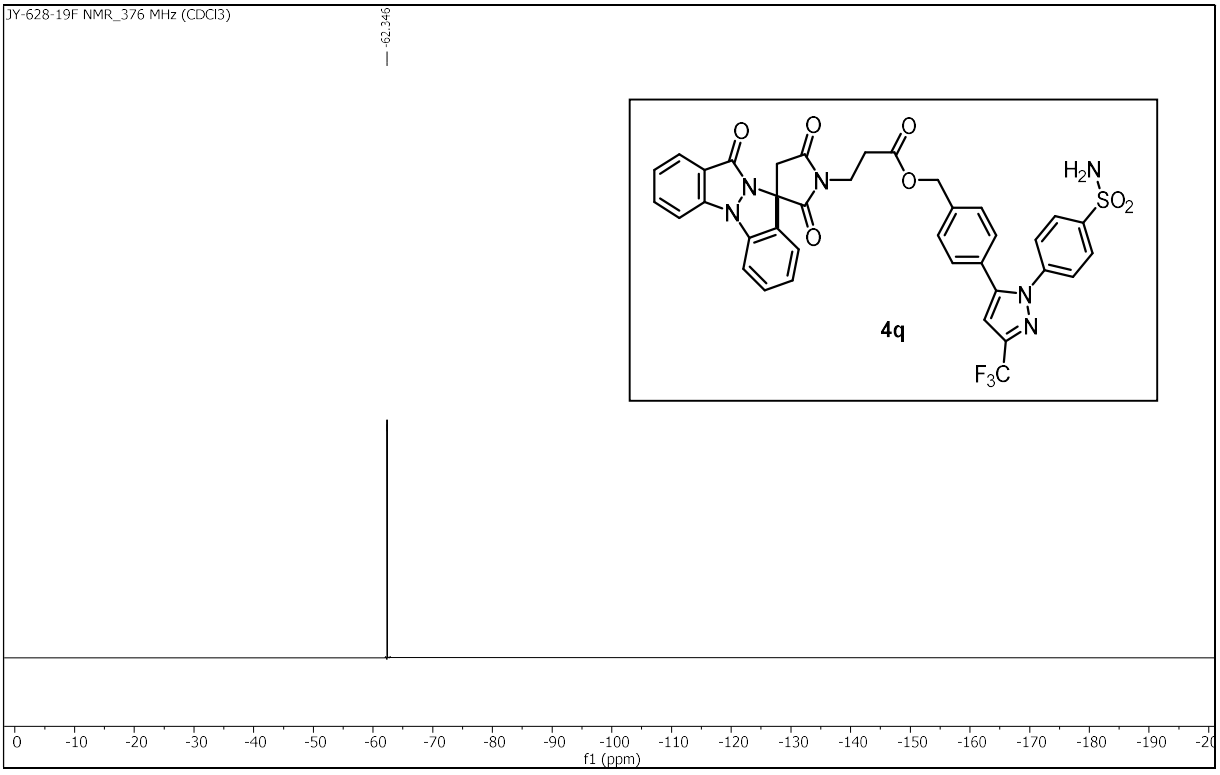

JY-573-19F NMR_376 MHz (CDCl3)
-117.321
O
O
N
NMe
N
O
F
3e
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)


JY-577-19F NMR-376 MHz (CDCl3)
-61.591
O
O
N
NMe
N
O
CF3
3f
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)


JY-576-19 F NMR_376 MHz (CDCl3)
-62.732
O
O
NMe
N
N
O
F3C
3i
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


JY-571-19F NMR_376 MHz (CDCl3)
-125.128
O
O
NMe
N
N
O
F
3k
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


JY-601-19F NMR-376 MHz (CDCl3)
-111.403
4g
f1 (ppm)


JY-628-19F NMR_376 MHz (CDCl3)
-62.346
4q
f1 (ppm)