Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Rh(III)-Catalyzed Spiroannulation of Ketimines with Cyclopropenones via Sequential C−H/C−C Bond Activation

Hong Hu,[#a] Bin-Shi Li,[#a] Jing-Lei Xu,[a] Wei Sun,[a] Yong Wang,*[c] Meng Sun*[a,b]

[a]*Key Laboratory of Synthetic and Natural Functional Molecule of the Ministry of Education, College of Chemistry and Materials Science, Northwest University, Xi'an 710127, China.*

[b]*State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116024, China.*

[c]*BGI-Shenzhen, Shenzhen 518083, China.*

M. S.: sunmeng@nwu.edu.cn

Contents:

1. General information.

All reactions involving air- and moisture-sensitive reagents were carried out under a nitrogen atmosphere. Toluene, DME, DCM, 1, 2- dichloroethane, 1, 4- dioxane and THF were distilled from appropriate drying agents prior to use. TFE (2,2,2-trifluoroethanol) and HFIP (hexafluoroisopropanol) were purchased from Energy, which were used without further purification. Other chemicals were purchased from Sigma-Aldrich and Energy, which were used without further purification. Thin-layer chromatography (TLC) was performed using 60 mesh silica gel plates visualized with short-wavelength UV light (254 nm). Silica gel 60 (230~400 mesh) was used for column chromatography. The hemiaminals[1] and cyclopropenones[2] were prepared according to the literatures.

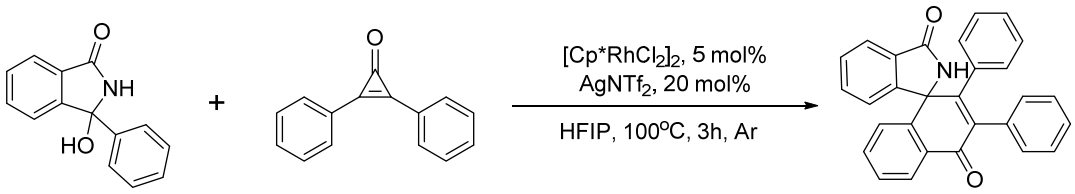
NMR: Spectra were recorded on a 400 MHz (Varian Unity Inova-400 or Bruker Ascend 400) NMR spectrometer. Chemical shifts (δ) are reported in ppm and quoted relative to the residual solvent peaks in $CDCl_3$ (^1H: 7.26 ppm, ^{13}C: 77.16 ppm), DMSO-d_6 (^1H: 2.50 ppm, ^{13}C: 39.52 ppm), and coupling constants (*J*) are given in Hertz (Hz). Multiplicities are indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), or br (broadened).

HRMS: High resolution mass spectra were acquired on a Bruker Daltonics MicroTof-Q II mass spectrometer with an ESI source.

Single crystal X-ray diffraction analysis: Diffraction data for complexe **3aa** were collected on a Bruker SMART APEX II diffractometer at 150 K with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). An empirical absorption correction using SADABS was applied for all data.[3] The structures were solved and refined to convergence on F^2 for all independent reflections by the full-matrix least squares method using the SHELXL−2016 programs.[4]

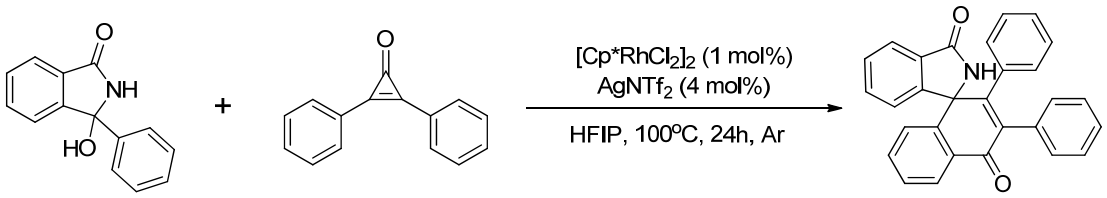
2. Experimental procedures.

General procedure for synthesis of 3aa.



A mixture of cyclopropenone (0.1 mmol, 20.6 mg, 1.0 equiv), 3-hydroxy-3-phenylisoindolin-1-one (0.12 mmol, 27.0 mg, 1.2 equiv), $[Cp^*RhCl_2]_2$ (0.005 mmol, 3.1 mg, 5 mol %), $AgNTf_2$ (0.02 mmol, 7.8 mg, 20 mol %) in HFIP (1.0 mL) was stirred under argon at 100 °C for 3 hours. After cooled to room temperature, the solvent was removed under reduced pressure. The contents were subjected to flash chromatography (petrol ether/EtOAc 3:1) to give the product as white solid (0.09 mmol, 36.4 mg, 88 %).

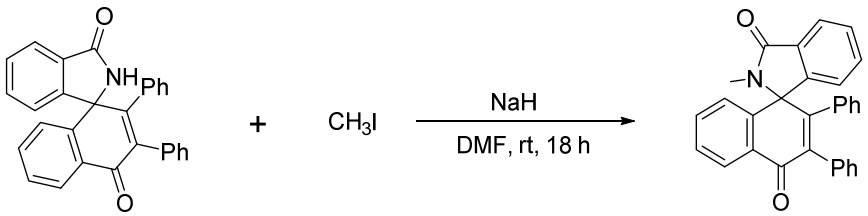
Experimental procedure for large scale synthesis of compound 3aa.



1a **2a** **3aa**

A mixture of cyclopropenone (10 mmol, 2.06 g, 1.0 equiv), 3-hydroxy-3-phenylisoindolin-1-one (12 mmol, 2.7 g, 1.2 equiv), $[Cp^*RhCl_2]_2$ (0.1 mmol, 61.8 mg, 1 mol %), $AgNTf_2$ (0.4 mmol, 155.2 mg, 4 mol %) in HFIP (50 mL) was stirred under argon at 100 °C for 24 hours. After cooled to room temperature, the solvent was removed under reduced pressure. The contents were subjected to flash chromatography (petrol ether/EtOAc 3:1) to give the product as white solid (8.3 mmol, 3.43 g, 83 %).

Experimental procedure for *N*-methylation of 3aa.

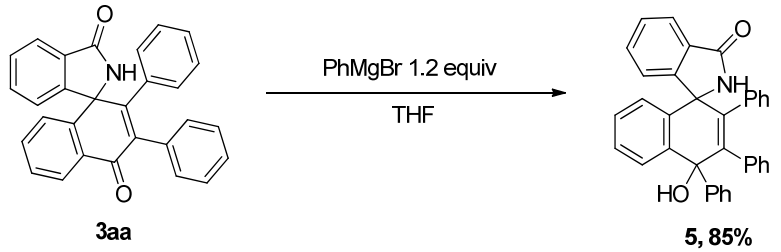


3aa **4, 87%**

Sodium hydride (0.24 mmol, 9.6 mg, 60 % oil dispersion) was added to a stirred solution of **3aa** (0.20 mmol, 82.63 mg) and methyl iodide (0.5 mmol, 71.0 mg, 2.5 eqiuv) in DMF (1.0 mL). After the initial exothermic reaction had subsided, the mixture was stirred at 25 °C for 18 h. The solvent

was removed in vacuo, and the residue was dissolved in H_2O (5.0 mL) and extracted with CH_2Cl_2 (3×10 mL). The organic phase was dried with Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel chromatography using PE/EA (3:1) to afford compound **4** as a white solid (0.17 mmol, 74.3 mg, 87 %).

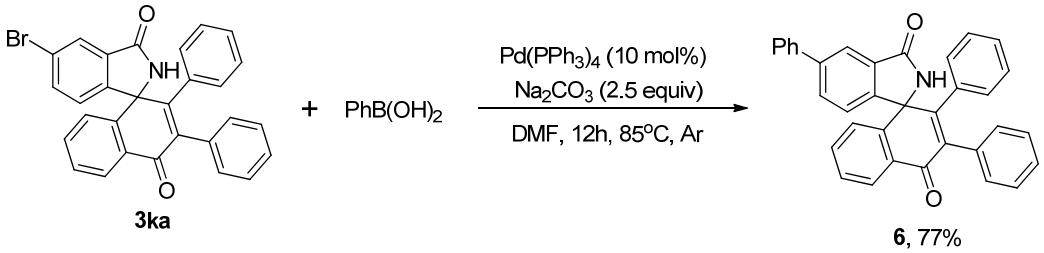
Experimental procedure for addition reaction of spiro compound 3aa with PhMgBr.



3aa **5, 85%**

To a solution of **3aa** (0.2 mmol, 82.63 mg) in THF (5.0 mL) was added PhMgBr (0.42 mmol, 1.2 M, 0.35 mL) at 0°C under N_2. The mixture was allowed to stir at room temperature for 2 h. The reaction was quenched with water saturated NH_4Cl aqueous solution (5 mL) and extracted with EtOAc (3x5 mL). The organic layers was combined and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum. Then the reaction mixture was purified by flash chromatography (petrol ether/ ethyl acetate, 1:1) to afford **5** (0.17 mmol, 83.5 mg, 85 %) as white solid.

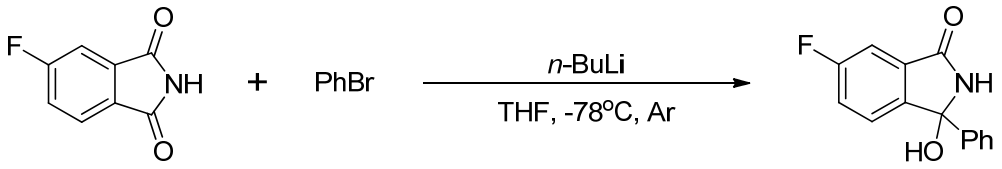
Experimental procedure for Suzuki coupling of 3ka with phenylboronic acid.



3ka **6**, 77%

A solution of **3ka** (0.1 mmol, 49.1 mg, 1.0 equiv.), $PhB(OH)_2$ (0.2 mmol, 24.4 mg, 2.0 equiv.), $Pd(PPh_3)_4$ (0.01 mmol, 11.6 mg, 10 mol%) and Na_2CO_3 (0.25 mmol, 26.5 mg, 2.5 equiv.) in 1.0 mL of DMF was heated in oil bath at 85 °C for 12 h. After cooled to room temperature, the reaction was quenched with water (5 mL) and extracted with EtOAc (3x5 mL). The organic layers was combined and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum. Then the reaction mixture was purified by flash chromatography (petrol ether/ ethyl acetate, 8:1) to afford **6** (0.08 mmol, 37.7 mg, 77 %) as white solid.

General procedure for synthesis of 3-hydroxy-3-aryl isoindolin-1-ones.



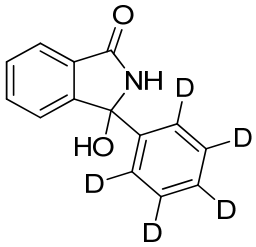
S1

To a solution of bromobenzene (20.0 mmol, 4.0 equiv) in THF (20 mL) was added dropwise *n*-BuLi in hexane (20.0 mmol, 4.0 equiv, 1.5 M) at -78°C. After stirring for 30 min, a solution of phthalimide (5.0 mmol, 1.0 equiv) in THF (15 mL) was added to the reaction mixture at -78°C. After stirring at room temperature for 2h, the reaction mixture was quenched with saturated NH_4Cl aqueous solution and extracted with ethyl acetate. The combined organic layers were washed with H_2O and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane: EA = 1:1) to afford the crude product. Then the crude product was recrystallized from EtOAc/Hexane to give compound **S1** (3.55 mmol, 862.7 mg, 71%).

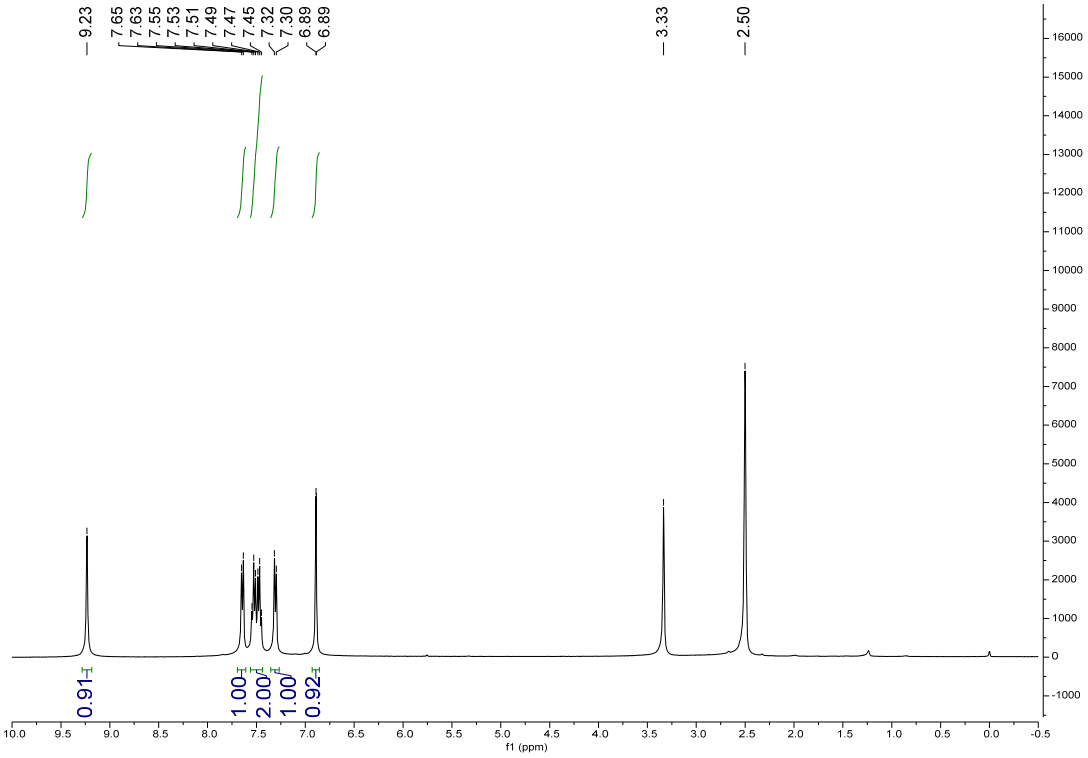
The 6-chloro-3-hydroxy-3-phenylisoindolin-1-one[7] and 6-methoxy-3-hydroxy-3-phenylisoindolin-1-one[8] were prepared according to the above procedures.

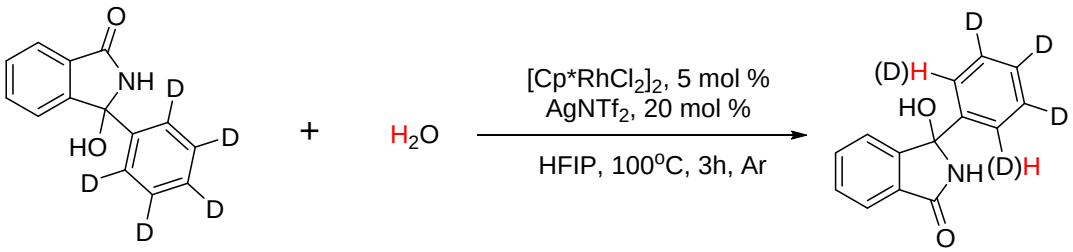
3. Mechanistic studies.

H/D scrambling experiments.

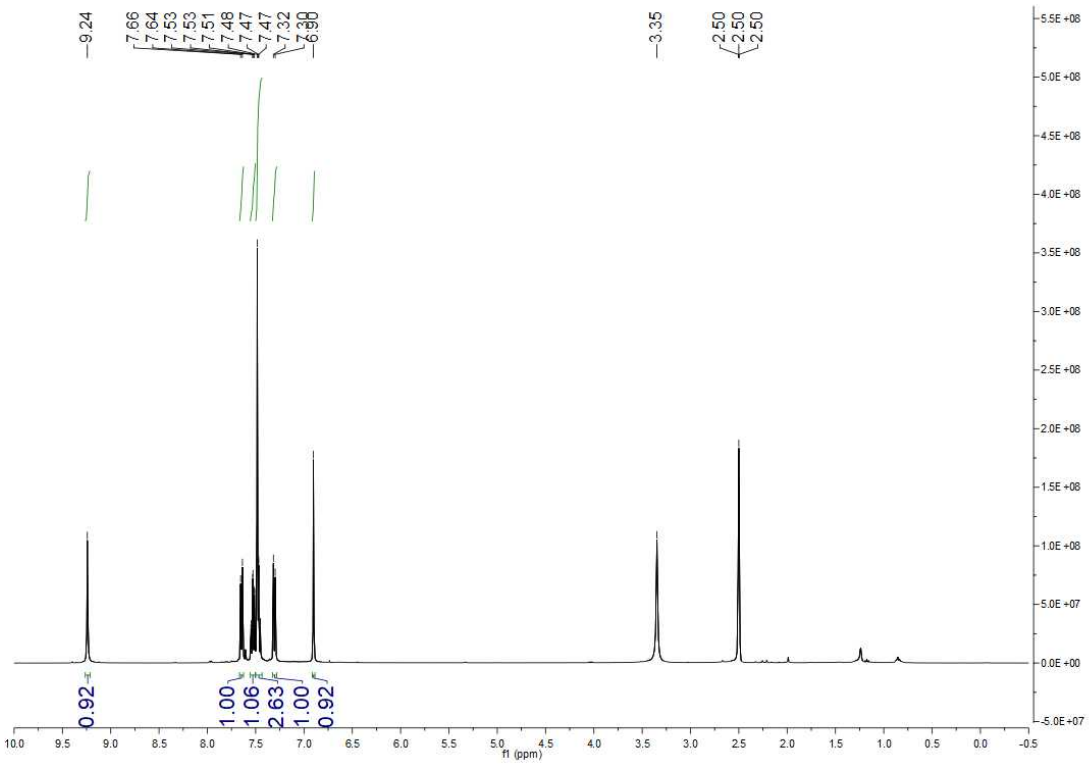


1a-d_5



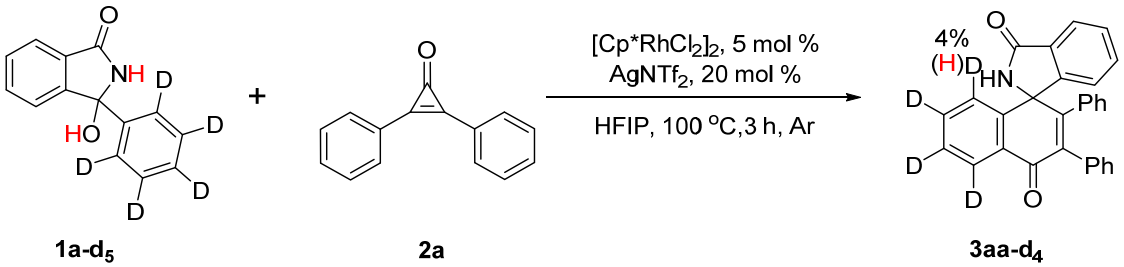


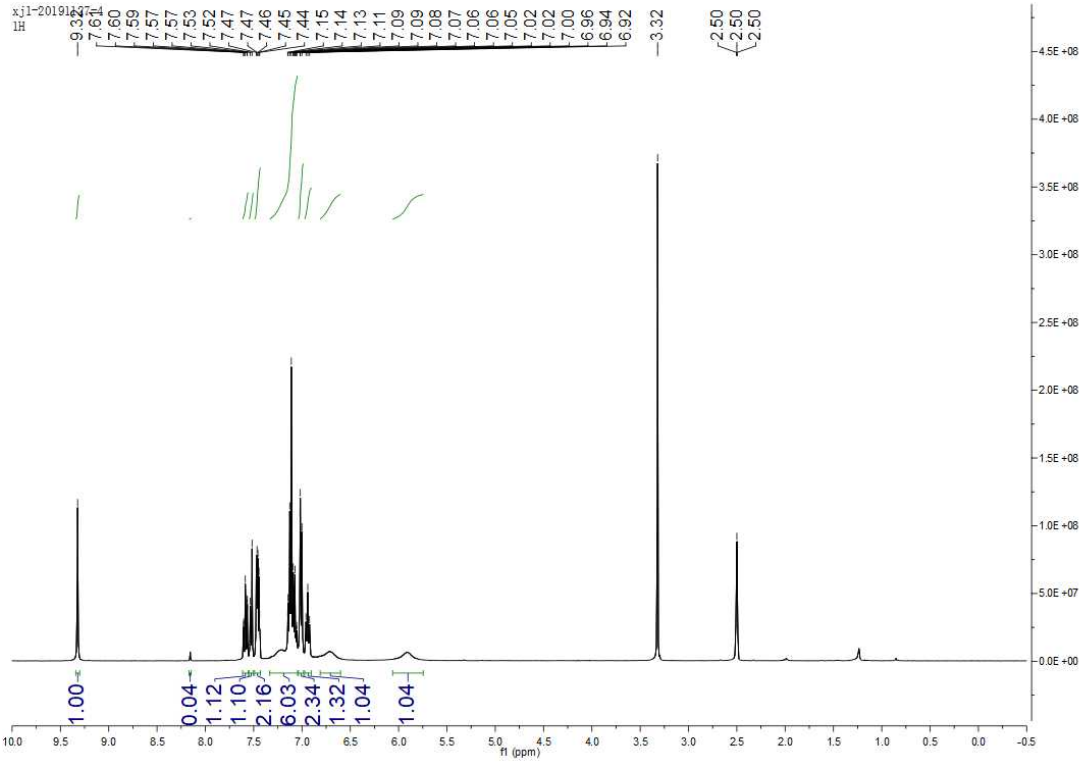
1a-d_5 **10 equiv** **81% H**



Compound **1a-*d*$_5$** (0.1 mmol, 23.0 mg),[5] [Cp*RhCl$_2$]$_2$ (0.005 mmol, 3.1 mg, 5 mol%) and AgNTf$_2$ (0.02 mmol, 7.8 mg, 20 mol%) were placed in a Schlenk tube under argon. HFIP (1.0 mL) and H_2O (18 μL, 1.0 mmol) were added successively. The Schlenk tube was capped with a glass stopper and heated at 100 °C for 3 h with stirring. The mixture was passed through a short column of silica gel with EtOAc as eluent, and the solvent was removed on a rotary evaporator. The residue was subjected to flash chromatography (petrol ether/EtOAc 3:1) to give **1a** (43%). A hydrogen content of the recovered **1a** at the *ortho*-position was determined to be 81% by ^{1}H NMR.

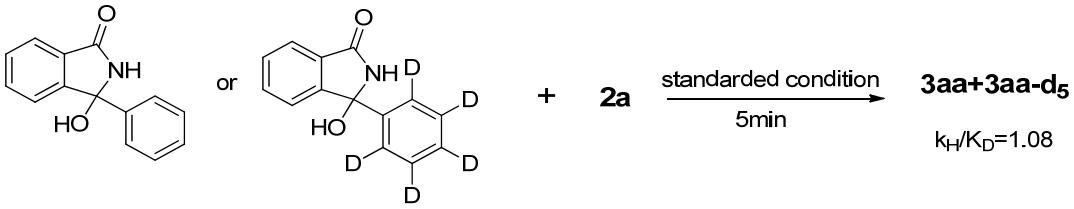
The reaction of 1a-d_5 with 2a



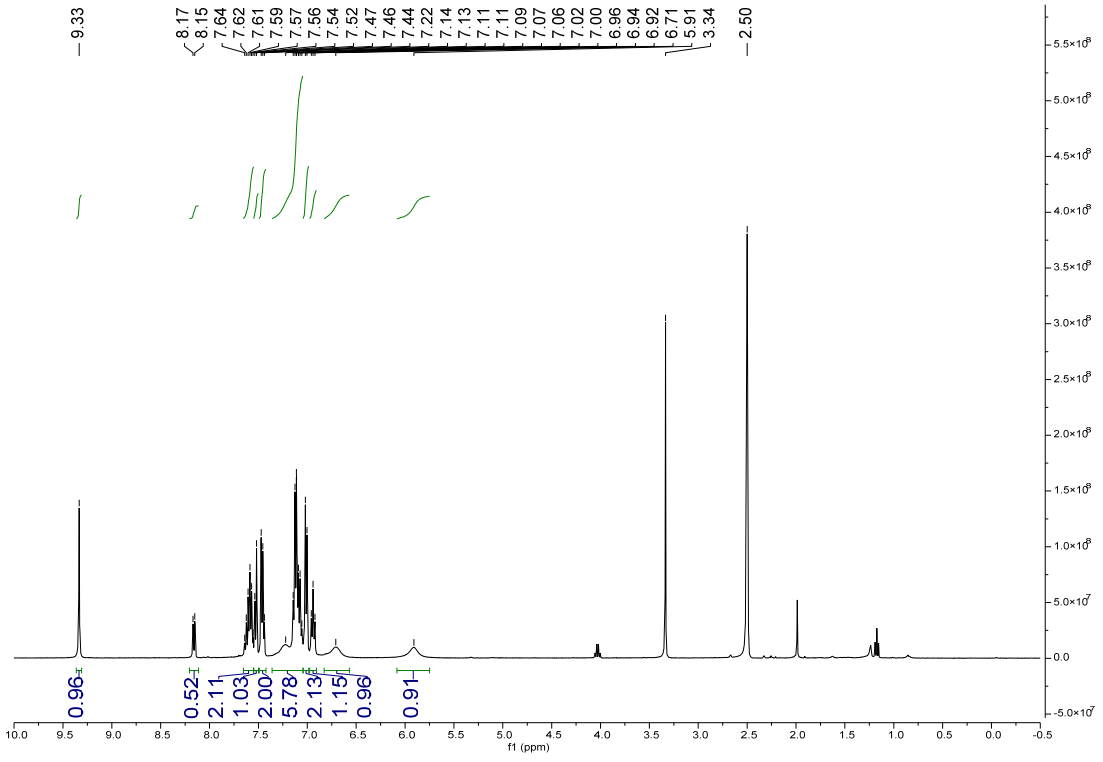


A mixture of cyclopropenone (0.1 mmol, 20.6 mg, 1.0 equiv), compound **1a-*d*$_5$** (27.6 mg, 0.12 mmol, 1.2 equiv), $[Cp^*RhCl_2]_2$ (0.005 mmol, 3.1 mg, 5 mol %), $AgNTf_2$ (0.02 mmol, 7.8 mg, 20 mol %) in HFIP (1.0 mL) was stirred under argon at 100 °C for 3 hours. After cooled to room temperature, the solvent was removed under reduced pressure. The contents were subjected to flash chromatography (petrol ether/EtOAc 3:1) to give the product as white solid **3aa-*d*$_4$** (0.09 mmol, 36.4 mg, 88 %). A hydrogen content of the annulation product **3aa-*d*$_4$** at the *ortho*-position was determined to be 4% by ^{1}H NMR.

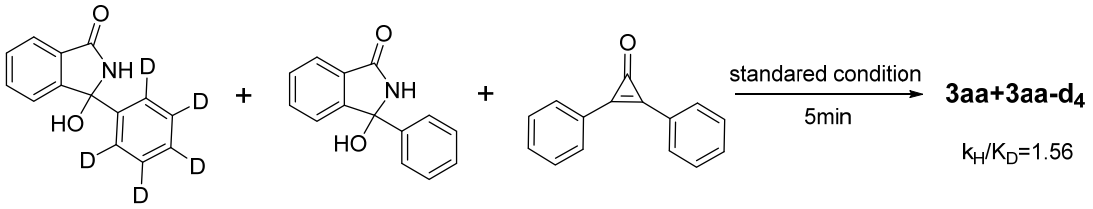
KIE by parallel experiments.



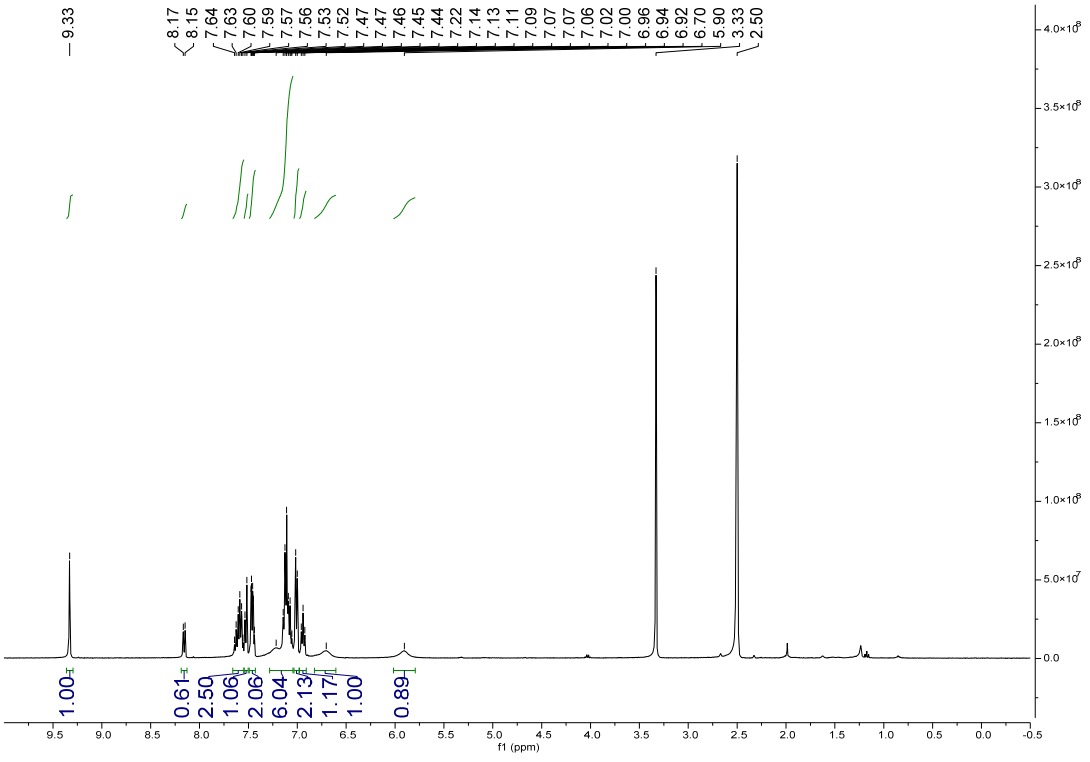
A mixture of **1a** (0.12 mmol, 27.0 mg, 1.2 equiv) or **1a-*d*$_5$** (0.12 mmol, 27.6 mg, 1.2 equiv), **2a** (0.1 mmol, 20.6 mg, 1.0 equiv), $[Cp^*RhCl_2]_2$ (0.005 mmol, 3.1 mg, 5 mol%) and $AgNTf_2$ (0.02 mmol, 7.8 mg, 20 mol%) in HFIP (1.0 mL) was stirred separately in an oil bath preheated at 100 °C for 5 min under argon. Afterwards, the resulting mixtures in the two tubes were combined, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (petrol ether/EtOAc 3:1) to give the corresponding products **3aa/3aa-d$_5$** (6.6 mg). The KIE value was determined to be K_H/K_D = 1.08 on the basis of ^{1}H NMR analysis.



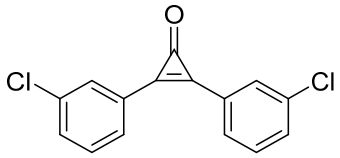
KIE by intermolecular competition experiments.



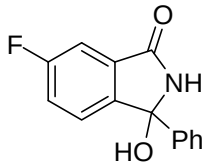
A mixture of **1a** (0.12 mmol, 27.0 mg, 1.2 equiv), **1a-*d*$_5$** (0.12 mmol, 27.6 mg, 1.2 equiv), **2a** (0.1 mmol, 20.6 mg, 1.0 equiv), $[Cp^*RhCl_2]_2$ (0.005 mmol, 3.1 mg, 5 mol%) and $AgNTf_2$ (0.02 mmol, 7.8 mg, 20 mol%) in HFIP (1.0 mL) was stirred in an oil bath preheated at 100 °C for 5 min under argon. After cooled to room temperature, the solvent was removed under reduced pressure. The residue was purified by column chromatography (petrol ether/EtOAc 3:1) to give the corresponding products **3aa/3aa-d$_5$** (4.1 mg). The KIE value was determined to be K_H/K_D = 1.56 on the basis of ^{1}H NMR analysis.



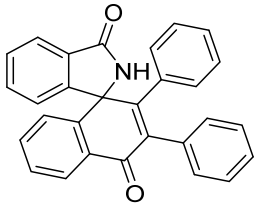
4. Characterization of the Products



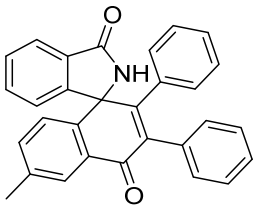
2j: This substrate was prepared according to the literature[6]. m.p. 179 – 180 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.92 (s, 2H), 7.84 (d, J = 8.0 Hz, 2H), 7.60 – 7.53 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 155.0, 148.6, 135.7, 133.2, 131.4, 131.0, 129.6, 125.2. IR ν 2928, 1832, 1632, 1405, 1344, 1077, 884, 790, 687, 660 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{15}H_8Cl_2ONa$ 296.9850; Found 296.9847.



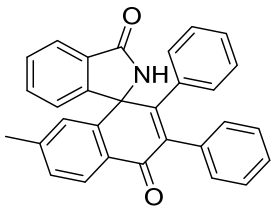
S1: m.p. 157 – 158 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.36 (s, 1H), 7.73 – 7.69 (m, 1H), 7.51 (d, J = 8.0 Hz, 2H), 7.36 – 7.31 (m, 4H), 7.16 – 7.13 (m, 1H), 7.07 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 167.4, 164.9 (d, J = 251.0 Hz), 153.7 (d, J = 9.0 Hz), 141.6, 128.4, 128.1, 126.9, 125.6, 125.2 (d, J = 9.0 Hz), 116.5 (d, J = 23.0 Hz), 110.1 (d, J = 24.0 Hz), 86.9. ^{19}F NMR (376 MHz, DMSO-d_6) δ: –107.0. IR ν 3305, 1710, 1618, 1482, 1453, 1262, 1055, 695, 598 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{10}FNO_2Na$ 266.0593; Found 266.0585.



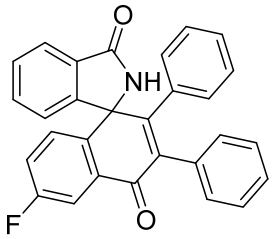
3aa: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 3:1) to afford **3aa** as white solid (36.4 mg, 88 %); m.p. 245 – 246 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.33 (s, 1H), 8.16 (d, J = 8.0 Hz, 1H), 7.64 – 7.55 (m, 3H), 7.53 (d, J = 8.0 Hz, 1H), 7.47 – 7.44 (m, 2H), 7.22 (s, 1H), 7.15 – 7.06 (m, 5H), 7.01 (d, J = 8.0 Hz, 2H), 6.94 (t, J = 8.0 Hz, 1H), 6.72 (s, 1H), 5.91 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 183.0, 169.4, 155.5, 147.7, 142.3, 139.6, 135.2, 135.0, 133.7, 132.8, 131.9, 130.3, 130.0, 129.1, 128.7, 127.2, 127.2, 126.8, 126.7, 126.5, 123.4, 123.1, 63.7. IR ν 3447, 3061, 1698, 1653, 1343, 1257, 742, 699, 585 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{19}NO_2Na$ 436.1308; Found 436.1317.



3ba: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 3:1) to afford **3ba** as white solid (38.5 mg, 90 %); m.p. 276 – 277 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.31 (s, 1H), 7.96 (s, 1H), 7.59 – 7.56 (m, 1H), 7.51 (d, J = 4.0 Hz, 1H), 7.46 – 7.41 (m, 3H), 7.21 (s, 1H), 7.14 – 7.05 (m, 4H), 7.00 (d, J = 8.0 Hz, 3H), 6.95 – 6.92 (t, J = 8.0 Hz, 1H), 6.70 (s, 1H), 5.90 (s, 1H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 183.0, 169.4, 155.4, 147.8, 139.6, 139.5, 138.1, 135.3, 135.0, 134.5, 132.7, 131.9, 130.2, 129.8, 128.9, 127.1, 127.1, 126.7, 126.6, 126.3, 123.3, 122.9, 63.5, 20.6. IR ν 3358, 3190, 3060, 1697, 1652, 1608, 755, 715, 695, 573 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{30}H_{21}NO_2Na$ 450.1465; Found 450.1469.

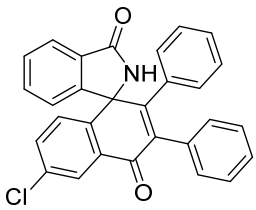


3ca: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 3:1) to afford **3ca** as white solid (29.9 mg, 70 %); m.p. ＞ 300 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.31 (s, 1H), 8.06 (d, J = 8.0 Hz, 1H), 7.61 – 7.57 (m, 1H), 7.52 (d, J = 8.0 Hz, 1H), 7.47 – 7.43 (m, 2H), 7.39 (d, J = 8.0 Hz, 1H), 7.22 (s, 1H), 7.13 – 7.05 (m, 4H), 6.99 (d, J = 8.0 Hz, 2H), 6.95 – 6.91 (m, 2H), 6.69 (s, 1H), 5.86 (s, 1H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 182.7, 169.4, 155.3, 147.8, 144.1, 142.3, 139.4, 135.3, 135.0, 132.8, 131.9, 130.2, 129.7, 129.1, 127.9, 127.2, 127.1, 126.8, 126.7, 126.4, 123.4, 123.0, 63.7, 21.3. IR ν 3356, 3190, 3062, 1694, 1653, 1342, 746, 716, 697, 577 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{30}H_{21}NO_2Na$ 450.1465; Found 450.1469.

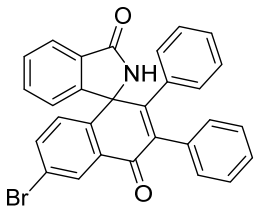


3ea: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 3:1) to afford **3ea** as white solid (41.8 mg, 97 %); m.p. 233 – 234 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ:

9.37 (s, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.60 (t, J = 8.0 Hz, 1H), 7.54 – 7.44 (m, 4H), 7.24 (s, 1H), 7.19 – 7.06 (m, 5H), 7.02 (d, J = 8.0 Hz, 2H), 6.94 (t, J = 8.0 Hz, 1H), 6.70 (s, 1H), 5.91 (s, 1H). ^{13}C NMR (101 MHz, DMSO-D_6) δ: 182.0, 169.4, 161.9 (d, J = 246.0 Hz), 156.0, 147.4, 139.4, 138.5 (d, J = 3.0 Hz), 134.9, 134.8, 132.9, 132.1 (d, J = 6.0 Hz), 131.9, 130.2, 130.0 (d, J = 8.0 Hz), 129.2, 127.3, 126.9, 123.5, 123.2, 121.5, 121.3, 112.0 (d, J = 22.0 Hz), 63.5. ^{19}F NMR (376 MHz, DMSO-d_6) δ: –112.3. IR ν 3442, 3063, 1699, 1653, 1333, 1266, 754, 717, 573 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{19}FNO_2$ 432.1400; Found 432.1402.

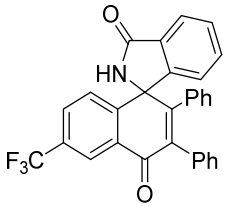


3fa: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 3:1) to afford **3fa** as white solid (45.9 mg, 96 %); m.p. 271 – 272 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.35 (s, 1H), 8.09 (s, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.60 (t, J = 8.0 Hz, 1H), 7.54 – 7.51 (m, 2H), 7.49 – 7.42 (m, 1H), 7.21 (s, 1H), 7.15 – 7.08 (m, 5H), 7.01 (d, J = 8.0 Hz, 2H), 6.94 (t, J = 8.0 Hz, 1H), 6.71 (s, 1H), 5.91 (s, 1H). ^{13}C NMR (101 MHz, DMSO-D_6) δ: 181.8, 169.3, 155.8, 147.2, 141.1, 139.4, 134.8, 134.7, 133.6, 133.5, 132.9, 131.9, 131.6, 130.2, 129.3, 129.2, 127.2, 126.9, 125.6, 123.4, 123.1, 63.3. IR ν 3467, 3062, 1700, 1652, 1333, 1250, 754, 711, 582 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{18}ClNO_2Na$ 470.0924; Found 470.0935.

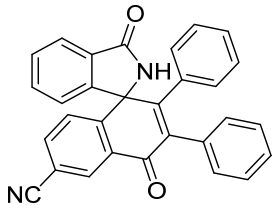


3ga: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 3:1) to afford **3ga** as white solid (46.8 mg, 95 %); m.p. 292 – 294 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.35 (s, 1H), 8.23 (s, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.60 (t, J = 8.0 Hz, 1H), 7.54 – 7.51 (m, 2H), 7.47 (t, J = 8.0 Hz, 1H), 7.21 (s, 1H), 7.15 – 7.06 (m, 5H), 7.01 (d, J = 8.0 Hz, 2H), 6.94 (t, J = 8.0 Hz, 1H), 6.71 (s, 1H), 5.91 (s, 1H). ^{13}C NMR (101 MHz, DMSO-D_6) δ: 181.7, 169.3, 155.8, 147.2, 141.5, 139.4, 136.4, 134.8, 134.7, 132.9, 131.8, 131.8, 130.2, 129.4, 129.3, 128.7, 127.2, 126.9, 123.5, 123.1, 122.0, 63.4. IR ν 3367, 3061, 1700, 1652, 1332, 1249, 754, 708, 641, 582 cm^{-1}. HRMS

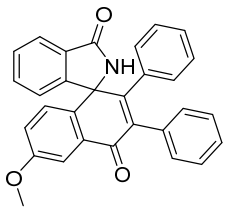
(ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{19}BrNO_2$ 492.0594; Found 492.0596.



3ha: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 3:1) to afford **3ha** as white solid (42.8 mg, 89 %); m.p. 274 – 275 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.43 (s, 1H), 8.40 (s, 1H), 7.98 (d, J = 8.0 Hz, 1H), 7.63 – 7.56 (m, 3H), 7.49 (t, J = 8.0 Hz, 1H), 7.36 (d, J = 8.0 Hz, 1H), 7.23 (s, 1H), 7.16 – 7.07 (m, 4H), 7.05 – 7.01 (m, 2H), 6.96 (t, J = 8.0 Hz, 1H), 6.71 (s, 1H), 5.92 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 181.8, 169.3, 155.8, 146.9, 146.4, 139.5, 134.7, 134.6, 133.0, 131.9, 130.6, 130.2, 129.6 (q, J = 34.0 Hz), 129.1, 128.6, 127.3, 127.2, 127.0, 123.6 (q, J = 271.0 Hz), 123.5, 123.3, 123.2 (q, J = 4.0 Hz), 63.5. ^{19}F NMR (376 MHz, DMSO-d_6) δ: –61.5. IR ν 3436, 1702, 1655, 1312, 1123, 755, 703 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{30}H_{18}F_3NO_2Na$ 504.1182; Found 504.1185.

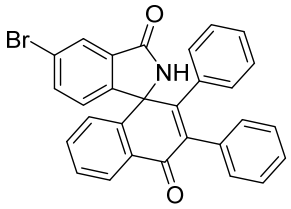


3ia: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 3:1) to afford **3ia** as white solid (24.6 mg, 56 %); m.p. 237 – 238 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.42 (s, 1H), 8.53 (s, 1H), 8.02 (d, J = 8.0 Hz, 1H), 7.61 (t, J = 8.0 Hz, 1H), 7.57 – 7.54 (m, 2H), 7.49 (t, J = 8.0 Hz, 1H), 7.30 (d, J = 8.0 Hz, 1H), 7.22 (s, 1H), 7.16 – 7.07 (m, 4H), 7.03 (d, J = 8.0 Hz, 2H), 6.95 (t, J = 8.0 Hz, 1H), 6.71 (s, 1H), 5.91 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 182.7, 167.8, 154.3, 146.9, 141.5, 139.8, 135.5, 135.1, 134.7, 134.2, 133.8, 130.2, 130.0, 128.8, 127.2, 127.1, 126.8, 126.7, 126.5, 126.0, 125.4, 122.2, 63.4. IR ν 3436, 1701, 1653, 1340, 1255, 757, 699 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{30}H_{18}N_2O_2Na$ 461.1260; Found 461.1254.

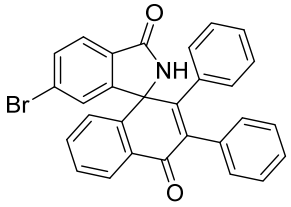


3ja: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 3:1) to

afford **3ja** as white solid (30.1 mg, 68 %); m.p. 272 – 273 ºC. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.30 (s, 1H), 7.61 – 7.56 (m, 2H), 7.52 (d, J = 8.0 Hz, 1H), 7.44 (t, J = 8.0 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.14 – 7.00 (m, 7H), 6.93 (t, J = 4.0 Hz, 1H), 6.71 (s, 1H), 5.92 (s, 1H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 182.8, 169.3, 159.2, 155.6, 147.8, 139.5, 135.2, 135.0, 134.5, 132.7, 131.9, 131.2, 130.2, 129.0, 128.4, 127.2, 127.1, 126.7, 123.3, 122.9, 121.3, 108.8, 63.5, 55.5. IR ν 3357, 3058, 2851, 1699, 1650, 1019, 753, 717, 592, 578 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{30}H_{22}NO_3$ 444.1600; Found 444.1609.

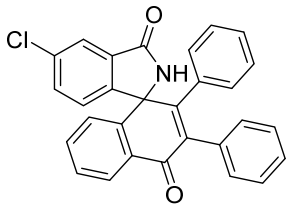


3ka: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 3:1) to afford **3ka** as white solid (47.3 mg, 96 %); m.p. 292 – 293 ºC. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.50 (s, 1H), 8.15 (d, J = 8.0 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.66 – 7.57 (m, 3H), 7.49 (d, J = 8.0 Hz, 1H), 7.23 (s, 1H), 7.15 – 7.08 (m, 5H), 7.02 (d, J = 8.0 Hz, 2H), 6.97 (t, J = 8.0 Hz, 1H), 6.78 (s, 1H), 6.02 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 182.8, 167.9, 154.4, 146.9, 141.5, 139.9, 135.6, 135.1, 134.8, 134.2, 133.8, 130.2, 130.0, 128.9, 127.3, 127.2, 126.9, 126.8, 126.6, 126.1, 125.5, 122.3, 63.5. IR ν 3459, 3052, 1687, 1655, 1341, 743, 700, 669 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{18}BrNO_2Na$ 514.0413; Found 514.0409.

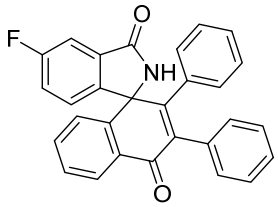


3la: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 3:1) to afford **3la** as white solid (35.4 mg, 72 %); m.p. ＞ 300 ºC. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.44 (s, 1H), 8.16 (d, J = 8.0 Hz, 1H), 7.88 (s, 1H), 7.66 – 7.57 (m, 3H), 7.43 (d, J = 8.0 Hz, 1H), 7.23 (s, 1H), 7.15 – 7.05 (m, 7H), 6.95 (d, J = 8.0 Hz, 1H), 6.77 (s, 1H), 6.07 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 182.7, 168.3, 153.7, 150.0, 141.4, 140.0, 135.2, 134.8, 133.7, 132.4, 131.2, 130.3, 130.1, 128.8, 127.2, 127.1, 126.9, 126.7, 126.5, 126.3, 126.3, 125.2, 63.1. IR ν 3440, 3053, 1704, 1653, 1597, 1343, 1311, 754, 702, 626 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for

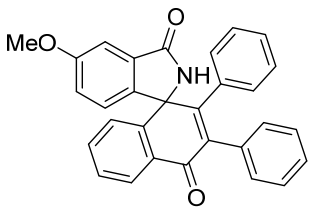
$C_{29}H_{18}BrNO_2Na$ 514.0413; Found 514.0406.



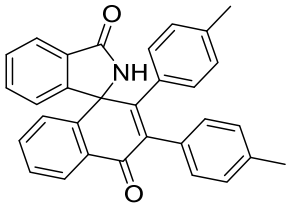
3ma: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 3:1) to afford **3ma** as white solid (42.0 mg, 94 %); m.p. 273 – 274 ºC. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.47 (s, 1H), 8.17 (d, J = 8.0 Hz, 1H), 7.75 (s, 1H), 7.66 – 7.57 (m, 2H), 7.53 – 7.48 (m, 2H), 7.26 (s, 1H), 7.15 – 7.05 (m, 7H), 6.95 (d, J = 8.0 Hz, 1H), 6.76 (s, 1H), 6.08 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 182.7, 168.3, 153.8, 149.9, 141.5, 140.0, 137.5, 135.2, 134.8, 133.7, 130.8, 130.3, 130.1, 129.6, 128.8, 127.2, 127.1, 126.9, 126.8, 126.6, 125.0, 123.5, 63.2. IR ν 3434, 3057, 1702, 1656, 1343, 757, 726, 701 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{18}ClNO_2Na$ 470.0924; Found 470.0920.



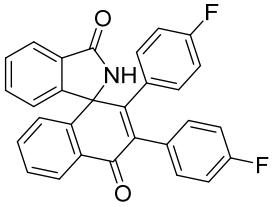
3na: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 3:1) to afford **3na** as white solid (37.9 mg, 88 %); m.p. 237 – 238 ºC. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.41 (s, 1H), 8.15 (d, J = 8.0 Hz, 1H), 7.63 – 7.51 (m, 4H), 7.27 (t, J = 8.0 Hz, 2H), 7.14 – 7.01 (m, 7H), 6.94 (t, J = 8.0 Hz, 1H), 6.75 (s, 1H), 6.10 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 182.7, 168.3, 164.9 (d, J = 249.0 Hz), 154.1, 150.6 (d, J = 106.0 Hz), 141.6, 140.0, 135.2, 134.8, 133.7, 130.3, 130.2 (d, J = 15.0 Hz), 128.8, 128.3, 127.2, 127.1, 126.9, 126.8, 126.6, 125.7 (d, J = 10.0 Hz), 116.8 (d, J = 23.0 Hz), 110.7 (d, J = 24.0 Hz), 63.2. ^{19}F NMR (376 MHz, DMSO-d_6) δ: –106.1. IR ν 3443, 3063, 1701, 1655, 1344, 1257, 755, 701 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{18}FNO_2Na$ 454.1219; Found 454.1222.



3oa: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 2:1) to afford **3oa** as white solid (40.3 mg, 91 %); m.p. ＞ 300 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.13 (s, 1H), 8.15 (d, J = 8.0 Hz, 1H), 7.65 – 7.55 (m, 2H), 7.41 (d, J = 8.0 Hz, 1H), 7.22 – 7.03 (m, 8H), 6.99 – 6.92 (m, 3H), 6.76 (s, 1H), 6.08 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 183.0, 169.2, 163.1, 155.2, 150.2, 142.5, 139.7, 135.3, 135.1, 133.6, 130.3, 130.0, 128.6, 127.2, 127.1, 126.9, 126.7, 126.4, 124.8, 124.6, 115.9, 107.4, 63.2, 56.0. IR ν 3355, 3062, 2846, 1698, 1653, 1602, 1345, 1275, 754, 701 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{30}H_{21}NO_3Na$ 466.1419; Found 466.1423.

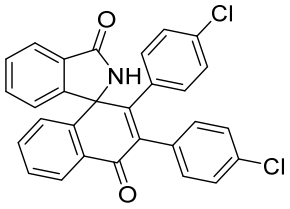


3ab: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 3:1) to afford **3ab** as white solid (39.7 mg, 90 %); m.p. 288 – 289 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.30 (s, 1H), 8.14 (d, J = 8.0 Hz, 1H), 7.62 – 7.53 (m, 4H), 7.47 – 7.40 (m, 2H), 7.10 (d, J = 4.0 Hz, 2H), 6.95 – 6.88 (m, 5H), 6.55 (s, 1H), 5.80 (s, 1H), 2.17 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 183.1, 169.4, 155.4, 147.9, 142.3, 139.4, 136.1, 135.7, 133.6, 132.7, 132.3, 132.3, 131.9, 130.1, 130.0, 129.0, 128.5, 127.9, 126.5, 123.4, 122.9, 63.8, 20.7, 20.6. IR ν 3438, 3072, 1702, 1660, 1341, 742, 639 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{31}H_{23}NO_2Na$ 464.1626; Found 464.1639.

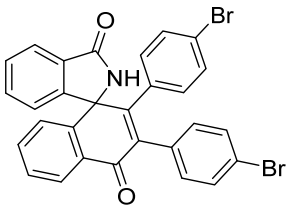


3ac: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 3:1) to afford **3ac** as white solid (43.6 mg, 97 %); m.p. 253 – 254 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.33 (s, 1H), 8.16 (d, J = 8.0 Hz, 1H), 7.64 – 7.61 (m, 1H), 7.59 – 7.54 (m, 3H), 7.50 – 7.45 (m, 2H), 7.28 (s, 1H), 7.11 (d, J = 4.0 Hz, 1H), 7.08 – 6.98 (m, 5H), 6.60 (s, 1H), 5.95 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 182.9, 169.7, 161.1 (d, J = 244.0 Hz), 154.8, 147.7, 142.2, 139.3, 133.9, 133.1, 132.4 (d, J = 9.0 Hz), 131.9, 131.4 (d, J = 3.0 Hz), 131.3 (d, J = 4.0 Hz), 130.0, 129.4, 128.8,

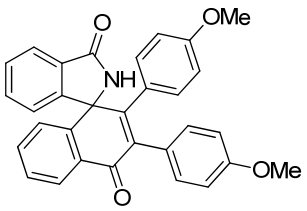
126.7 (d, J = 11.0 Hz), 123.4 (d, J = 36.0 Hz), 114.4 (d, J = 22.0 Hz), 63.7. ^{19}F NMR (376 MHz, DMSO-d_6) δ: –114.1, –115.0. IR ν 3453, 3075, 1736, 1706, 1656, 1225, 807, 759, 750, 544 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{17}F_2NO_2Na$ 472.1120; Found 472.1116.



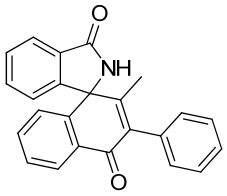
3ad: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 3:1) to afford **3ad** as white solid (42.9 mg, 89 %); m.p. 282 – 283 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.34 (s, 1H), 8.16 (d, J = 8.0 Hz, 1H), 7.63 (t, J = 8.0 Hz, 1H), 7.61 – 7.55 (m, 3H), 7.53 – 7.45 (m, 2H), 7.24 (d, J = 8.0 Hz, 4H), 7.10 (d, J = 8.0 Hz, 1H), 7.06 (d, J = 8.0 Hz, 2H), 6.84 (s, 1H), 5.95 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 182.5, 169.3, 154.4, 147.3, 142.1, 138.8, 133.8, 133.6, 132.9, 132.2, 132.1, 131.8, 129.8, 129.3, 128.7, 127.4, 126.7, 126.5, 123.4, 123.2, 63.4. IR ν 3324, 3063, 1702, 1650, 1489, 1090, 1015, 759, 726, 513 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{17}Cl_2NO_2Na$ 504.0529; Found 504.0527.



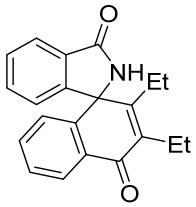
3ae: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 3:1) to afford **3ae** as white solid (52.6 mg, 92 %); m.p. 291 – 292 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.33 (s, 1H), 8.16 (d, J = 8.0 Hz, 1H), 7.64 – 7.56 (m, 4H), 7.52 – 7.45 (m, 2H), 7.38 (d, J = 8.0 Hz, 3H), 7.20 (s, 1H), 7.10 (d, J = 8.0 Hz, 1H), 7.00 (d, J = 8.0 Hz, 3H), 5.89 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 182.4, 169.3, 154.3, 147.3, 142.1, 138.7, 134.2, 134.0, 133.8, 132.9, 132.4, 131.8, 130.4, 129.8, 129.3, 128.7, 126.7, 126.5, 123.5, 123.2, 120.9, 120.5, 63.4. IR ν 3325, 3059, 2849, 1700, 1656, 1338, 1009, 758, 726, 587 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{17}Br_2NO_2Na$ 591.9524; Found 591.9530.



3af: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 3:1) to afford **3af** as white solid (50.0 mg, 95 %); m.p. 294 – 295 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.31 (s, 1H), 8.15 (d, J = 8.0 Hz, 1H), 7.62 – 7.55 (m, 5H), 7.47 – 7.39 (m, 2H), 7.11 – 6.92 (m, 4H), 6.71 (d, J = 8.0 Hz, 2H), 6.48 – 5.87 (m, 2H), 3.65 (s, 3H), 3.54 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 183.1, 169.5, 157.8, 157.8, 155.1, 148.0, 142.3, 139.3, 133.5, 132.7, 131.9, 131.5, 130.1, 129.0, 128.5, 128.2, 127.5, 127.4, 126.5, 125.5, 123.4, 122.8, 112.7, 63.9, 54.8, 54.7. IR ν 3400, 3020, 1845, 1600, 1512, 1257, 1012, 832, 759, 511 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{31}H_{23}NO_4Na$ 496.1525; Found 496.1529.

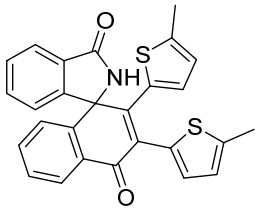


3ag: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 3:1) to afford **3ag** as white solid (27.8 mg, 79 %); m.p. 245 – 246 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.36 (s, 1H), 8.08 (d, J = 8.0 Hz, 1H), 7.84 – 7.82 (m, 1H), 7.59 – 7.54 (m, 3H), 7.51 (t, J = 8.0 Hz, 1H), 7.44 (t, J = 8.0 Hz, 2H), 7.37 (t, J = 8.0 Hz, 1H), 7.22 – 7.18 (m, 3H), 7.08 (d, J = 8.0 Hz, 1H), 1.41 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 181.9, 170.2, 153.1, 148.7, 142.3, 138.8, 135.6, 133.3, 133.2, 131.4, 130.1, 129.6, 129.2, 128.4, 128.1, 127.4, 126.4, 126.2, 123.8, 122.2, 63.8, 16.3. IR ν 3435, 1700, 1651, 1597, 1340, 1024, 757, 698 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{17}NO_2Na$ 374.1157; Found 374.1165.

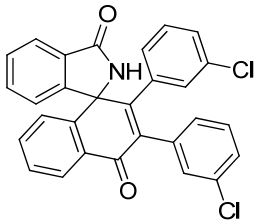


3ah: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 3:1) to afford **3ah** as white solid (15.9 mg, 50 %); m.p. 232 – 233 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ:

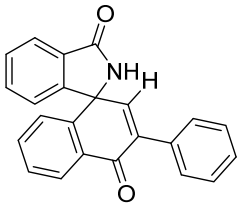
9.35 (s, 1H), 8.06 (d, J = 8.0 Hz, 1H), 7.80 (d, J = 4.0 Hz, 1H), 7.52 – 7.44 (m, 4H), 7.00 (d, J = 8.0 Hz, 1H), 6.90 (d, J = 8.0 Hz, 1H), 2.56 – 2.50 (m, 2H), 2.14 – 2.05 (m, 1H), 1.64 – 1.55 (m, 1H), 1.06 (t, J = 8.0 Hz, 3H), 0.92 (t, J = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 182.8, 170.2, 155.7, 148.6, 142.4, 138.5, 133.0, 132.9, 131.5, 129.9, 129.0, 128.2, 126.2, 125.9, 123.7, 122.2, 63.9, 21.8, 19.5, 14.3, 13.7. IR ν 3436, 3065, 1704, 1647, 1344, 1314, 766, 724, 713 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{19}NO_2Na$ 340.1308; Found 340.1313.



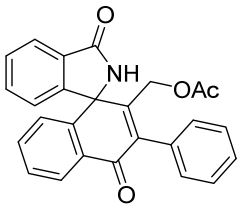
3ai: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 3:1) to afford **3ai** as white solid (23.1 mg, 51 %); m.p. 202 – 203 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.28 – 8.24 (m, 1H), 7.82 – 7.79 (m, 1H), 7.50 – 7.45 (m, 4H), 7.18 – 7.11 (m, 2 H), 6.96 (s, 1H), 6.67 (d, J = 4.0 Hz, 1H), 6.53 (d, J = 4.0 Hz, 1H), 6.35 (d, J = 4.0 Hz, 1H), 6.11 (d, J = 4.0 Hz, 1H), 2.41 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 182.8, 171.3, 148.4, 147.5, 142.7, 142.6, 141.1, 134.8, 133.6, 133.6, 133.4, 132.7, 131.7, 130.6, 130.5, 129.6, 129.4, 128.9, 127.9, 126.3, 125.2, 124.7, 124.5, 122.5, 64.9, 15.3, 15.2. IR ν 3437, 3066, 1700, 1652, 1597, 1310, 795, 759, 742, 717 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{19}NO_2S_2Na$ 476.0749; Found 476.0737.



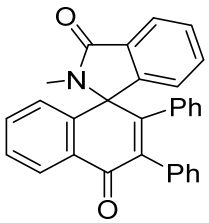
3aj: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 3:1) to afford **3aj** as white solid (43.8 mg, 91 %); m.p. ＞ 300 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.37 (s, 1H), 8.17 (d, J = 8.0 Hz, 1H), 7.65 – 7.56 (m, 5H), 7.49 (s, 1H), 7.23 – 7.16 (m, 4H), 7.12 (d, J = 8.0 Hz, 1H), 7.07 (1H), 7.06 (d, J = 4.0 Hz, 1H), 6.99 (t, J = 4.0 Hz, 1H), 5.97 (d, J = 16.0 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 182.4, 169.4, 154.1, 147.3, 142.1, 138.7, 137.0, 136.6, 134.0, 133.0, 132.1, 130.1, 129.8, 129.4, 129.3, 128.9, 128.8, 127.5, 127.2, 126.9, 126.6, 123.5, 63.4. IR ν 3446, 3065, 1706, 1657, 1338, 762, 714, 691 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{17}Cl_2NO_2Na$ 504.0534; Found 504.0550.



3ak: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 3:1) to afford **3ak** as white solid (28.3 mg, 84 %); m.p. 188 – 189 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.16 (s, 1H), 8.13 (s, 1H), 7.76 (d, J = 12.0 Hz, 2H), 7.52 – 7.34 (m, 10H), 7.24 (d, J = 8.0 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 195.2, 170.8, 145.2, 143.4, 139.7, 135.0, 134.3, 132.5, 130.9, 130.5, 130.2, 130.1, 129.3, 129.0, 128.4, 128.3, 128.1, 125.4, 124.4, 121.3, 72.3. IR ν 3446, 3211, 3076, 1696, 1463, 765, 695, 639cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{15}NO_2Na$ 360.1000; Found 360.1017.

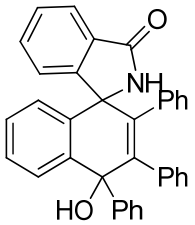


3al: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 3:1) to afford **3al** as white solid (35.6 mg, 87 %); m.p. 237 – 238 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.42 (s, 1H), 8.08 (d, J = 8.0 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.60 (t, J = 8.0 Hz, 1H), 7.56 – 7.51 (m, 3H), 7.46 – 7.40 (m, 3H), 7.25 (d, J = 8.0 Hz, 3H), 7.10 (d, J = 8.0 Hz, 1H), 4.46 (d, J = 12.0 Hz, 1H), 4.17 (d, J = 12.0 Hz, 1H), 1.47 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 182.7, 170.2, 169.1, 148.3, 147.9, 142.6, 142.0, 134.1, 134.0, 133.0, 131.3, 129.7, 129.5, 129.1, 128.6, 128.0 (2C), 126.7, 125.9, 123.8, 122.8, 62.9, 60.3, 19.7. IR ν 3415, 1741, 1705, 1656, 1463, 1221, 1025, 1000, 767, 704 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{19}NO_4Na$ 432.1212; Found 432.1205.

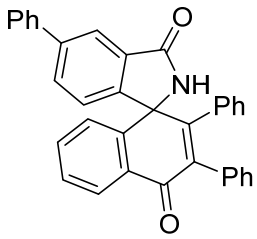


4: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 3:1) to afford **4** as white solid (74.3 mg, 87 %); m.p. 220 – 221 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.23 – 8.20 (m, 1H), 7.66 – 7.60 (m, 4H), 7.54 – 7.51 (m, 2H), 7.14 – 7.06 (m, 6H), 6.97 – 6.94 (m, 2H),

6.84 – 6.81 (m, 2H), 5.85 (s, 1H), 2.78 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 182.7, 167.8, 153.4, 146.0, 142.1, 139.6, 135.2, 135.0, 134.1, 132.9, 131.8, 131.0, 130.5, 129.4, 129.0, 127.6, 127.1, 127.0, 126.9, 126.1, 123.3, 123.1, 68.3, 26.1. IR ν 3382, 3027, 1699, 1652, 1597, 1344, 1312, 737, 701, 585 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{30}H_{21}NO_2Na$ 450.1465; Found 450.1460.



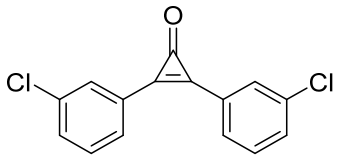
5: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 3:1) to afford **5** as white solid (41.8 mg, 85 %); m.p. 172 – 173 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.71 (s, 1H), 7.67 – 7.58 (m, 2H), 7.47 – 7.41 (m, 2H), 7.33 (d, J = 4.0 Hz, 2H), 7.27 – 7.21 (m, 3H), 7.16 (t, J = 8.0 Hz, 3H), 7.02 (d, J = 8.0 Hz, 1H), 6.89 (t, J = 8.0 Hz, 1H), 6.78 (t, J = 4.0 Hz, 3H), 6.75 – 6.66 (m, 4H), 6.55 (t, J = 4.0 Hz, 1H), 6.10 (d, J = 4.0 Hz, 1H), 6.05 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 168.7, 151.1, 145.9, 143.5, 142.2, 138.1, 136.7, 135.4, 134.3, 132.6, 132.3, 131.8, 131.4, 131.0, 129.9, 129.7, 128.8, 128.5, 127.7, 127.5, 127.4, 127.0, 126.5, 126.4, 126.0, 125.8, 125.6, 123.6, 122.8, 73.0, 63.3. IR ν 3255, 3021, 1693, 1489, 1444, 1311, 1024, 1000, 748, 696 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{35}H_{25}NO_2Na$ 514.1783; Found 514.1792.



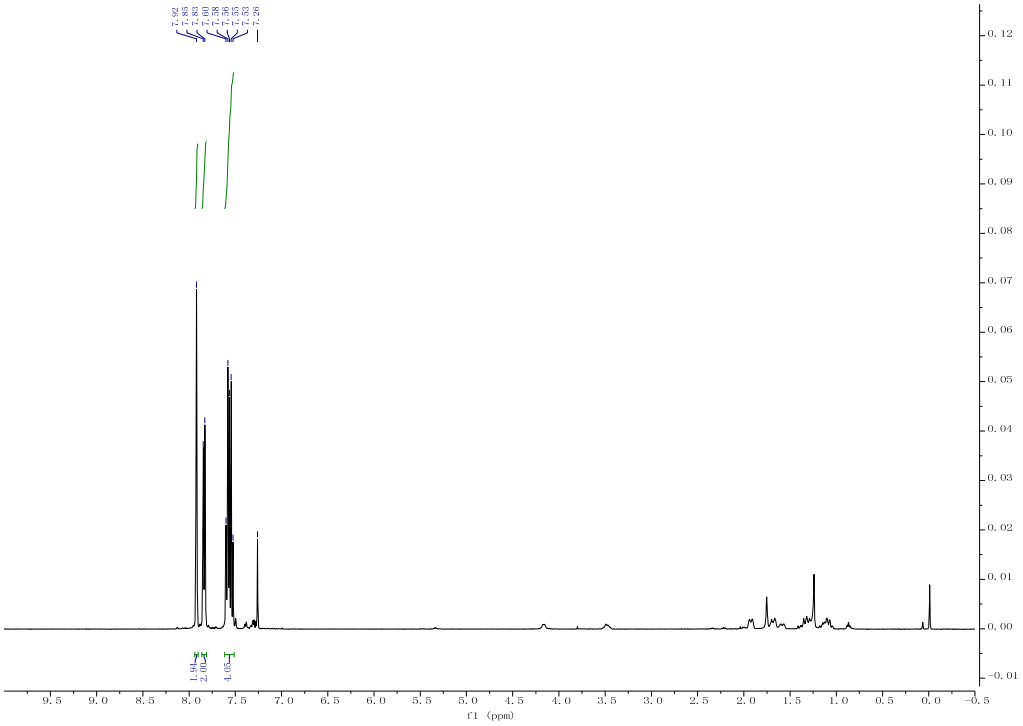
6: The crude product was purified by column chromatography (petrol ether/ethyl acetate, 3:1) to afford 6 as white solid (37.7 mg, 77 %); m.p. 245 – 246 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.41 (s, 1H), 8.18 (d, J = 7.6 Hz, 1H), 7.91 (dd, J = 8.0, 1.6 Hz, 1H), 7.77 (s, 1H), 7.70 (d, J = 7.5 Hz, 2H), 7.66 – 7.55 (m, 3H), 7.49 – 7.45 (t, J = 7.6 Hz, 2H), 7.41 – 7.37 (m, 1H), 7.26 – 7.02 (m, 8H), 6.97 – 6.93 (m, 1H), 6.74 (s, 1H), 6.03 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 182.9, 169.2, 155.3, 146.7, 142.2, 141.1, 139.6, 138.7, 135.2, 135.0, 133.7, 132.8, 131.4, 130.2, 130.0, 129.1, 128.6, 128.1, 127.2, 126.9, 126.8, 126.7, 126.5, 123.6, 121.0, 63.5. IR ν 3448, 3060, 1843, 1698, 1444, 1342, 765, 742, 699, 585 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{35}H_{23}NO_2Na$ 512.1621;

Found 512.1629.

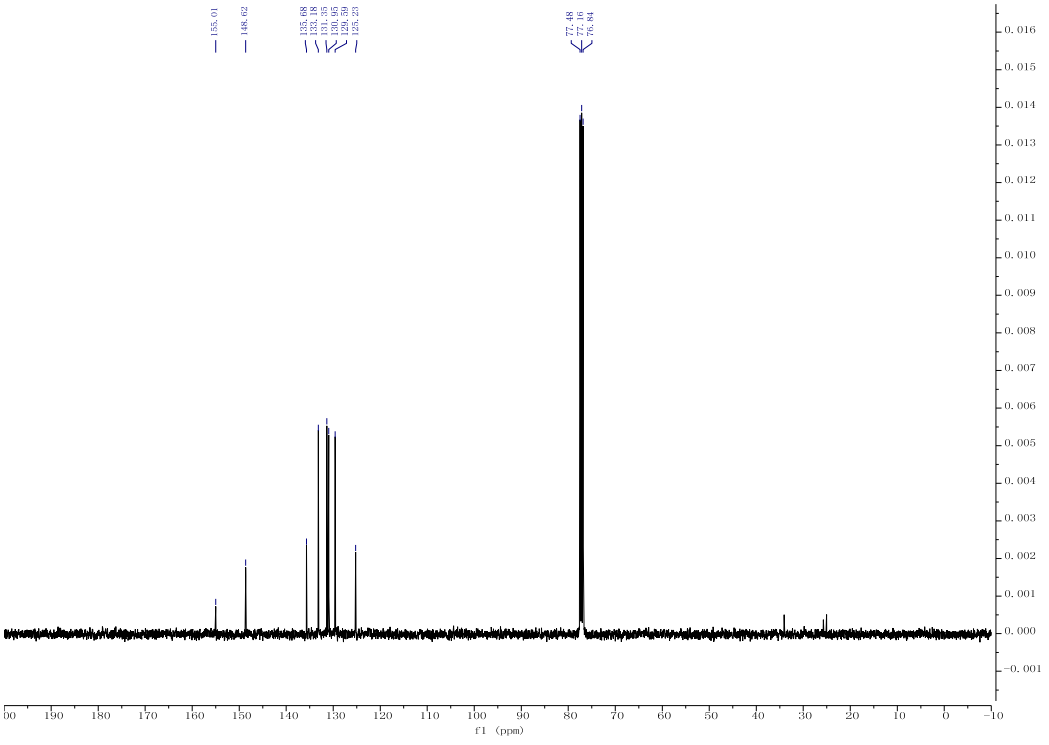
5. **NMR Chart and crystal structure.**

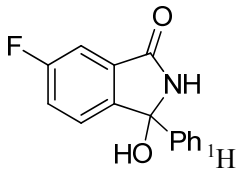


^{1}H NMR (400 MHz, $CDCl_3$) Compound **2j**

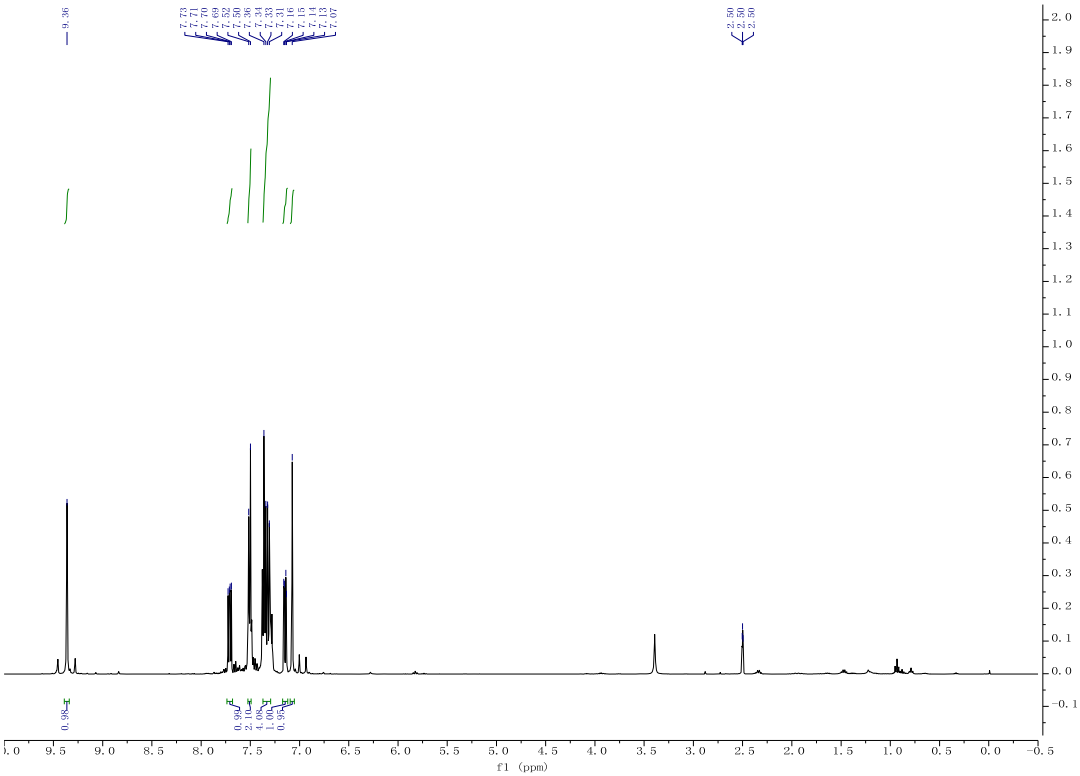


^{13}C NMR (101 MHz, $CDCl_3$) Compound **2j**

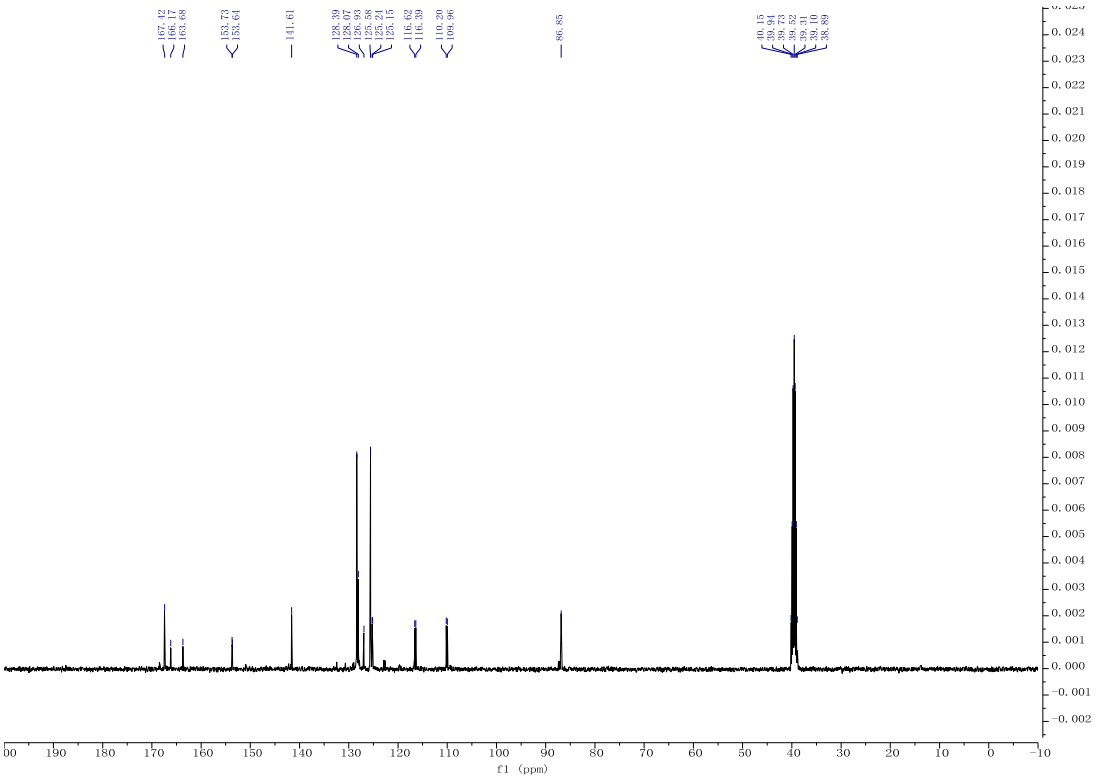




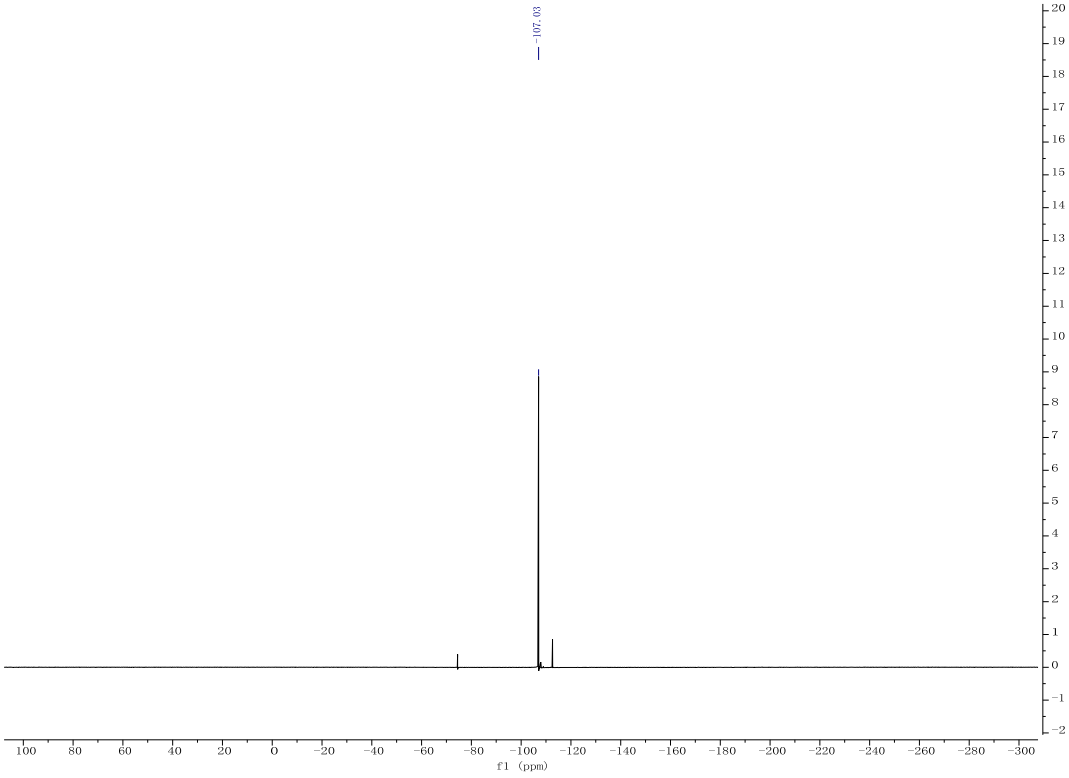
^{1}H NMR (400 MHz, DMSO-d_6) Compound **S1**

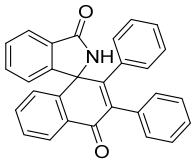


^{13}C NMR (101 MHz, DMSO-d_6) Compound **S1**

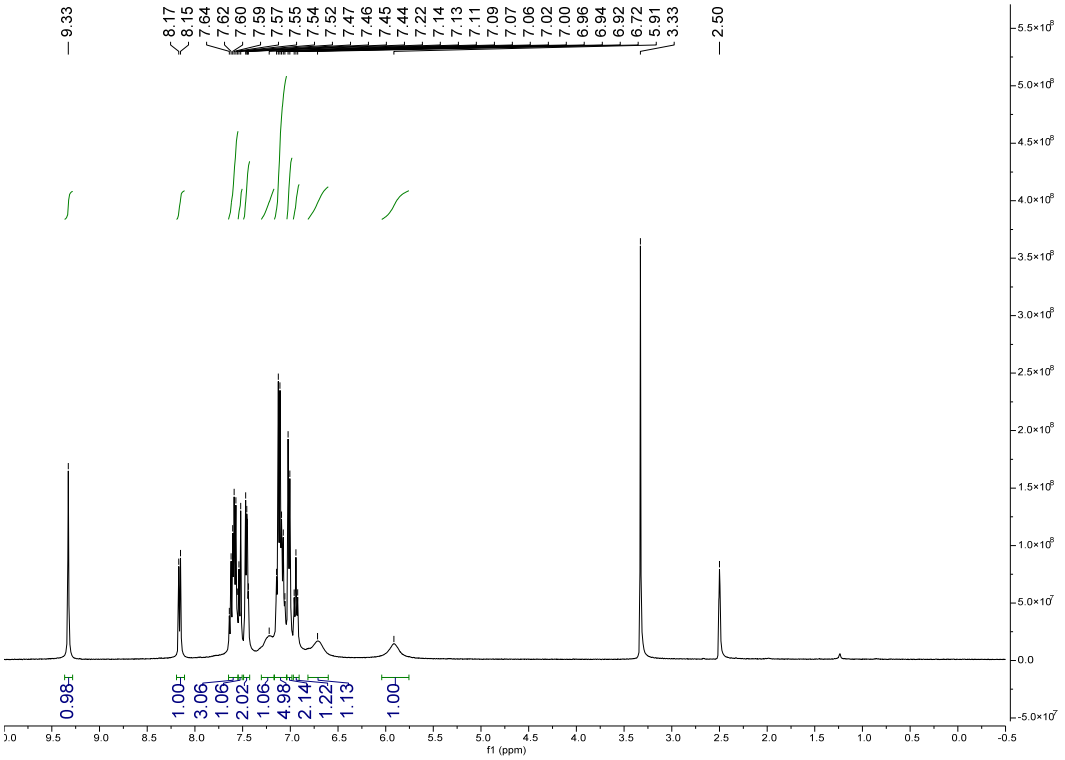


^{19}F NMR (376 MHz, DMSO-d_6) Compound **S1**

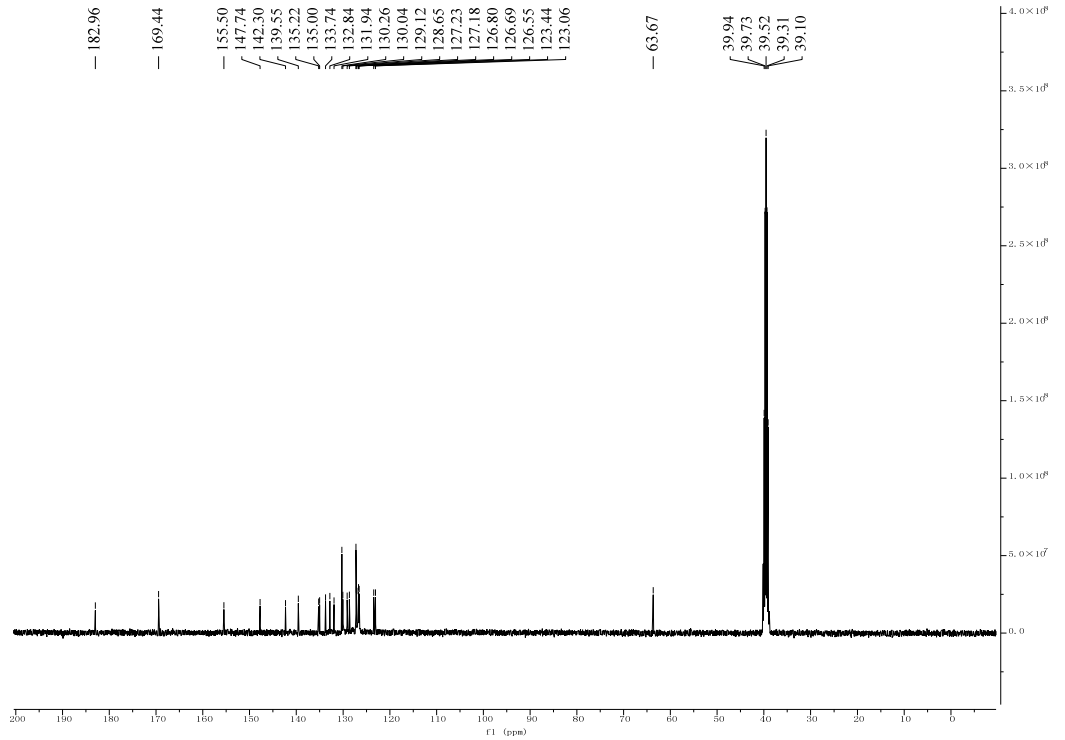


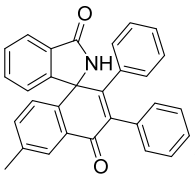


^{1}H NMR (400 MHz, DMSO-d_6) Compound **3aa**

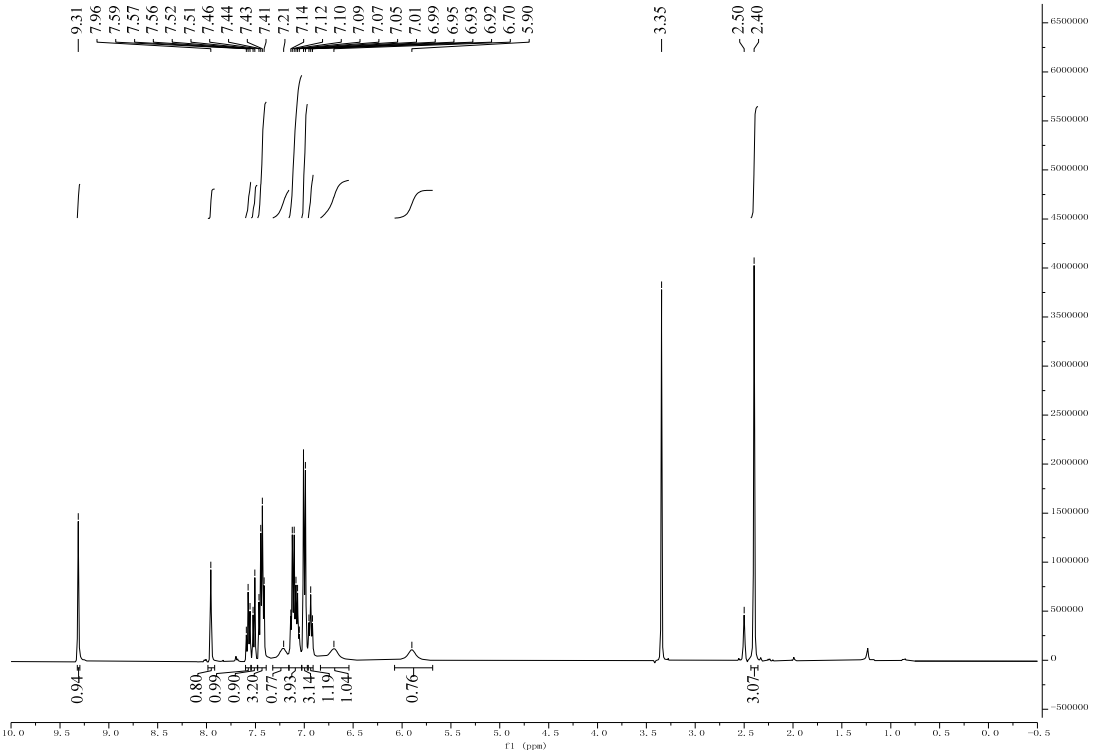


^{13}C NMR (101 MHz, DMSO-d_6) Compound **3aa**

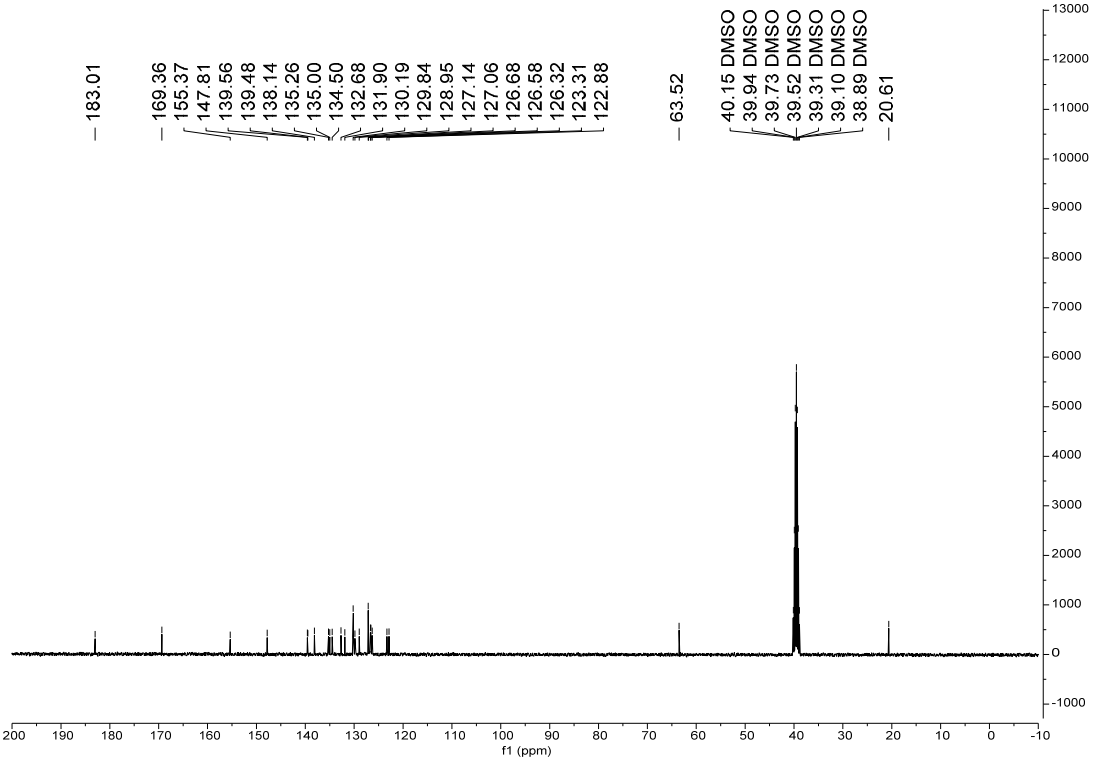


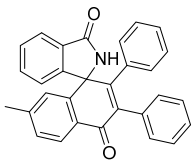


^{1}H NMR (400 MHz, DMSO-d_6) Compound **3ba**

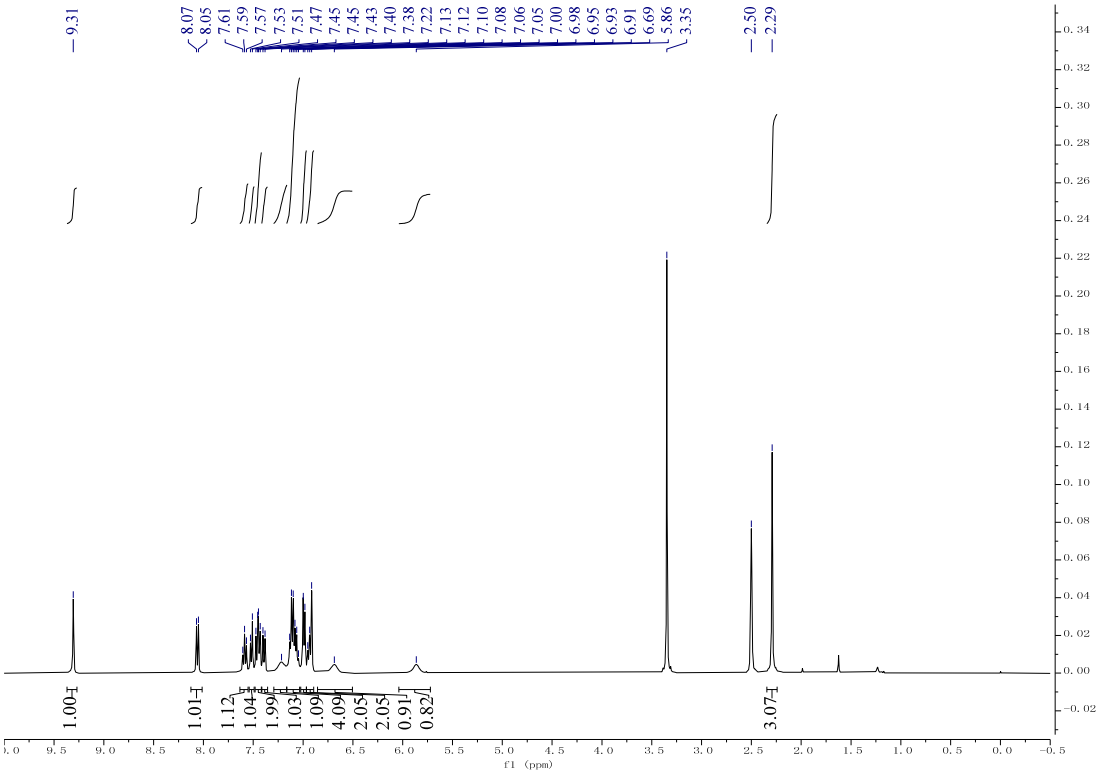


^{13}C NMR (101 MHz, DMSO-d_6) Compound **3ba**

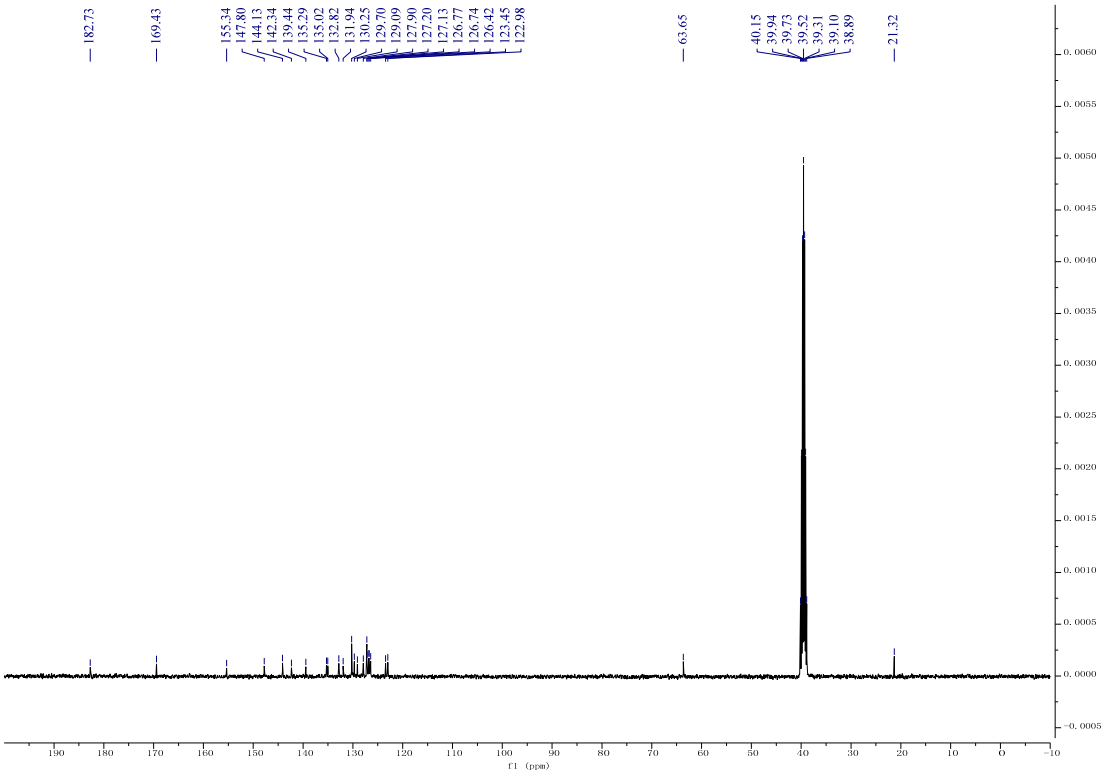


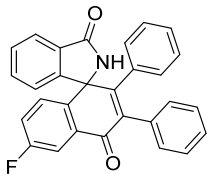


^{1}H NMR (400 MHz, DMSO-d_6) Compound **3ca.**

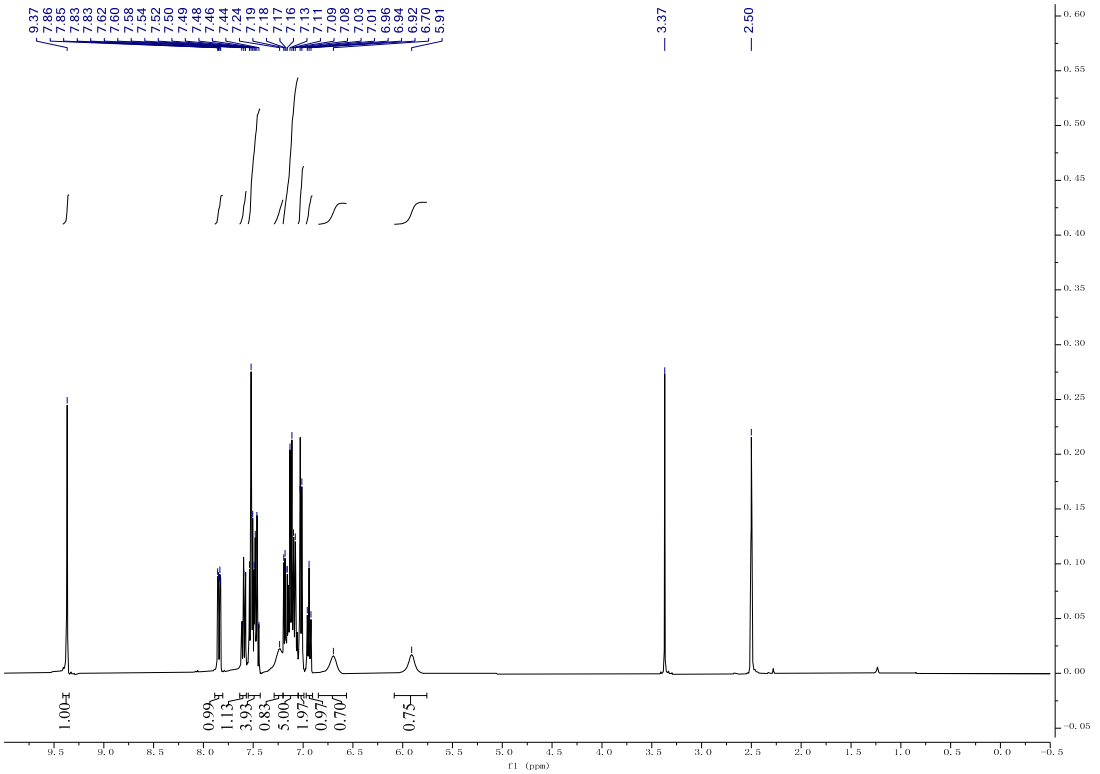


^{13}C NMR (101 MHz, DMSO-d_6) Compound **3ca**

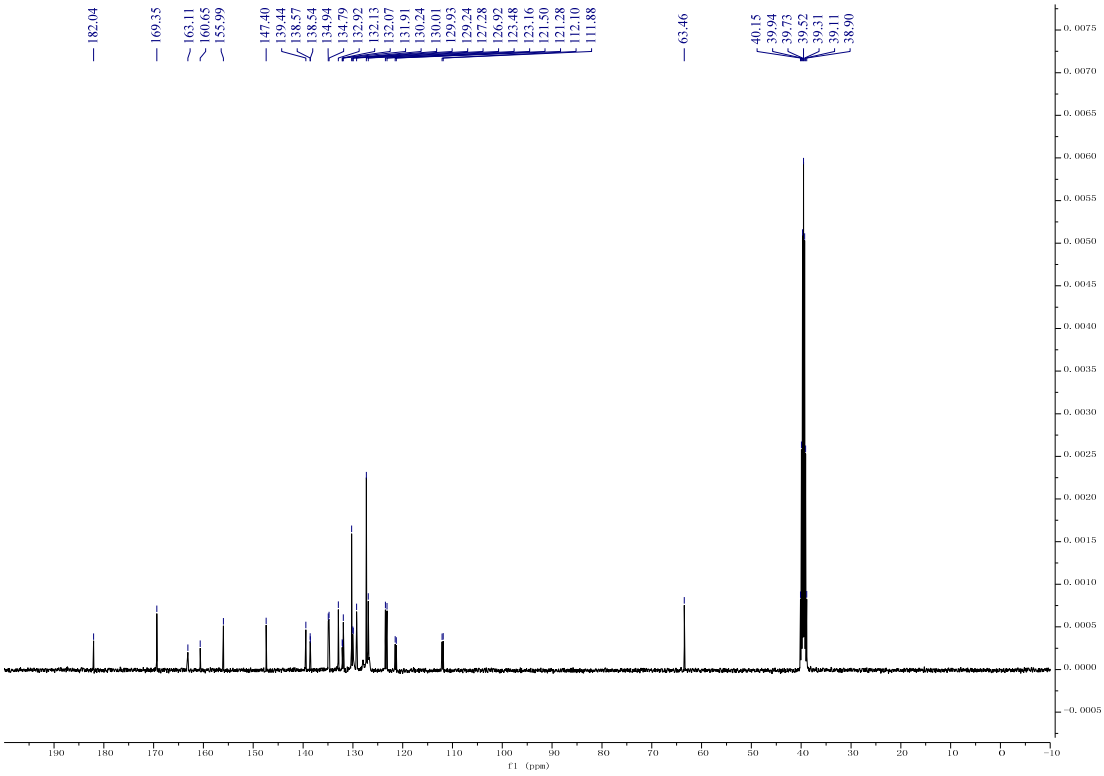




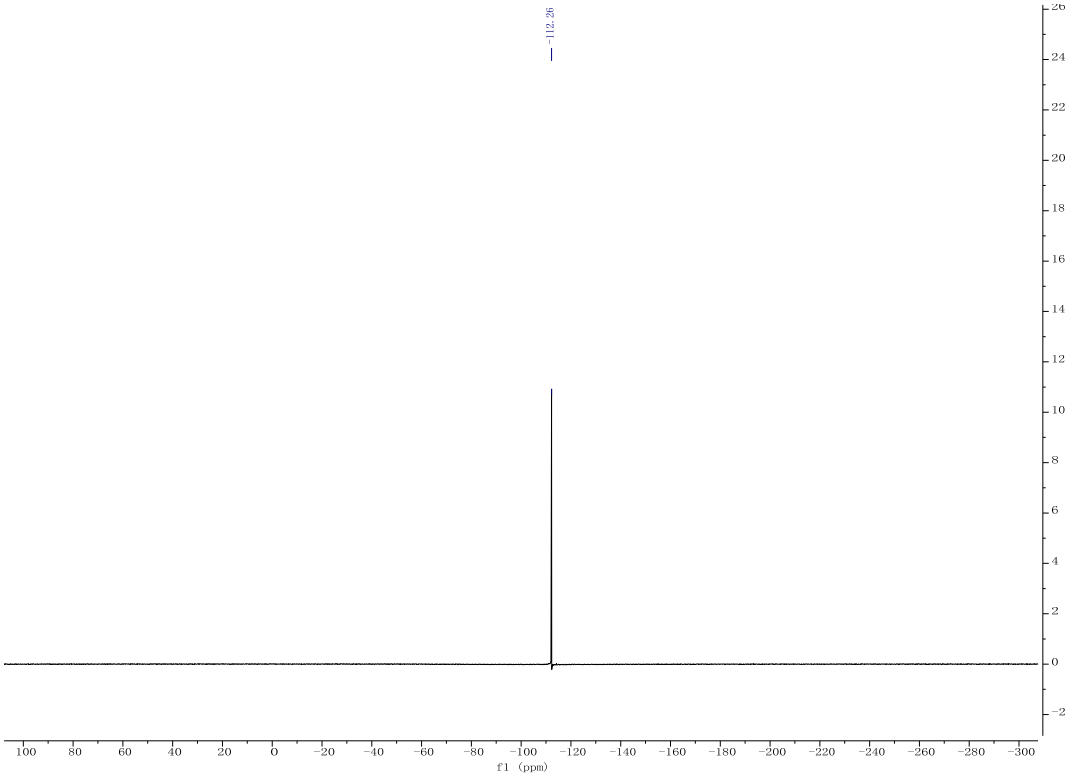
^{1}H NMR (400 MHz, DMSO-d_6) Compound **3ea**

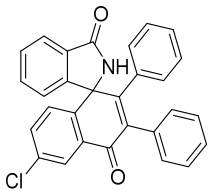


^{13}C NMR (101 MHz, DMSO-d_6) Compound **3ea**

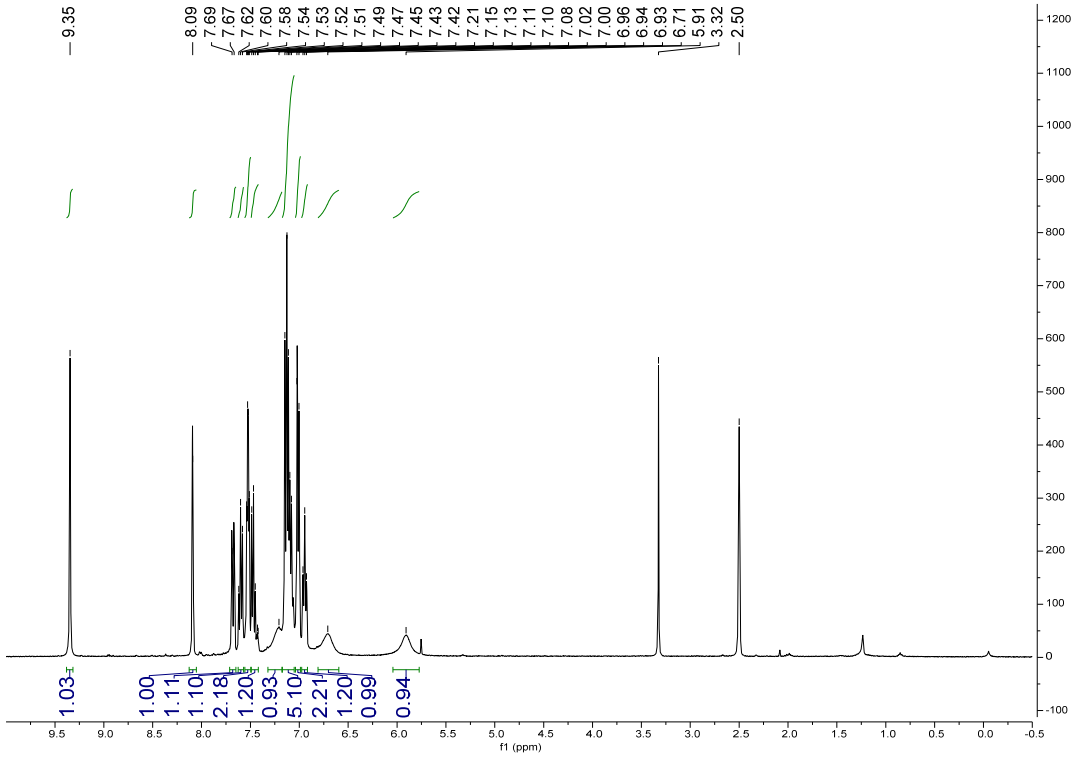


^{19}F NMR (376 MHz, DMSO-d_6) Compound 3**ea**

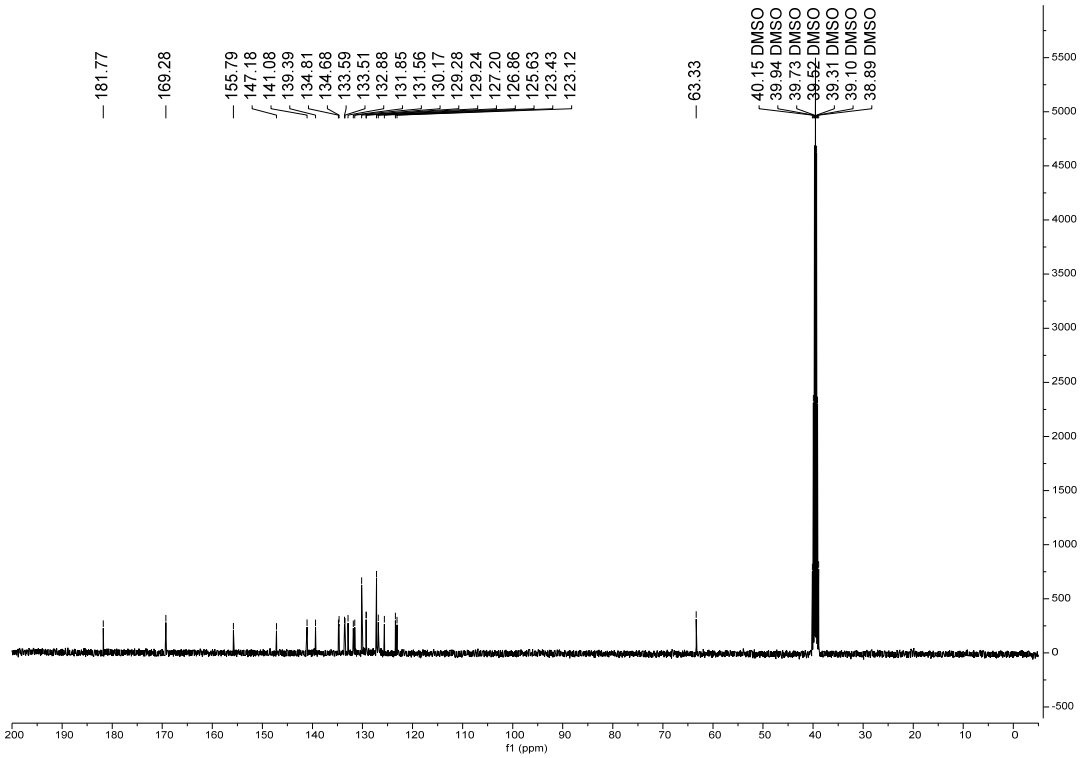


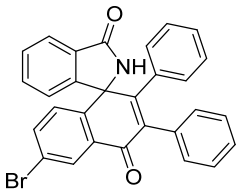


^{1}H NMR (400 MHz, DMSO-d_6) Compound **3fa**

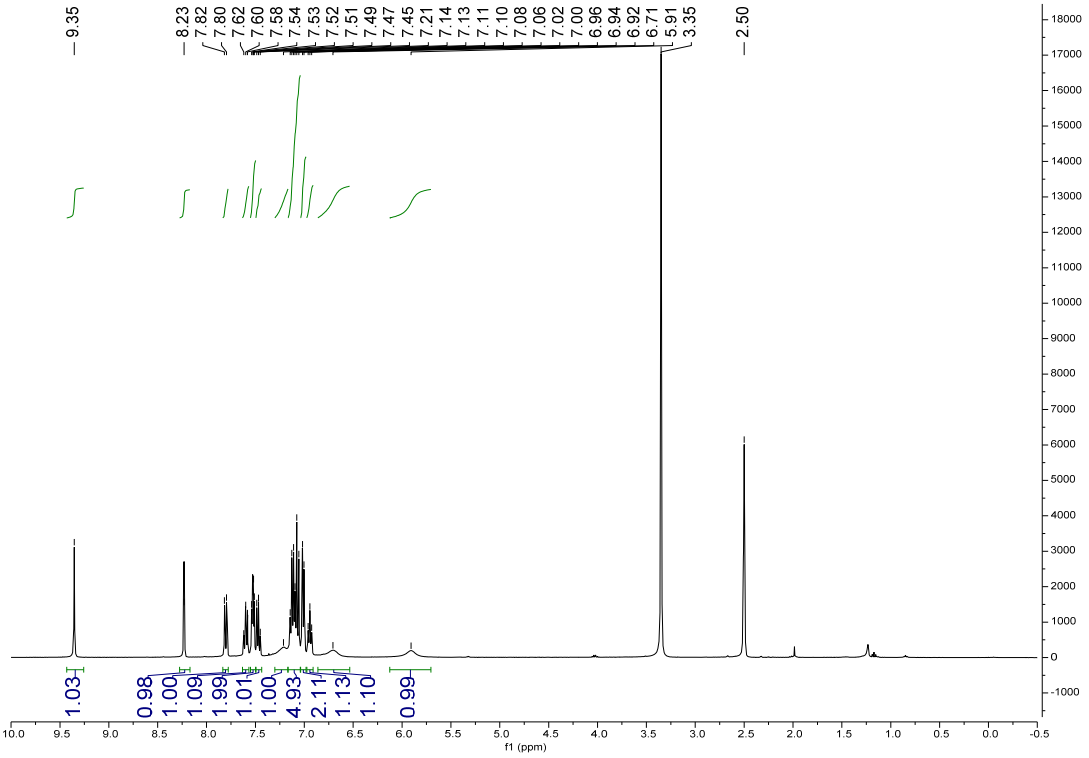


^{13}C NMR (101 MHz, DMSO-d_6) Compound **3fa**

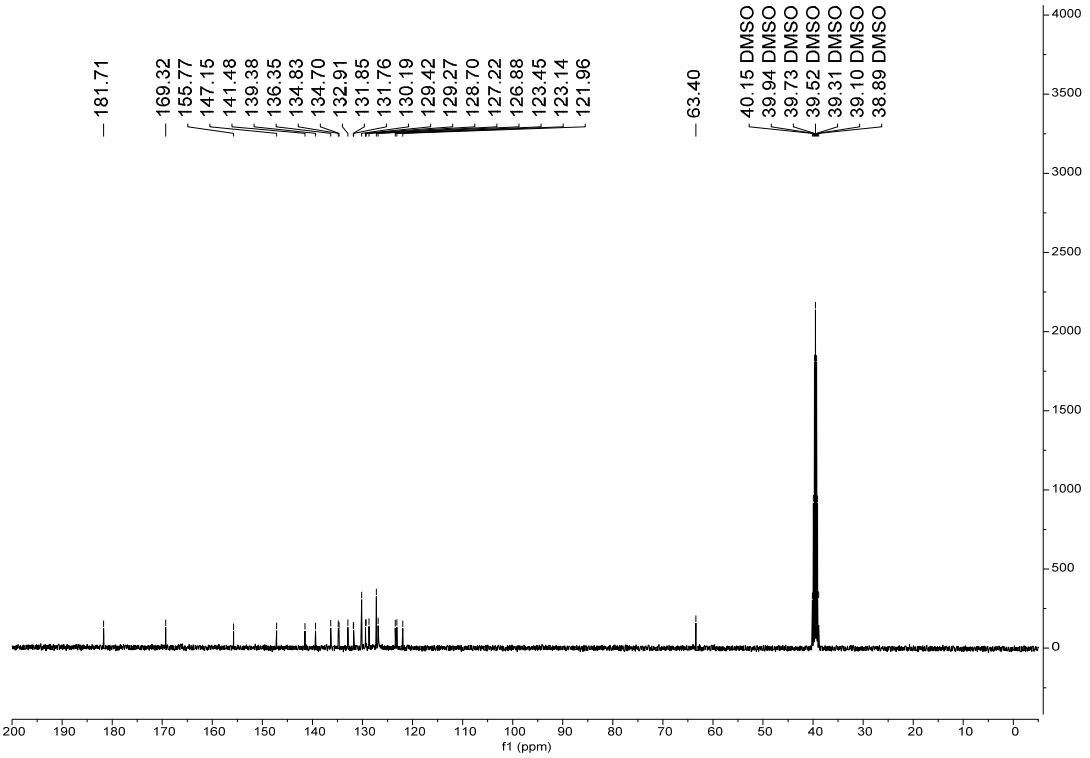


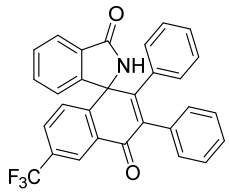


^{1}H NMR (400 MHz, DMSO-d_6) Compound **3ga**

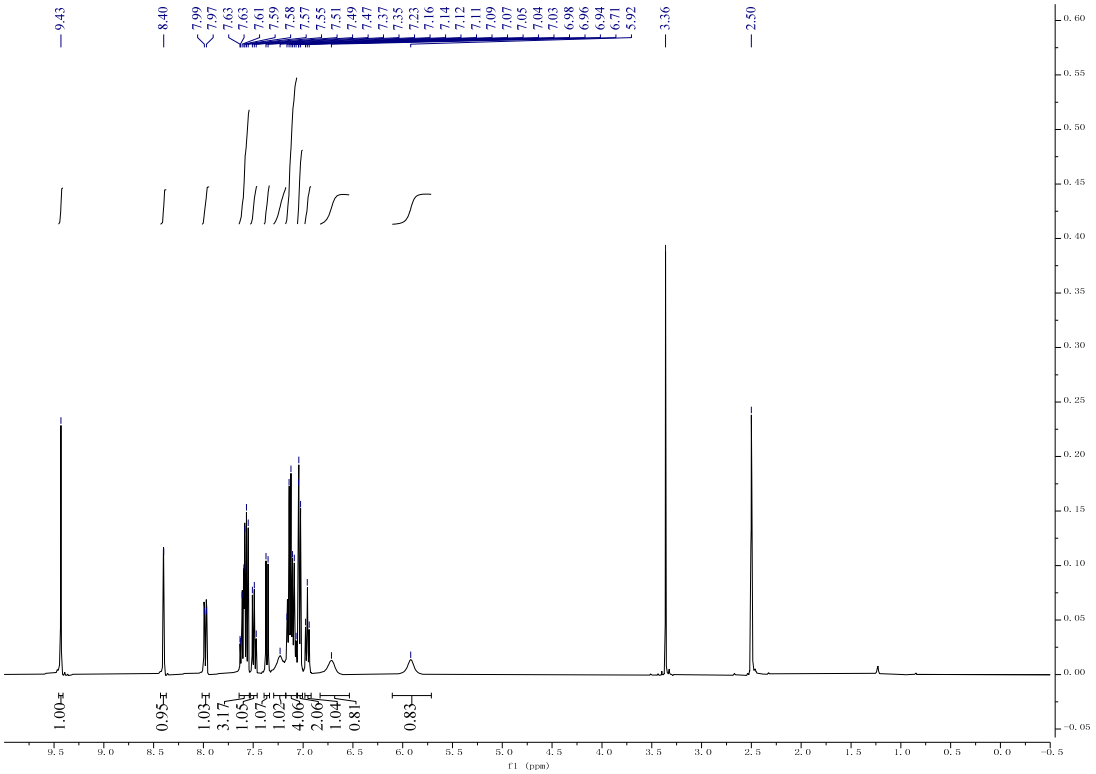


^{13}C NMR (101 MHz, DMSO-d_6) Compound **3ga**

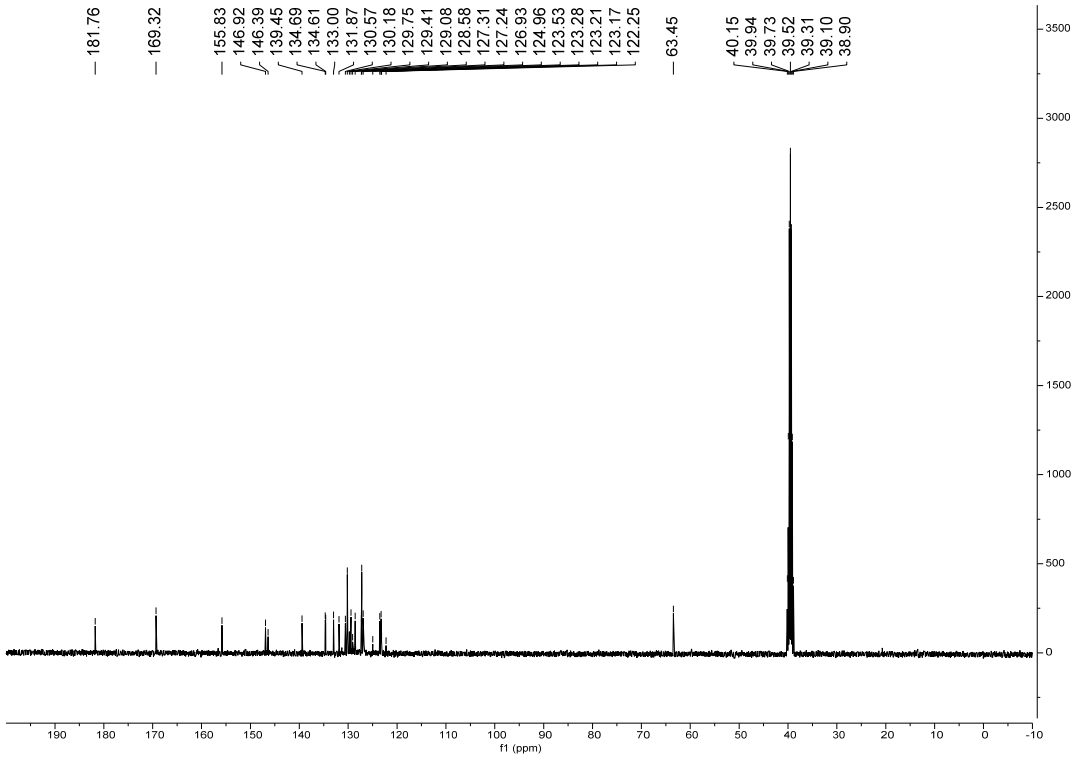




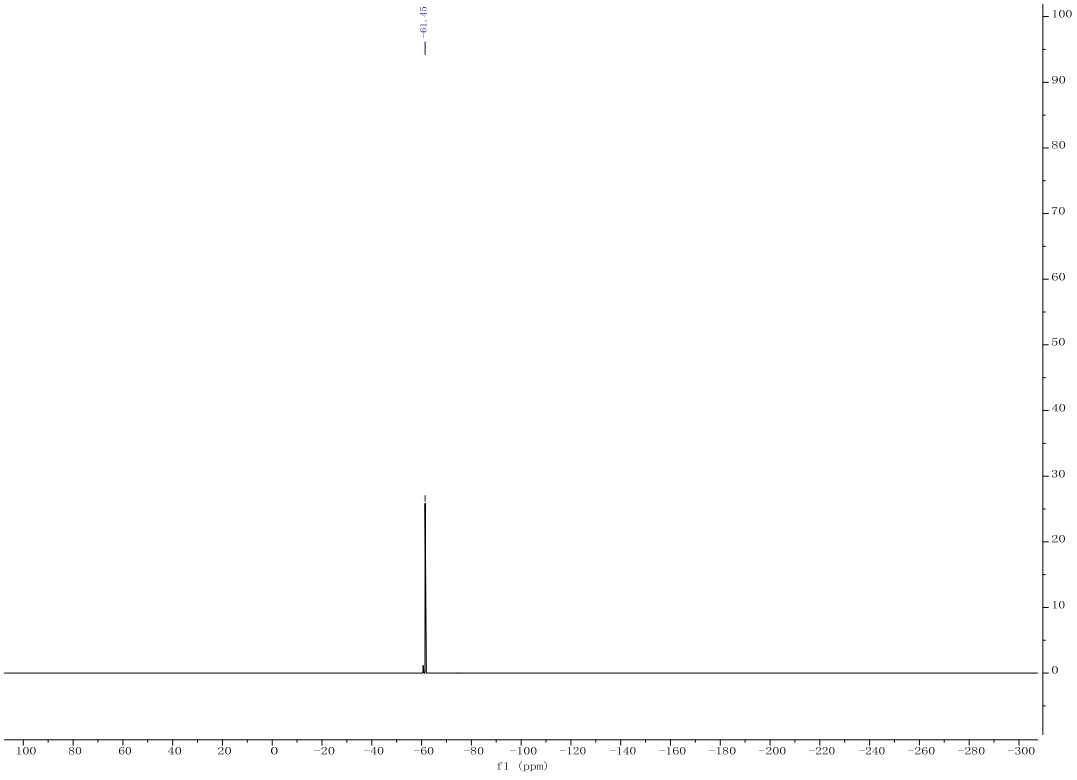
^{1}H NMR (400 MHz, DMSO-d_6) Compound **3ha**

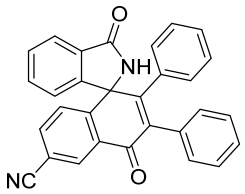


^{13}C NMR (101 MHz, DMSO-d_6) Compound **3ha**

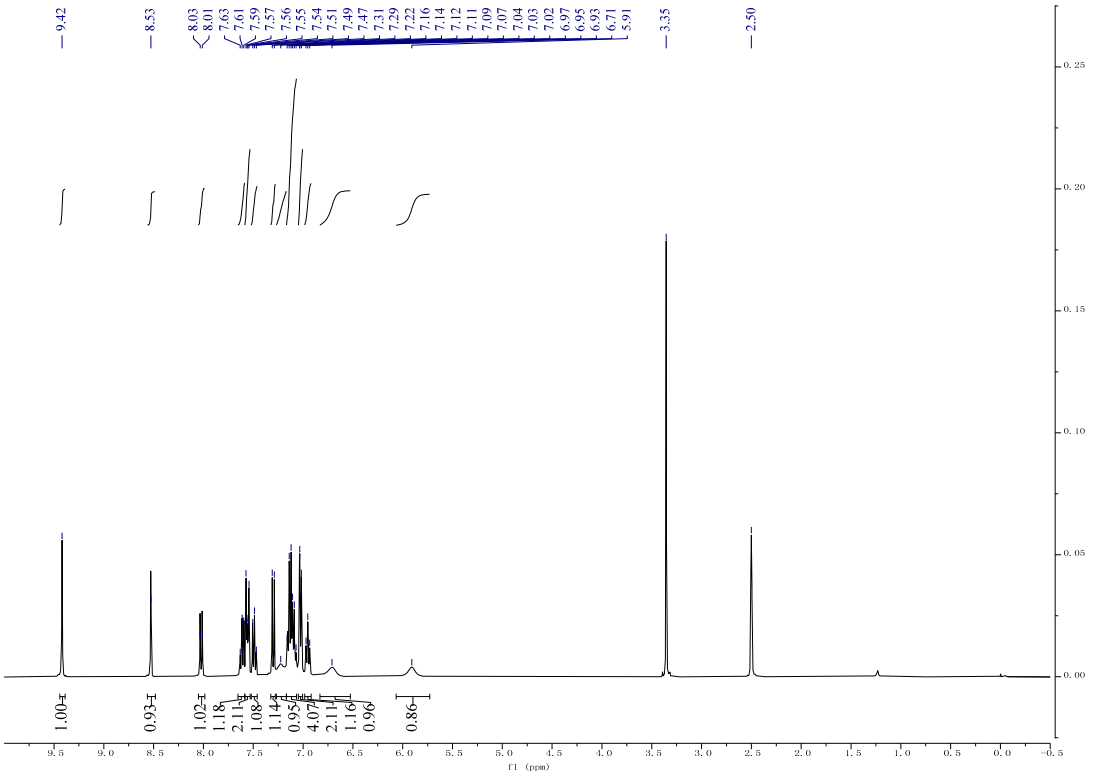


^{19}F NMR (376 MHz, DMSO-d_6) Compound 3**ha**

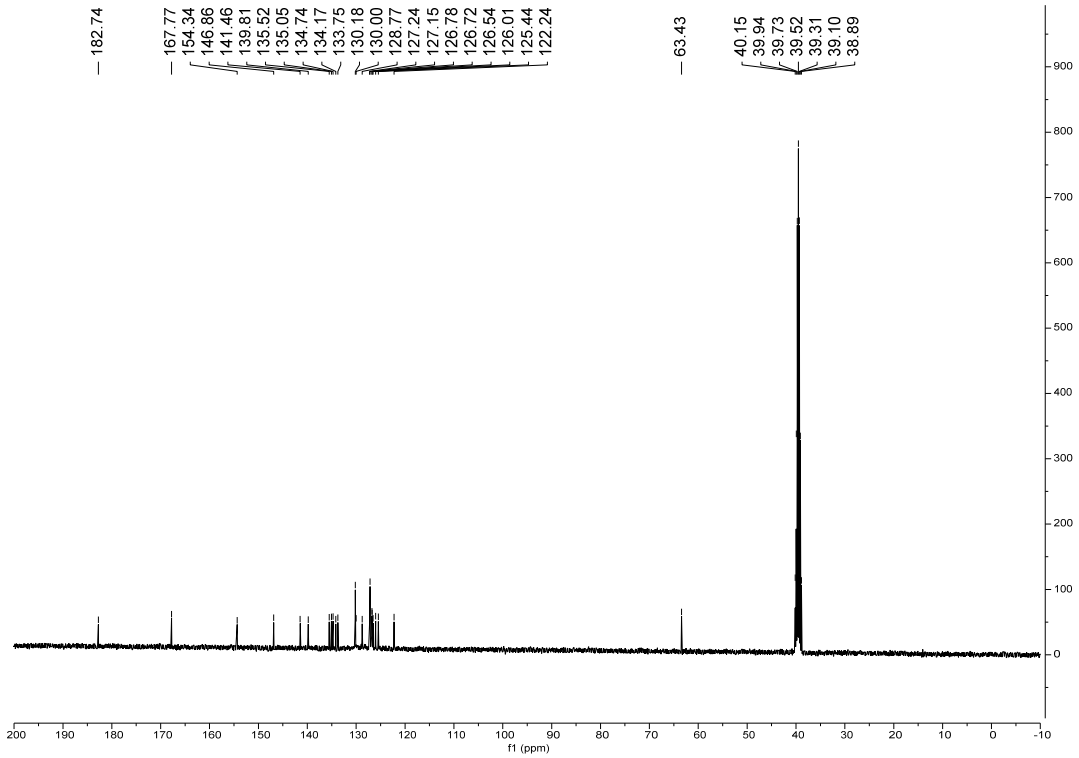


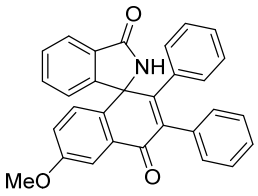


^{1}H NMR (400 MHz, DMSO-d_6) Compound **3ia**

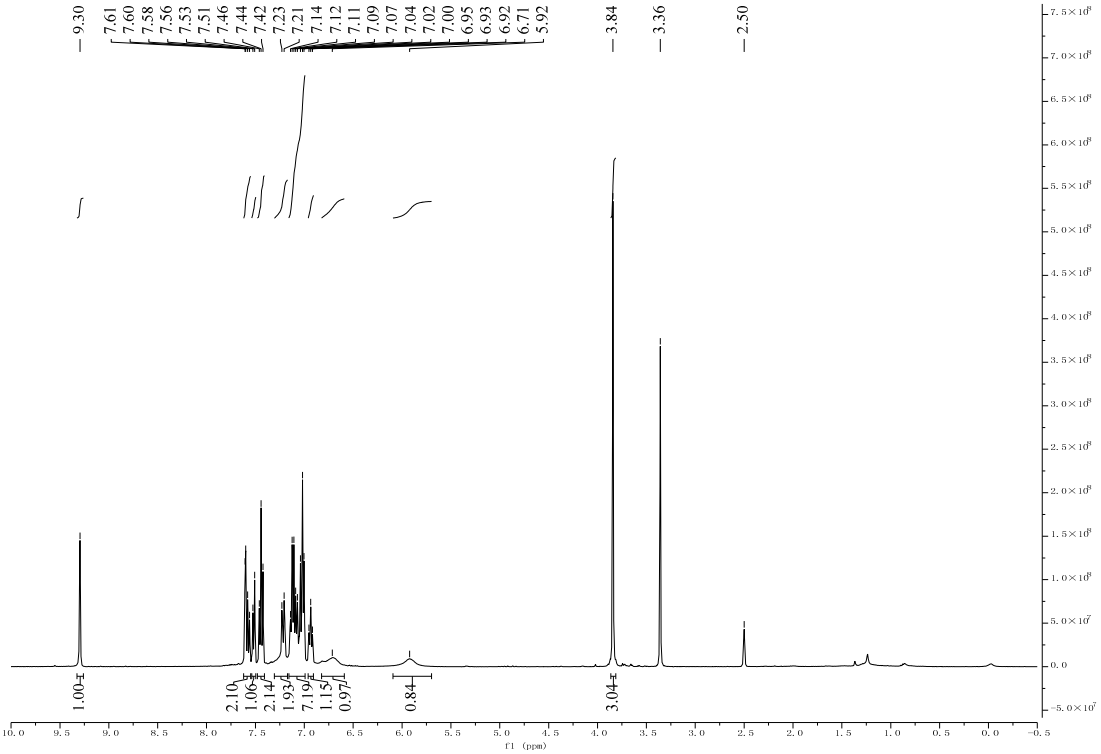


^{13}C NMR (101 MHz, DMSO-d_6) Compound **3ia**

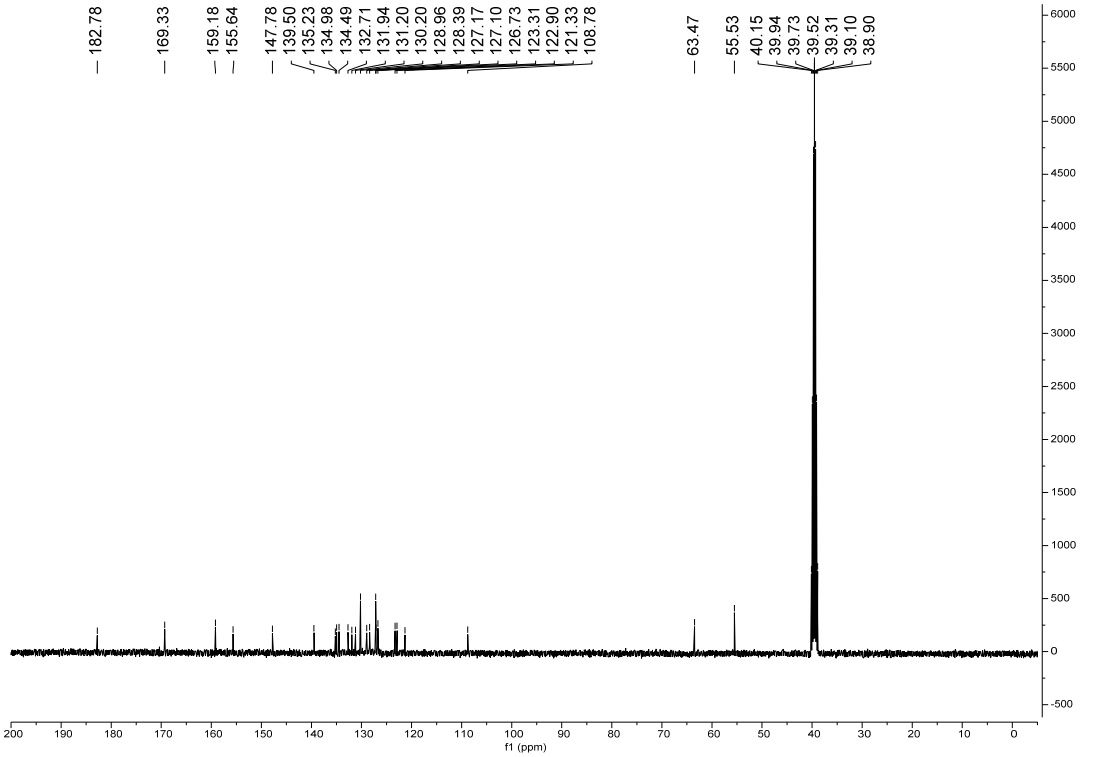


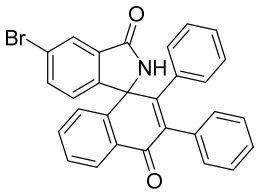


^{1}H NMR (400 MHz, DMSO-d_6) Compound **3ja**

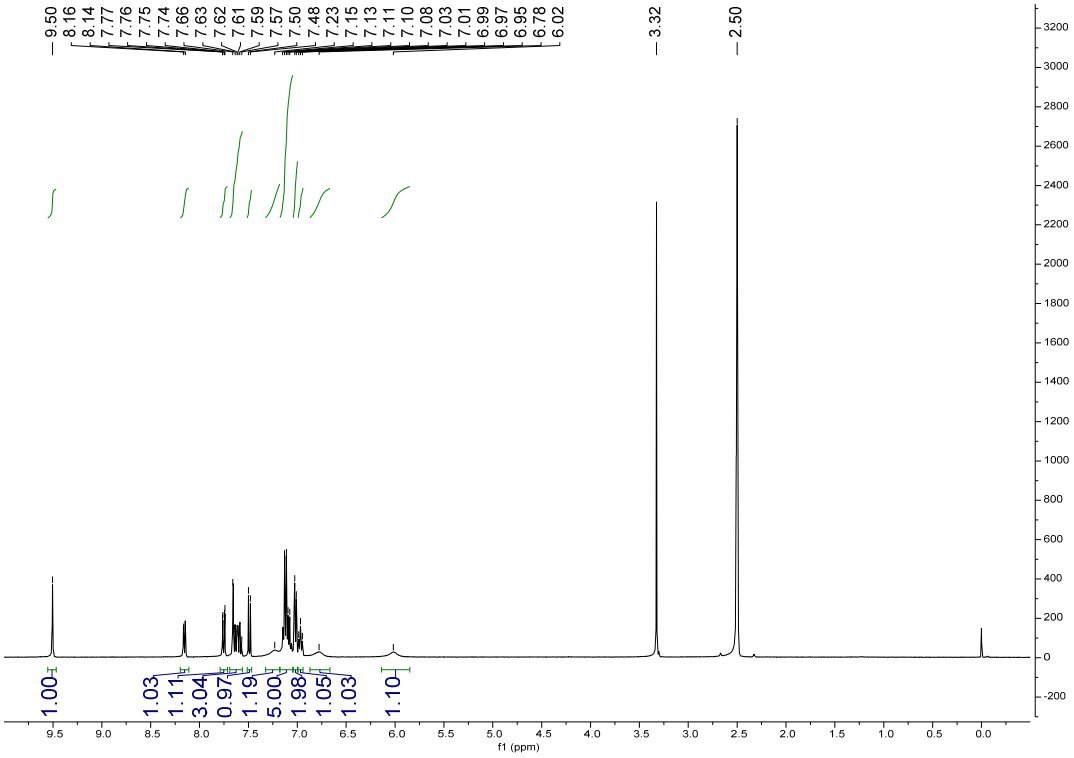


^{13}C NMR (101 MHz, DMSO-d_6) Compound **3ja**

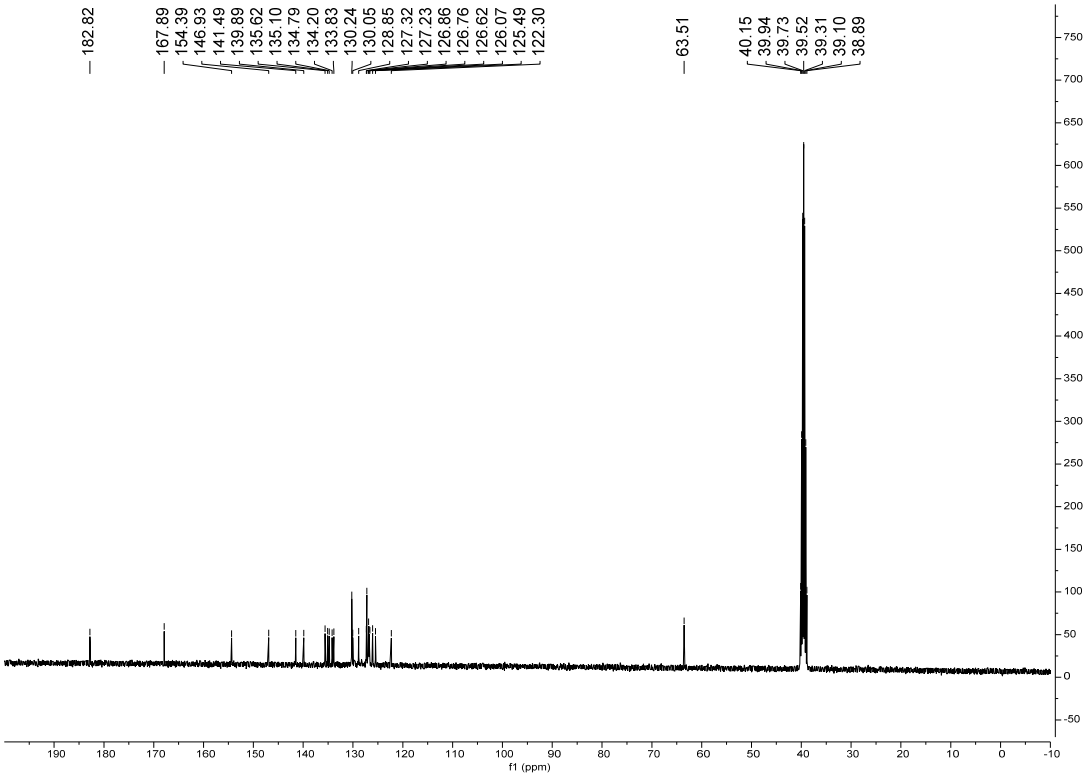


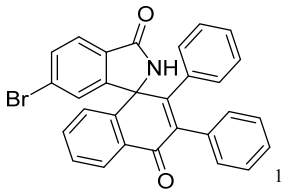


^{1}H NMR (400 MHz, DMSO-d_6) Compound **3ka**

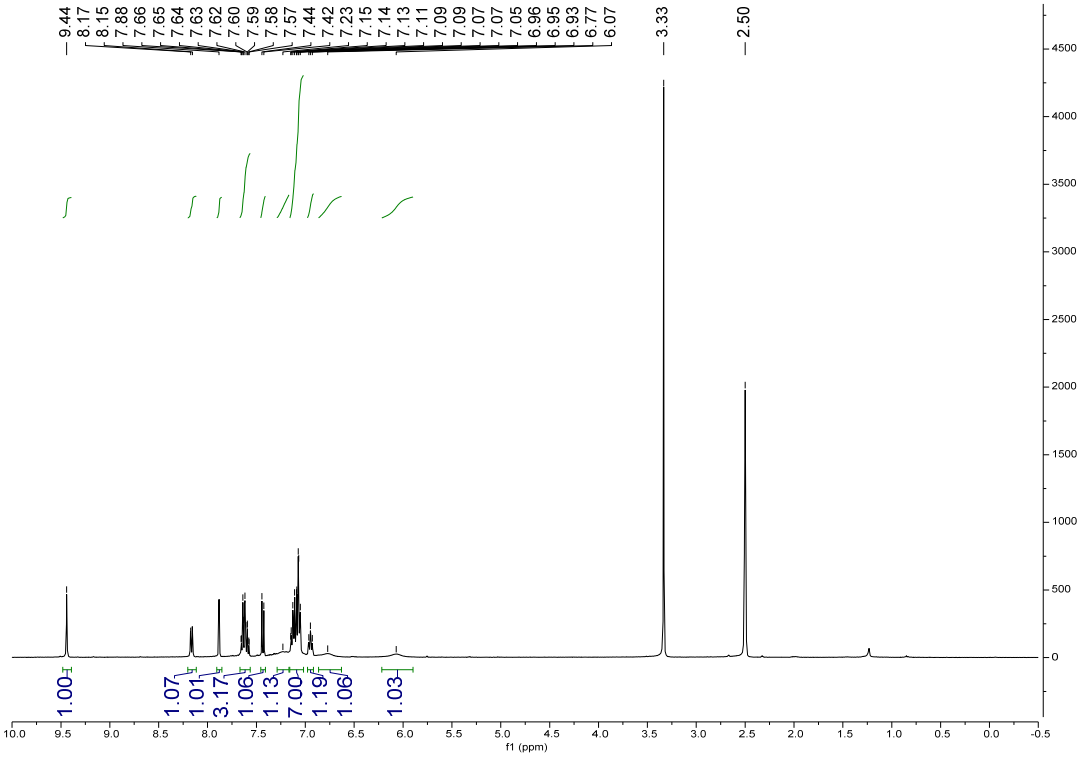


^{13}C NMR (101 MHz, DMSO-d_6) Compound **3ka**

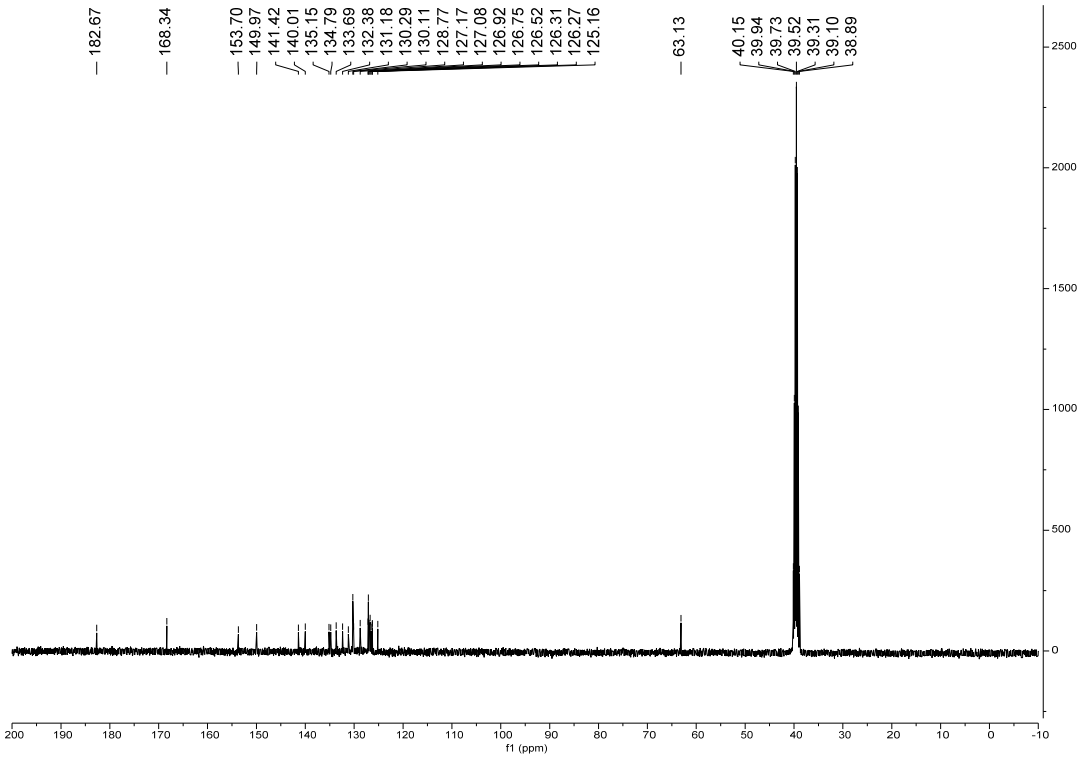


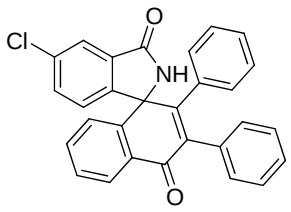


^{1}H NMR (400 MHz, DMSO-d_6) Compound **3la**

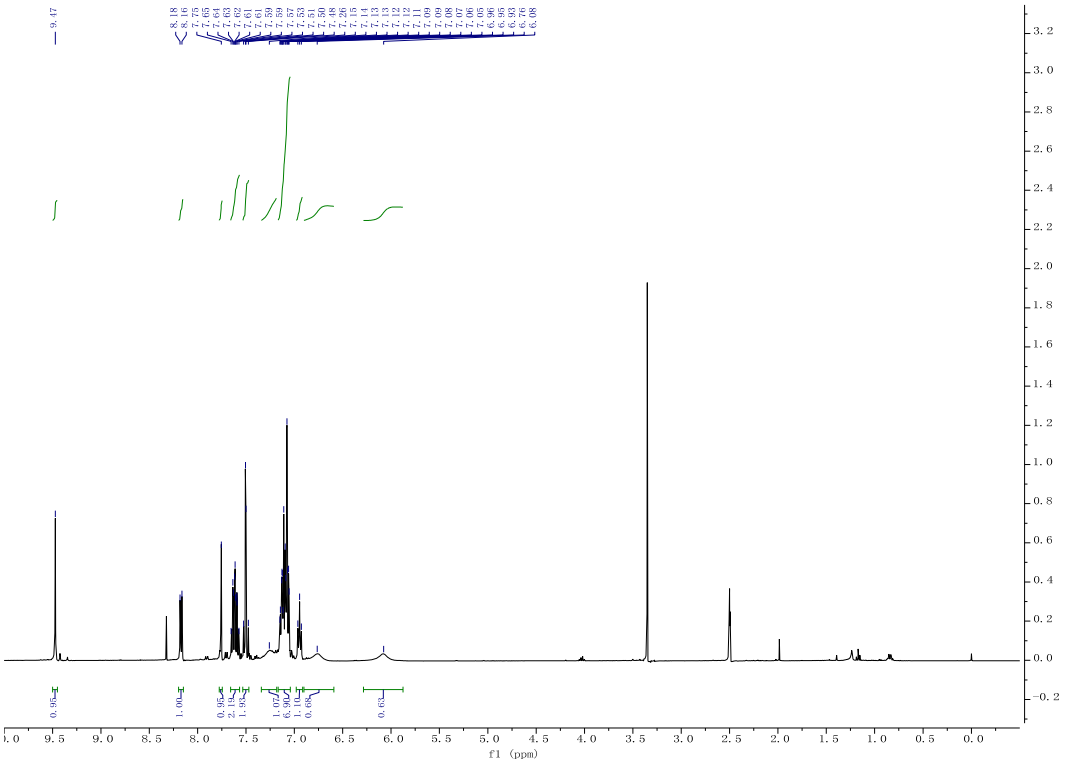


^{13}C NMR (101 MHz, DMSO-d_6) Compound **3la**

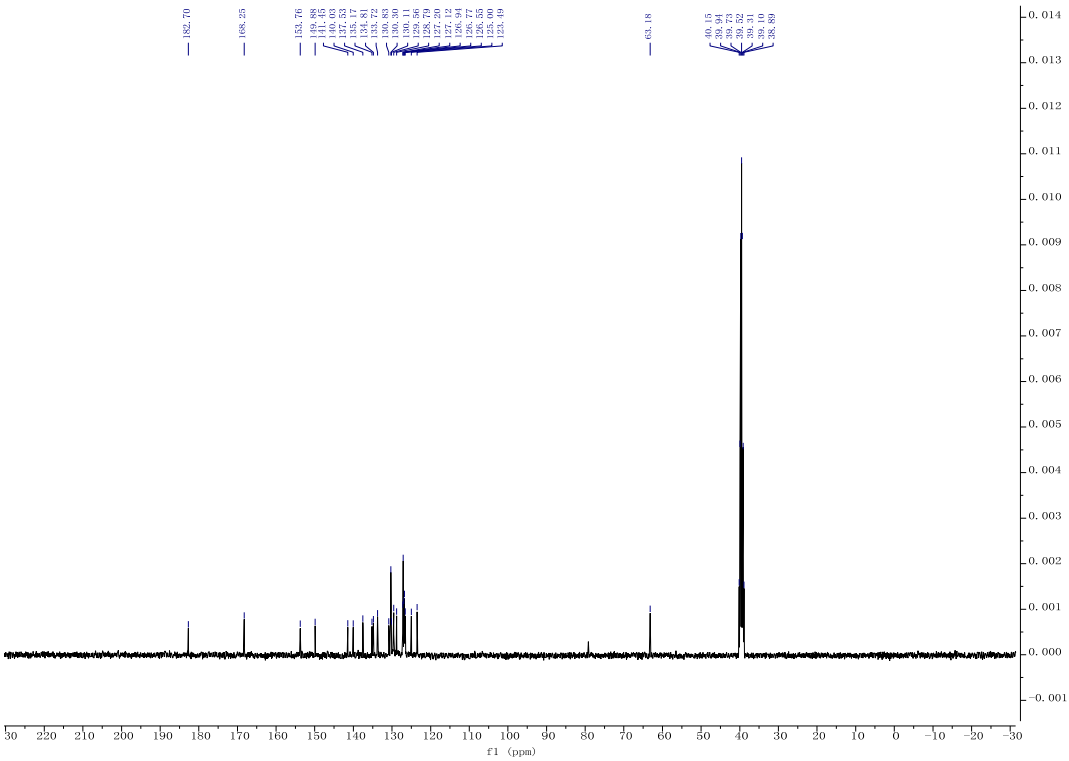


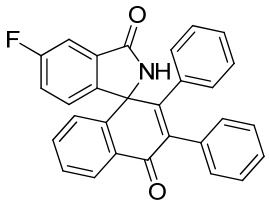


^{1}H NMR (400 MHz, DMSO-d_6) Compound **3ma**

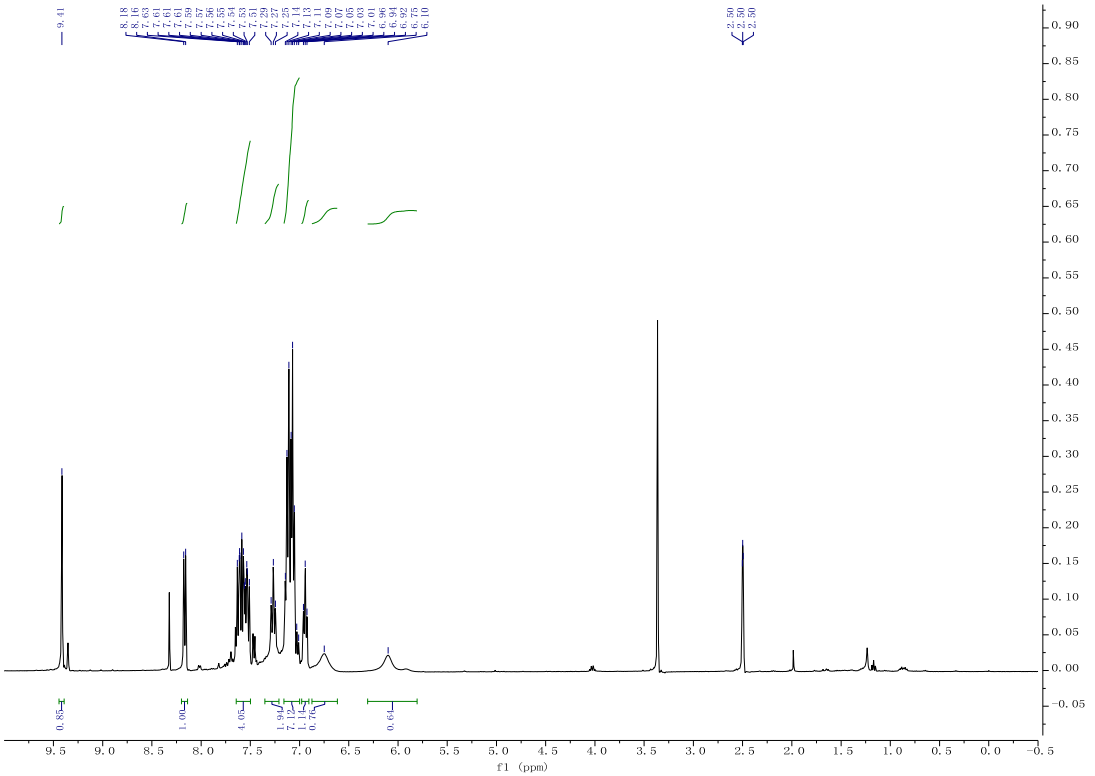


^{13}C NMR (101 MHz, DMSO-d_6) Compound **ma**

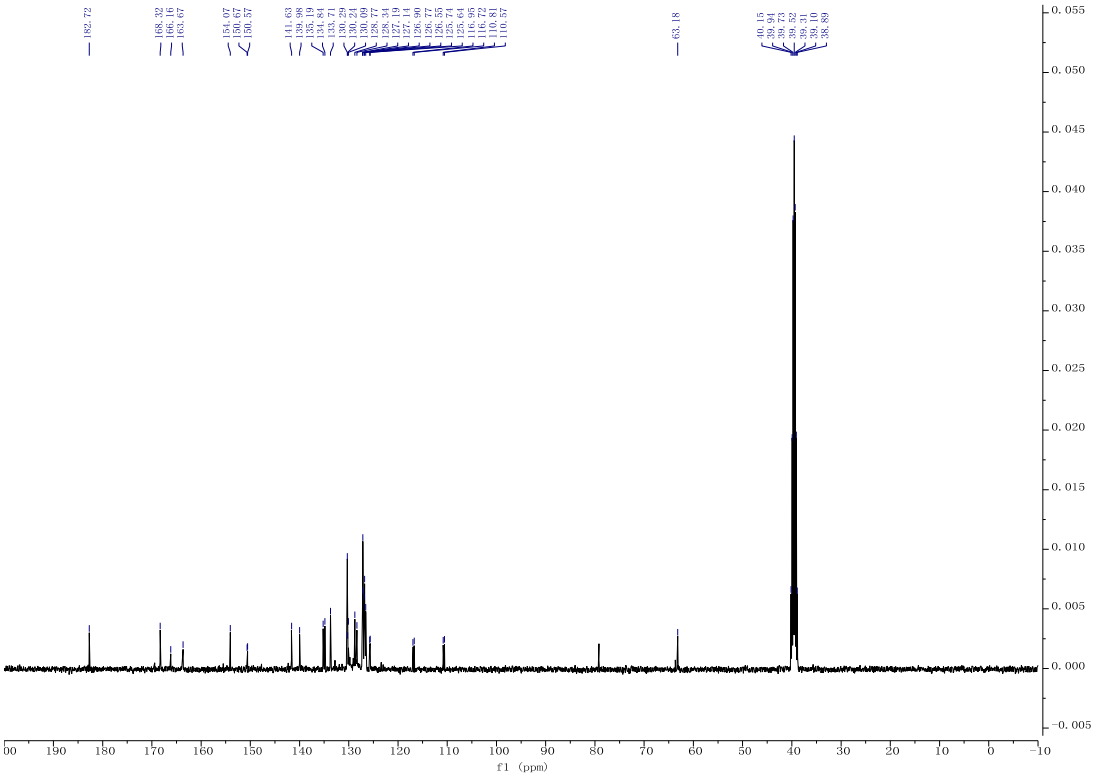




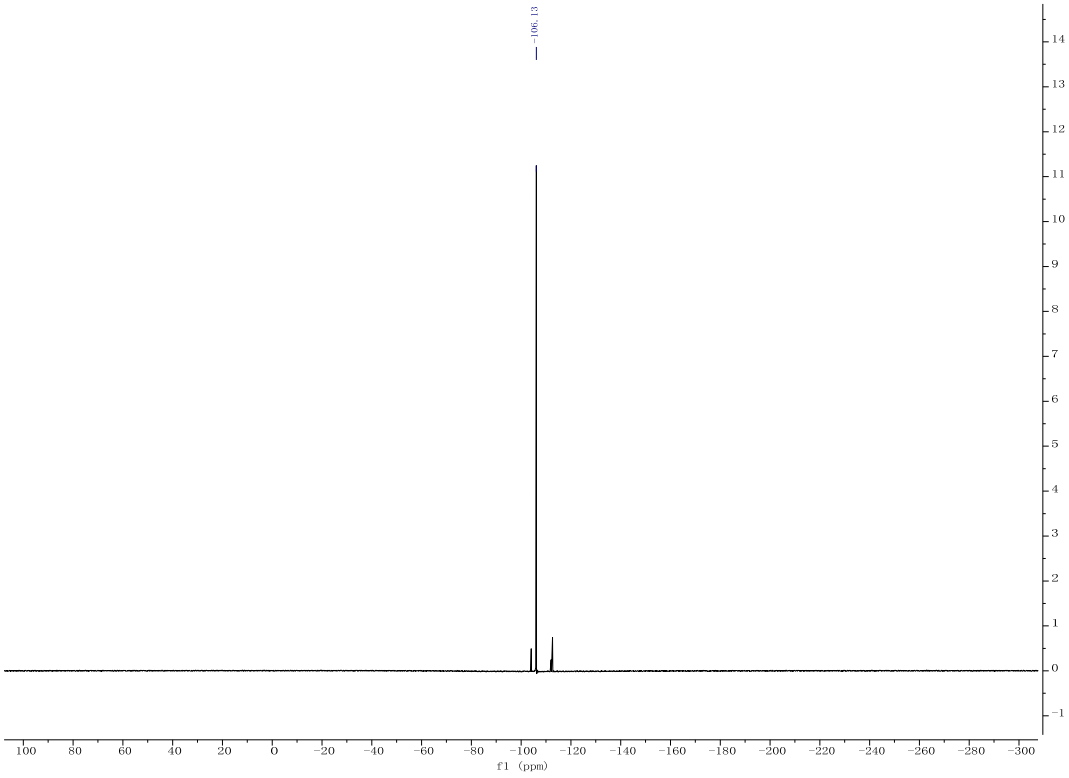
^{1}H NMR (400 MHz, DMSO-d_6) Compound **3na**

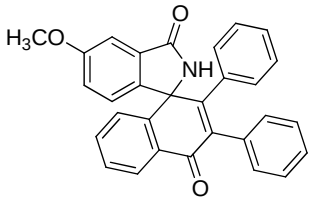


^{13}C NMR (101 MHz, DMSO-d_6) Compound **3na**

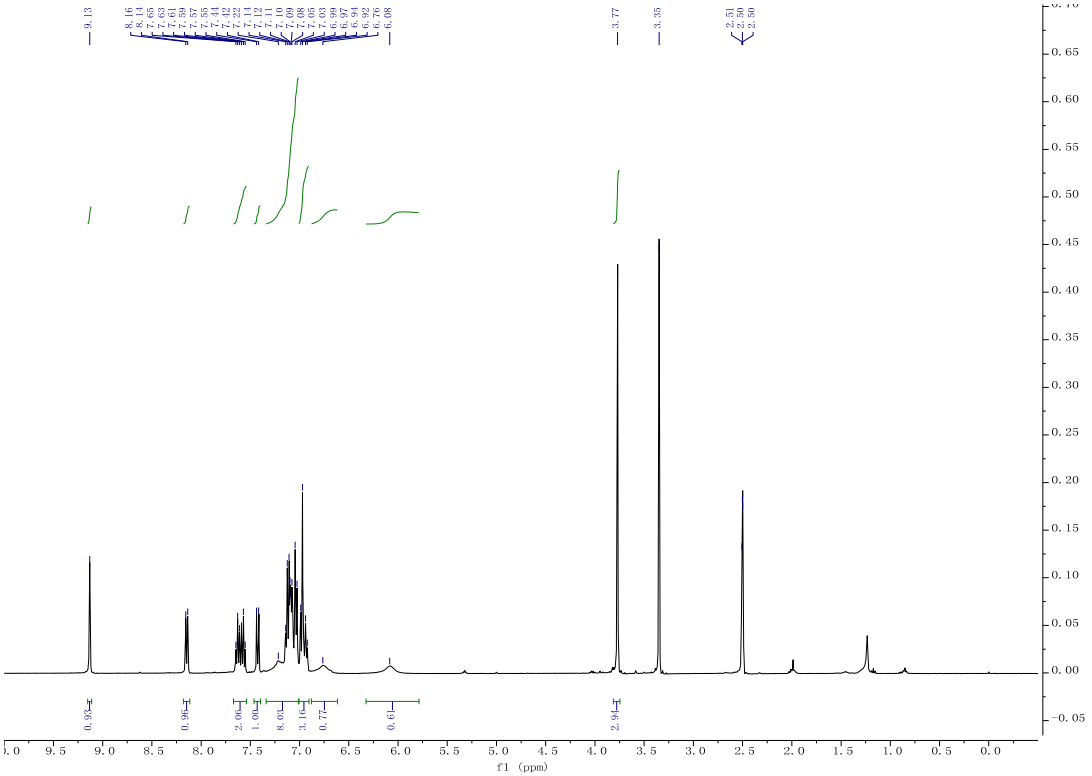


^{19}F NMR (376 MHz, DMSO-d_6) Compound 3**na**

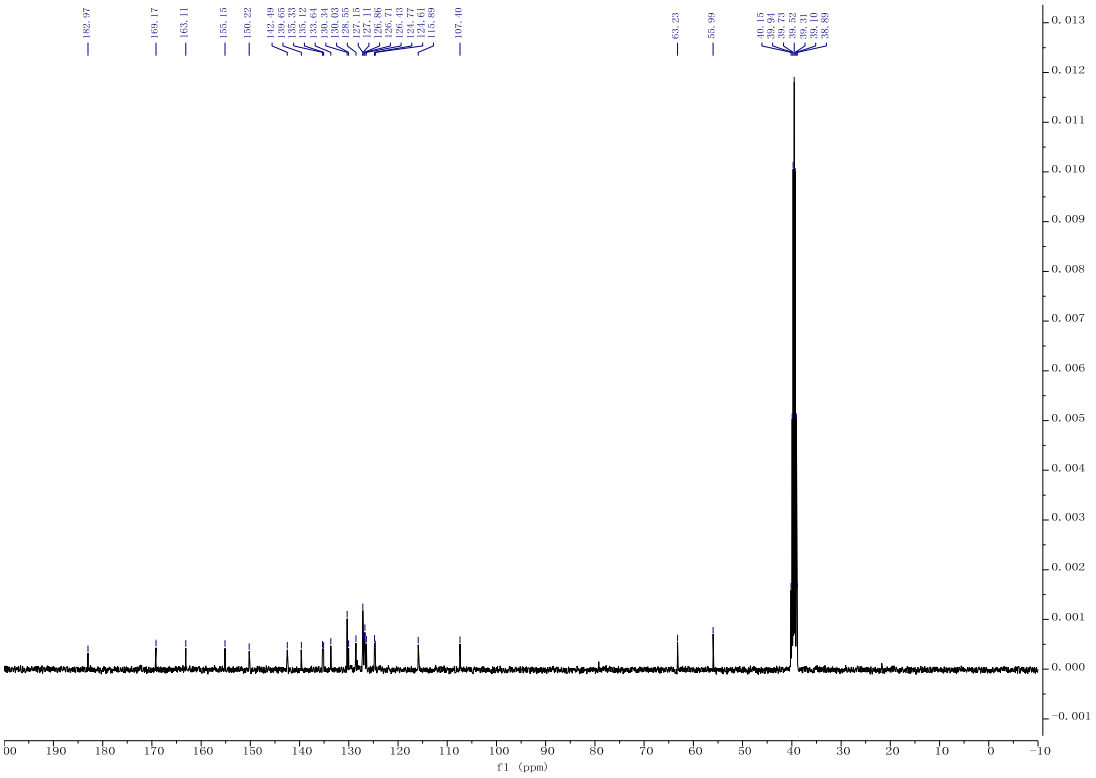


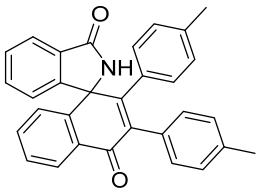


^{1}H NMR (400 MHz, DMSO-d_6) Compound **3oa**

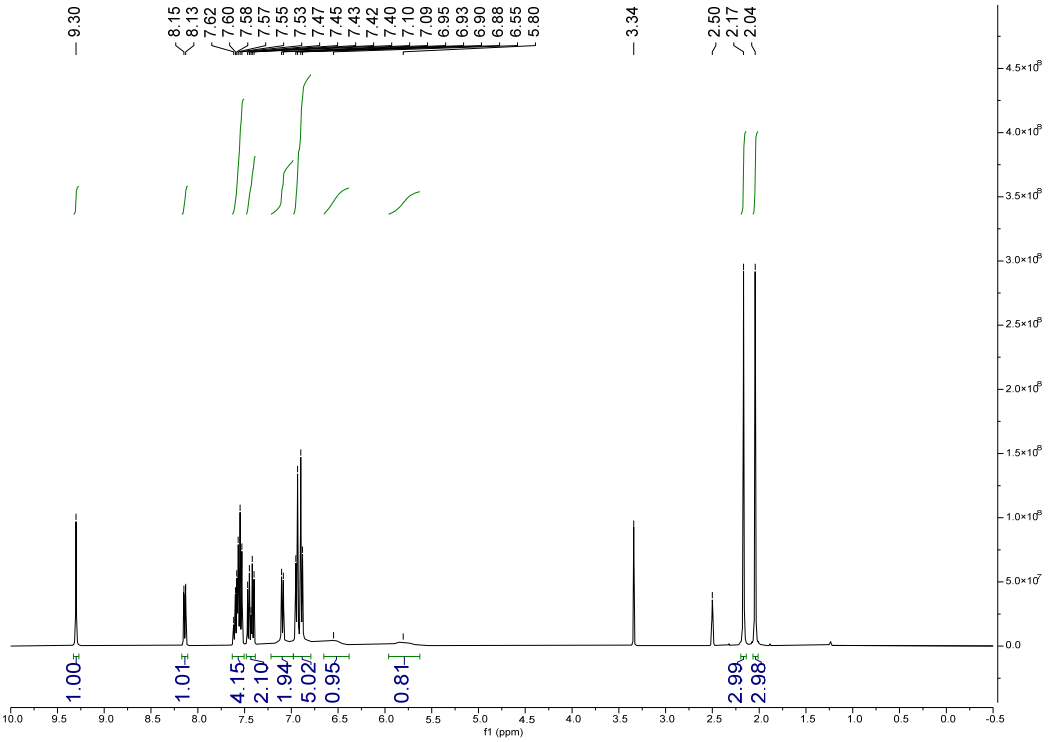


^{13}C NMR (101 MHz, DMSO-d_6) Compound **3oa**

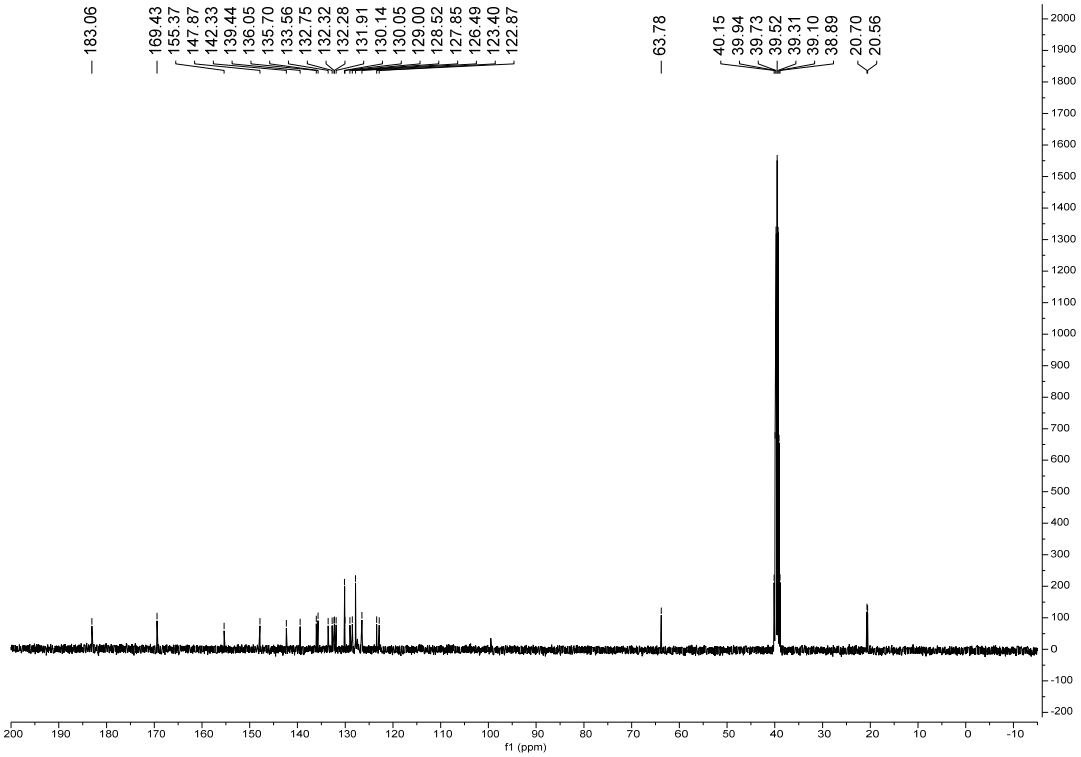


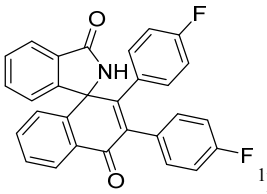


^{1}H NMR (400 MHz, DMSO-d_6) Compound **3ab**



^{13}C NMR (101 MHz, DMSO-d_6) Compound **3ab**





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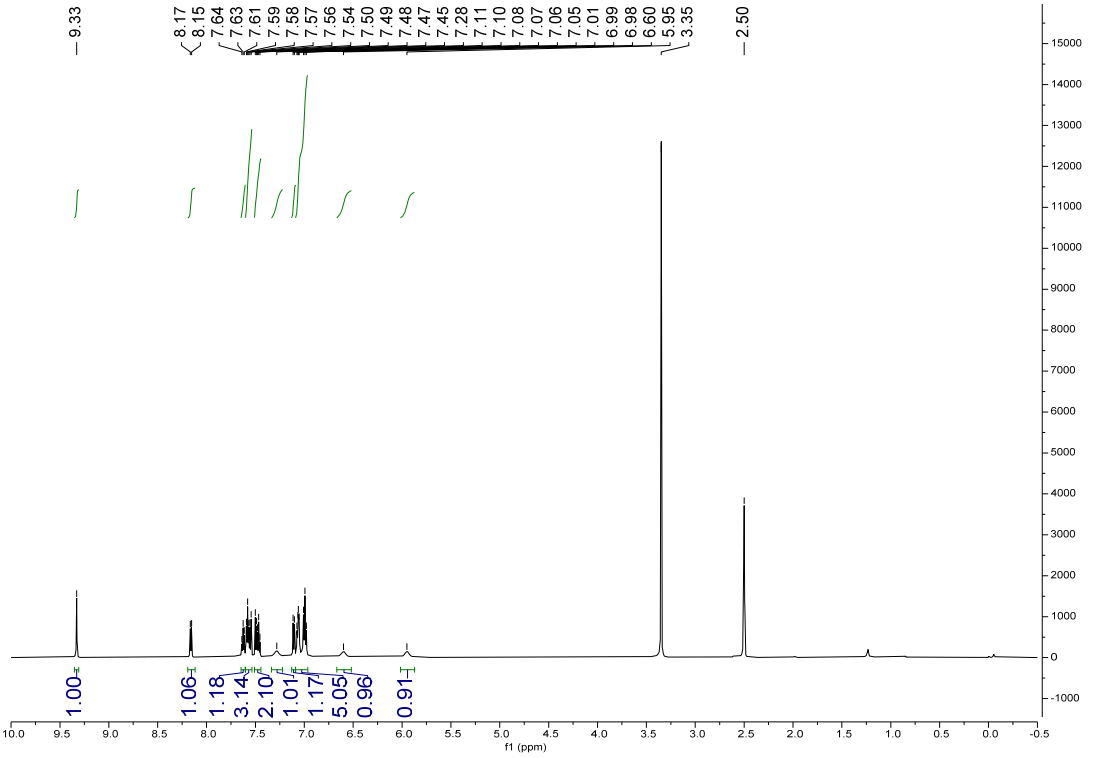
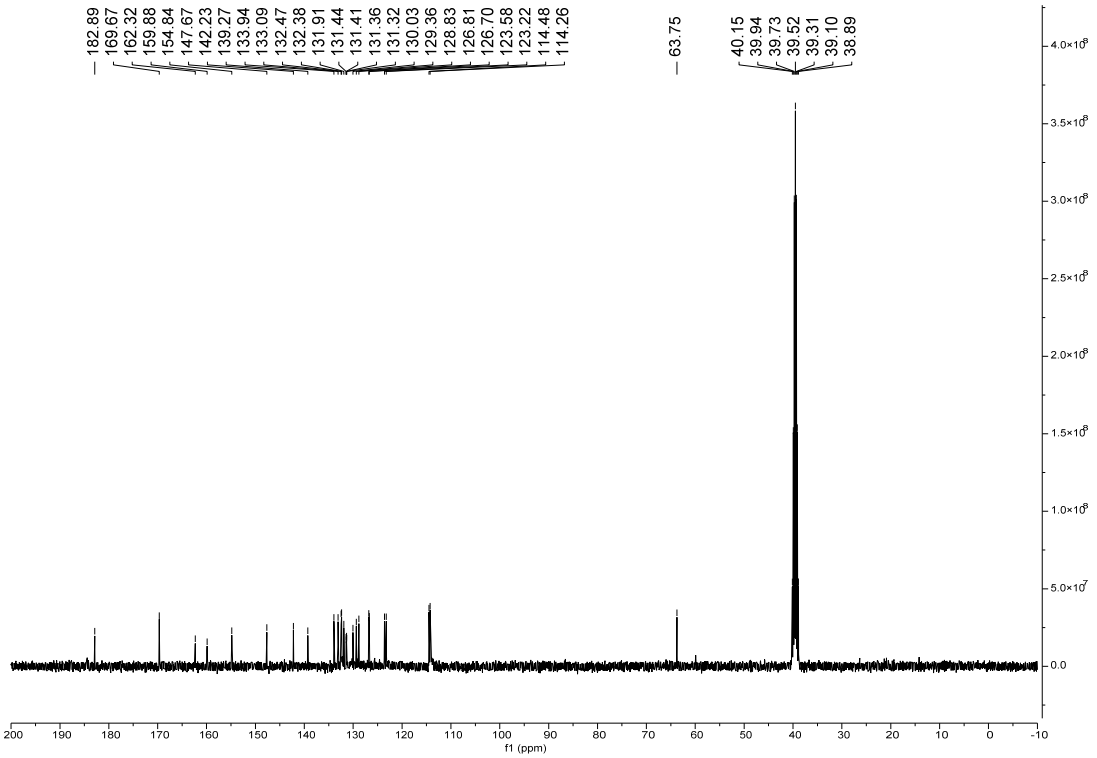
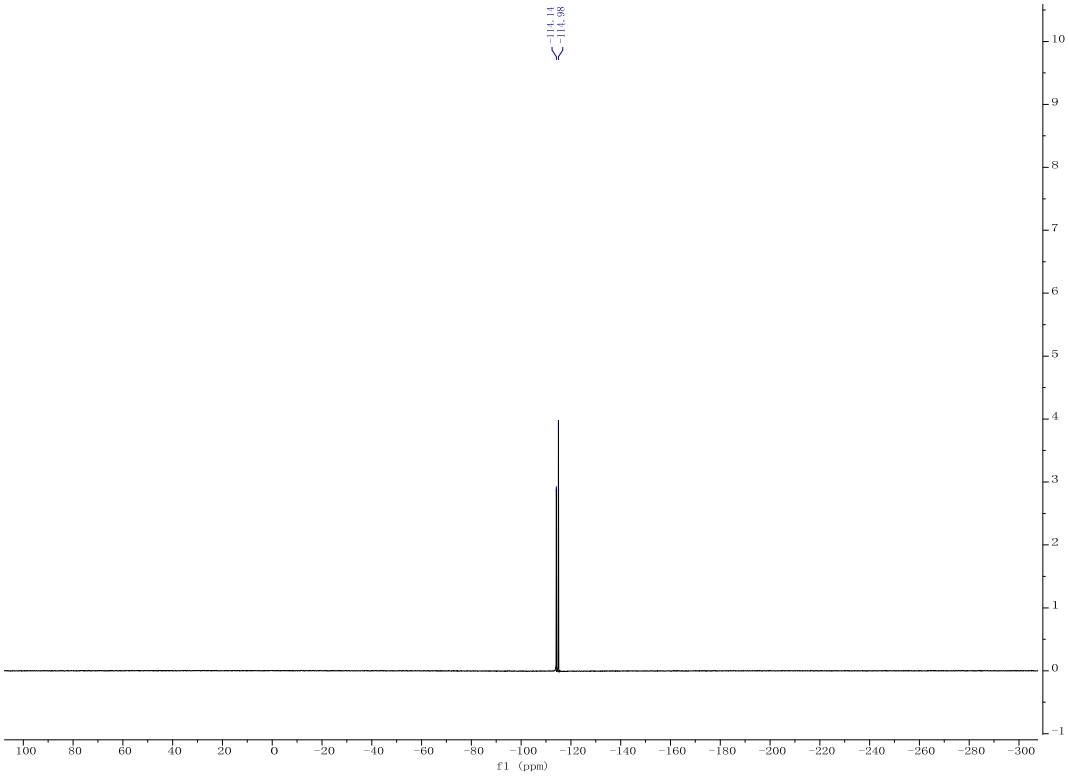
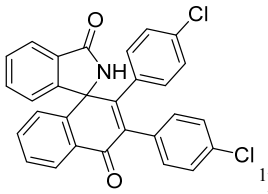


^{13}C NMR (101 MHz, DMSO-d_6) Compound **3ac**

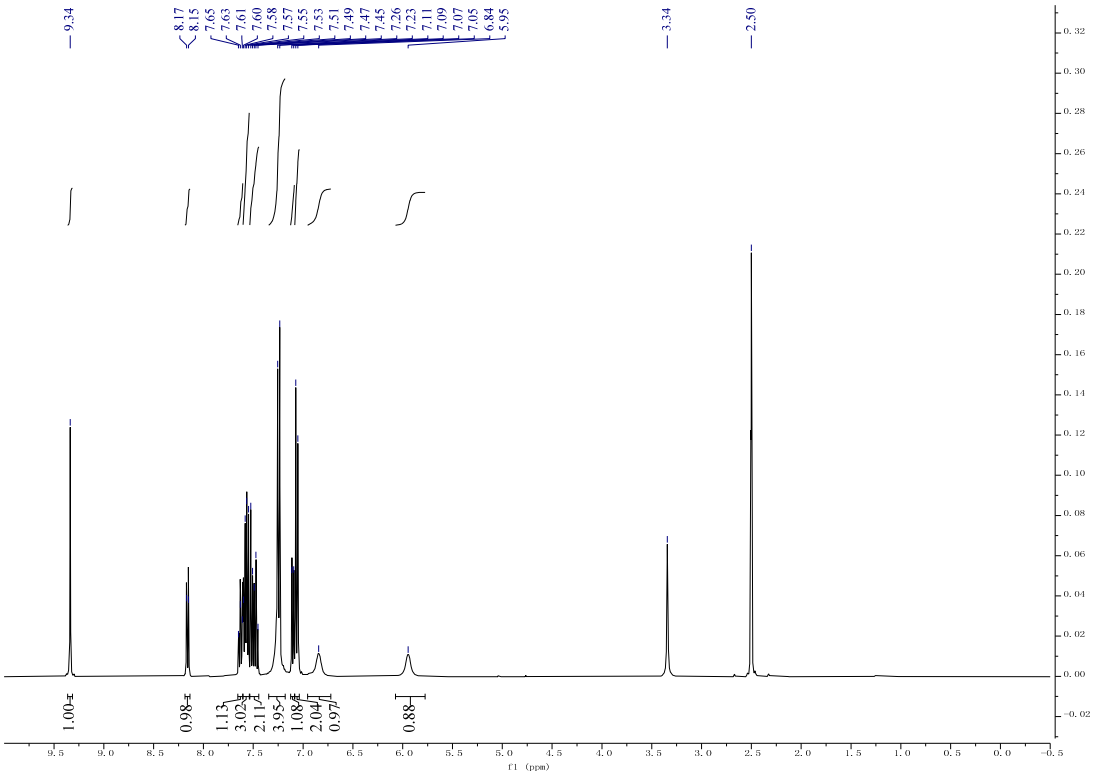


^{19}F NMR (376 MHz, DMSO-d_6) Compound 3**ac**

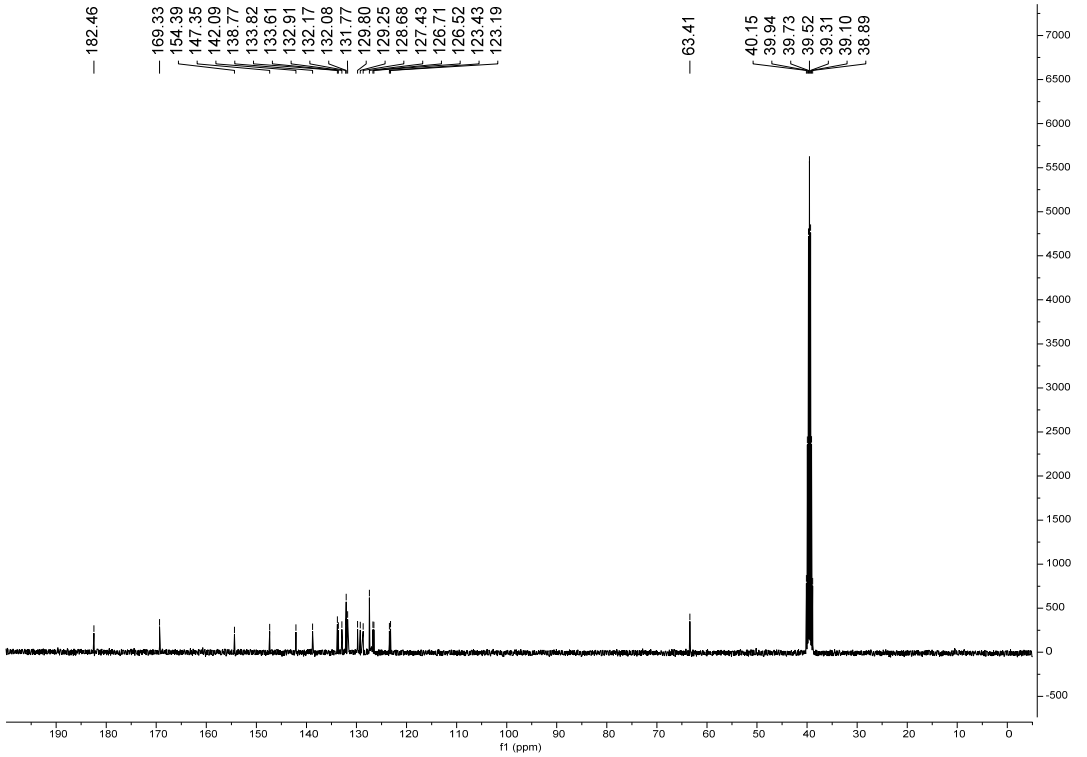


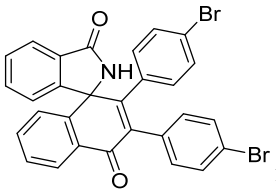


^{1}H NMR (400 MHz, DMSO-d_6) Compound **3ad**

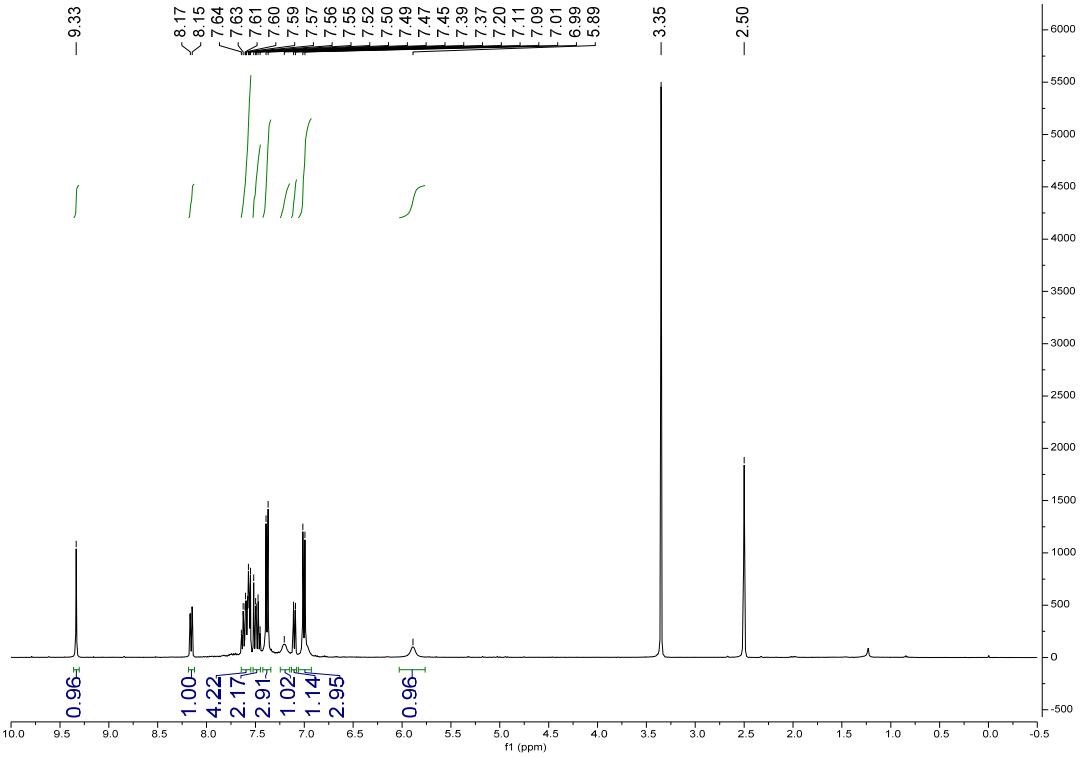


^{13}C NMR (101 MHz, DMSO-d_6) Compound **3ad**

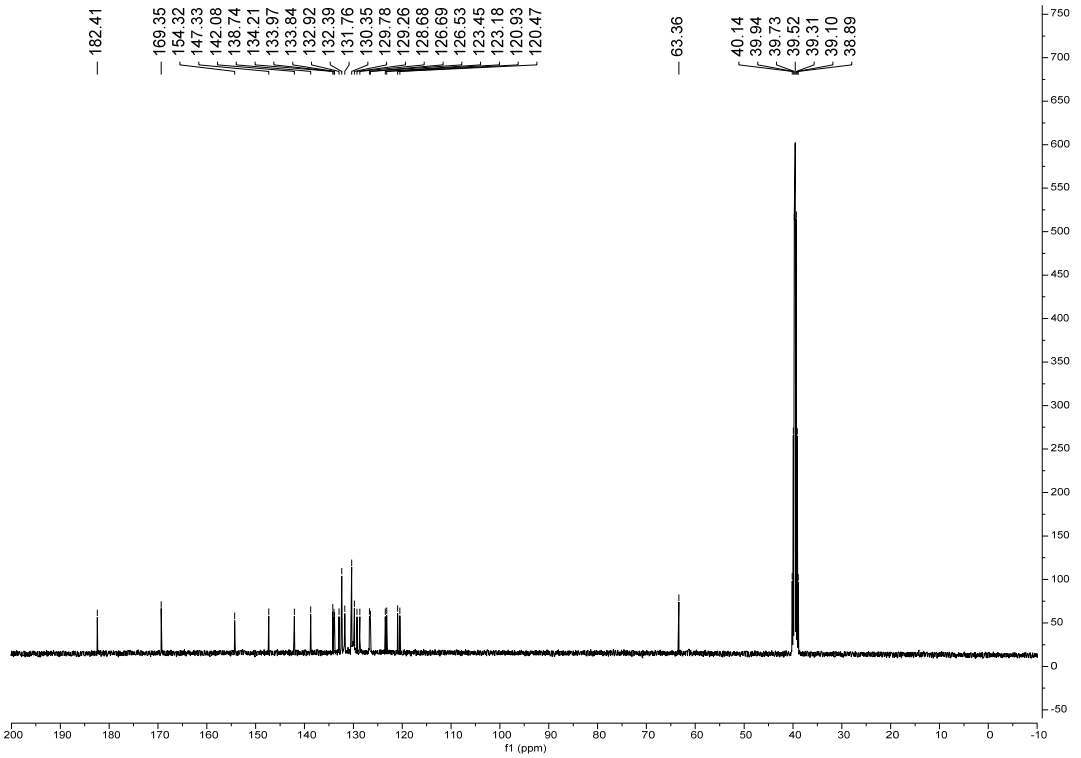


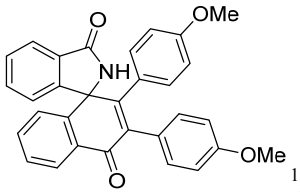


^{1}H NMR (400 MHz, DMSO-d_6) Compound **3ae**



^{13}C NMR (101 MHz, DMSO-d_6) Compound **3ae**





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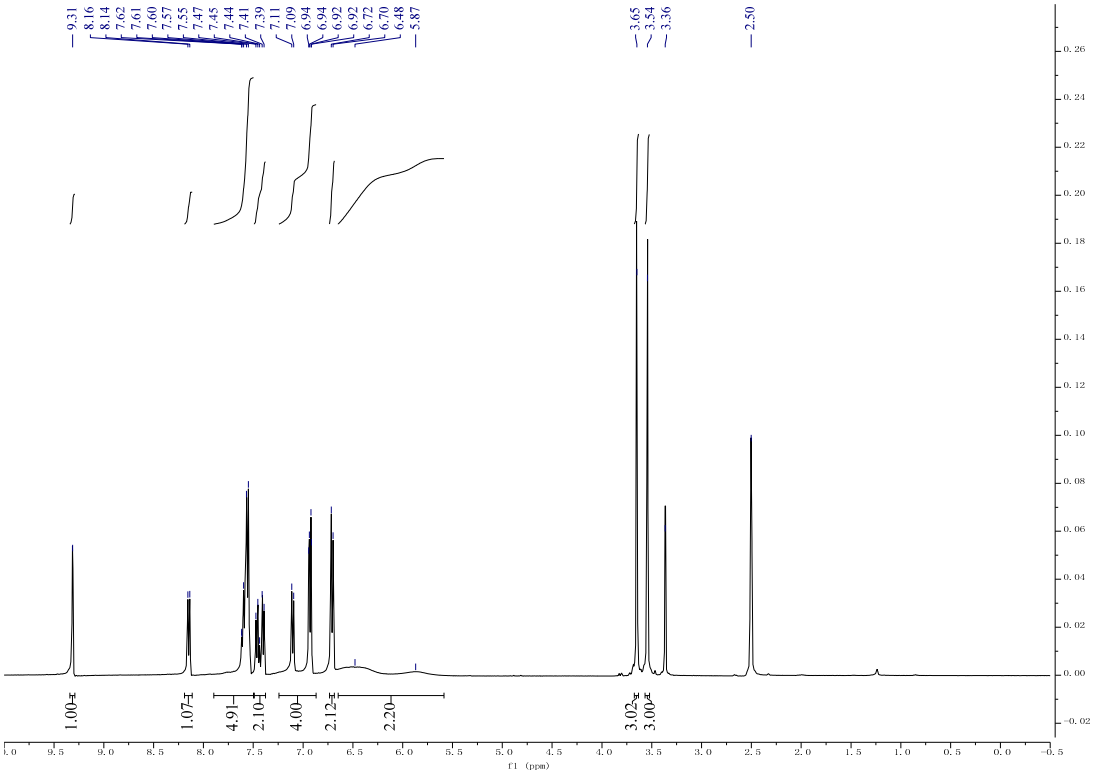

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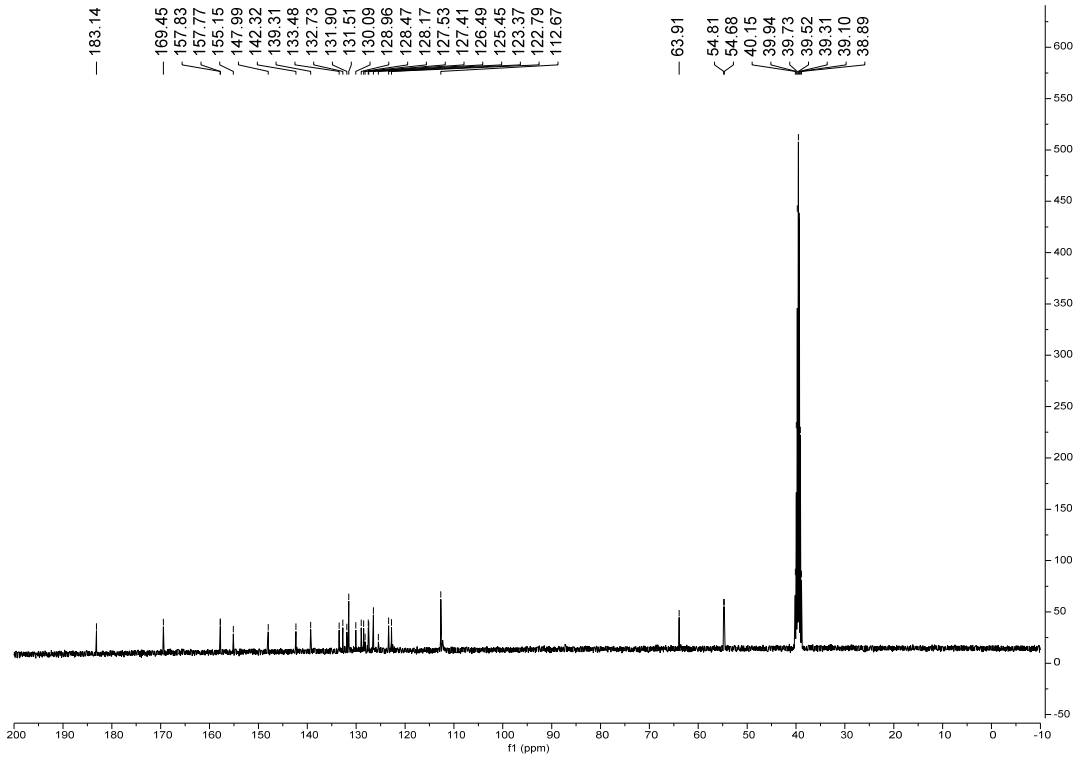

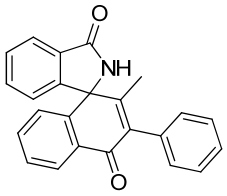

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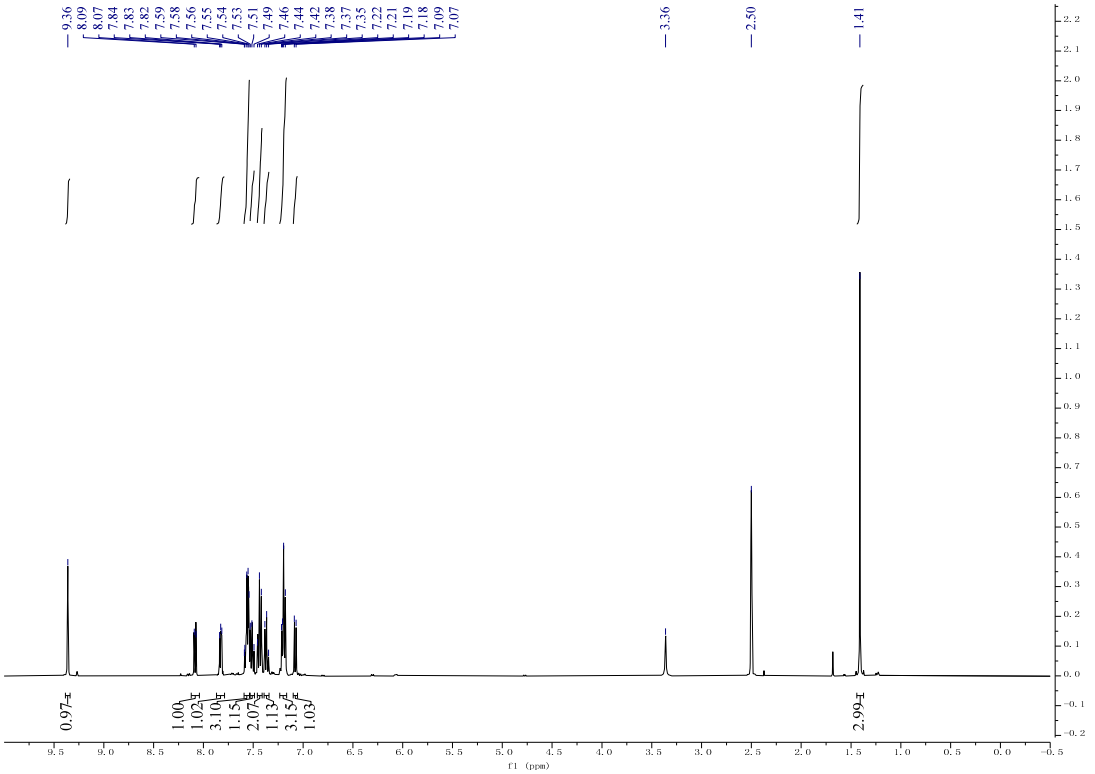
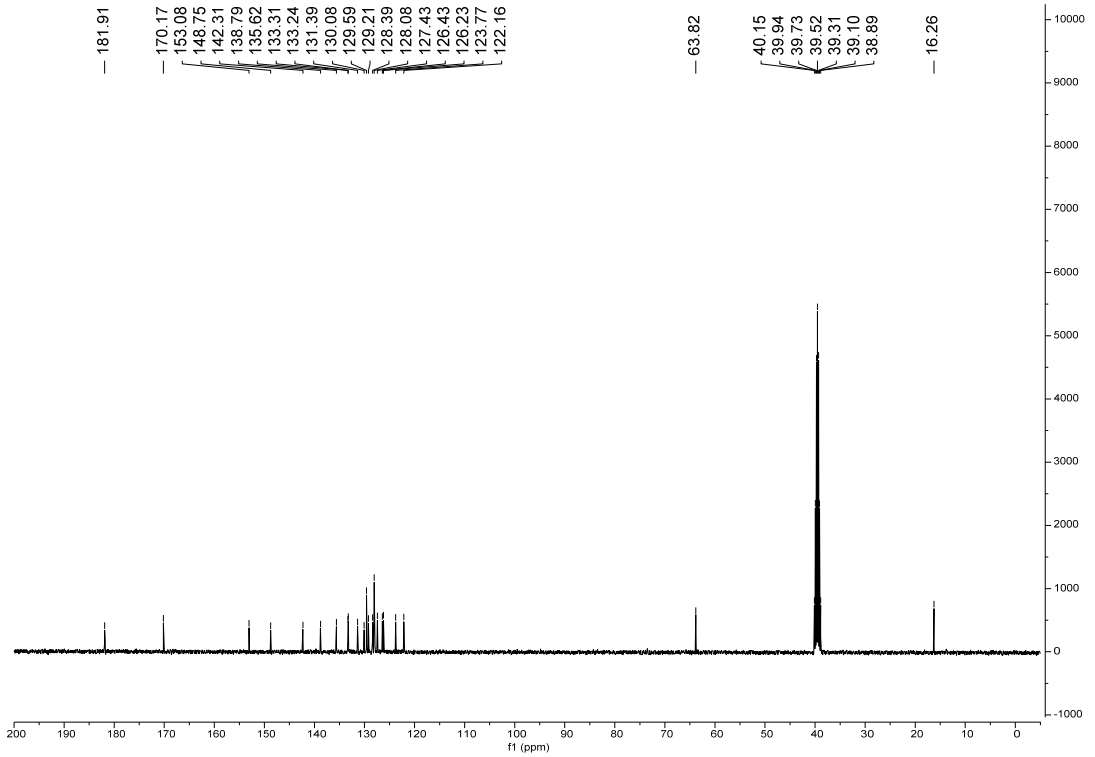
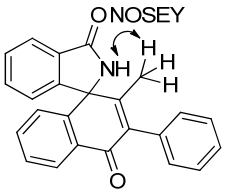
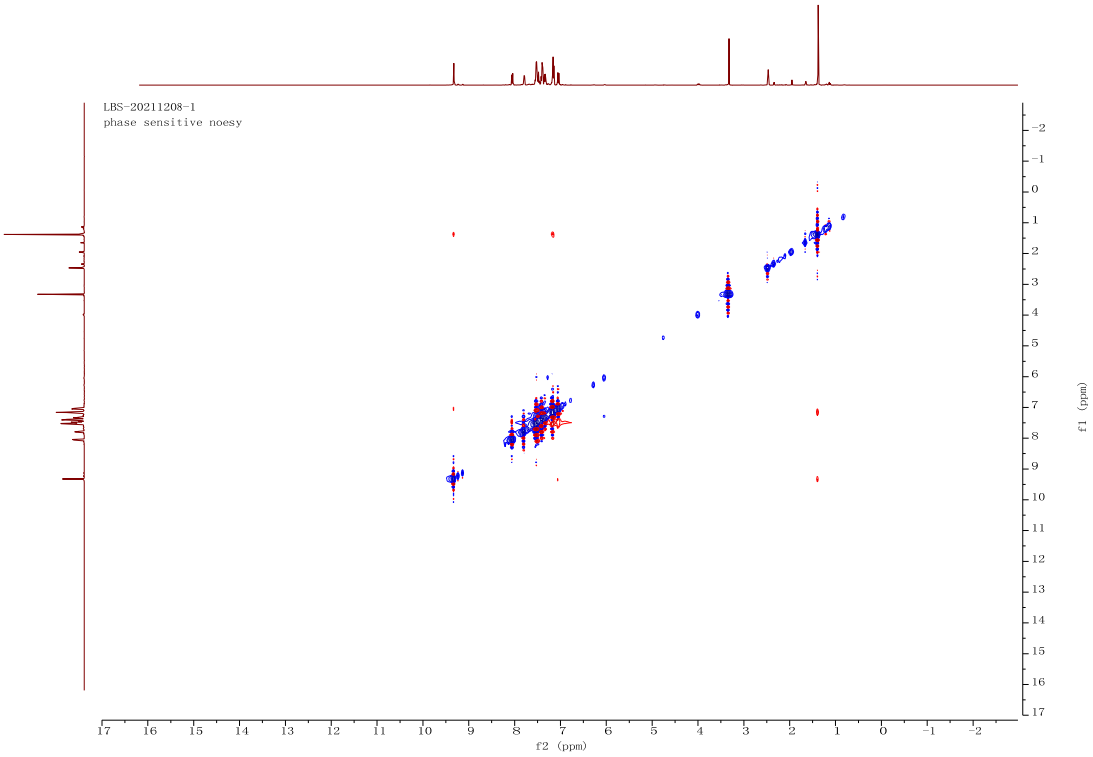


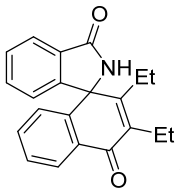
^{13}C NMR (101 MHz, DMSO-d_6) Compound **3ag**



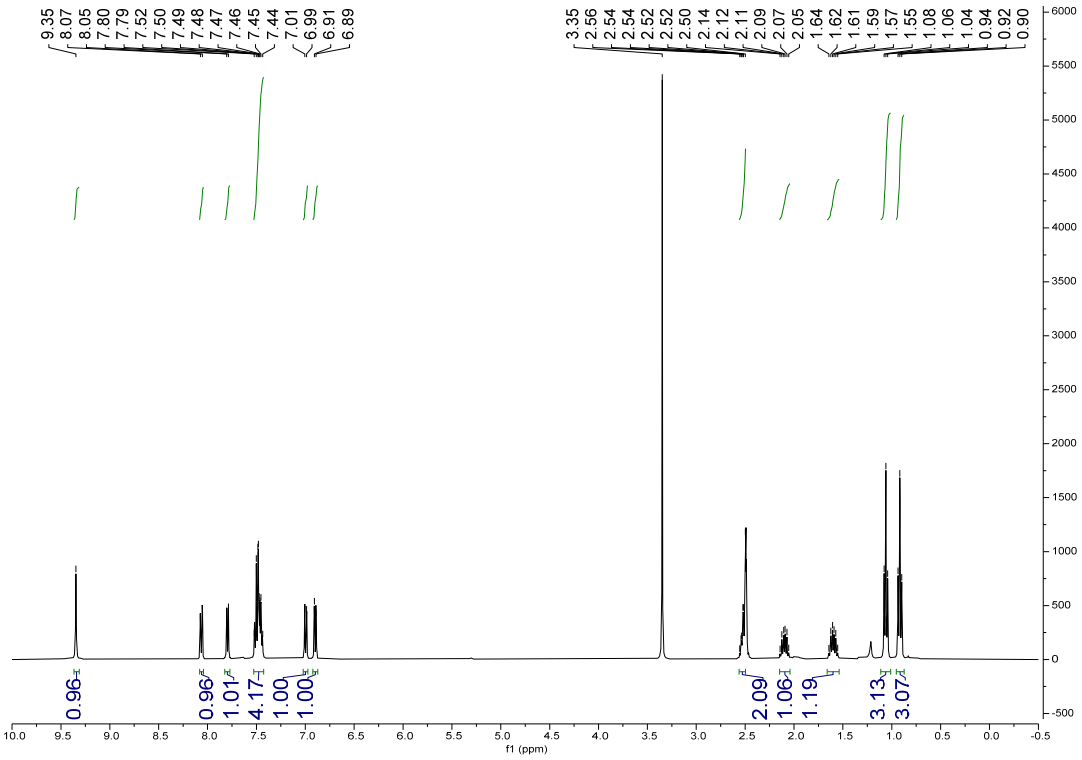


NOE experiment of compound **3ag**

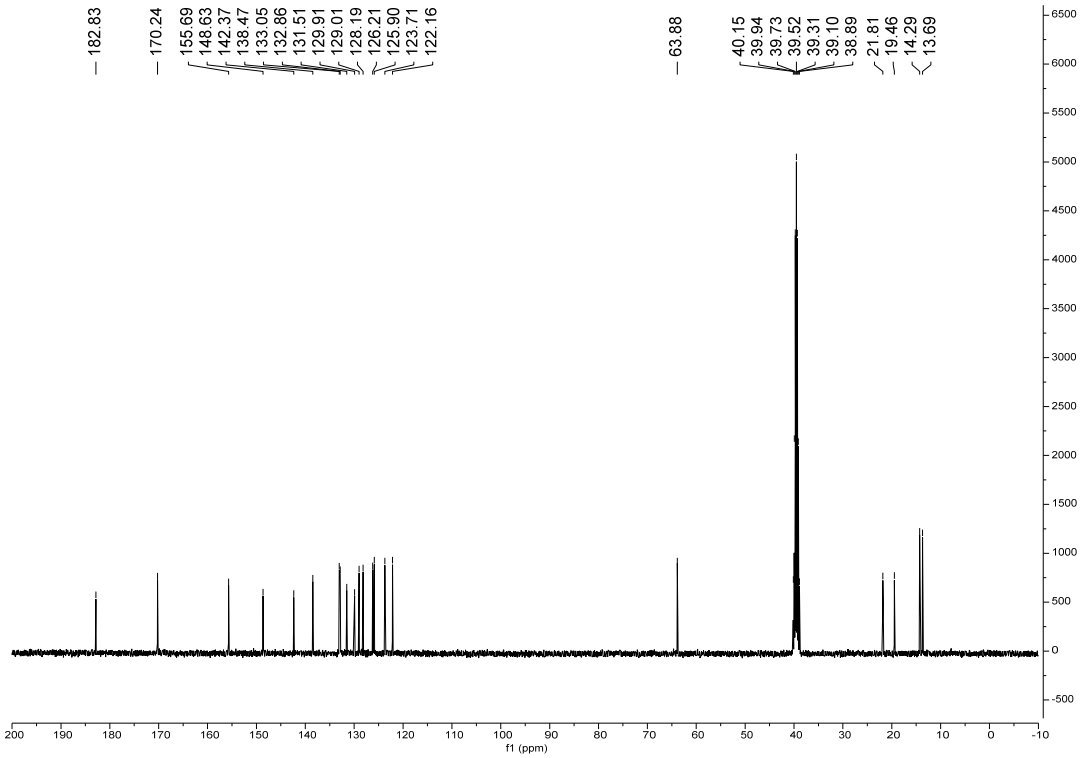


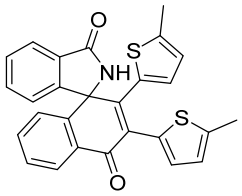


^{1}H NMR (400 MHz, DMSO-d_6) Compound **3ah**

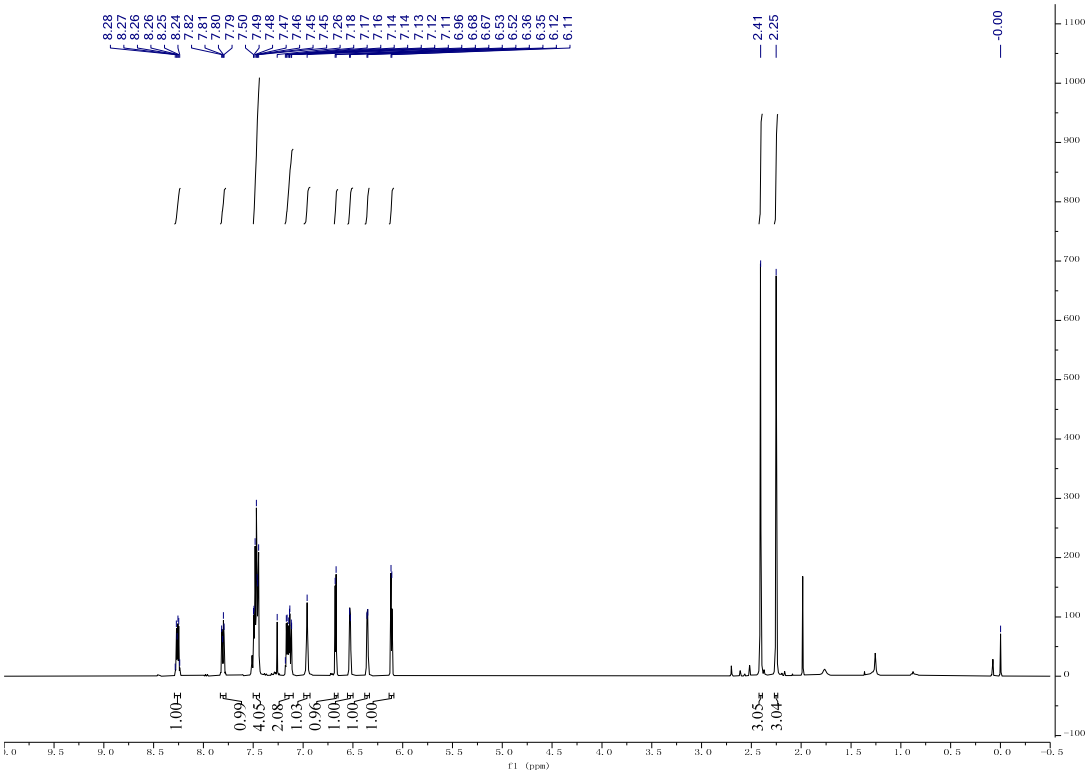


^{13}C NMR (101 MHz, DMSO-d_6) Compound **3ah**

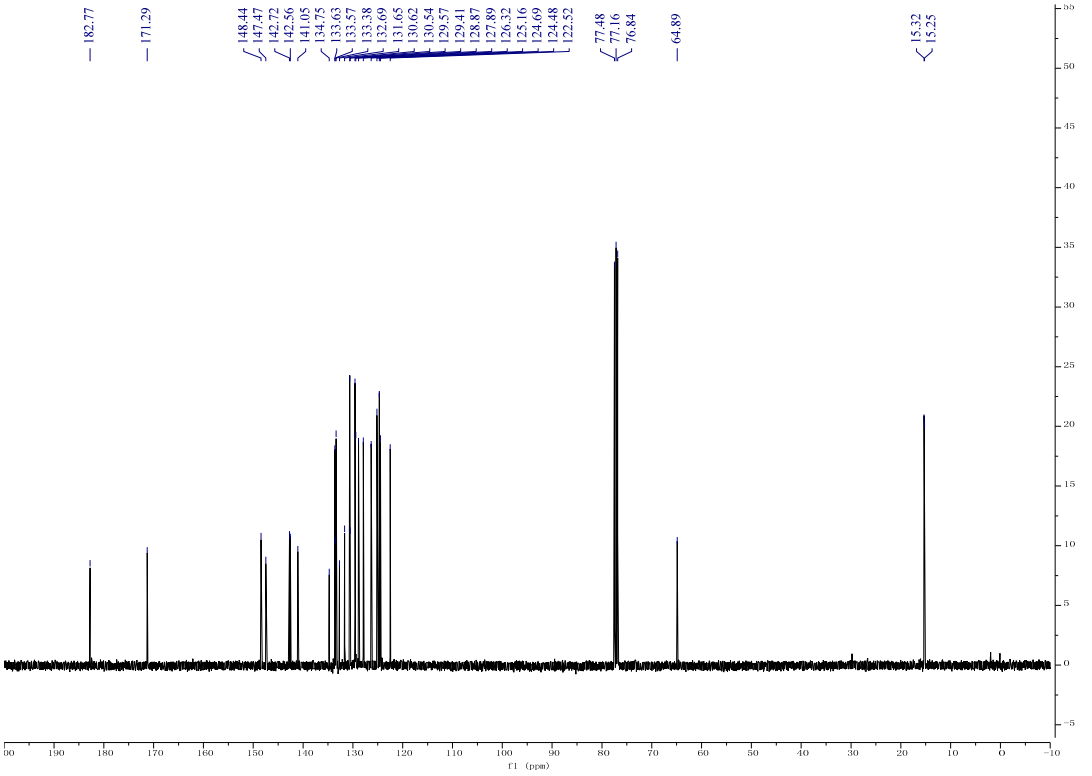


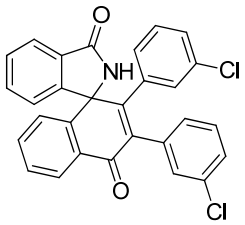


^{1}H NMR (400 MHz, DMSO-d_6) Compound **3ai**

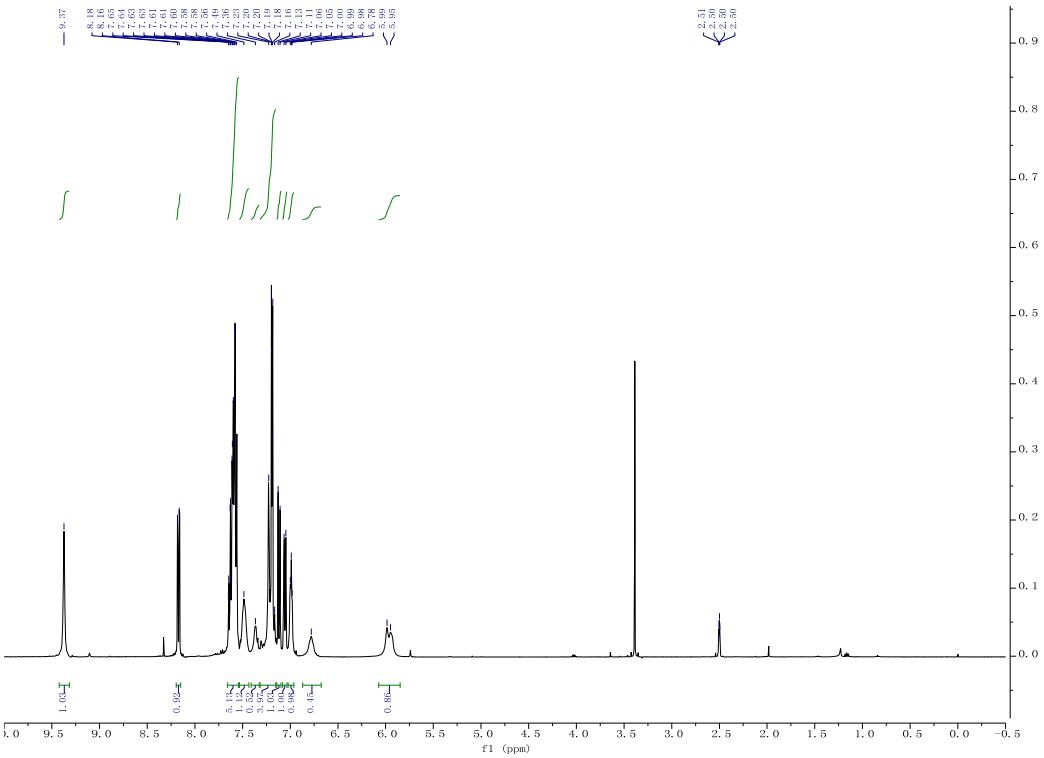


^{13}C NMR (101 MHz, DMSO-d_6) Compound **3ai**

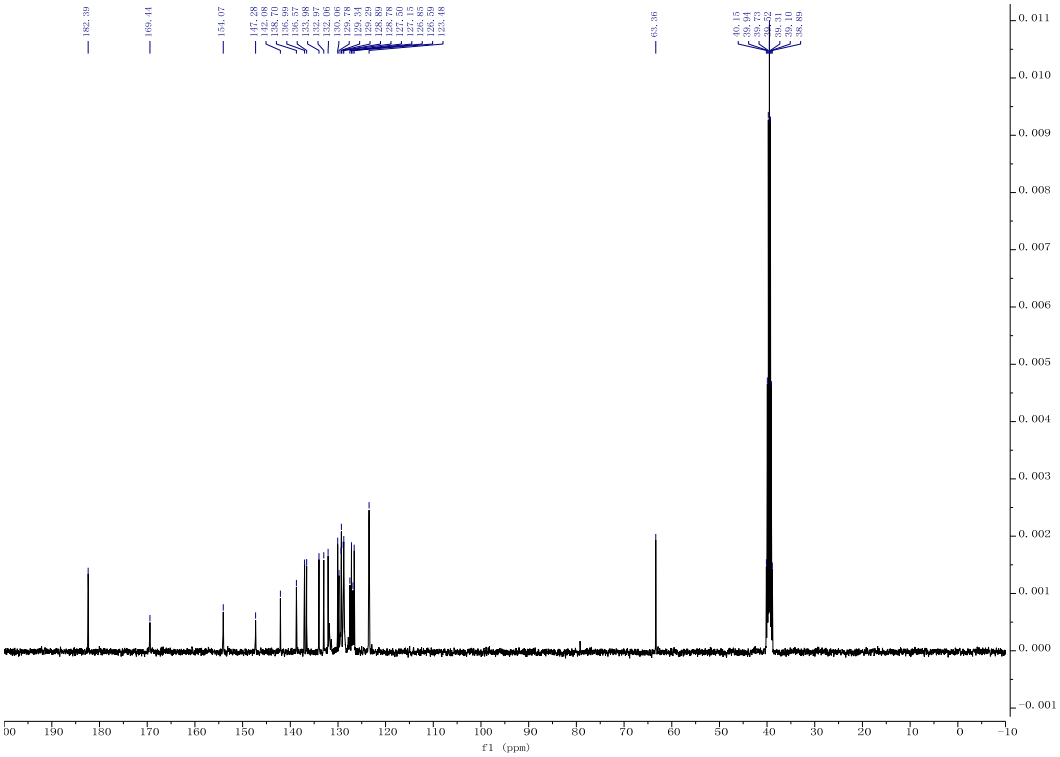


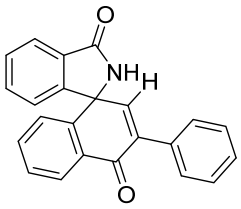


^{1}H NMR (400 MHz, DMSO-d_6) Compound **3aj**

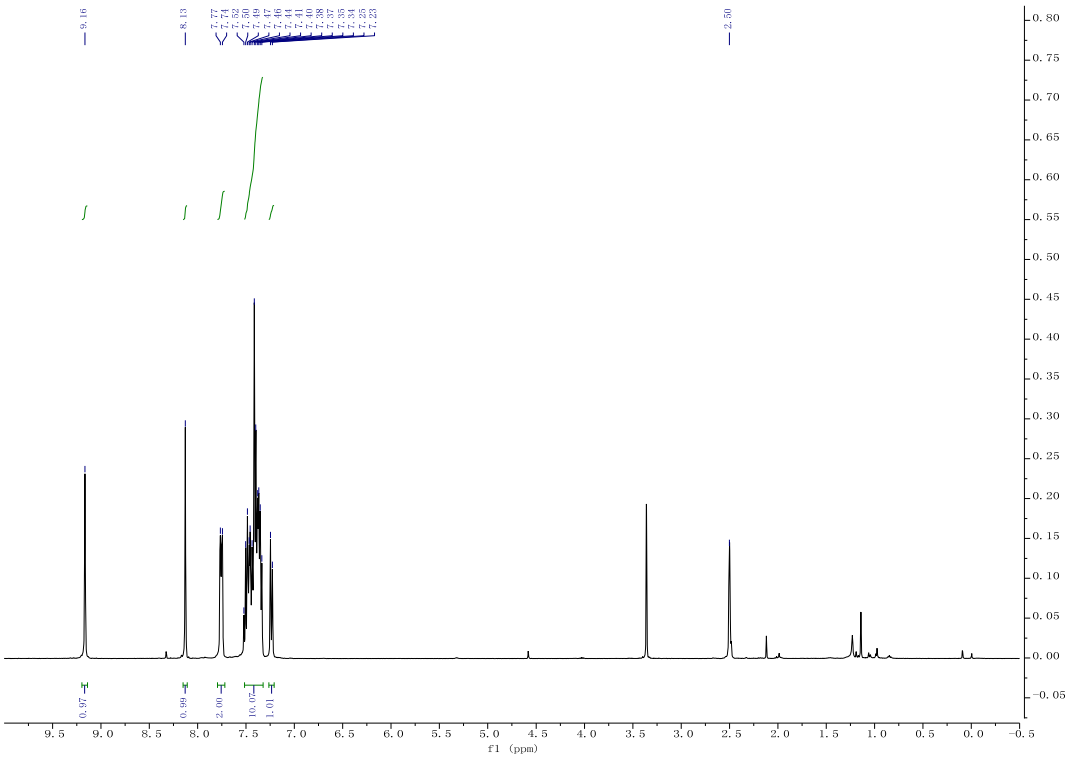


^{13}C NMR (101 MHz, DMSO-d_6) Compound **3aj**

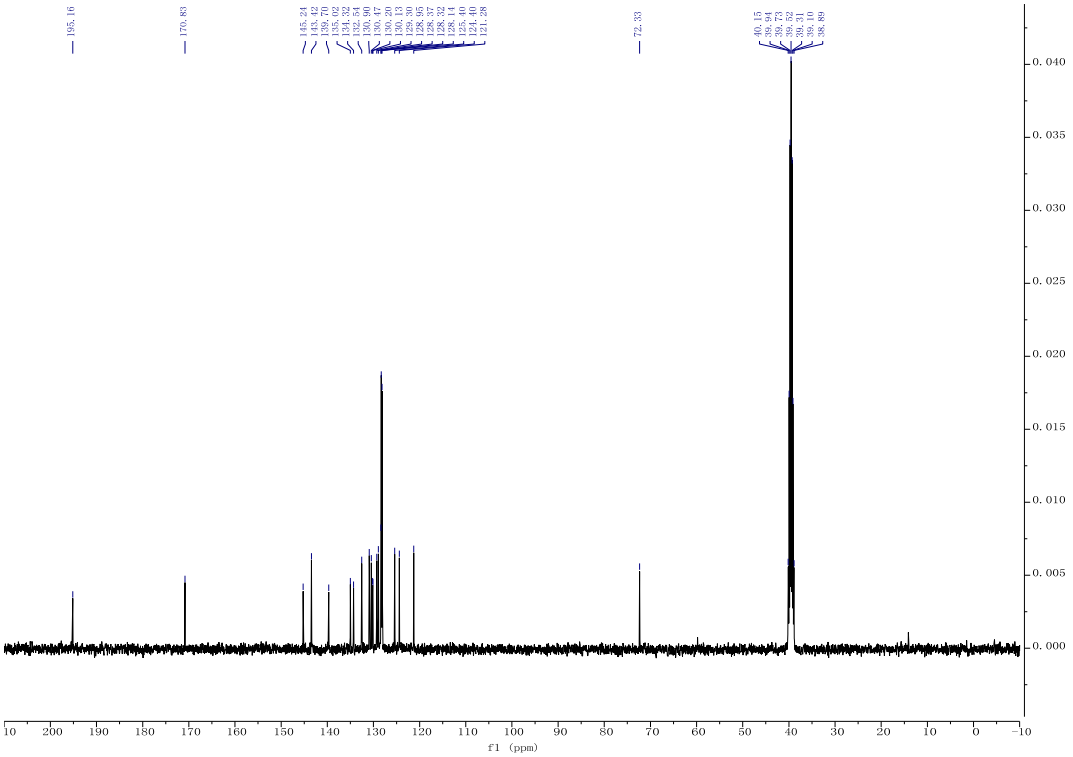


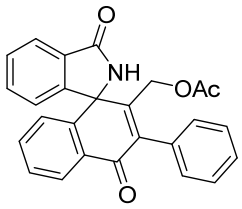


^{1}H NMR (400 MHz, DMSO-d_6) Compound **3ak**

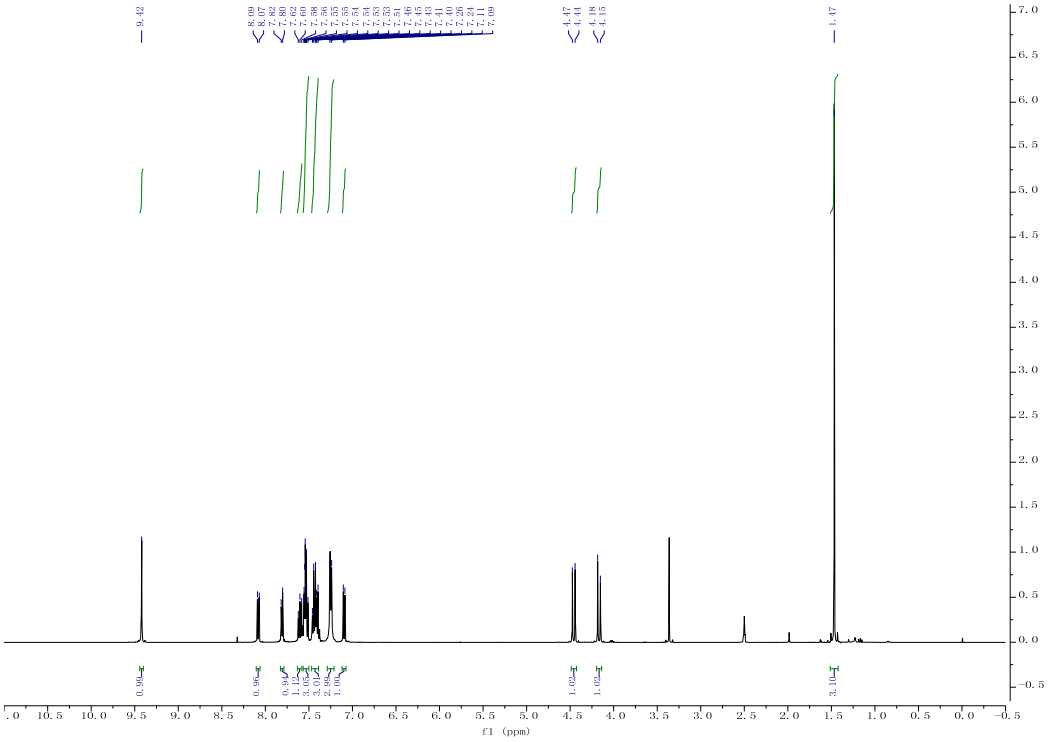


^{13}C NMR (101 MHz, DMSO-d_6) Compound **3ak**

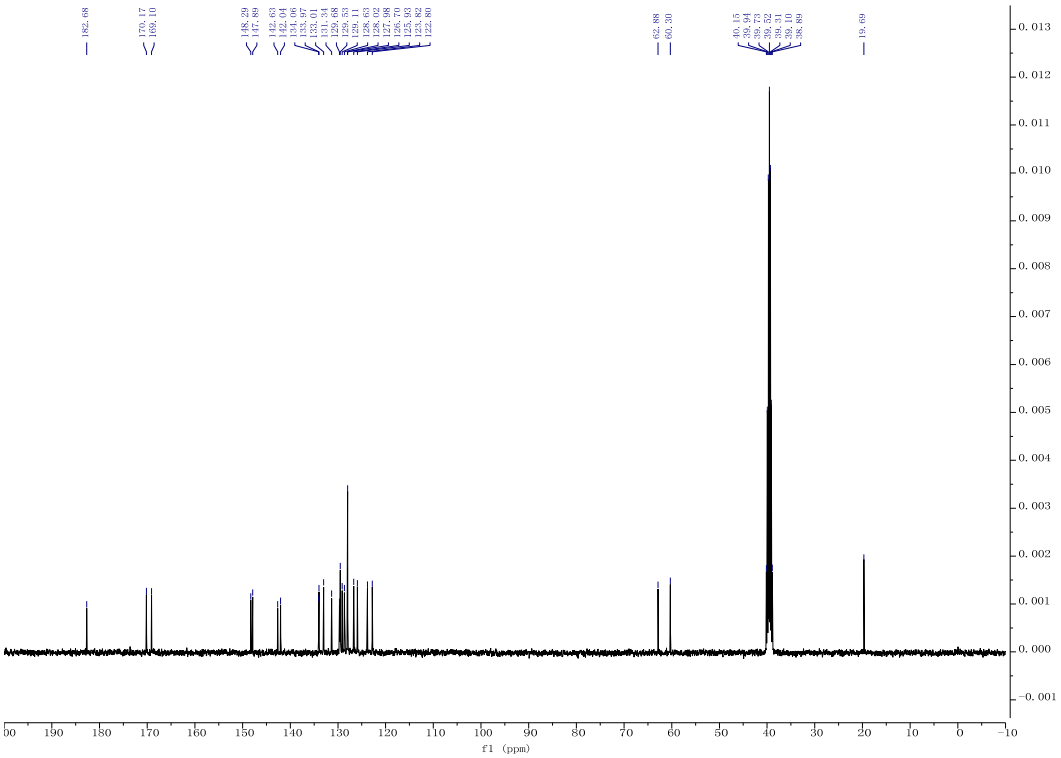


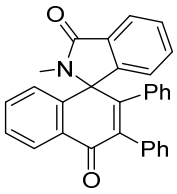


^{1}H NMR (400 MHz, DMSO-d_6) Compound **3al**

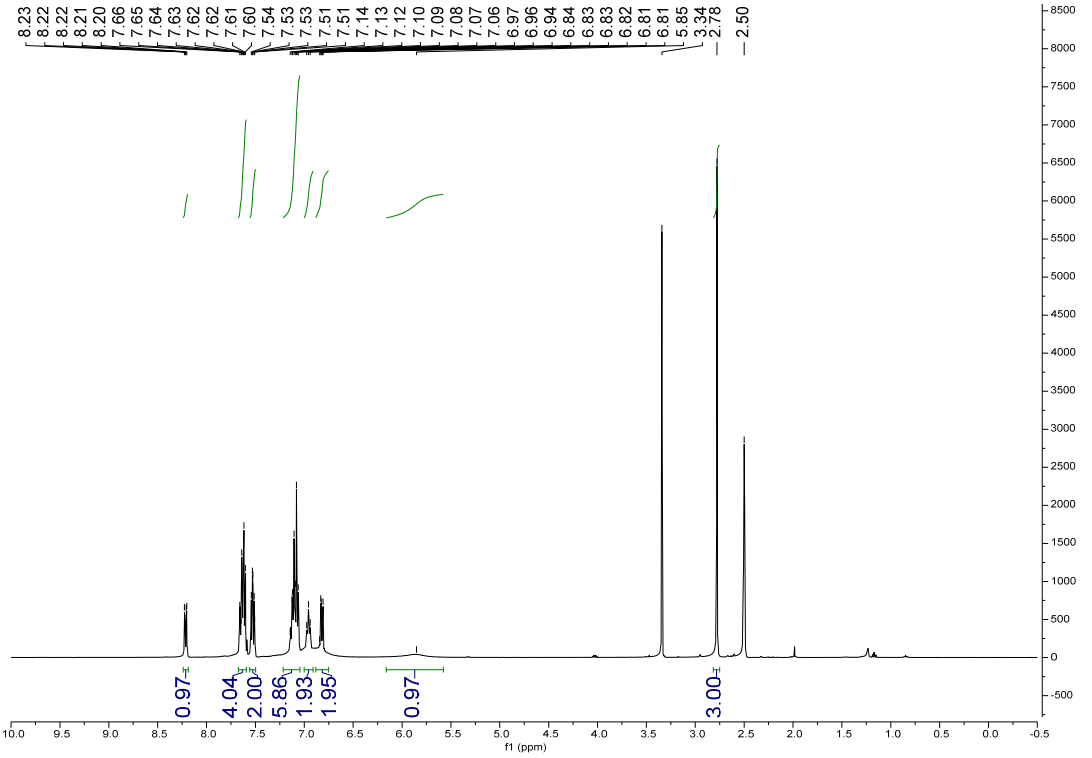


^{13}C NMR (101 MHz, DMSO-d_6) Compound **3al**

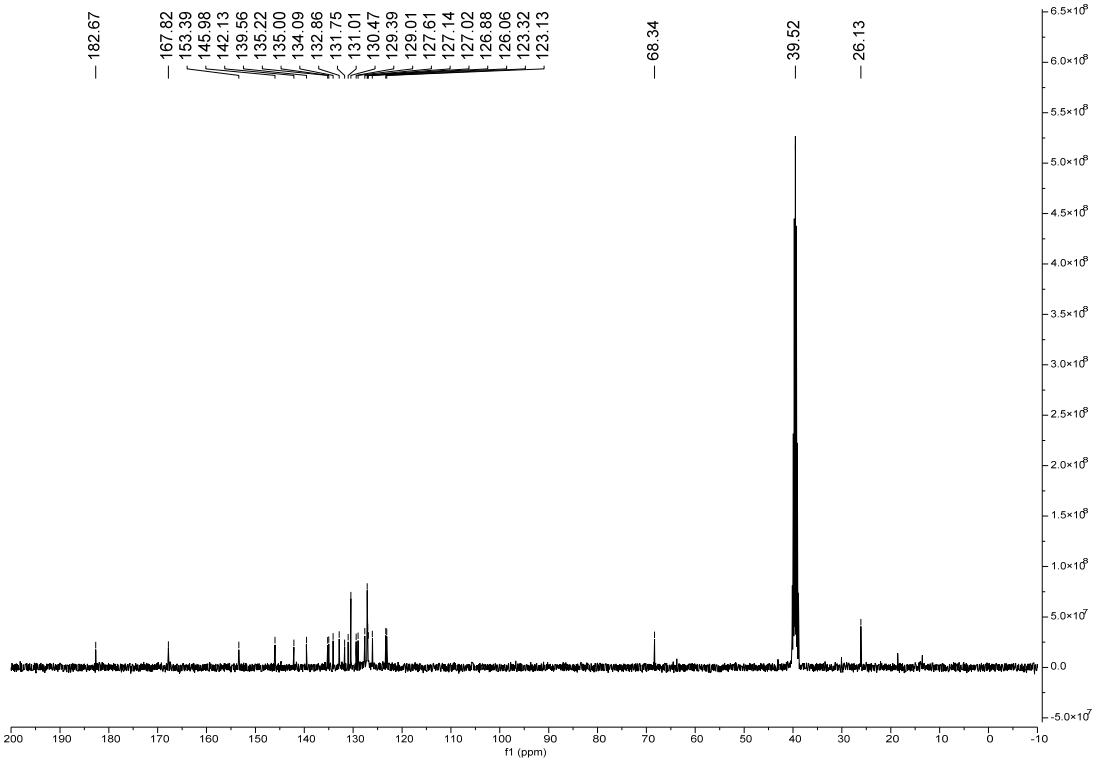


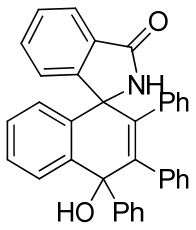


^{1}H NMR (400 MHz, DMSO-d_6) Compound **4**

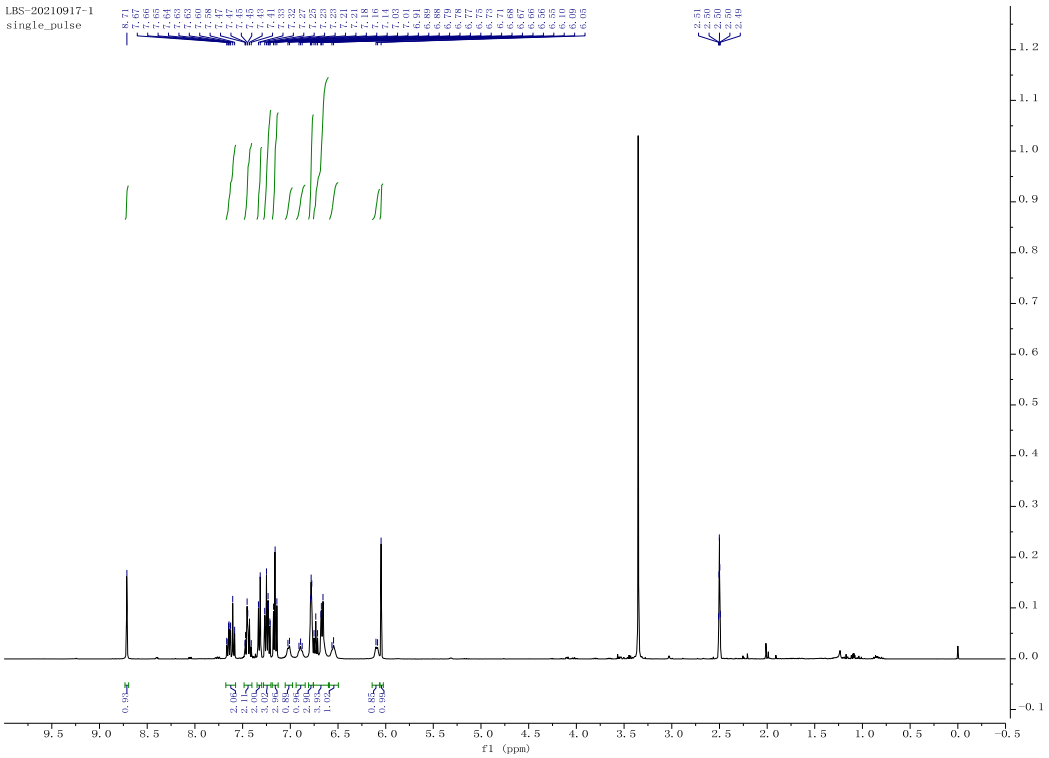


^{13}C NMR (101 MHz, DMSO-d_6) Compound **4**

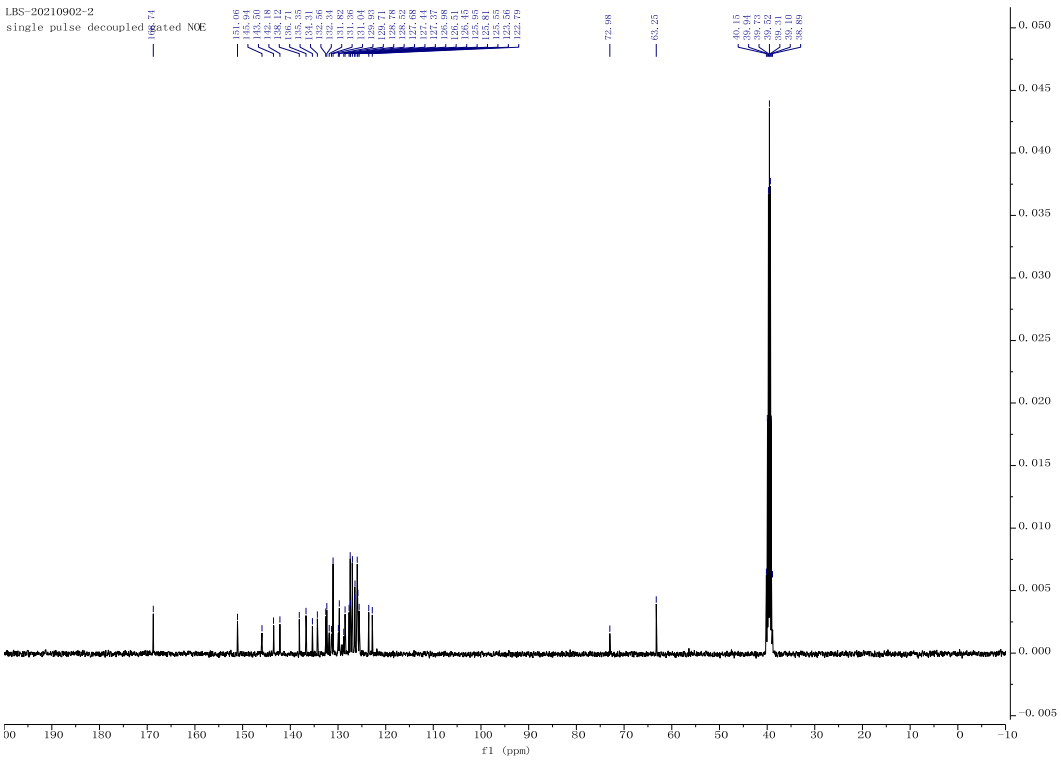


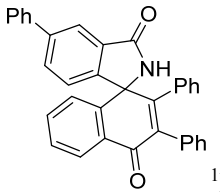


^{1}H NMR (400 MHz, DMSO-d_6) Compound **5**

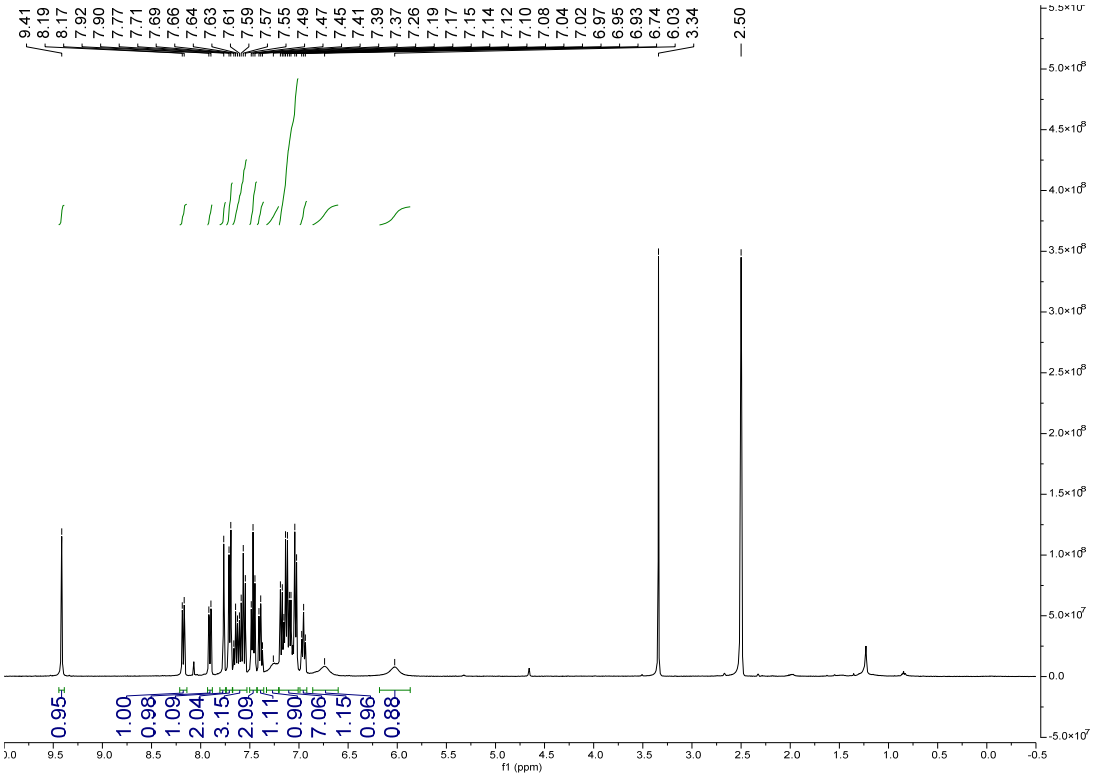


^{13}C NMR (101 MHz, DMSO-d_6) Compound **5**

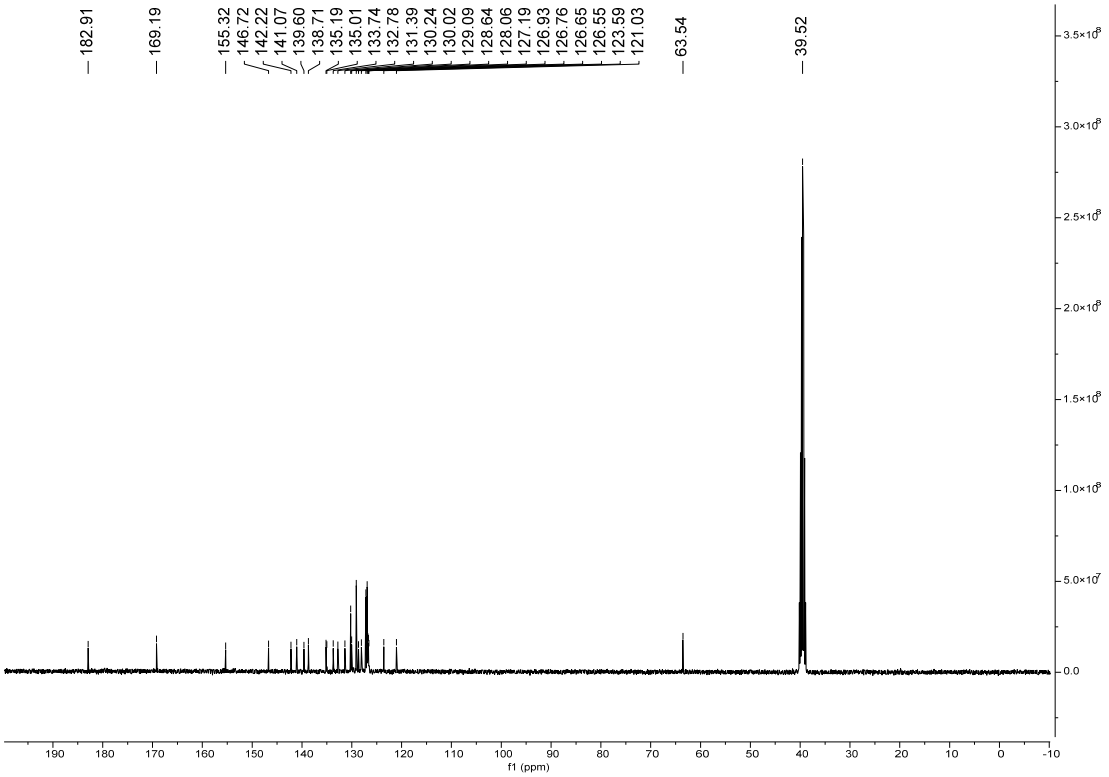




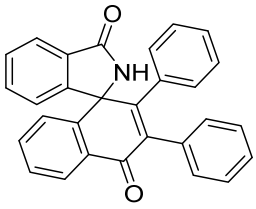
^{1}H NMR (400 MHz, DMSO-d_6) Compound **6**



^{13}C NMR (101 MHz, DMSO-d_6) Compound **6**



X-ray Structures



3aa

The preparation of crystals:

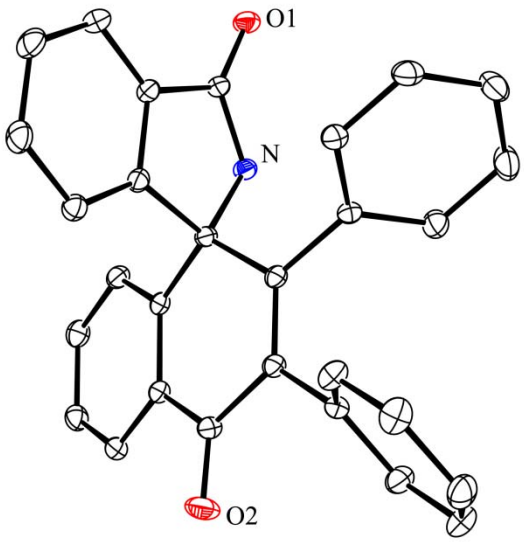
The crystals of **3aa** were obtained by dissolving **3aa** in a mixture of petrol ether and ethyl acetate (1:1) followed by slow evaporation of solvents at room temperature.

X-ray crystal sturcture analysis of 3aa:

Diffraction data for complexe **3aa** were collected on a Bruker SMART APEX II diffractometer at 150 K with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). An empirical absorption correction using SADABS was applied for all data.[3] The structures were solved and refined to convergence on F^2 for all independent reflections by the full-matrix least squares method using the SHELXL−2016 programs.[4]

Crystallographic data and refinement details for compound **3aa** are given in Table S1. CCDC number 2115545. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre www.ccdc.cam.ac.uk/data_request/cif.

X-ray Sturcture of 3aa (CCDC 2115545)



Molecular structure of **3aa** (thermal ellipsoids are set at the 30% probability level; H atoms are

omitted for clarity).

Table S1

Compound	**3aa**
Empirical formula	$C_{29}H_{19}NO_2$
Fw	413.45
Crystal system	triclinic
Space group	*P*-1
a /Å	10.336(3)
b /Å	10.907(3)
c /Å	11.626(3)
α /°	117.746(12)
β /°	101.702(16)
γ /°	100.621(16)
V /Å^3	1075.5(5)
Z	2
D_{calc}/g cm^{-3}	1.277
F (000)	432
μ /mm^{-1}	0.080
θ range	2.441−25.242
Reflns collected	3888
Independent reflns	2967
Reflns [$I > 2\sigma(I)$]	3888
R_{int}	0.0702
R_1;wR_2 [$I > 2\sigma(I)$]	0.0438; 0.0986
R_1; wR_2 (all data)	0.0658; 0.1082
GOF (F^2)	1.013

6. References.

[1] (a) Nishimura, T.; Noishiki, A.; Ebe, Y.; Hayashi, T. Hydroxorhodium/Chiral Diene Complexes as Effective Catalysts for the Asymmetric Arylation of 3-Aryl-3-hydroxyisoindolin-1-ones. *Angew. Chem. Int. Ed.* **2013**, *52*, 1777–1780. (b) Sharma, S.; Oh, Y.; Mishra, N. K.; De, U.; Jo, H.; Sachan, R.; Kim, H. S.; Jung, Y. H.; Kim, I. S. Rhodium-Catalyzed [3 + 2] Annulation of Cyclic *N*-Acyl Ketimines with Activated Olefins: Anticancer Activity of Spiroisoindolinones. *J. Org. Chem.* **2017**, *82*, 3359–3367.

[2] (a) Vanos, C. M.; Lambert, T. H. Development of a Catalytic Platform for Nucleophilic Substitution: Cyclopropenone-Catalyzed Chlorodehydration of Alcohols. *Angew. Chem. Int. Ed.* **2011**, *50*, 12222−12226. (b) Poloukhtine, A.; Popik, V. V. Highly Efficient Photochemical Generation of a Triple Bond: Synthesis, Properties, and Photodecarbonylation of Cyclopropenones. *J. Org. Chem.* **2003**, *68*, 7833−7840.

[3] Sheldrick, G. M. Program SADABS: Area-Detector Absorption Correction, **1996**, University of Göttingen, Germany.

[4] Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun*., **2015**, *71*, 3−8.

[5] Nishimura, T.; Nagamoto, M.; Ebe, Y.; Hayashi, T. Enantioselective [3 + 2] annulation *via* C–H activation between cyclic *N*-acyl ketimines and 1,3-dienes catalyzed by iridium/chiral diene complexes. *Chem. Sci.* **2013**, *4*, 4499–4504.

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[8] Nishimura, T.; Noishiki, A.; Ebe, Y.; Hayashi, T. Hydroxorhodium/chiral diene complexes as effective catalysts for the asymmetric arylation of 3-aryl-3-hydroxyisoindolin-1-ones. *Angew. Chem., Int. Ed.*, **2013**, *52*, 1777−1780.