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Electronic Supplementary Information

Cobalt(III)-Catalyzed C-H Amidation of Weakly Coordinating Sulfoxonium Ylides and α-Benzoylketene Dithioacetals

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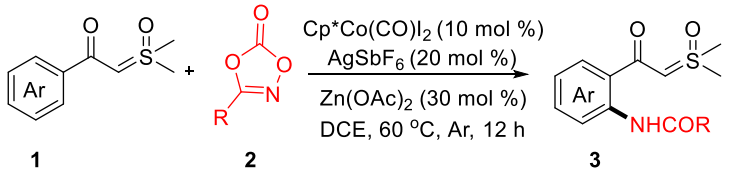
Contents

Experimental Section

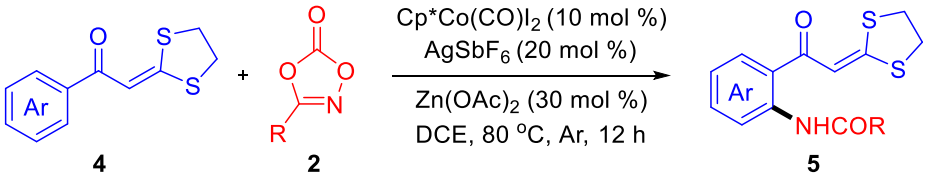
General Considerations: All the reactions were carried out under argon atmosphere using standard Schlenk technique. The ^{1}H NMR spectra were recorded on a 400 MHz or 600 MHz NMR spectrometer. The ^{13}C NMR spectra were recorded at 100 MHz or 150 MHz. The ^{19}F NMR spectra were recorded at 565 MHz. The residual solvent signals were used as references and the chemical shifts were converted to the TMS scale. The coupling constants were given in Hz. HRMS data were obtained using a TOF mode. The conversion of starting materials was monitored by thin layer chromatography (TLC) using silica gel plates (silica gel 60 F254 0.25 mm), and components were visualized under UV light (254 and 365 nm). Column chromatography was performed on silica gel 200-300 mesh. Unless otherwise noted, all other compounds have been reported in the literature or are commercially available. Commercial reagents were used without further purification.

General Procedure: Preparation of the Substrates

The substrates **1a-1u**,[1] **1a**-d_5,[1] **2a-2t**,[2] and **4a-4k**[3] were prepared according to the literature reports.



General procedure for synthesis of 3. A mixture of sulfoxonium ylide **1** (0.2 mmol), **2** (0.2 mmol), Cp*Co(CO)I_2 (9.5 mg, 0.02 mmol, 10 mol %), $AgSbF_6$ (13.7 mg, 0.04 mmol, 20 mol %) and $Zn(OAc)_2$ (11.0 mg, 0.06 mmol, 30 mol %) were added to a Schlenk tube equipped with a stir bar. Dry DCE (2.0 mL) was added and the mixture was stirred at 60 °C for 12 h under Ar atmosphere. Afterwards, the solvent was removed under reduced pressure and the residue was adsorbed onto small amounts of silica. The purification was performed by flash column chromatography on silica gel (eluent: PE/EA = 1:1).



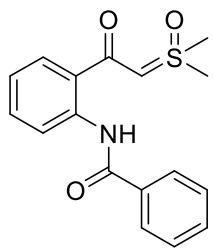
General procedure for synthesis of 5. A mixture of ketene dithioacetal **4** (0.2 mmol), amidating reagent **2** (0.2 mmol), Cp*Co(CO)I_2 (9.5 mg, 0.02 mmol, 10 mol %), $AgSbF_6$ (13.7 mg, 0.04 mmol, 20 mol %) and $Zn(OAc)_2$ (11.0 mg, 0.06 mmol, 30 mol %) were added to a Schlenk tube equipped with a stir bar. Dry DCE (2.0 mL) was added and the mixture was stirred at 80 °C for 12 h under Ar atmosphere. The solvent was removed under reduced pressure and the residue was adsorbed onto small amounts of silica. The purification was performed by flash column chromatography on silica gel (eluent: PE/EA = 5:1).

Gram-scale Synthesis of 3aa. A mixture of **1a** (3.17 mmol), **2a** (3.17 mmol), Cp*Co(CO)I_2 (151.0 mg, 0.317 mmol, 10 mol %), $AgSbF_6$ (218.0 mg, 0.643 mmol, 20 mol %) and $Zn(OAc)_2$ (175.0 mg, 0.951 mmol, 30 mol %) were added to a Schlenk tube equipped with a stir bar. Dry DCE (32 mL) was added and the mixture was stirred at 60 ^oC for 15 h under Ar atmosphere. Afterwards, the solvent was removed under reduced pressure, and the residue was adsorbed onto small amounts of silica. Purification was performed by flash column chromatography on silica gel and moderate yield of 91% (910.0 mg) was attained (eluent: PE/EA = 1:1).

1.5 mmol-Scale Synthesis of 5a

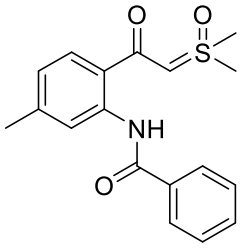
A mixture of **2a** (1.5 mmol), ketene dithioacetal **4a** (1.5 mmol), Cp*Co(CO)I_2 (71.3 mg, 0.15 mmol, 10 mol %), $AgSbF_6$ (103.0 mg, 0.3 mmol, 20 mol %) and $Zn(OAc)_2$ (82.5 mg, 0.45 mmol, 30 mol %) were added to a Schlenk tube equipped with a stir bar. Dry DCE (15 mL) was added and the mixture was stirred at 80 ^oC for 15 h under Ar atmosphere. Afterwards, the solvent was removed under reduced pressure and the residue was adsorbed onto small amounts of silica. Purification was performed by flash column chromatography on silica gel and moderate yield of 79 % (393.0 mg) was attained (eluent: PE/EA = 5:1).

Characterization of Products



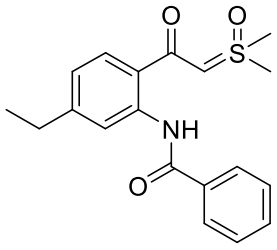
***N*-(2-(2-(dimethyl(oxo)-λ^6-sulfanylidene)acetyl)phenyl)benzamide (3aa)**

The title compound was isolated as a pale-yellow solid (PE/EA = 1:1, 59.9 mg, 95%). M.p.: 140-141 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.14 (s, 1H), 8.81 (d, *J* = 8.4 Hz, 1H), 8.06 (dd, *J* = 7.9, 1.5 Hz, 2H), 7.60 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.52 - 7.42 (m, 4H), 7.06 - 7.01 (m, 1H), 5.08 (s, 1H), 3.51 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 185.8, 165.7, 140.2, 135.5, 132.1, 131.6, 128.7, 128.5, 127.6, 124.0, 122.6, 121.1, 72.2, 42.3. HRMS (ESI): Calcd for $C_{17}H_{17}NO_3S$ $[M+Na]^+$ 388.0821, Found: 388.0816.



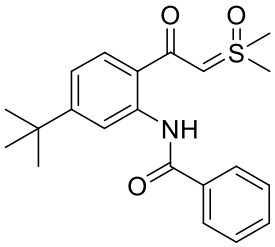
***N*-(2-(2-(dimethyl(oxo)-λ^6-sulfanylidene)acetyl)-5-methylphenyl)benzamide (3ba)**

The title compound was isolated as a pale-yellow solid (PE/EA = 1:1, 62.3 mg, 94%). M.p.: 142-143 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 13.24 (s, 1H), 8.69 (s, 1H), 8.10 - 8.04 (m, 2H), 7.56 - 7.45 (m, 4H), 6.85 (dd, *J* = 8.0, 1.0 Hz, 1H), 5.04 (s, 1H), 3.51 (s, 6H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.9, 165.7, 142.9, 140.3, 135.6, 131.6, 128.7, 128.5, 127.6, 123.4, 121.4, 121.3, 71.4, 42.4, 22.0. HRMS (ESI): Calcd for $C_{18}H_{19}NO_3S$ $[M+Na]^+$ 352.0978, Found: 352.0981.



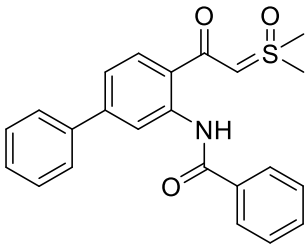
***N*-(2-(2-(dimethyl(oxo)-λ^6-sulfanylidene)acetyl)-5-ethylphenyl)benzamide (3ca)**

The title compound was isolated as a white solid (PE/EA = 1:1, 62.3 mg, 90%). M.p.: 160-161 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 13.24 (s, 1H), 8.73 (s, 1H), 8.07 (d, *J* = 7.1 Hz, 2H), 7.55 - 7.48 (m, 4H), 6.89 (d, *J* = 8.0 Hz, 1H), 5.04 (s, 1H), 3.53 (s, 6H), 2.70 (q, *J* = 7.6 Hz, 2H), 1.27 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.8, 165.7, 149.1, 140.5, 135.6, 131.6, 128.7, 128.6, 127.6, 122.2, 121.5, 120.3, 71.4, 42.4, 29.3, 15.4. HRMS (ESI): Calcd for $C_{19}H_{21}NO_3S$ $[M+Na]^+$ 366.1134, Found: 366.1137.



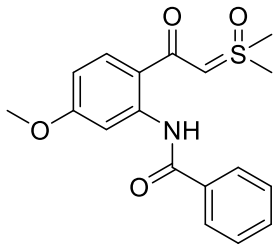
_N_-(5-(tert-butyl)-2-(2-(dimethyl(oxo)-λ^6-sulfanylidene)acetyl)phenyl)benzamide (3da)

The title compound was isolated as a pale-yellow solid (PE/EA = 1:1, 70.7 mg, 94%). M.p.: 126-127 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 13.25 (s, 1H), 8.96 (d, *J* = 1.9 Hz, 1H), 8.12 - 8.05 (m, 2H), 7.55 (d, *J* = 8.3 Hz, 1H), 7.53 - 7.47 (m, 3H), 7.07 (dd, *J* = 8.3, 1.9 Hz, 1H), 5.05 (s, 1H), 3.50 (s, 6H), 1.37 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.7, 165.7, 155.9, 140.4, 135.7, 131.5, 128.7, 128.3, 127.6, 121.2, 119.7, 118.1, 71.4, 42.5, 35.3, 31.2. HRMS (ESI): Calcd for $C_{21}H_{25}NO_3S$ $[M+Na]^+$ 394.1447, Found: 394.1454.



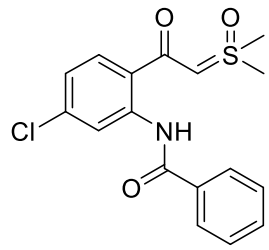
_N_-(4-(2-(dimethyl(oxo)-λ^6-sulfanylidene)acetyl)-[1,1'-biphenyl]-3-yl)benzamide (3ea)

The title compound was isolated as a pale-yellow solid (PE/EA = 1:1, 63.0 mg, 80%). M.p.: 160-161 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 13.30 (s, 1H), 9.19 (d, *J* = 1.7 Hz, 1H), 8.14 - 8.08 (m, 2H), 7.72 (d, *J* = 7.3 Hz, 2H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.55 - 7.49 (m, 3H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.30 (dd, *J* = 8.2, 1.8 Hz, 1H), 5.10 (s, 1H), 3.54 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.5, 165.8, 144.7, 140.9, 140.2, 135.5, 131.7, 129.0, 128.9, 128.8, 128.1, 127.7, 127.5, 122.6, 121.1, 119.6, 71.8, 42.5. HRMS (ESI): Calcd for $C_{23}H_{21}NO_3S$ $[M+Na]^+$ 414.1134, Found: 414.1126.



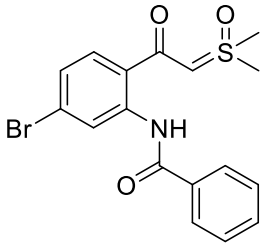
_N_-(2-(2-(dimethyl(oxo)-λ^6-sulfanylidene)acetyl)-5-methoxyphenyl)benzamide (3fa)

The title compound was isolated as a pale-yellow solid (PE/EA = 1:1, 46.0 mg, 66%). M.p.: 176-177 °C. ^{1}H NMR (600 MHz, DMSO) δ 14.16 (s, 1H), 8.41 (d, *J* = 2.6 Hz, 1H), 7.98 (t, *J* = 12.4 Hz, 2H), 7.73 (d, *J* = 8.9 Hz, 1H), 7.69 - 7.49 (m, 3H), 6.67 (dd, *J* = 8.8, 2.6 Hz, 1H), 5.76 (d, *J* = 5.3 Hz, 1H), 3.82 (s, 3H), 3.6 (s, 6H). ^{13}C NMR (100 MHz, DMSO) δ 183.8, 164.5, 161.4, 141.9, 134.8, 131.9, 130.3, 128.9, 127.0, 116.2, 108.2, 104.6, 75.5, 55.2, 40.5. HRMS (ESI): Calcd for $C_{18}H_{19}NO_4S$ $[M+Na]^+$ 368.0927, Found: 368.0924.



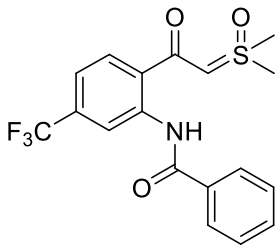
_N_-(5-chloro-2-(2-(dimethyl(oxo)-λ^6-sulfanylidene)acetyl)phenyl)benzamide (3ga)

The title compound was isolated as a pale-yellow solid (PE/EA = 1:1, 64.8 mg, 92%). M.p.: 192-193 °C. ^{1}H NMR (600 MHz, DMSO) δ 14.00 (s, 1H), 8.82 (d, *J* = 2.2 Hz, 1H), 7.99 - 7.97 (m, 2H), 7.81 (d, *J* = 8.6 Hz, 1H), 7.67 - 7.60 (m, 3H), 7.19 (dd, *J* = 8.5, 2.1 Hz, 1H), 5.91 (s, 1H), 3.63 (s, 6H). ^{13}C NMR (100 MHz, DMSO) δ 182.6, 164.7, 141.1, 135.6, 134.3, 132.1, 130.2, 129.0, 127.0, 122.2, 122.1, 119.1, 77.5, 40.3. HRMS (ESI): Calcd for $C_{17}H_{16}ClNO_3S$ $[M+Na]^+$ 372.0432, Found: 372.0426.



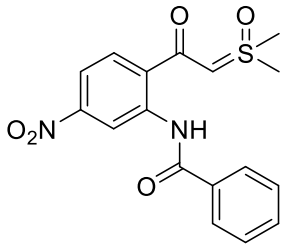
_N_-(5-bromo-2-(2-(dimethyl(oxo)-λ^6-sulfanylidene)acetyl)phenyl) Benzamide (3ha)

The title compound was isolated as a white solid (PE/EA = 1:1, 68.8 mg, 86%). M.p.: 211-212 °C. ^{1}H NMR (600 MHz, Acetone) δ 13.92 (s, 1H), 9.16 (d, *J* = 2.0 Hz, 1H), 8.10 - 8.07 (m, 2H), 7.71 (d, *J* = 8.5 Hz, 1H), 7.61 (d, *J* = 7.3 Hz, 1H), 7.57 (t, *J* = 7.4 Hz, 2H), 7.24 (dd, *J* = 8.4, 2.0 Hz, 1H), 5.66 (s, 1H), 3.69 (s, 6H). ^{13}C NMR (100 MHz, Acetone) δ 184.6, 165.8, 142.8, 136.0, 132.7, 131.0, 129.6, 128.2, 125.8, 125.7, 123.7, 123.5, 76.4, 41.6. HRMS (ESI): Calcd for $C_{17}H_{16}BrNO_3S$ $[M+Na]^+$ 415.9926, Found: 415.9919.



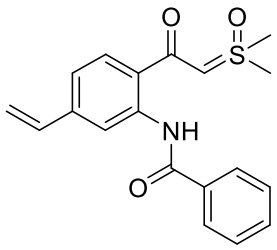
_N_-(2-(2-(dimethyl(oxo)-λ^6-sulfanylidene)acetyl)-5-(trifluoromethyl)phenyl)benzamide (3ia)

The title compound was isolated as a white solid (PE/EA = 1:1, 54.1 mg, 71%). M.p.: 209-210 °C. ^{1}H NMR (600 MHz, DMSO) δ 13.89 (s, 1H), 9.11 (s, 1H), 7.99 (d, *J* = 7.1 Hz, 3H), 7.68 - 7.60 (m, 3H), 7.47 (d, *J* = 8.2 Hz, 1H), 5.98 (s, 1H), 3.66 (s, 6H). ^{13}C NMR (150 MHz, DMSO) δ 182.5, 165.3, 140.7, 134.7, 132.7, 131.4 (q, $J_{C\text{-}F}$ = 31.7 Hz), 130.0, 129.5, 127.5, 127.4, 124.3 (q, $J_{C\text{-}F}$ = 270.8 Hz), 119.3 (q, $J_{C\text{-}F}$ = 2.6 Hz), 116.7 (q, $J_{C\text{-}F}$ = 4.2 Hz), 79.1, 40.8. ^{19}F NMR (565 MHz, DMSO) δ -61.71. HRMS (ESI): Calcd for $C_{18}H_{16}F_3NO_3S$ $[M+Na]^+$ 406.0695, Found: 406.0690.



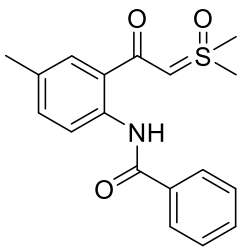
_N_-(2-(2-(dimethyl(oxo)-λ^6-sulfanylidene)acetyl)-5-nitrophenyl)benzamide (3ja)

The title compound was isolated as a pale-yellow solid (PE/EA = 1:1, 59.6 mg, 82%). M.p.: 160-161 °C. ^{1}H NMR (600 MHz, DMSO) δ 13.92 (s, 1H), 9.59 (d, *J* = 2.3 Hz, 1H), 8.01 (dd, *J* = 15.5, 8.0 Hz, 3H), 7.94 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.7 - 7.6 (m, 3H), 6.03 (s, 1H), 3.67 (s, 6H). ^{13}C NMR (100 MHz, DMSO) δ 181.2, 164.9, 148.4, 140.5, 134.0, 132.4, 129.7, 129.1, 128.8, 127.0, 116.9, 114.2, 79.6, 40.2. HRMS (ESI): Calcd for $C_{17}H_{16}N_2O_5S$ $[M+Na]^+$ 383.0672, Found: 383.0670.



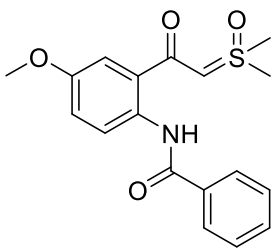
_N_-(2-(2-(dimethyl(oxo)-λ^6-sulfanylidene)acetyl)-5-vinylphenyl)benzamide (3ka)

The title compound was isolated as a pale-yellow solid (PE/EA = 1:1, 53.0 mg, 77%). M.p.: 150-151 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 13.24 (s, 1H), 8.94 (d, *J* = 1.5 Hz, 1H), 8.09 - 8.06 (m, 2H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.54 - 7.48 (m, 3H), 7.11 (dd, *J* = 8.2, 1.6 Hz, 1H), 6.75 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.90 (d, *J* = 17.6 Hz, 1H), 5.36 (d, *J* = 10.9 Hz, 1H), 5.30 (s, 1H), 5.05 (s, 1H), 3.54 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.4, 165.8, 141.3, 140.8, 136.5, 135.6, 131.6, 128.8, 127.7, 123.0, 120.2, 118.9, 116.2, 77.4, 71.7, 42.6. HRMS (ESI): Calcd for $C_{19}H_{19}NO_3S$ $[M+Na]^+$ 364.0978, Found: 364.0984.



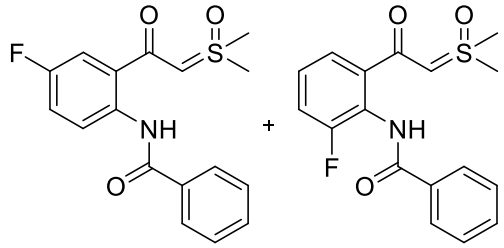
_N_-(2-(2-(dimethyl(oxo)-λ^6-sulfanylidene)acetyl)-4-methylphenyl)benzamide (3la)

The title compound was isolated as a pale-yellow solid (PE/EA = 1:1, 63.0 mg, 95%). M.p.: 135-136 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.99 (s, 1H), 8.70 (d, *J* = 8.5 Hz, 1H), 8.13 - 7.96 (m, 2H), 7.55 - 7.44 (m, 3H), 7.42 (d, *J* = 1.6 Hz, 1H), 7.28 - 7.25 (m, 1H), 5.06 (s, 1H), 3.52 (s, 6H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.9, 165.5, 137.8, 135.6, 132.7, 131.9, 131.5, 128.8, 128.7, 127.6, 124.0, 121.0, 71.9, 42.4, 21.0. HRMS (ESI): Calcd for $C_{18}H_{19}NO_3S$ $[M+Na]^+$ 352.0978, Found: 352.0982.



_N_-(2-(2-(dimethyl(oxo)-λ^6-sulfanylidene)acetyl)-4-methoxyphenyl) benzamide (3ma)

The title compound was isolated as a white solid (PE/EA = 1:1, 56.0 mg, 81%). M.p.: 169-170 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.74 (s, 1H), 8.73 (d, *J* = 8.7 Hz, 1H), 8.03 (d, *J* = 6.9 Hz, 2H), 7.52 - 7.44 (m, 3H), 7.12 (s, 1H), 7.01 (d, *J* = 8.9 Hz, 1H), 5.03 (s, 1H), 3.81 (s, 3H), 3.51 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.4, 165.2, 154.7, 135.6, 133.6, 131.5, 128.7, 127.5, 125.6, 122.5, 117.1, 113.8, 72.2, 55.8, 42.3. HRMS (ESI): Calcd for $C_{18}H_{19}NO_4S$ $[M+Na]^+$ 368.0927, Found: 368.0918.

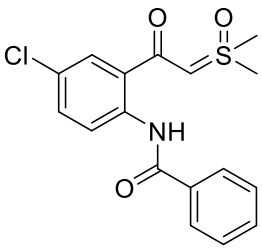


3na 3na'

2.3:1

_N_-(2-(2-(dimethyl(oxo)-λ^6-sulfanylidene)acetyl)-4-fluorophenyl)benzamide (3na) and _N_-(2-(2-(dimethyl(oxo)-λ^6-sulfanylidene)acetyl)-6-fluorophenyl)benzamide (3na')

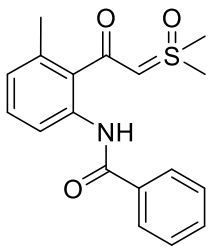
The title compound was isolated as a pale-yellow solid (PE/EA = 1:1, 42.7 mg, 64%). M.p.: 119-120 °C. ^{1}H NMR (600 MHz, DMSO) δ 11.09 (s, 1H), 7.96 (d, *J* = 7.7 Hz, 2H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 2H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 9.1 Hz, 1H), 7.29 (m, 1H), 5.49 (s, 1H), 3.51 (s, 6H). ^{13}C NMR (150 MHz, DMSO) δ181.9 (d, $J_{C\text{-}F}$ = 2.0 Hz), 173.4 (d, $J_{C\text{-}F}$ = 2.9 Hz,), 164.9, 159.9, 158.8, 157.8, 157.1, 156.1, 141.1, 138.8 (d, $J_{C\text{-}F}$ = 10.4 Hz), 135.8, 134.3, 132.5, 129.3, 129.3, 128.7, 128.5, 128.0, 127.6, 126.6 (d, $J_{C\text{-}F}$ = 8.1 Hz), 125.3 (d, $J_{C\text{-}F}$ = 13.6 Hz), 124.3 (d, $J_{C\text{-}F}$ = 7.9 Hz), 124.0 (d, $J_{C\text{-}F}$ = 2.6 Hz), 120.0 (d, $J_{C\text{-}F}$ = 3.6 Hz), 117.8 (d, $J_{C\text{-}F}$ = 20.8 Hz), 117.2 (d, $J_{C\text{-}F}$ = 18.9 Hz), 102.9, 77.0, 41.8, 40.7. ^{19}F NMR (565 MHz, DMSO) δ -115.50, -125.86. HRMS (ESI): Calcd for $C_{17}H_{16}FNO_3S$ $[M+Na]^+$ 356.0727, Found: 356.0735.



_N_-(4-chloro-2-(2-(dimethyl(oxo)-λ^6-sulfanylidene)acetyl)phenyl)benzamide (3oa)

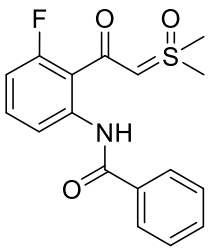
The title compound was isolated as a pale-yellow solid (PE/EA = 1:1, 36.6 mg, 52%). M.p.: 156-157 °C. ^{1}H NMR (600 MHz, Acetone) δ 13.66 (s, 1H), 8.88 (d, *J* = 8.9 Hz, 1H), 8.08 - 8.06 (m, 2H), 7.75 (d, *J* = 2.5 Hz, 1H), 7.62 - 7.55 (m, 3H), 7.46 (dd, *J* = 8.9, 2.5 Hz, 1H), 5.76 (s, 1H), 3.70 (s, 6H). ^{13}C

NMR (100 MHz, Acetone) δ 184.1, 165.5, 140.3, 136.1, 132.6, 131.7, 129.6, 128.9, 128.2, 127.5, 126.7, 122.7, 77.0, 41.5. HRMS (ESI): Calcd for $C_{17}H_{16}ClNO_3S$ $[M+Na]^+$ 372.0432, Found: 372.0442.



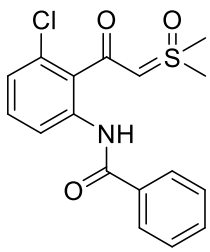
_N_-(2-(2-(dimethyl(oxo)-λ^6-sulfanylidene)acetyl)-3-methylphenyl)benzamide (3pa)

The title compound was isolated as a white solid (PE/EA = 1:1, 37.9 mg, 57%). M.p.: 170-171 °C. ^{1}H NMR (600 MHz, DMSO) δ 10.38 (s, 1H), 8.01 (d, *J* = 8.1 Hz, 1H), 7.88 (d, *J* = 7.6 Hz, 2H), 7.61 (t, *J* = 7.2 Hz, 1H), 7.55 (t, *J* = 7.4 Hz, 2H), 7.24 (t, *J* = 7.8 Hz, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 5.21 (s, 1H), 3.58 (s, 6H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 182.7, 164.1, 135.1, 134.5, 134.3, 133.0, 131.8, 128.8, 128.1, 126.9, 126.1, 119.1, 80.1, 40.3, 20.4. HRMS (ESI): Calcd for $C_{18}H_{19}NO_3S$ $[M+Na]^+$ 352.0978, Found: 352.0974.



_N_-(2-(2-(dimethyl(oxo)-λ^6-sulfanylidene)acetyl)-3-fluorophenyl)benzamide (3qa)

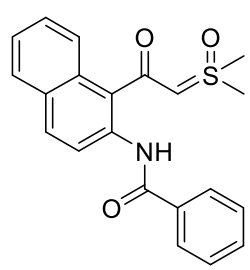
The title compound was isolated as a white solid (PE/EA = 1:1, 63.5 mg, 95%). M.p.: 157-158 °C. ^{1}H NMR (600 MHz, DMSO) δ 12.79 (s, 1H), 8.41 (d, *J* = 8.3 Hz, 1H), 7.94 (d, *J* = 7.5 Hz, 2H), 7.62 (m, 3H), 7.49 - 7.43 (m, 1H), 7.00 (dd, *J* = 10.8, 8.6 Hz, 1H), 5.52 (d, *J* = 1.9 Hz, 1H), 3.65 (s, 6H). ^{13}C NMR (100 MHz, DMSO) δ 177.6 (d, $J_{C\text{-}F}$ = 1.1 Hz), 164.2, 159.8 (d, $J_{C\text{-}F}$ = 246.9 Hz), 140.2 (d, $J_{C\text{-}F}$ = 5.2 Hz), 134.39, 132.06, 131.4 (d, $J_{C\text{-}F}$ = 10.6 Hz), 129.0, 126.9, 116.2 (d, $J_{C\text{-}F}$ = 2.8 Hz), 115.1 (d, $J_{C\text{-}F}$ = 17.0 Hz), 110.6 (d, $J_{C\text{-}F}$ = 24.6 Hz), 82.3 (d, $J_{C\text{-}F}$ = 13.2 Hz), 40.4. ^{19}F NMR (565 MHz, DMSO) δ -108.69. HRMS (ESI): Calcd for $C_{17}H_{16}FNO_3S$ $[M+Na]^+$ 356.0727, Found: 356.0723.



_N_-(3-chloro-2-(2-(dimethyl(oxo)-λ^6-sulfanylidene)acetyl)phenyl)benzamide (3ra)

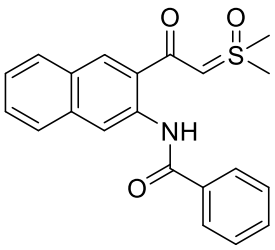
The title compound was isolated as a white solid (PE/EA = 1:1, 66.1 mg, 93%). M.p.: 141-142 °C. ^{1}H NMR (600 MHz, DMSO) δ 10.38 (s, 1H), 8.13 (d, *J* = 8.1 Hz, 1H), 7.92 - 7.86 (m, 2H), 7.63 (t, *J* = 7.3 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 8.1 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 1H), 5.29 (s, 1H), 3.59 (s, 6H). ^{13}C NMR (150 MHz, DMSO) δ 179.6, 164.9, 137.4, 134.5, 132.6, 132.4, 130.2, 130.1,

129.4, 127.5, 125.9, 121.2, 81.1, 40.8. HRMS (ESI): Calcd for $C_{17}H_{16}ClNO_3S$ $[M+Na]^+$ 372.0432, Found: 372.0437.



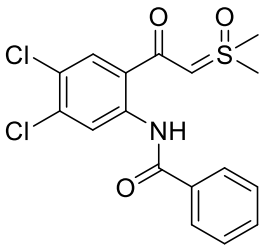
_N_-(1-(2-(dimethyl(oxo)-λ^6-sulfanylidene)acetyl)naphthalen-2-yl)benzamide (3sa)

The title compound was isolated as a gray solid (PE/EA = 1:1, 22.6 mg, 31%). M.p.: 130-131 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.83 (s, 1H), 8.61 (d, *J* = 9.0 Hz, 1H), 8.34 (d, *J* = 8.4 Hz, 1H), 8.06 - 7.98 (m, 2H), 7.87 (d, *J* = 9.0 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.55 - 7.52 (m, 1H), 7.52 - 7.44 (m, 3H), 7.41 (m, *J* = 7.9, 6.9, 1.1 Hz, 1H), 4.94 (s, 1H), 3.55 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.3, 165.3, 135.0, 134.5, 131.9, 130.8, 130.5, 130.2, 128.9, 128.4, 127.4, 126.6, 125.9, 125.6, 124.9, 121.1, 78.3, 42.4. HRMS (ESI): Calcd for $C_{21}H_{19}NO_3S$ $[M+Na]^+$ 388.0978, Found: 388.0980.



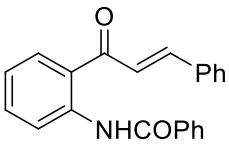
_N_-(3-(2-(dimethyl(oxo)-λ^6-sulfanylidene)acetyl)naphthalen-2-yl)benzamide (3ta)

The title compound was isolated as a pale-yellow solid (PE/EA = 1:1, 58.5 mg, 80%). M.p.: 145-146 °C. ^{1}H NMR (600 MHz, Acetone) δ 13.55 (s, 1H), 9.31 (s, 1H), 8.38 (s, 1H), 8.14 (d, *J* = 6.9 Hz, 2H), 7.88 (d, *J* = 7.7 Hz, 2H), 7.6 - 7.5 (m, 4H), 7.43 (t, *J* = 6.8 Hz, 1H), 5.79 (s, 1H), 3.73 (m, 6H). ^{13}C NMR (100 MHz, Acetone) δ 185.8, 165.4, 138.0, 136.5, 135.9, 132.4, 129.9, 129.6, 129.3, 128.7, 128.1, 126.3, 125.9, 117.5, 76.4, 41.7. HRMS (ESI): Calcd for $C_{21}H_{19}NO_3S$ $[M+H]^+$ 366.1158, Found: 366.1159.



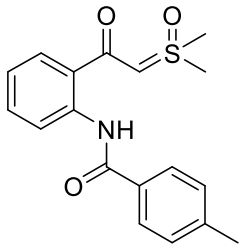
_N_-(4,5-dichloro-2-(2-(dimethyl(oxo)-λ^6-sulfanylidene)acetyl)phenyl)benzamide (3ua)

The title compound was isolated as a pale-yellow solid (PE/EA = 1:1, 56.6 mg, 73%). M.p.: 175-176 °C. ^{1}H NMR (600 MHz, DMSO) δ 13.94 (s, 1H), 8.99 (s, 1H), 8.03 (s, 1H), 7.98 - 7.96 (m, 2H), 7.66 (t, *J* = 7.2 Hz, 1H), 7.61 (t, *J* = 7.3 Hz, 2H), 6.09 (s, 1H), 3.63 (s, 6H). ^{13}C NMR (100 MHz, DMSO) δ 181.1, 164.7, 139.6, 134.1, 133.3, 132.3, 130.0, 129.0, 127.0, 124.2, 123.9, 121.0, 78.2, 40.3. HRMS (ESI): Calcd for $C_{17}H_{15}Cl_2NO_3S$ $[M+Na]^+$ 406.0042, Found: 406.0041.



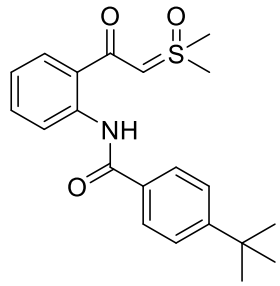
***N*-(2-cinnamoylphenyl)benzamide (3va)**

The title compound was isolated as a pale-yellow solid (PE/EA = 5:1, 23.6 mg, 36%). M.p.: 88-89 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.63 (s, 1H), 8.97 (d, *J* = 8.4 Hz, 1H), 8.11 (dd, *J* = 8.0, 1.4 Hz, 2H), 8.06 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.87 (d, *J* = 15.5 Hz, 1H), 7.68 - 7.62 (m, 4H), 7.59 - 7.53 (m, 3H), 7.45 - 7.43 (m, 3H), 7.23 - 7.20 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.8, 166.2, 145.8, 141.7, 135.1, 135.0, 134.8, 132.1, 131.0, 130.9, 129.2, 129.0, 128.7, 127.6, 123.7, 122.9, 122.7, 121.4. HRMS (ESI): Calcd for $C_{22}H_{17}NO_2$ $[M+Na]^+$ 350.1151, Found: 350.1145.



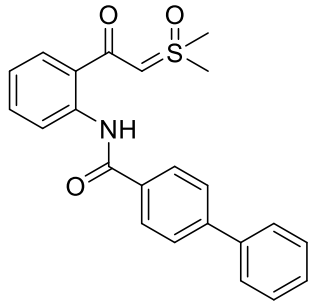
***N*-(2-(2-(dimethyl(oxo)-λ^6-sulfanylidene)acetyl)phenyl)-4-methylbenzamide (3ab)**

The title compound was isolated as a pale-yellow solid (PE/EA = 1:1, 46.1 mg, 70%). M.p.: 136-137 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.04 (s, 1H), 8.81 (d, *J* = 8.3 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 2H), 7.61 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.48 - 7.41 (m, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.08 - 6.99 (m, 1H), 5.05 (s, 1H), 3.52 (s, 6H), 2.42 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 185.8, 165.7, 142.0, 140.3, 132.7, 132.0, 129.4, 128.4, 127.6, 124.0, 122.4, 121.1, 72.1, 42.3, 21.6. HRMS (ESI): Calcd for $C_{18}H_{19}NO_3S$ $[M+H]^+$ 330.1158, Found: 330.1150.



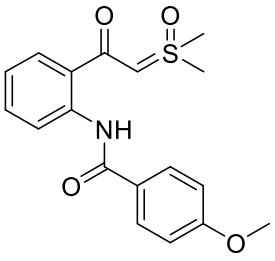
4-(tert-butyl)-*N*-(2-(2-(dimethyl(oxo)-λ^6-sulfanylidene)acetyl)phenyl)benzamide (3ac)

The title compound was isolated as a pale-yellow liquid (PE/EA = 1:1, 62.6 mg, 84%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 13.12 (s, 1H), 8.82 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 5.09 (s, 1H), 3.49 (s, 7H), 1.34 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 185.7, 165.6, 155.0, 140.3, 132.6, 131.9, 128.4, 127.3, 125.6, 123.9, 122.4, 120.9, 72.4, 42.1, 35.0, 31.2. HRMS (ESI): Calcd for $C_{21}H_{25}NO_3S$ $[M+Na]^+$ 394.1447, Found: 394.1145.



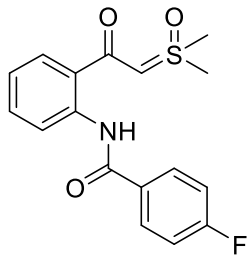
_N_-(2-(2-(dimethyl(oxo)-λ^6-sulfanylidene)acetyl)phenyl)-[1,1'-biphenyl]-4-carboxamide (3ad)

The title compound was isolated as a pale-yellow solid (PE/EA = 1:1, 51.9 mg, 66%). M.p.: 182-183 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.21 (s, 1H), 8.84 (d, *J* = 8.4 Hz, 1H), 8.14 (d, *J* = 8.2 Hz, 2H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.63 (t, *J* = 7.7 Hz, 3H), 7.47 (t, *J* = 7.3 Hz, 3H), 7.38 (t, *J* = 7.3 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 5.08 (s, 1H), 3.53 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 185.8, 165.4, 144.3, 140.3, 140.3, 134.3, 132.1, 129.0, 128.5, 128.1, 128.0, 127.4, 127.3, 123.9, 122.6, 121.1, 72.2, 42.4. HRMS (ESI): Calcd for $C_{23}H_{21}NO_3S$ $[M+Na]^+$ 414.1134, Found: 414.1127.



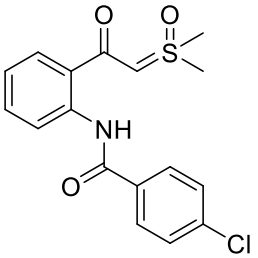
_N_-(2-(2-(dimethyl(oxo)-λ^6-sulfanylidene)acetyl)phenyl)-4-methoxybenzamide (3ae)

The title compound was isolated as a pale-yellow solid (PE/EA = 1:1, 32.5 mg, 47%). M.p.: 146-147 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.02 (s, 1H), 8.80 (d, *J* = 8.3 Hz, 1H), 8.03 (d, *J* = 8.6 Hz, 2H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.00 (m, 3H), 5.08 (s, 1H), 3.86 (s, 3H), 3.52 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.9, 165.3, 162.4, 140.5, 132.1, 129.5, 128.5, 127.9, 123.9, 122.3, 121.0, 113.9, 72.0, 55.5, 42.4. HRMS (ESI): Calcd for $C_{18}H_{19}NO_4S$ $[M+Na]^+$ 368.0927, Found: 368.0918.



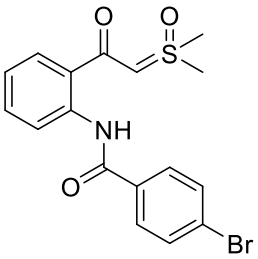
_N_-(2-(2-(dimethyl(oxo)-λ^6-sulfanylidene)acetyl)phenyl)-4-fluorobenzamide (3af)

The title compound was isolated as a white solid (PE/EA = 1:1, 54.0 mg, 81%). M.p.: 158-159 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.20 (s, 1H), 8.79 (d, *J* = 8.2 Hz, 1H), 8.11 - 8.03 (m, 2H), 7.62 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.49 - 7.41 (m, 1H), 7.16 (t, *J* = 8.6 Hz, 2H), 7.05 (t, *J* = 7.2 Hz, 1H), 5.09 (s, 1H), 3.54 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 185.8, 164.9 (d, *J* = 250 Hz), 164.6, 140.3, 132.2, 131.8 (d, *J* = 2.9 Hz), 130.0 (d, *J* = 8.9 Hz), 128.5, 123.8, 122.6, 121.0, 115.7 (d, *J* = 21.8 Hz), 72.1, 42.4. ^{19}F NMR (565 MHz, $CDCl_3$) δ -108.52. HRMS (ESI): Calcd for $C_{17}H_{16}FNO_3S$ $[M+H]^+$ 334.0908, Found: 414.0910.



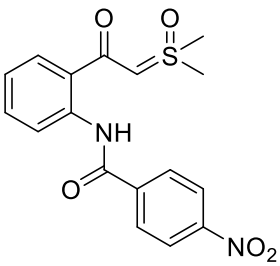
4-chloro-*N*-(2-(2-(dimethyl(oxo)-λ^6-sulfanylidene)acetyl)phenyl)benzamide (3ag)

The title compound was isolated as a white solid (PE/EA = 1:1, 52.5 mg, 75%). M.p.: 181-182 °C. ^{1}H NMR (400 MHz, DMSO) δ 13.86 (s, 1H), 8.67 (d, *J* = 8.3 Hz, 1H), 7.98 (d, *J* = 8.3 Hz, 2H), 7.77 (d, *J* = 7.7 Hz, 1H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 5.85 (s, 1H), 3.62 (s, 6H). ^{13}C NMR (150 MHz, DMSO) δ 184.3, 163.7, 140.2, 137.2, 134.1, 131.9, 129.6, 129.4, 129.1, 124.2, 123.2, 120.3, 77.7, 40.8. HRMS (ESI): Calcd for $C_{17}H_{16}ClNO_3S$ $[M+Na]^+$ 372.0432, Found: 372.0425.



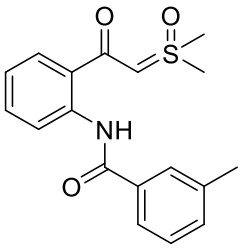
4-bromo-*N*-(2-(2-(dimethyl(oxo)-λ^6-sulfanylidene)acetyl)phenyl)benzamide (3ah)

The title compound was isolated as a pale-yellow solid (PE/EA = 1:1, 61.3 mg, 78%). M.p.: 160-161 °C. ^{1}H NMR (400 MHz, DMSO) δ 13.87 (s, 1H), 8.68 (d, *J* = 8.2 Hz, 1H), 7.93 - 7.76 (m, 5H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.12 (t, *J* = 7.3 Hz, 1H), 5.86 (s, 1H), 3.64 (s, 6H). ^{13}C NMR (150 MHz, DMSO) δ 184.3, 163.9, 140.2, 134.5, 132.5, 131.9, 129.5, 129.0, 126.2, 124.2, 123.1, 120.4, 77.6, 40.9. HRMS (ESI): Calcd for $C_{17}H_{16}BrNO_3S$ $[M+Na]^+$ 415.9926, Found: 415.9919.



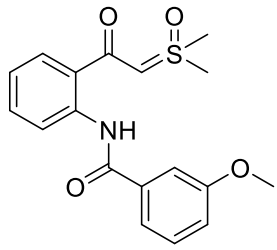
***N*-(2-(2-(dimethyl(oxo)-λ^6-sulfanylidene)acetyl)phenyl)-4-nitrobenzamide (3ai)**

The title compound was isolated as a pale-yellow solid (PE/EA = 1:1, 46.7 mg, 64%). M.p.: 198-199 °C. ^{1}H NMR (400 MHz, DMSO) δ 14.15 (s, 1H), 8.68 (d, *J* = 8.2 Hz, 1H), 8.45 (d, *J* = 8.8 Hz, 2H), 8.19 (d, *J* = 8.8 Hz, 2H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 5.89 (s, 1H), 3.64 (s, 6H). ^{13}C NMR (150 MHz, DMSO) δ 184.1, 163.0, 149.8, 140.9, 140.0, 132.0, 129.1, 129.0, 124.7, 124.3, 123.5, 120.4, 77.8, 40.9. HRMS (ESI): Calcd for $C_{17}H_{16}N_2O_5S$ $[M+Na]^+$ 383.0672, Found: 383.0662.



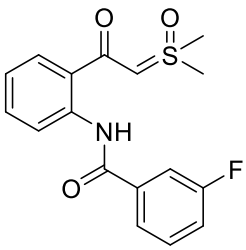
_N_-(2-(2-(dimethyl(oxo)-λ^6-sulfanylidene)acetyl)phenyl)-3-methylbenzamide (3aj)

The title compound was isolated as a pale-yellow solid (PE/EA = 1:1, 32.3 mg, 49%). M.p.: 148-149 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.05 (s, 1H), 8.80 (d, *J* = 8.4 Hz, 1H), 7.88 (s, 1H), 7.83 (d, *J* = 7.4 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.40 - 7.31 (m, 2H), 7.03 (t, *J* = 7.5 Hz, 1H), 5.06 (s, 1H), 3.50 (s, 6H), 2.43 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 185.8, 165.9, 140.2, 138.5, 135.5, 132.4, 132.0, 128.6, 128.4, 124.4, 124.1, 122.5, 121.1, 72.0, 42.4, 21.6. HRMS (ESI): Calcd for $C_{18}H_{19}NO_3S$ $[M+Na]^+$ 352.0978, Found: 352.0972.



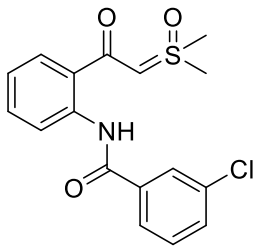
_N_-(2-(2-(dimethyl(oxo)-λ^6-sulfanylidene)acetyl)phenyl)-3-methoxybenzamide (3ak)

The title compound was isolated as a pale-yellow solid (PE/EA = 1:1, 19.1 mg, 28%). M.p.: 168-169 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.13 (s, 1H), 8.81 (d, *J* = 8.3 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 3H), 7.45 (t, *J* = 7.3 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.09 - 7.02 (m, 2H), 5.06 (s, 1H), 3.89 (s, 3H), 3.53 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.7, 165.5, 159.9, 140.2, 137.1, 132.1, 129.7, 128.5, 124.0, 122.6, 121.0, 119.5, 118.2, 112.6, 71.9, 55.5, 42.4. HRMS (ESI): Calcd for $C_{18}H_{19}NO_4S$ $[M+Na]^+$ 368.0927, Found: 368.0927.



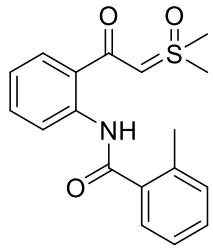
_N_-(2-(2-(dimethyl(oxo)-λ^6-sulfanylidene)acetyl)phenyl)-3-fluorobenzamide (3al)

The title compound was isolated as a white solid (PE/EA = 1:1, 39.6 mg, 59%). M.p.: 179-180 °C. ^{1}H NMR (400 MHz, DMSO) δ 13.90 (s, 1H), 8.67 (d, *J* = 8.3 Hz, 1H), 7.80 (dd, *J* = 16.2, 7.8 Hz, 2H), 7.73 - 7.64 (m, 2H), 7.56 - 7.43 (m, 2H), 7.13 (t, *J* = 7.6 Hz, 1H), 5.87 (s, 1H), 3.63 (s, 6H). ^{13}C NMR (150 MHz, DMSO) δ 184.3, 163.4 (d, $J_{C\text{-}F}$ = 2.4 Hz), 162.7 (d, $J_{C\text{-}F}$ = 243 Hz), 140.1, 137.9 (d, $J_{C\text{-}F}$ = 6.6 Hz), 131.9, 131.7 (d, $J_{C\text{-}F}$ = 8.0 Hz), 129.1, 124.2, 123.4 (d, $J_{C\text{-}F}$ = 2.6 Hz), 123.2, 120.3, 119.3 (d, $J_{C\text{-}F}$ = 21.2 Hz), 114.4 (d, $J_{C\text{-}F}$ = 22.9 Hz), 77.7, 40.9. ^{19}F NMR (565 MHz, DMSO) δ -111.85. HRMS (ESI): Calcd for $C_{17}H_{16}FNO_3S$ $[M+Na]^+$ 356.0727, Found: 356.0718.



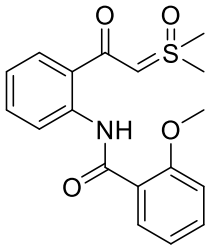
3-chloro-*N*-(2-(2-(dimethyl(oxo)-λ^6-sulfanylidene)acetyl)phenyl)benzamide (3am)

The title compound was isolated as a pale-yellow solid (PE/EA = 1:1, 40.4 mg, 58%). M.p.: 150-151 °C. ^{1}H NMR (400 MHz, DMSO) δ 13.91 (s, 1H), 8.67 (d, *J* = 8.2 Hz, 1H), 7.99 - 7.88 (m, 2H), 7.78 (d, *J* = 7.4 Hz, 1H), 7.75 - 7.62 (m, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 5.87 (s, 1H), 3.64 (s, 6H). ^{13}C NMR (100 MHz, DMSO) δ 184.2, 163.3, 140.1, 137.4, 134.2, 132.2, 131.9, 131.4, 129.0, 127.6, 125.9, 124.3, 123.3, 120.4, 77.7, 40.9. HRMS (ESI): Calcd for $C_{17}H_{16}ClNO_3S$ $[M+Na]^+$ 372.0432, Found: 372.0437.



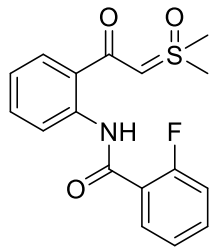
***N*-(2-(2-(dimethyl(oxo)-λ^6-sulfanylidene)acetyl)phenyl)-2-methylbenzamide (3an)**

The title compound was isolated as a pale-yellow solid (PE/EA = 1:1, 40.7 mg, 62%). M.p.: 125-126 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.46 (s, 1H), 8.80 (d, *J* = 8.3 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 2H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.25 (t, *J* = 6.4 Hz, 2H), 7.04 (t, *J* = 7.6 Hz, 1H), 5.03 (s, 1H), 3.44 (s, 6H), 2.55 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 185.5, 168.5, 140.0, 137.2, 136.9, 132.0, 131.4, 130.1, 128.5, 127.4, 126.0, 124.2, 122.6, 120.9, 71.9, 42.3, 20.4. HRMS (ESI): Calcd for $C_{18}H_{19}NO_3S$ $[M+Na]^+$ 352.0978, Found: 352.0982.



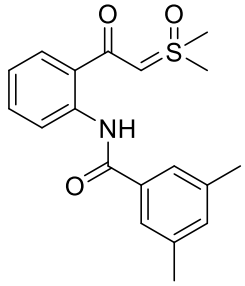
***N*-(2-(2-(dimethyl(oxo)-λ^6-sulfanylidene)acetyl)phenyl)-2-methoxybenzamide (3ao)**

The title compound was isolated as a pale-yellow liquid (PE/EA = 1:1, 52.9 mg, 76%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.27 (s, 1H), 8.73 (d, *J* = 8.3 Hz, 1H), 8.13 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.46 - 7.43 (m, 1H), 7.41 (dd, *J* = 11.5, 4.2 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.99 (d, *J* = 8.3 Hz, 1H), 4.97 (s, 1H), 4.07 (s, 3H), 3.48 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.0, 164.5, 157.7, 138.5, 132.8, 132.1, 131.3, 128.2, 127.5, 123.6, 122.7, 122.5, 121.0, 111.5, 71.9, 55.8, 42.2. HRMS (ESI): Calcd for $C_{18}H_{19}NO_4S$ $[M+Na]^+$ 368.0927, Found: 368.0926.



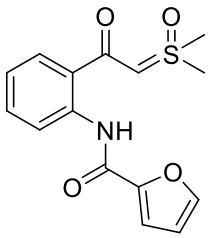
_N_-(2-(2-(dimethyl(oxo)-λ^6-sulfanylidene)acetyl)phenyl)-2-fluorobenzamide (3ap)

The title compound was isolated as a pale-yellow solid (PE/EA = 1:1, 37.8 mg, 57%). M.p.: 142-143 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.48 (s, 1H), 8.78 (d, *J* = 8.3 Hz, 1H), 8.03 (t, *J* = 7.7 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.51 - 7.44 (m, 2H), 7.29 (d, *J* = 7.1 Hz, 1H), 7.20 - 7.13 (m, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 5.00 (s, 1H), 3.53 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 185.2, 162.4, 160.2 (d, $J_{C\text{-}F}$ = 250.8 Hz), 138.9, 133.0 (d, $J_{C\text{-}F}$ = 8.7 Hz), 131.6, 131.6, 128.2, 125.9, 124.6 (d, $J_{C\text{-}F}$ = 2.8 Hz), 123.8 (d, $J_{C\text{-}F}$ = 12.3 Hz), 123.1, 121.7, 116.4 (d, $J_{C\text{-}F}$ = 23.2 Hz), 71.8, 42.4. ^{19}F NMR (565 MHz, $CDCl_3$) δ -112.97. HRMS (ESI): Calcd for $C_{17}H_{16}FNO_3S$ $[M+Na]^+$ 356.0727, Found: 356.0732.



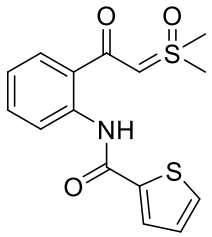
_N_-(2-(2-(dimethyl(oxo)-λ^6-sulfanylidene)acetyl)phenyl)-3,5-dimethylbenzamide (3aq)

The title compound was isolated as a pale-yellow solid (PE/EA = 1:1, 44.5 mg, 65%). M.p.: 176-177 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.95 (s, 1H), 8.77 (d, *J* = 7.9 Hz, 1H), 7.64 (s, 2H), 7.59 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.46 - 7.40 (m, 1H), 7.15 (s, 1H), 7.07 - 6.98 (m, 1H), 5.07 (s, 1H), 3.51 (s, 6H), 2.39 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 185.8, 166.2, 140.1, 138.2, 135.6, 133.2, 131.9, 128.4, 125.4, 124.2, 122.5, 121.1, 72.2, 42.3, 21.5. HRMS (ESI): Calcd for $C_{19}H_{21}NO_3S$ $[M+Na]^+$ 366.1134, Found: 366.1132.



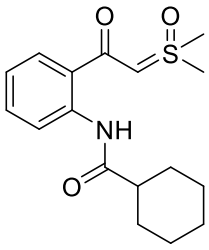
_N_-(2-(2-(dimethyl(oxo)-λ^6-sulfanylidene)acetyl)phenyl)furan-2-carboxamide (3ar)

The title compound was isolated as a pale-yellow solid (PE/EA = 1:1, 21.4 mg, 35%). M.p.: 105-106 °C. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 12.97 (s, 1H), 8.60 (d, *J* = 8.3 Hz, 1H), 7.55 (d, *J* = 7.7 Hz, 2H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.10 (d, *J* = 3.3 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.48 (dd, *J* = 3.2, 1.6 Hz, 1H), 3.45 (s, 6H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 185.8, 156.9, 149.3, 145.1, 139.9, 132.0, 128.7, 124.6, 122.8, 121.1, 114.7, 112.4, 73.1, 42.4. HRMS (ESI): Calcd for $C_{15}H_{15}NO_4S$ $[M+H]^+$ 306.0795, Found: 306.0795.



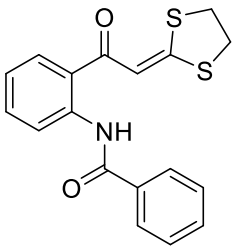
_N_-(2-(2-(dimethyl(oxo)-λ^6-sulfanylidene)acetyl)phenyl)thiophene-2-carboxamide (3as)

The title compound was isolated as a pale-yellow solid (PE/EA = 1:1, 36.2 mg, 56%). M.p.: 164-165 °C. ^{1}H NMR (400 MHz, DMSO) δ 13.88 (s, 1H), 8.58 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.89 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.83 - 7.73 (m, 2H), 7.50 - 7.40 (m, 1H), 7.28 (dd, *J* = 4.9, 3.8 Hz, 1H), 7.16 - 7.03 (m, 1H), 5.86 (s, 1H), 3.64 (s, 6H). ^{13}C NMR (100 MHz, DMSO) δ 184.3, 159.8, 141.0, 140.1, 132.4, 131.9, 129.0, 128.9, 128.7, 123.8, 122.9, 120.1, 77.5, 40.9. HRMS (ESI): Calcd for $C_{15}H_{15}NO_3S_2$ $[M+Na]^+$ 344.0386, Found: 344.0382.



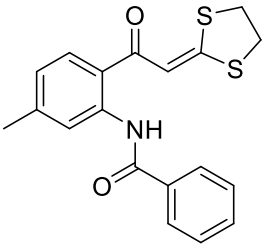
_N_-(2-(2-(dimethyl(oxo)-λ^6-sulfanylidene)acetyl)phenyl)cyclohexanecarboxamide (3at)

The title compound was isolated as a pale-yellow solid (PE/EA = 1:1, 34.6 mg, 54%). M.p.: 130-131 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.99 (s, 1H), 8.64 (d, *J* = 8.3 Hz, 1H), 7.55 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.42 - 7.31 (m, 1H), 6.98 (t, *J* = 7.3 Hz, 1H), 5.03 (s, 1H), 3.52 (s, 6H), 2.35 - 2.23 (m, 1H), 1.98 (d, *J* = 13.2 Hz, 2H), 1.85 - 1.78 (m, 2H), 1.69 (d, *J* = 11.0 Hz, 1H), 1.6 - 1.5 (m, 2H), 1.35 - 1.25 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.9, 175.3, 140.1, 131.9, 128.3, 124.0, 122.2, 121.0, 71.9, 47.2, 42.4, 29.8, 26.0, 25.9. HRMS (ESI): Calcd for $C_{17}H_{23}NO_3S$ $[M+Na]^+$ 344.1291, Found: 344.1288.



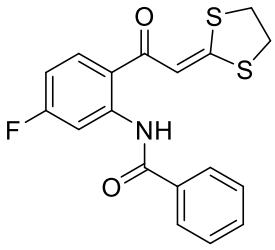
_N_-(2-(2-(1,3-dithiolan-2-ylidene)acetyl)phenyl)benzamide (5a)

The title compound was isolated as a pale-yellow solid (PE/EA = 5:1, 60.8 mg, 89%). M.p.: 113-114 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.57 (s, 1H), 8.79 (d, *J* = 8.4 Hz, 1H), 8.01 (d, *J* = 7.4 Hz, 2H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.54 - 7.35 (m, 4H), 7.03 (t, *J* = 7.6 Hz, 1H), 3.38 (t, *J* = 6.3 Hz, 2H), 3.28 (t, *J* = 6.3 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 189.2, 170.4, 166.0, 141.1, 135.2, 133.8, 131.9, 129.4, 128.8, 127.7, 124.1, 122.7, 121.3, 109.6, 39.1, 35.6. HRMS (ESI): Calcd for $C_{18}H_{15}NO_2S_2$ $[M+Na]^+$ 364.0436, Found: 364.0426.



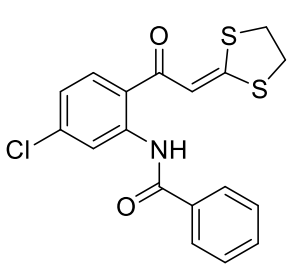
_N_-(2-(2-(1,3-dithiolan-2-ylidene)acetyl)-5-methylphenyl)benzamide (5b)

The title compound was isolated as a pale-yellow solid (PE/EA = 5:1, 56.0 mg, 78%). M.p.: 149-150 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.78 (s, 1H), 8.75 (s, 1H), 8.16 - 8.05 (m, 2H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.60 - 7.46 (m, 3H), 7.37 (s, 1H), 6.94 (dd, *J* = 8.1, 1.0 Hz, 1H), 3.50 (dd, *J* = 7.4, 5.5 Hz, 2H), 3.40 (dd, *J* = 7.3, 5.5 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 189.0, 169.4, 166.1, 145.1, 141.4, 135.3, 131.8, 129.5, 128.8, 127.7, 123.6, 121.6, 121.5, 109.6, 39.1, 35.6, 22.3. HRMS (ESI): Calcd for $C_{19}H_{17}NO_2S_2$ $[M+Na]^+$ 378.0593, Found: 378.0598.



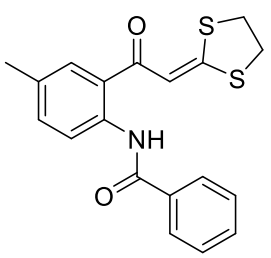
_N_-(2-(2-(1,3-dithiolan-2-ylidene)acetyl)-5-fluorophenyl)benzamide (5c)

The title compound was isolated as a pale-yellow solid (PE/EA = 5:1, 66.8 mg, 92%). M.p.: 139-140 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.97 (s, 1H), 8.74 (dd, *J* = 12.0, 2.6 Hz, 1H), 8.09 (dd, *J* = 5.2, 3.3 Hz, 2H), 7.85 (dd, *J* = 8.9, 6.3 Hz, 1H), 7.58 - 7.49 (m, 3H), 7.30 (s, 1H), 6.81 (ddd, *J* = 8.9, 7.5, 2.6 Hz, 1H), 3.49 (dd, *J* = 7.3, 5.5 Hz, 2H), 3.40 (dd, *J* = 7.3, 5.5 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 188.1, 170.7, 166.2, 165.6 (d, J_{C-F} = 252.8 Hz), 143.7 (d, J_{C-F} = 12.9 Hz), 134.8, 132.1, 131.6 (d, J_{C-F} = 10.7 Hz), 128.9, 127.7, 120.2 (d, J_{C-F} = 2.7 Hz), 109.8 (d, J_{C-F} = 22.3 Hz), 109.2, 108.3 (d, J_{C-F} = 27.9 Hz). 39.2, 35.6. ^{19}F NMR (565 MHz, $CDCl_3$) δ -102.03. HRMS (ESI): Calcd for $C_{18}H_{14}FNO_2S_2$ $[M+Na]^+$ 382.0342, Found: 382.0332.



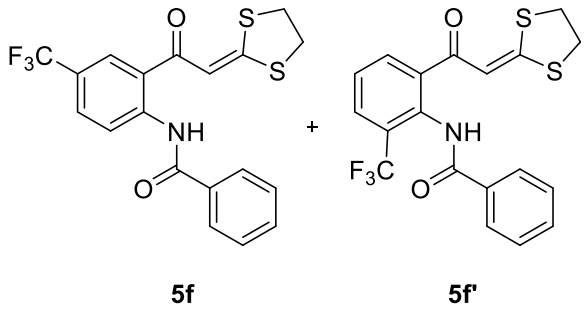
_N_-(2-(2-(1,3-dithiolan-2-ylidene)acetyl)-5-chlorophenyl)benzamide (5d)

The title compound was isolated as a pale-yellow solid (PE/EA = 5:1, 73.4 mg, 97%). M.p.: 157-158 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.81 (s, 1H), 9.01 (s, 1H), 8.09 (d, *J* = 7.4 Hz, 2H), 7.76 (d, *J* = 8.5 Hz, 1H), 7.58 - 7.51 (m, 3H), 7.30 (s, 1H), 7.09 (d, *J* = 8.5 Hz, 1H), 3.50 (t, *J* = 6.3 Hz, 2H), 3.41 (t, *J* = 6.3 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 188.2, 171.3, 166.0, 142.2, 139.9, 134.8, 132.1, 130.4, 128.9, 127.7, 122.8, 122.1, 121.1, 109.2, 39.2, 35.7. HRMS (ESI): Calcd for $C_{18}H_{14}ClNO_2S_2$ $[M+Na]^+$ 398.0047, Found: 398.0046.



***N*-(2-(2-(1,3-dithiolan-2-ylidene)acetyl)-4-methylphenyl)benzamide (5e)**

The title compound was isolated as a pale-yellow solid (PE/EA = 5:1, 46.9 mg, 66%). M.p.: 136-137 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.53 (s, 1H), 8.76 (d, *J* = 8.5 Hz, 1H), 8.09 (dd, *J* = 7.8, 1.4 Hz, 2H), 7.62 (s, 1H), 7.60 - 7.44 (m, 3H), 7.39 - 7.31 (m, 2H), 3.49 (t, *J* = 6.4 Hz, 2H), 3.39 (t, *J* = 6.4 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 189.3, 170.0, 165.8, 138.7, 135.3, 134.5, 132.2, 131.7, 129.7, 128.8, 127.6, 124.1, 121.3, 109.7, 39.1, 35.6, 21.0. HRMS (ESI): Calcd for $C_{19}H_{17}NO_2S_2$ $[M+H]^+$ 356.0773, Found: 356.0766.



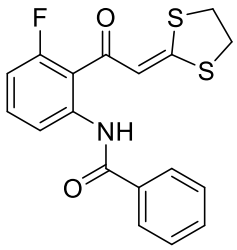
5f **5f'**

3:1

***N*-(2-(2-(1,3-dithiolan-2-ylidene)acetyl)-4-(trifluoromethyl)phenyl)benzamide (5f) and**

***N*-(2-(2-(1,3-dithiolan-2-ylidene)acetyl)-6-(trifluoromethyl)phenyl)benzamide (5f')**

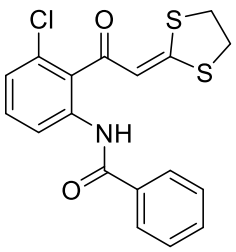
The title compound was isolated as a pale-yellow solid (PE/EA = 5:1, 63.8 mg, 78%). M.p.: 78-79 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.80 (s, 1H), 9.04 (d, *J* = 8.8 Hz, 1H), 8.20 (s, 0.31H), 8.13 - 8.07 (m, 2.32H), 8.05 (s, 1H), 7.78 - 7.75 (m, 1.30H), 7.59 - 7.51 (m, 3.32H), 7.34 (s, 1H), 7.33 (s, 0.31H), 3.54 - 3.48 (m, 2.64H), 3.44 - 3.40 (m, 2.67H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 187.9, 184.4, 172.8, 170.5, 166.2, 143.9, 139.0, 134.6, 132.3, 131.06, 130.17 (q, J_{C-F} = 3.3 Hz), 129.24, 128.94, 128.53, 128.51, 128.48, 128.46, 127.7, 126.7, 126.3 (q, J_{C-F} = 3.8 Hz), 124.9, 124.8 (q, J_{C-F} = 3.8 Hz), 124.7, 124.5, 124.3, 124.0, 123.7, 123.1, 121.4, 108.9, 107.7, 39.3, 39.1, 35.8, 35.7. ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.06, -62.67. HRMS (ESI): Calcd for $C_{19}H_{14}F_3NO_2S_2$ $[M+H]^+$ 432.0310, Found: 432.0307.



***N*-(2-(2-(1,3-dithiolan-2-ylidene)acetyl)-3-fluorophenyl)benzamide (5g)**

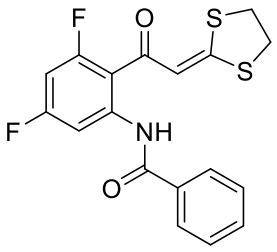
The title compound was isolated as a pale-yellow solid (PE/EA = 5:1, 64.9 mg, 90%). M.p.: 87-88 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.80 (s, 1H), 8.55 (d, *J* = 8.4 Hz, 1H), 8.04 (dd, *J* = 5.2, 3.2 Hz, 2H), 7.59 - 7.49 (m, 3H), 7.46 (td, *J* = 8.3, 6.4 Hz, 1H), 7.22 (d, *J* = 4.4 Hz, 1H), 6.87 (dd, *J* = 10.4, 8.4

Hz, 1H), 3.50 (t, J = 6.5 Hz, 2H), 3.40 (t, J = 6.4 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 185.9 (d, J_{C-F} = 2.1 Hz), 171.1 (d, J_{C-F} = 1.5 Hz), 165.7, 161.4 (d, J_{C-F} = 248.9 Hz), 140.9 (d, J_{C-F} = 4.7 Hz), 134.8, 133.5 (d, J_{C-F} = 11.0 Hz), 132.1, 128.9, 127.6, 117.3 (d, J_{C-F} = 3.0 Hz), 115.5 (d, J_{C-F} = 15.6 Hz), 114.1 (d, J_{C-F} = 12.0 Hz), 110.8 (d, J_{C-F} = 24.0 Hz), 39.3, 35.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.52. HRMS (ESI): Calcd for $C_{18}H_{14}FNO_2S_2$ $[M+Na]^+$ 382.0342, Found: 382.0339.



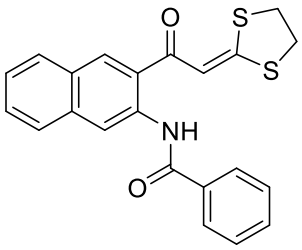
***N*-(2-(2-(1,3-dithiolan-2-ylidene)acetyl)-3-chlorophenyl)benzamide (5h)**

The title compound was isolated as a pale-yellow solid (PE/EA = 5:1, 53.8 mg, 71%). M.p.: 131-132 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.14 (s, 1H), 8.45 (dd, J = 8.3, 0.8 Hz, 1H), 7.93 (dd, J = 5.2, 3.4 Hz, 2H), 7.56 - 7.53 (m, 1H), 7.51 - 7.48 (m, 2H), 7.37 (t, J = 8.2 Hz, 1H), 7.18 (dd, J = 8.0, 0.9 Hz, 1H), 7.08 (s, 1H), 3.53 (dd, J = 7.4, 5.6 Hz, 2H), 3.41 (dd, J = 7.4, 5.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 188.0, 171.0, 165.2, 138.4, 134.4, 132.1, 131.5, 131.5, 128.9, 128.8, 127.5, 125.6, 120.6, 114.3, 39.3, 35.9. HRMS (ESI): Calcd for $C_{18}H_{14}ClNO_2S_2$ $[M+Na]^+$ 398.0047, Found: 398.0041.



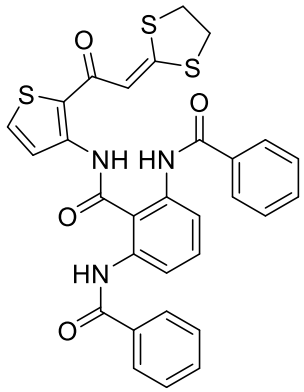
***N*-(2-(2-(1,3-dithiolan-2-ylidene)acetyl)-3,5-difluorophenyl)benzamide (5i)**

The title compound was isolated as a pale-yellow solid (PE/EA = 5:1, 61.4 mg, 81%). M.p.: 100-101 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.22 (s, 1H), 8.62 - 8.34 (m, 1H), 8.04 (dd, J = 5.2, 3.4 Hz, 2H), 7.58 - 7.51 (m, 3H), 7.20 (d, J = 4.3 Hz, 1H), 6.60 (ddd, J = 11.1, 8.3, 2.5 Hz, 1H), 3.51 (dd, J = 7.4, 5.5 Hz, 2H), 3.42 (dd, J = 7.4, 5.5 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 185.1 (d, J_{C-F} = 3.0 Hz), 171.7 (d, J_{C-F} = 1.7 Hz), 165.8, 165.7, 164.1 (d, J_{C-F} = 15.9 Hz), 163.2 (d, J_{C-F} = 14.9 Hz), 161.6 (d, J_{C-F} = 15.2 Hz), 142.9 (d, J_{C-F} = 7.2 Hz), 142.8 (d, J_{C-F} = 6.9 Hz), 134.4, 132.3, 129.0, 127.7, 113.6 (d, J_{C-F} = 13.2 Hz), 111.5 (d, J_{C-F} = 3.9 Hz), 111.4 (d, J_{C-F} = 3.8 Hz), 104.8 (d, J_{C-F} = 3.3 Hz), 104.6 (d, J_{C-F} = 3.2 Hz), 99.4 (d, J_{C-F} = 26.0 Hz), 99.2 (d, J_{C-F} = 26.0 Hz), 39.3, 35.8. ^{19}F NMR (565 MHz, $CDCl_3$) δ -101.09, -101.12, -103.12, -103.15. HRMS (ESI): Calcd for $C_{18}H_{13}F_2NO_2S_2$ $[M+Na]^+$ 400.0248, Found: 400.0242.



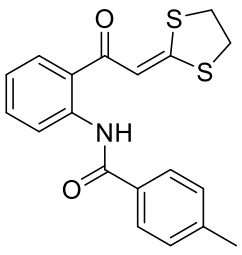
_N_-(3-(2-(1,3-dithiolan-2-ylidene)acetyl)naphthalen-2-yl)benzamide (5j)

The title compound was isolated as a pale-yellow solid (PE/EA = 5:1, 62.8 mg, 80%). M.p.: 186-187 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.46 (s, 1H), 9.31 (s, 1H), 8.37 (s, 1H), 8.20 - 8.11 (m, 2H), 7.92 - 7.81 (m, 2H), 7.59 - 7.52 (m, 5H), 7.47 - 7.39 (m, 1H), 3.53 (t, *J* = 6.3 Hz, 2H), 3.43 (t, *J* = 6.3 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 189.4, 170.8, 165.9, 136.4, 136.1, 135.3, 131.8, 131.2, 129.1, 128.9, 128.8, 128.7, 127.9, 127.6, 125.6, 125.2, 118.3, 109.8, 39.2, 35.7. HRMS (ESI): Calcd for $C_{22}H_{17}NO_2S_2$ $[M+H]^+$ 392.0773, Found: 392.0780.



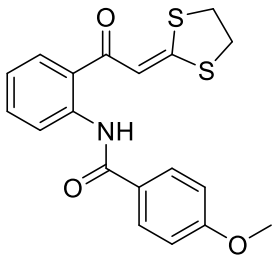
***N,N'*-(2-((2-(2-(1,3-dithiolan-2-ylidene)acetyl)thiophen-3-yl)carbamoyl)-1,3-phenylene)dibenzamide (5k)**

The title compound was isolated as a pale-yellow solid (PE/EA = 5:1, 32.8 mg, 28%). M.p.: 93-94 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.50 (s, 1H), 11.98 (s, 1H), 11.76 (s, 1H), 8.16 (t, *J* = 7.7 Hz, 4H), 8.07 (d, *J* = 7.4 Hz, 2H), 7.66 - 7.48 (m, 9H), 7.09 (s, 1H), 3.51 (t, *J* = 6.0 Hz, 2H), 3.41 (t, *J* = 5.8 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 181.1, 167.9, 167.5, 166.1, 164.7, 136.4, 134.3, 133.3, 133.1, 132.9, 132.9, 132.8, 132.8, 132.6, 132.5, 132.5, 129.1, 129.1, 128.9, 128.4, 128.2, 127.8, 117.8, 114.9, 109.5, 39.4, 35.8. HRMS (ESI): Calcd for $C_{30}H_{23}N_3O_4S_3$ $[M+Na]^+$ 608.0743, Found: 608.0750.



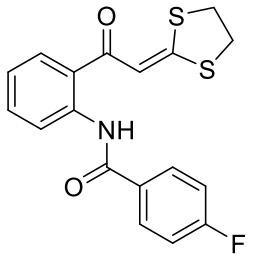
***N*-(2-(2-(1,3-dithiolan-2-ylidene)acetyl)phenyl)-4-methylbenzamide (5l)**

The title compound was isolated as a pale-yellow solid (PE/EA = 5:1, 51.0 mg, 77%). M.p.: 130-131 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.62 (s, 1H), 8.88 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 2H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.36 (s, 1H), 7.32 (d, *J* = 7.9 Hz, 2H), 7.12 (t, *J* = 7.6 Hz, 1H), 3.48 (t, *J* = 6.4 Hz, 2H), 3.38 (t, *J* = 6.4 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 189.2, 170.2, 166.0, 142.3, 141.2, 133.7, 132.4, 129.5, 129.4, 127.7, 124.0, 122.5, 121.3, 109.6, 39.1, 35.6, 21.6. HRMS (ESI): Calcd for $C_{19}H_{17}NO_2S_2$ $[M+Na]^+$ 378.0593, Found: 378.0601.



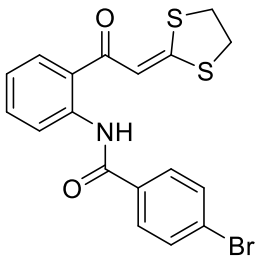
_N_-(2-(2-(1,3-dithiolan-2-ylidene)acetyl)phenyl)-4-methoxybenzamide (5m)

The title compound was isolated as a pale-yellow solid (PE/EA = 5:1, 44.2 mg, 64%). M.p.: 129-130 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.58 (s, 1H), 8.87 (d, *J* = 7.9 Hz, 1H), 8.09 - 8.04 (m, 2H), 7.83 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.56 - 7.51 (m, 1H), 7.37 (s, 1H), 7.13 - 7.09 (m, 1H), 7.04 - 6.98 (m, 2H), 3.87 (s, 3H), 3.49 (dd, *J* = 7.2, 5.6 Hz, 2H), 3.39 (dd, *J* = 7.3, 5.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 189.3, 170.1, 165.6, 162.6, 141.4, 133.8, 129.6, 129.4, 127.5, 124.0, 122.4, 121.2, 114.0, 109.7, 55.6, 39.2, 35.6. HRMS (ESI): Calcd for $C_{19}H_{17}NO_3S_2$ $[M+Na]^+$ 394.0542, Found: 394.0533.



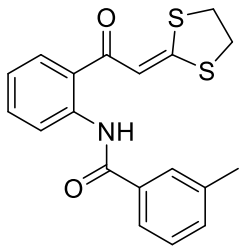
_N_-(2-(2-(1,3-dithiolan-2-ylidene)acetyl)phenyl)-4-fluorobenzamide (5n)

The title compound was isolated as a pale-yellow solid (PE/EA = 5:1, 58.1 mg, 87%). M.p.: 120-121 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.70 (s, 1H), 8.85 (d, *J* = 8.4 Hz, 1H), 8.11 (dd, *J* = 8.7, 5.3 Hz, 2H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 1H), 7.36 (s, 1H), 7.19 (t, *J* = 8.6 Hz, 2H), 7.13 (t, *J* = 7.6 Hz, 1H), 3.50 (t, *J* = 6.4 Hz, 2H), 3.39 (t, *J* = 6.4 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 189.3, 170.6, 165.1 (d, J_{C-F} = 250.5 Hz), 164.9, 141.1, 133.9, 131.4 (d, J_{C-F} = 3.0 Hz), 130.1 (d, J_{C-F} = 9.0 Hz), 129.5, 124.0, 122.8, 121.2, 115.9 (d, J_{C-F} = 21.9 Hz), 109.5, 39.2, 35.7. ^{19}F NMR (565 MHz, $CDCl_3$) δ -108.02. HRMS (ESI): Calcd for $C_{18}H_{14}FNO_2S_2$ $[M+Na]^+$ 382.0342, Found: 382.0341.



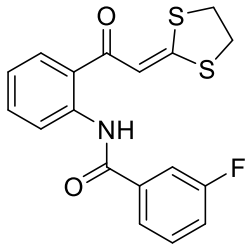
_N_-(2-(2-(1,3-dithiolan-2-ylidene)acetyl)phenyl)-4-bromobenzamide (5o)

The title compound was isolated as a pale-yellow solid (PE/EA = 5:1, 70.5 mg, 89%). M.p.: 159-160 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.75 (s, 1H), 8.83 (d, *J* = 8.3 Hz, 1H), 7.96 (d, *J* = 8.5 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.65 (t, *J* = 6.9 Hz, 2H), 7.56 - 7.51 (m, 1H), 7.36 (d, *J* = 11.4 Hz, 1H), 7.16 - 7.09 (m, 1H), 3.50 - 3.44 (m, 2H), 3.40 - 3.35 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 189.2, 170.8, 165.0, 141.0, 134.1, 133.9, 132.1, 129.4, 129.3, 126.7, 124.0, 122.9, 121.2, 109.5, 39.2, 35.7. HRMS (ESI): Calcd for $C_{18}H_{14}BrNO_2S_2$ $[M+H]^+$ 419.9722, Found: 419.9719.



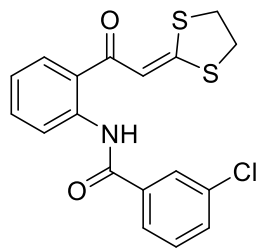
_N_-(2-(2-(1,3-dithiolan-2-ylidene)acetyl)phenyl)-3-methylbenzamide (5p)

The title compound was isolated as a pale-yellow solid (PE/EA = 5:1, 56.0 mg, 85%). M.p.: 95-96 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.63 (s, 1H), 8.88 (d, *J* = 8.4 Hz, 1H), 7.92 (s, 1H), 7.89 (d, *J* = 7.7 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 8.6 Hz, 2H), 7.13 (t, *J* = 7.6 Hz, 1H), 3.48 (t, *J* = 6.0 Hz, 2H), 3.38 (t, *J* = 6.1 Hz, 2H), 2.46 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 189.2, 170.3, 166.2, 141.1, 138.6, 135.1, 133.7, 132.6, 129.4, 128.7, 128.5, 124.6, 124.1, 122.6, 121.3, 109.6, 77.4, 77.2, 77.0, 39.2, 35.6, 21.6. HRMS (ESI): Calcd for $C_{19}H_{17}NO_2S_2$ $[M+Na]^+$ 378.0593, Found: 378.0586.



_N_-(2-(2-(1,3-dithiolan-2-ylidene)acetyl)phenyl)-3-fluorobenzamide (5q)

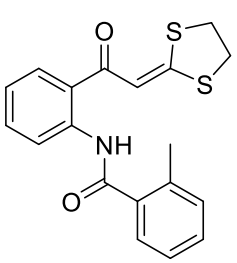
The title compound was isolated as a pale-yellow solid (PE/EA = 5:1, 60.9 mg, 91%). M.p.: 120-121 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.75 (s, 1H), 8.85 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.86 - 7.83 (m, 1H), 7.82 - 7.79 (m, 1H), 7.57 - 7.53 (m, 1H), 7.50 (td, *J* = 8.0, 5.7 Hz, 1H), 7.37 (s, 1H), 7.24 (td, *J* = 8.5, 2.5 Hz, 1H), 7.16 - 7.13 (m, 1H), 3.50 (t, *J* = 6.4 Hz, 2H), 3.40 (t, *J* = 6.4 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 189.2, 170.8, 164.6 (d, *J* = 2.4 Hz), 163.0 (d, *J* = 245.7 Hz), 140.9, 137.5(d, *J* = 6.9 Hz), 133.8, 130.5 (d, *J* = 7.8 Hz), 129.4, 124.0, 123.1 (d, *J* = 2.9 Hz), 123.0, 121.3, 118.9 (d, *J* = 21.3 Hz), 115.0 (d, *J* = 22.8 Hz), 109.4, 39.2, 35.7. ^{19}F NMR (565 MHz, $CDCl_3$) δ -111.87. HRMS (ESI): Calcd for $C_{18}H_{14}FNO_2S_2$ $[M+Na]^+$ 382.0342, Found: 382.0347.



_N_-(2-(2-(1,3-dithiolan-2-ylidene)acetyl)phenyl)-3-chlorobenzamide (5r)

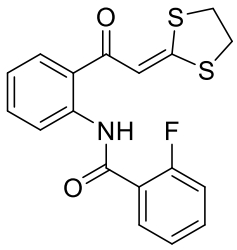
The title compound was isolated as a pale-yellow solid (PE/EA = 5:1, 67.5 mg, 96%). M.p.: 100-101 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.76 (s, 1H), 8.84 (d, *J* = 8.4 Hz, 1H), 8.09 (s, 1H), 7.97 (d, *J* = 7.6 Hz, 1H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.58 - 7.49 (m, 2H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.37 (s, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 3.51 (t, *J* = 6.3 Hz, 2H), 3.41 (t, *J* = 6.2 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 189.1, 170.9, 164.5, 140.8, 137.0, 135.0, 133.8, 131.8, 130.1, 129.4, 128.2, 125.5, 124.0,

123.0, 121.2, 109.3, 39.2, 35.6. HRMS (ESI): Calcd for $C_{18}H_{14}ClNO_2S_2$ $[M+Na]^+$ 398.0047, Found: 398.0053.



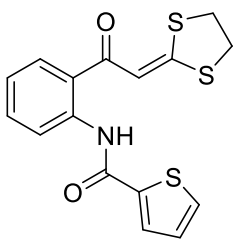
_N_-(2-(2-(1,3-dithiolan-2-ylidene)acetyl)phenyl)-2-methylbenzamide (5s)

The title compound was isolated as a pale-yellow solid (PE/EA = 5:1, 52.7 mg, 80%). M.p.: 136-137 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.99 (s, 1H), 8.86 (d, *J* = 8.3 Hz, 1H), 7.82 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.65 (d, *J* = 6.9 Hz, 1H), 7.57 - 7.53 (m, 1H), 7.36 (td, *J* = 7.5, 1.1 Hz, 1H), 7.33 (s, 1H), 7.30 – 7.25 (m, 2H), 7.16 - 7.12 (m, 1H), 3.45 (dd, *J* = 7.3, 5.5 Hz, 2H), 3.37 (dd, *J* = 7.2, 5.4 Hz, 2H), 2.56 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 189.0, 170.1, 168.7, 140.9, 137.1, 136.7, 133.7, 131.5, 130.3, 129.4, 127.5, 126.1, 124.3, 122.8, 121.3, 109.6, 39.1, 35.6, 20.4. HRMS (ESI): Calcd for $C_{19}H_{17}NO_2S_2$ $[M+Na]^+$ 378.0593, Found: 378.0584.



_N_-(2-(2-(1,3-dithiolan-2-ylidene)acetyl)phenyl)-2-fluorobenzamide (5t)

The title compound was isolated as a pale-yellow solid (PE/EA = 5:1, 54.7 mg, 82%). M.p.: 101-102 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.26 (d, *J* = 6.0 Hz, 1H), 8.82 (d, *J* = 8.4 Hz, 1H), 8.06 - 8.02 (m, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.49 (dd, *J* = 13.0, 6.3 Hz, 1H), 7.30 (s, 1H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.20 (dd, *J* = 10.9, 8.5 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 3.47 (t, *J* = 6.4 Hz, 2H), 3.37 (t, *J* = 6.3 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 188.7, 170.0, 162.6 (d, J_{C-F} = 2.4 Hz), 160.5 (d, J_{C-F} = 250.2 Hz), 140.0, 133.4 (d, J_{C-F} = 9.0 Hz), 133.3, 131.6 (d, J_{C-F} = 2.0 Hz), 129.2, 125.3, 124.6 (d, J_{C-F} = 3.6 Hz), 123.2 (d, J_{C-F} = 11.9 Hz), 123.2, 122.1, 116.6 (d, J_{C-F} = 23.4 Hz), 109.7, 39.1, 35.6. ^{19}F NMR (565 MHz, $CDCl_3$) δ -112.07. HRMS (ESI): Calcd for $C_{18}H_{14}FNO_2S_2$ $[M+Na]^+$ 382.0342, Found: 382.0333.

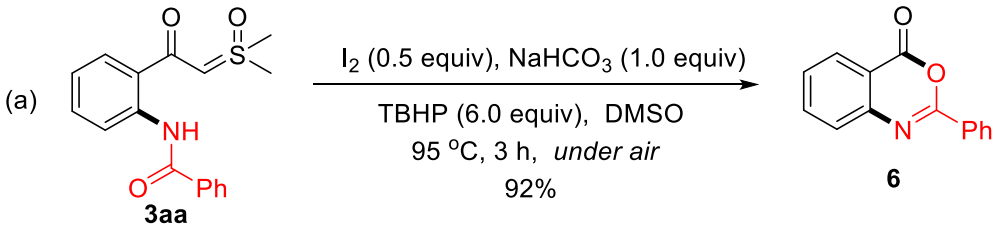


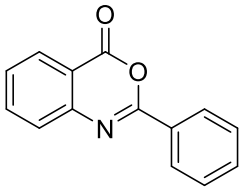
_N_-(2-(2-(1,3-dithiolan-2-ylidene)acetyl)phenyl)thiophene-2-carboxamide (5u)

The title compound was isolated as a pale-yellow solid (PE/EA = 5:1, 52.1 mg, 81%). M.p.: 155-156 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.76 (s, 1H). 8.80 - 8.78 (m, 1H). 7.86 (dd, *J* = 3.7, 0.9 Hz, 1H), 7.82 (dd, *J* = 8.0, 1.2 Hz, 1H). 7.54 (dd, *J* = 5.0, 0.9 Hz, 1H), 7.54 - 7.50 (m, 1H). 7.36 (s, 1H), 7.15 (dd, *J*

= 4.9, 3.8 Hz, 1H), 7.13 - 7.09 (m, 1H). 3.49 (dd, *J* = 7.4, 5.5 Hz, 2H), 3.39 (dd, *J* = 7.3, 5.5 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 189.1, 170.6, 160.6, 141.0, 140.8, 133.8, 131.1, 129.4, 128.7, 128.0, 123.5, 122.6, 121.0, 109.4, 39.2, 35.6. HRMS (ESI): Calcd for $C_{16}H_{13}NO_2S_3$ $[M+Na]^+$ 370.0001, Found: 370.0009.

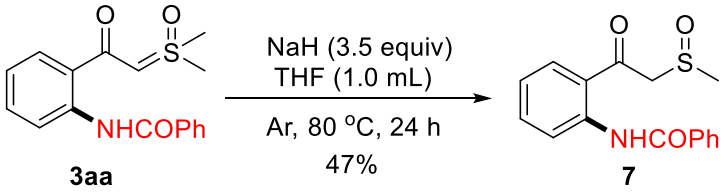
Derivatization Reactions

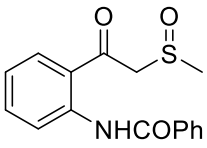




2-phenyl-4*H*-benzo[*d*][1,3]oxazin-4-one (6)

A mixture of **3aa** (0.1 mmol), I_2 (6.5 mg, 0.05 mmol, 0.5 equiv), $NaHCO_3$ (8.5 mg, 0.1 mmol, 1.0 equiv) and TBHP (78.0 mg, 0.6 mmol, 6.0 equiv) was added to a Schlenk tube equipped with a stir bar. DMSO (1.0 mL) was added and the mixture was stirred at 95 °C for 3 h under air atmosphere. The mixture was evaporated under reduced pressure and the residue was adsorbed onto small amounts of silica. The purification was performed by flash column chromatography on silica gel (eluent: PE/EA = 5:1). The title compound was isolated as a pale-yellow solid (PE/EA = 5:1, 20.4 mg, 92%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.32 (d, *J* = 7.9 Hz, 2H), 8.25 (d, *J* = 7.8 Hz, 1H), 7.83 (t, *J* = 7.7 Hz, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.7, 157.3, 147.2, 136.7, 132.8, 130.4, 128.9, 128.8, 128.5, 128.4, 127.4, 117.2. HRMS (ESI): Calcd for $C_{14}H_9NO_2$ $[M+H]^+$ 224.0706, Found: 224.0711.

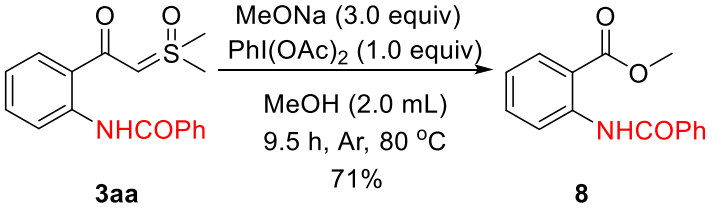




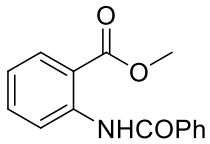
***N*-(2-(2-(methylsulfinyl)acetyl)phenyl)benzamide (7)**

A mixture of **3aa** (0.1 mmol) and NaH (60%, dispersion in paraffin liquid) (14.0 mg, 0.35 mmol, 3.5 equiv) was added to a Schlenk tube equipped with a stir bar. Dry THF (1.0 mL) was added and the mixture was stirred at 80 °C for 24 h under Ar atmosphere. The mixture was evaporated under reduced pressure and the residue was adsorbed onto small amounts of silica. Purification was performed by flash column chromatography on silica gel (eluent: EA). The title compound was isolated as a pale-yellow solid (EA, 14.0 mg, 47%). M.p.: 71-72 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.33 (s, 1H), 9.01

(d, *J* = 8.5 Hz, 1H), 8.05 (d, *J* = 7.8 Hz, 2H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.70 (t, *J* = 7.9 Hz, 1H), 7.60 - 7.57 (m, 1H), 7.54 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.6 Hz, 1H), 4.54 (d, *J* = 14.3 Hz, 1H), 4.38 (d, *J* = 14.3 Hz, 1H), 2.80 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.3, 166.3, 142.3, 137.0, 134.6, 132.4, 132.4, 129.1, 127.6, 123.0, 121.4, 121.3, 63.8, 39.7. HRMS (ESI): Calcd for $C_{16}H_{15}NO_3S$ $[M+Na]^+$ 324.0665, Found: 324.0675.



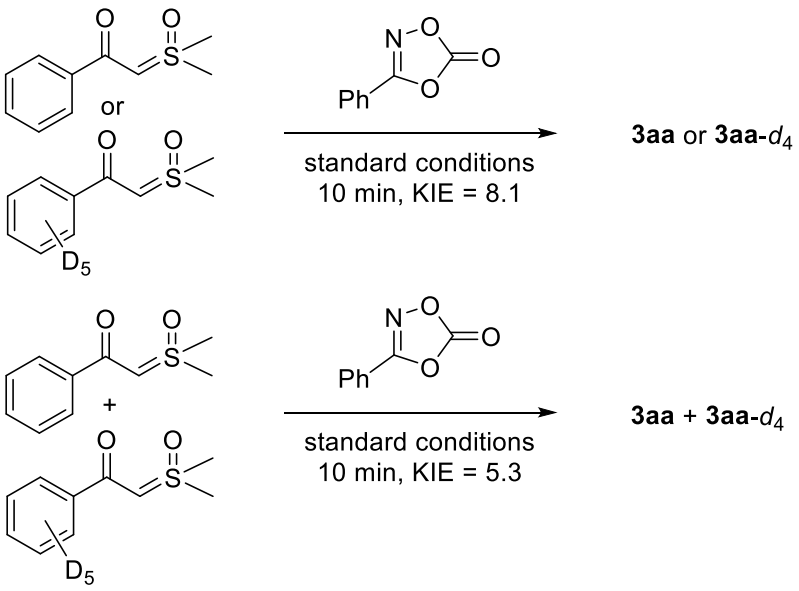
3aa **8**



methyl 2-benzamidobenzoate (8)

A mixture of **3aa** (0.1 mmol), MeONa (16.2 mg, 0.3 mmol, 3.0 equiv) and $PhI(OAc)_2$ (32.2 mg, 0.1 mmol, 1.0 equiv) was added to a Schlenk tube equipped with a stir bar. Dry MeOH (2.0 mL) was added and the mixture was stirred at 80 °C for 9.5 h under Ar atmosphere. The mixture was evaporated under reduced pressure and the residue was adsorbed onto small amounts of silica. The purification was performed by flash column chromatography on silica gel (eluent: PE/EA = 5:1). The title compound was isolated as a pale-yellow solid (PE/EA = 5:1, 18.0 mg, 71%). M.p.: 79-80 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.04 (s, 1H), 8.94 (d, *J* = 8.5 Hz, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 8.06 (d, *J* = 7.7 Hz, 2H), 7.61 (t, *J* = 7.9 Hz, 1H), 7.58 - 7.55 (m, 1H), 7.53 (t, *J* = 7.2 Hz, 2H), 7.13 (t, *J* = 7.6 Hz, 1H), 3.97 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.2, 165.9, 142.0, 135.1, 135.0, 132.1, 131.1, 129.0, 127.5, 122.8, 120.6, 115.3, 52.6. HRMS (ESI): Calcd for $C_{15}H_{13}NO_3$ $[M+Na]^+$ 278.0788, Found:278.0779.

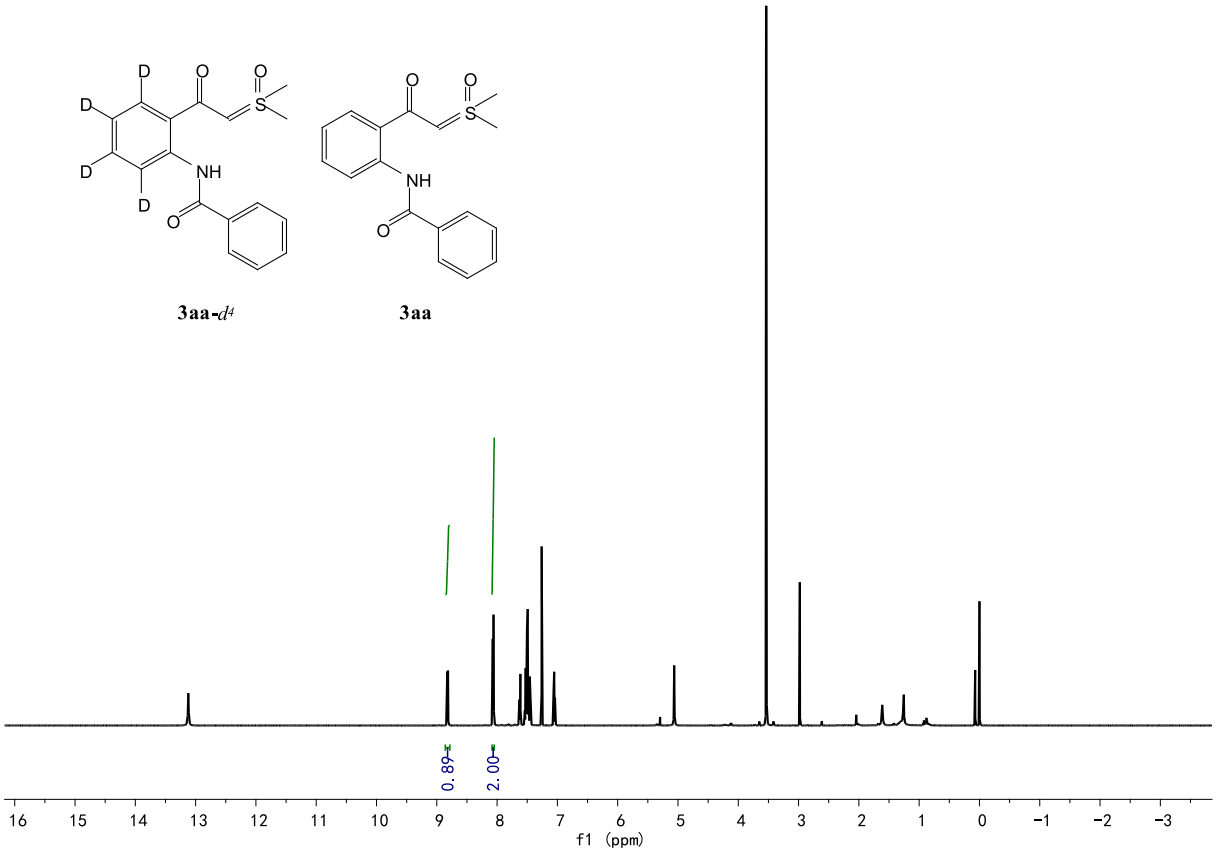
KIE Experiments

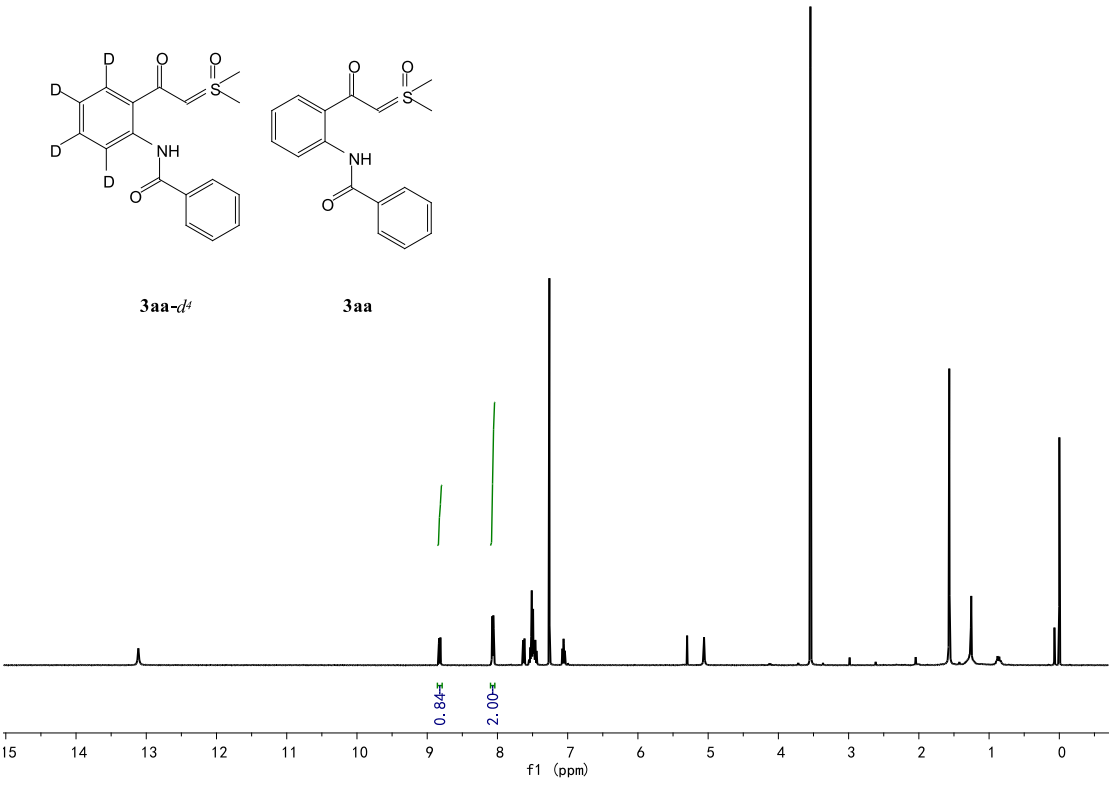


Intermolecular, Competitive KIE Studies. A mixture of **1a** (0.1 mmol) and **1a**-d_5 (0.1 mmol), **2a** (0.2 mmol), Cp*Co(CO)I_2 (9.5 mg, 0.02 mmol, 10 mol %), $AgSbF_6$ (13.7 mg, 0.04 mmol, 20 mol %) and $Zn(OAc)_2$ (11.0 mg, 0.06 mmol, 30 mol %) was weighted into a Schlenk tube equipped with a stir bar. Dry DCE (2.0 mL) was added. The reaction mixtures were stirred in an oil bath at 60 ^oC for 10 minutes under Ar atmosphere. Afterwards, the solvent was evaporated under reduced pressure and the residue was absorbed to small amounts of silica. Purification was performed by flash column chromatography on silica gel (eluent: PE/EA = 1:1). ^1H NMR analysis revealed KIE = 8.1.

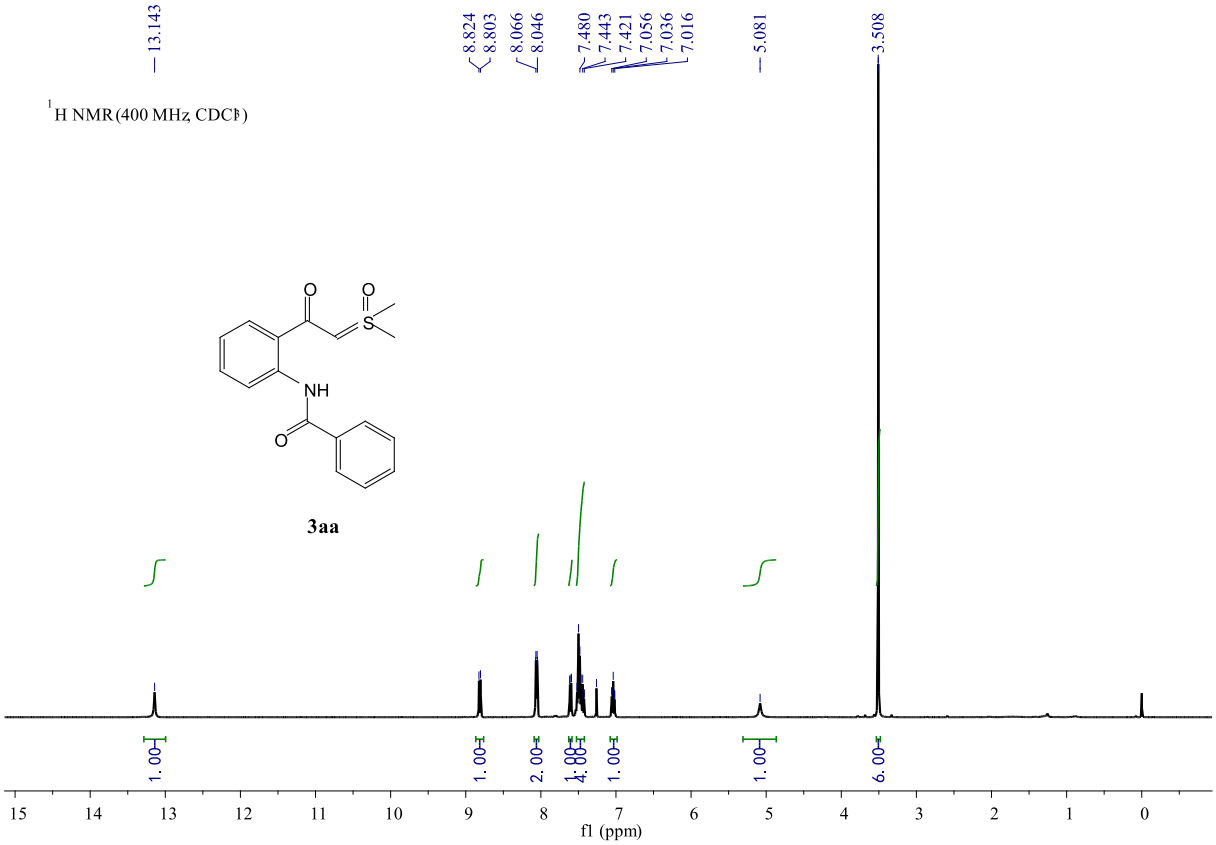
Independent, Parallel KIE Studies. Substrate **1a** (0.1 mmol) and **1a**-d_5 (0.1 mmol) were changed into two Schlenk tubes equipped with a stir bar, to each tube was added a mixture of **2a** (0.2 mmol), Cp*Co(CO)I_2 (9.5 mg, 0.02 mmol, 10 mol %), $AgSbF_6$ (13.7 mg, 0.04 mmol, 20 mol %) and $Zn(OAc)_2$ (11.0 mg, 0.06 mmol, 30 mol %). Dry DCE (2.0 mL) was then added. Thee two reaction mixtures were stirred side-by-side in an oil bath at 60 ^oC for 10 minutes under Ar atmosphere. Afterwards, these two reactions were quenched in an oil bath, and the reaction mixtures were rapidly combined. The solvent was evaporated under reduced pressure and the residue was absorbed to small amounts of silica. Purification was performed by flash column chromatography on silica gel (eluent: PE/EA = 1:1). ^1H NMR analysis revealed KIE = 5.3.

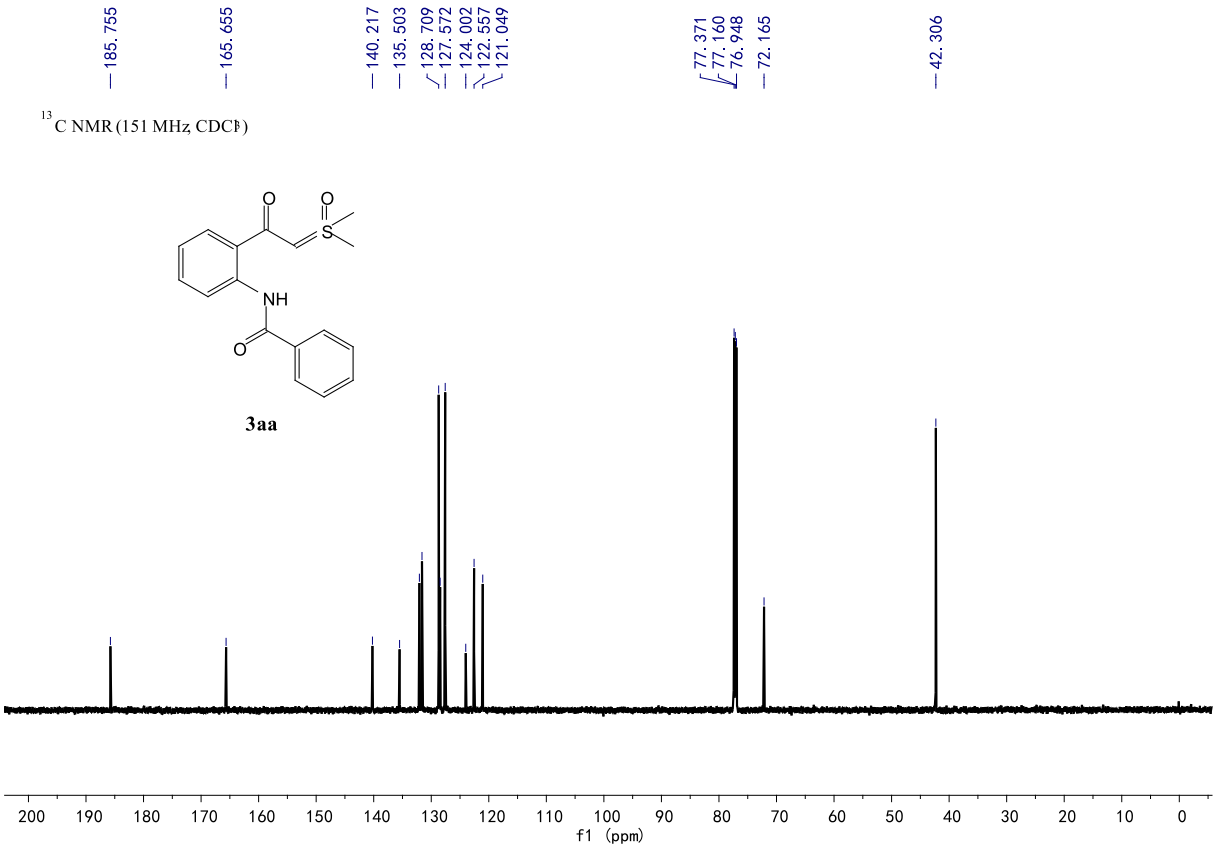
^{1}H NMR of product **3aa** and **3aa**-d_4 obtained from the KIE experiment.

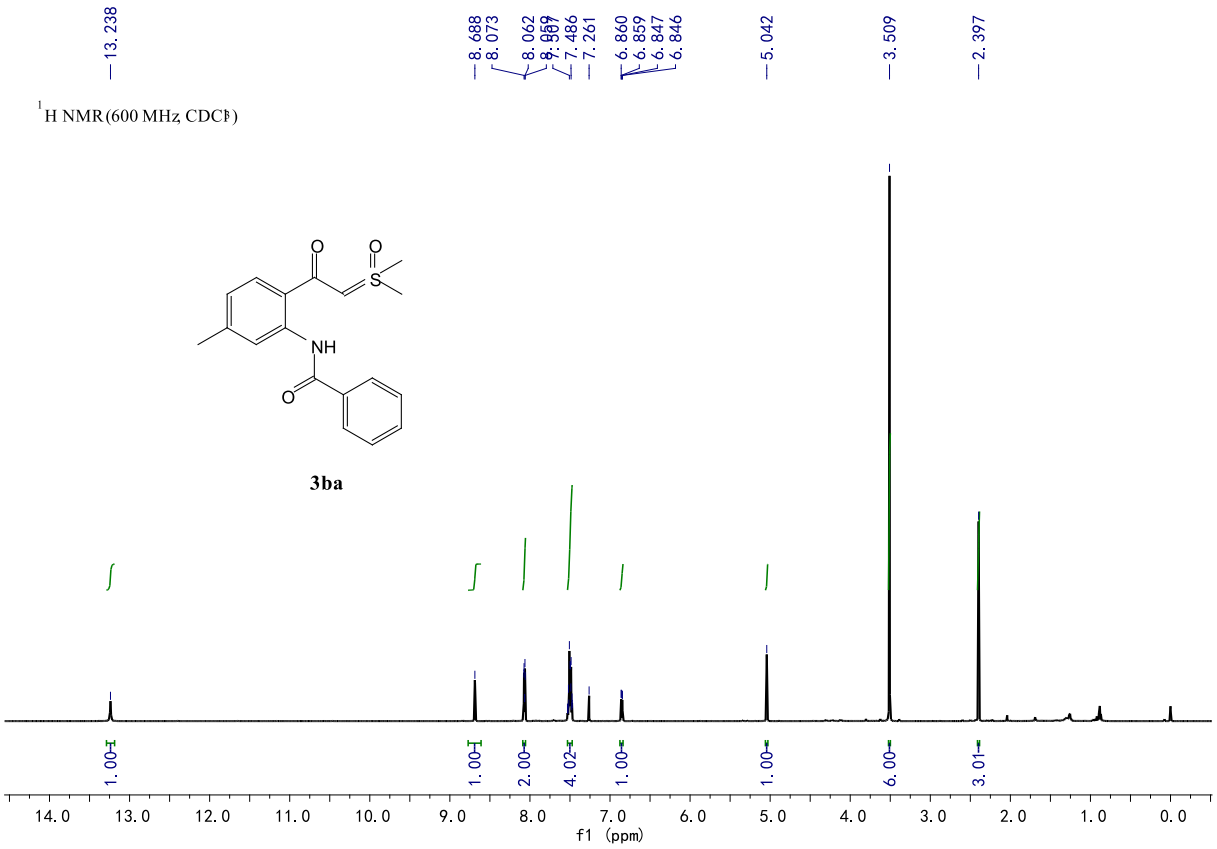




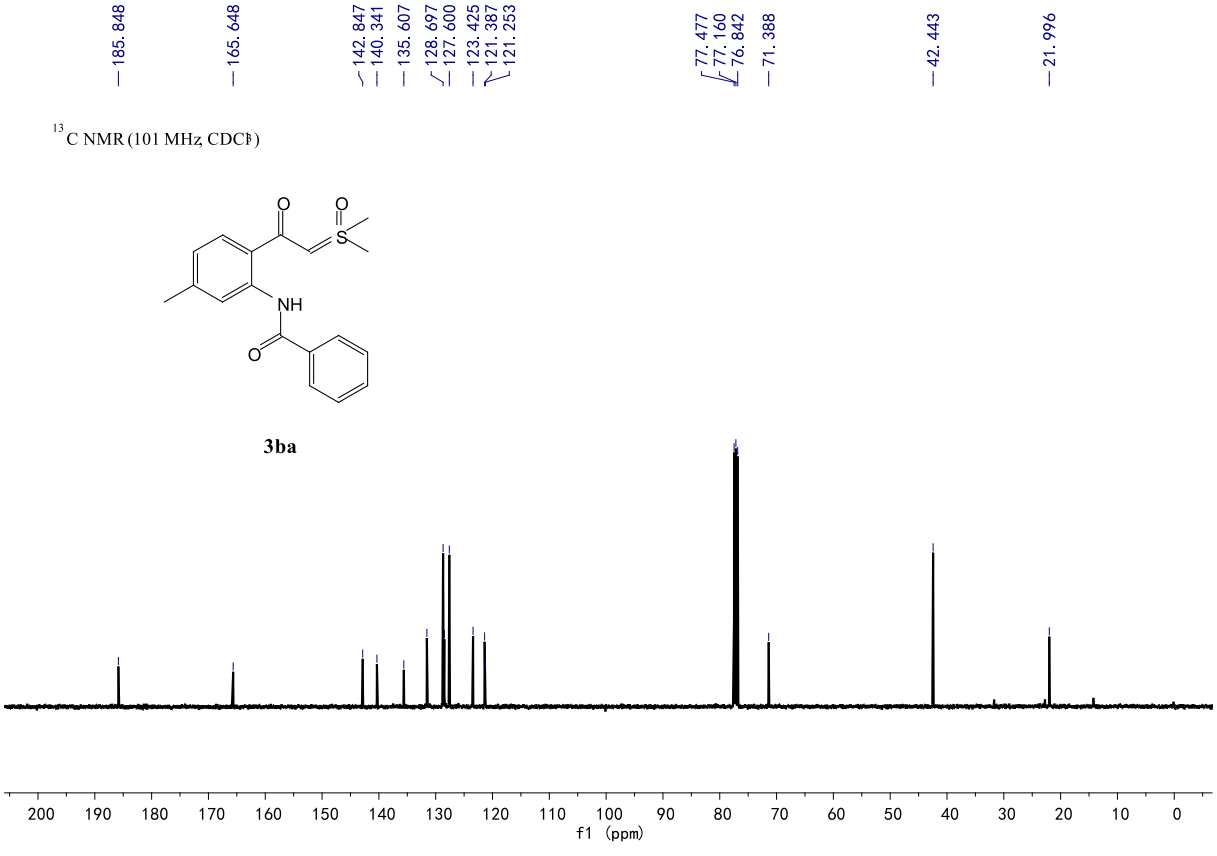
Copies of ^{1}H, ^{13}C, and ^{19}F NMR Spectra of the Products



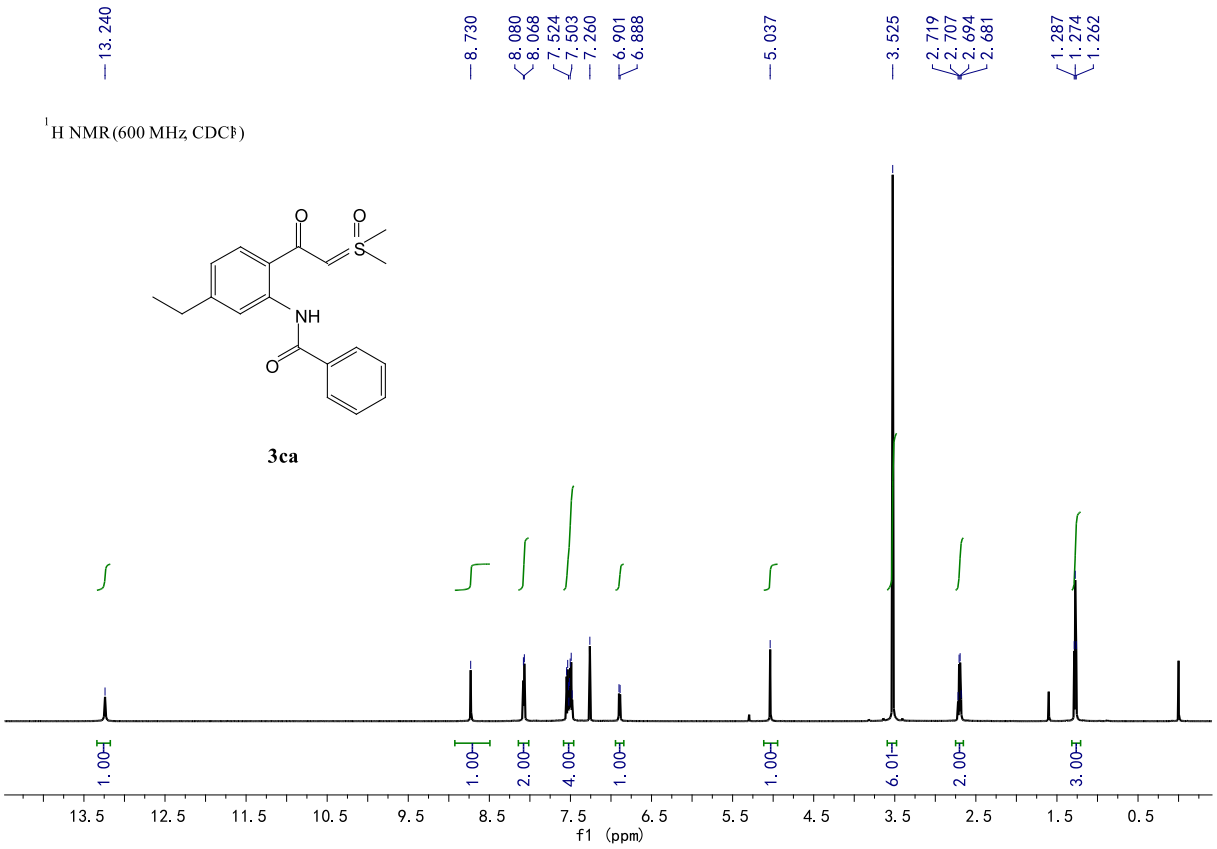


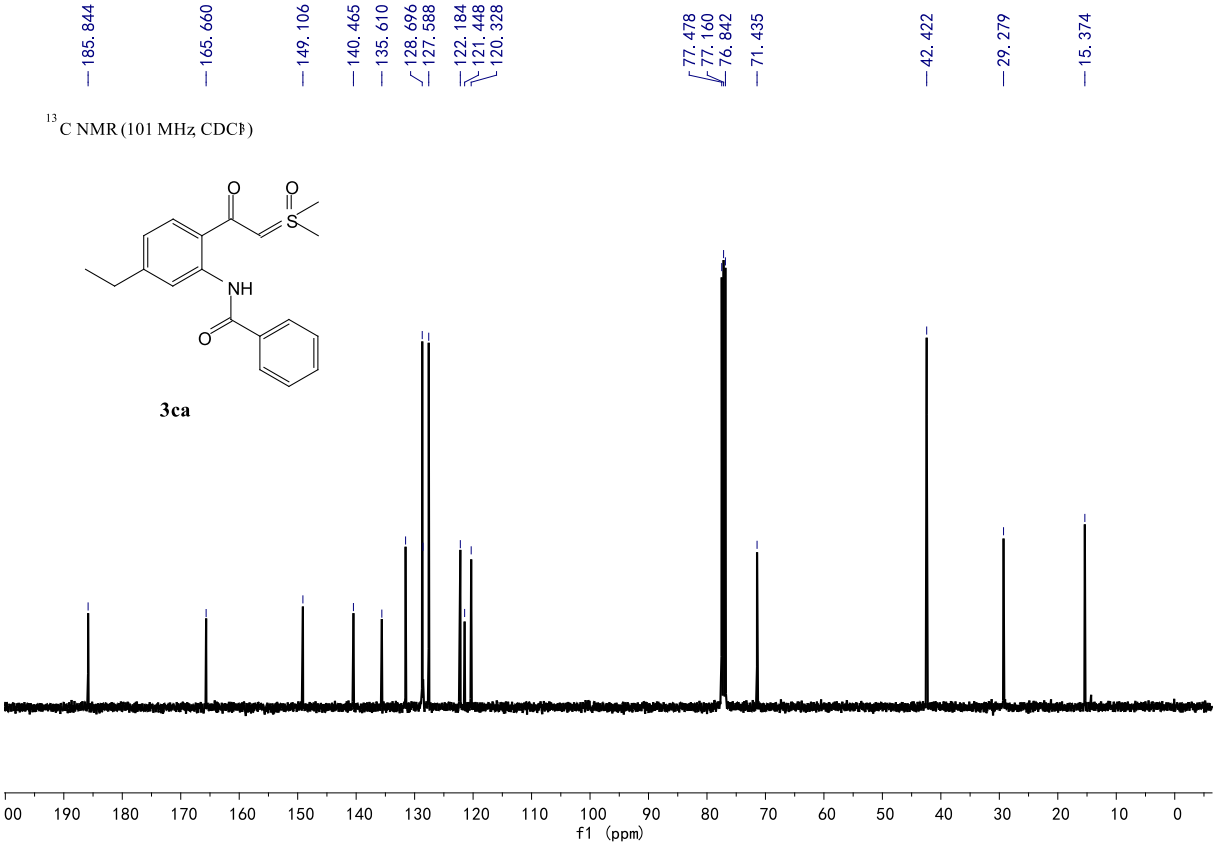

13.238
8.688
8.073
8.062
7.486
7.261
6.860
6.859
6.847
6.846
5.042
3.509
2.397
1H NMR (600 MHz, CDCl3)
O
O
S
NH
O
1.00
1.00
2.00
4.02
1.00
1.00
6.00
3.01
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

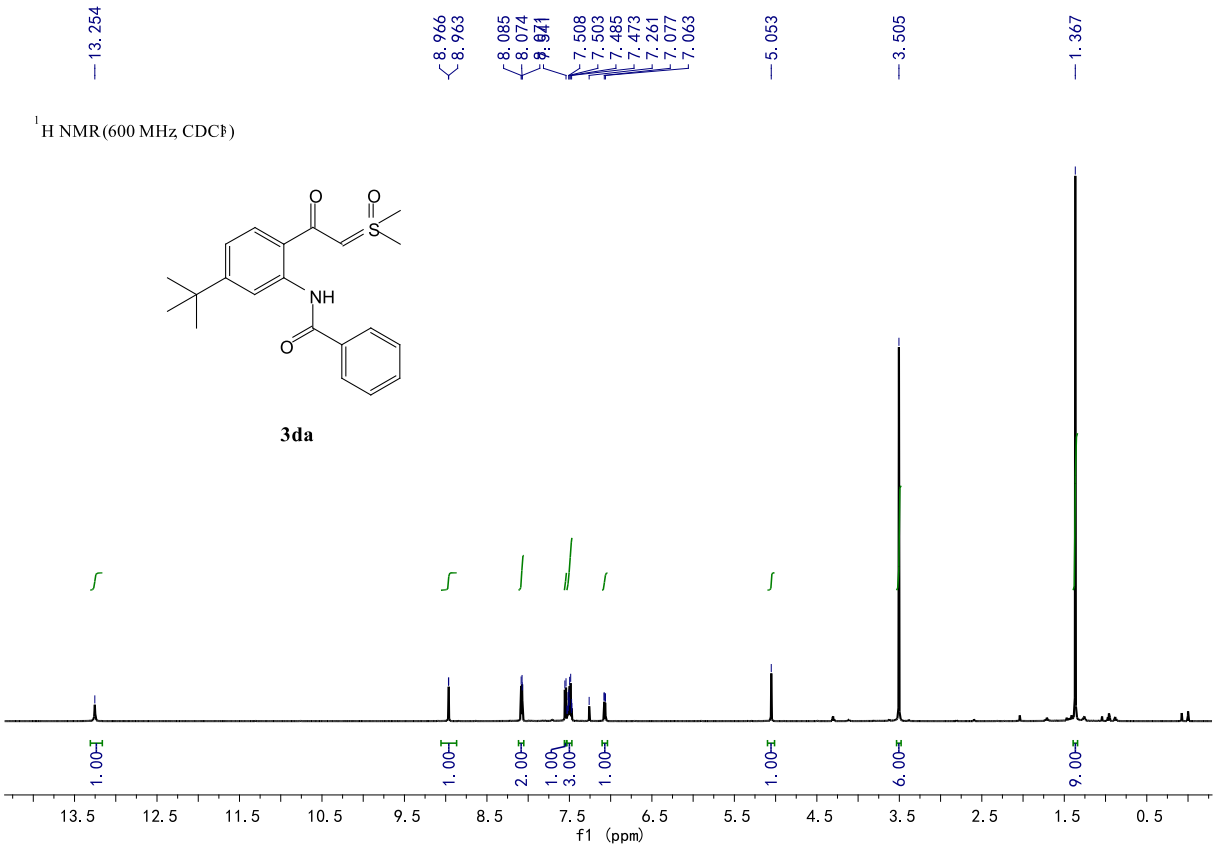
3ba


185.848
165.648
142.847
140.341
135.607
128.697
127.600
123.425
121.387
121.253
77.477
77.160
76.842
71.388
42.443
21.996
13C NMR (101 MHz, CDCl3)
O
O
S
NH
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3ba

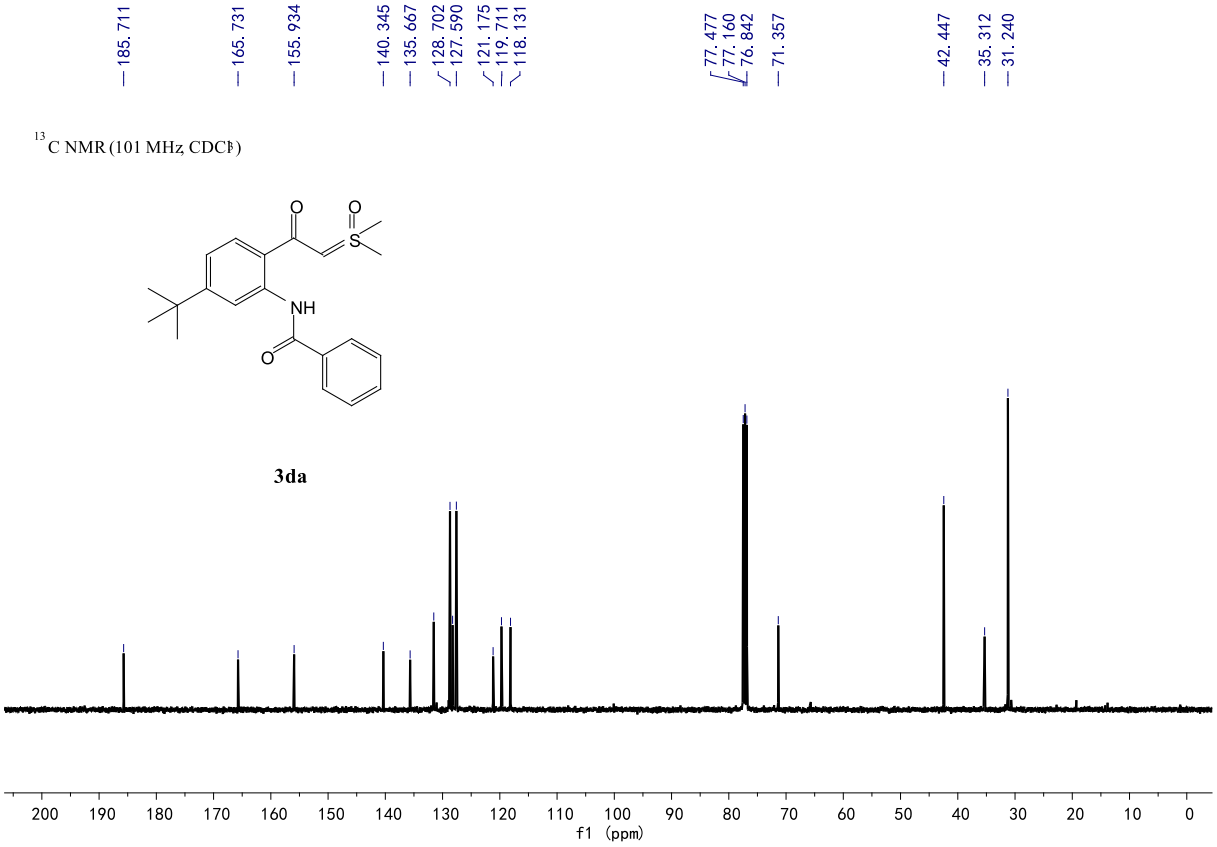

13.240
8.730
8.080
8.068
7.524
7.503
7.260
6.901
6.888
5.037
3.525
2.719
2.707
2.694
2.681
1.287
1.274
1.262
1H NMR (600 MHz, CDCl3)
O
O
S
NH
O
3ca
1.00
1.00
2.00
4.00
1.00
1.00
6.01
2.00
3.00
13.5
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


185.844
165.660
149.106
140.465
135.610
128.696
127.588
122.184
121.448
120.328
77.478
77.160
76.842
71.435
42.422
29.279
15.374
13C NMR (101 MHz, CDCl3)
O
O
S
NH
O
3ca
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



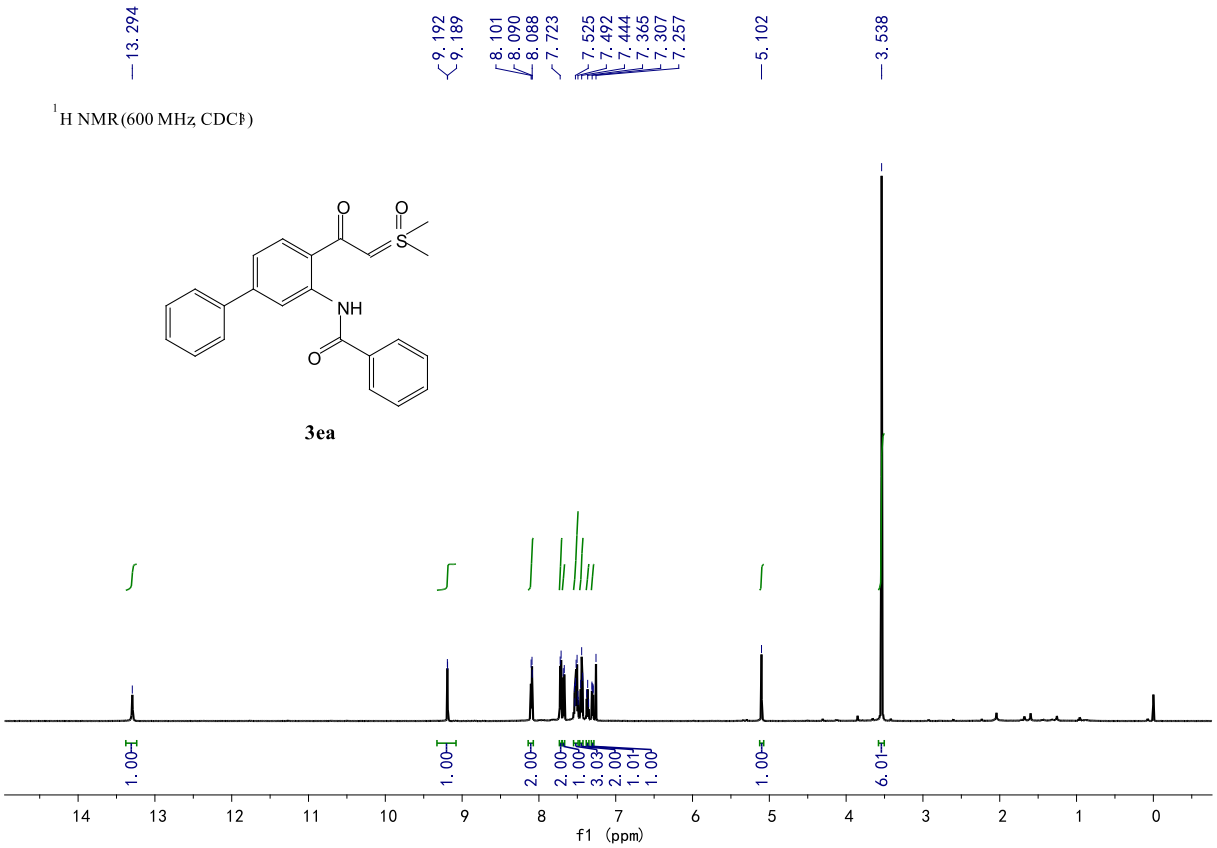
^{1}H NMR (600 MHz, CDCl$_3$)

3da



^{13}C NMR (101 MHz, CDCl$_3$)

3da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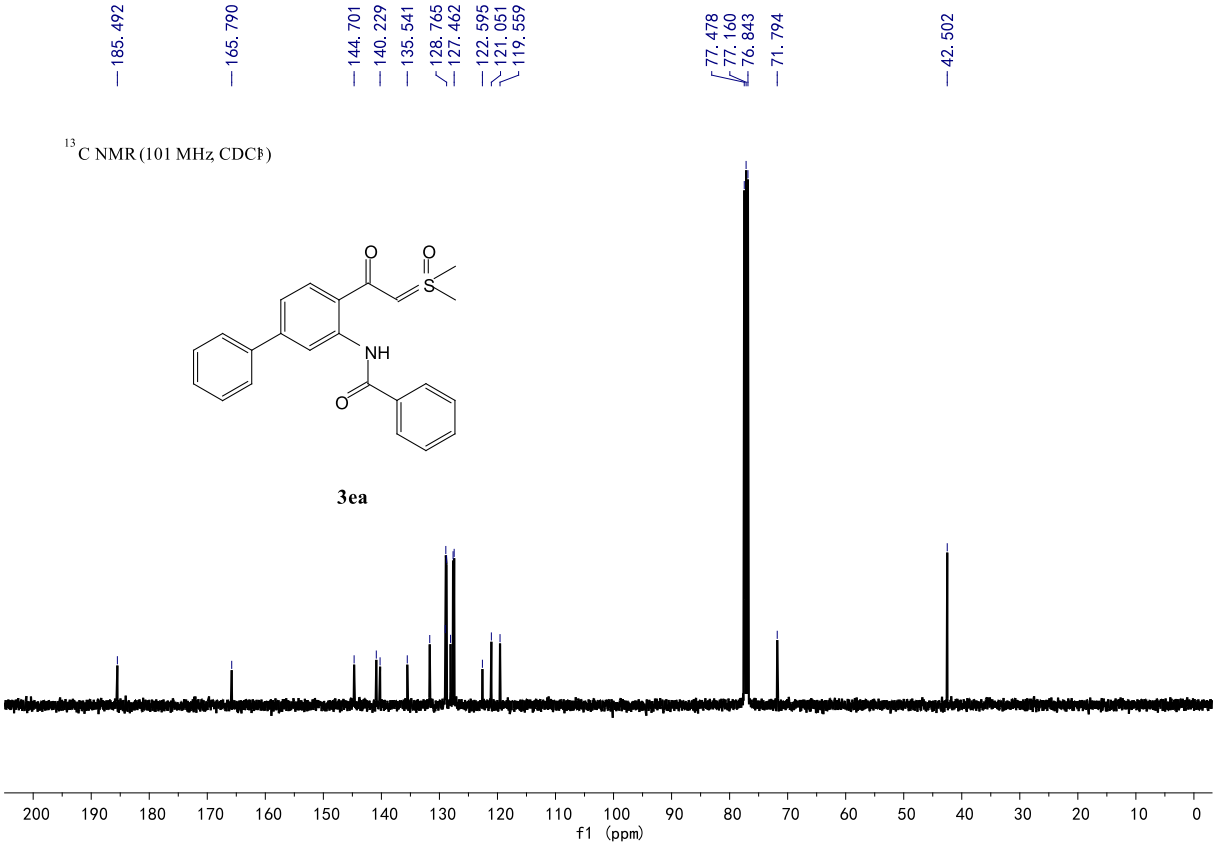
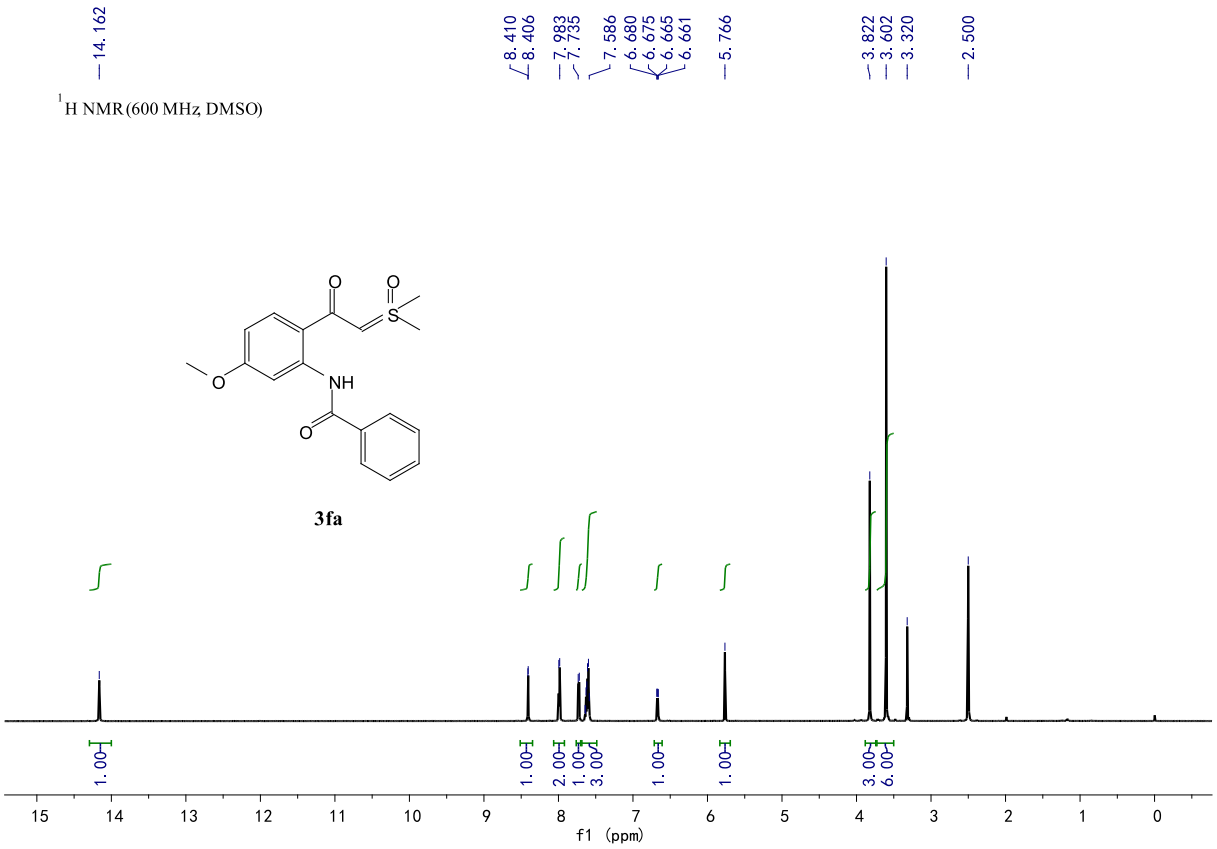
9.192
9.189
8.101
8.090
8.088
7.723
7.525
7.492
7.444
7.365
7.307
7.257
5.102
3.538
1H NMR (600 MHz, CDCl3)
O
O
S
NH
O
3ea
1.00
1.00
2.00
2.00
1.00
3.03
2.00
1.01
1.00
1.00
6.01
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


185.492
165.790
144.701
140.229
135.541
128.765
127.462
122.595
121.051
119.559
77.478
77.160
76.843
71.794
42.502
13C NMR (101 MHz, CDCl3)
O
O
S
NH
O
3ea
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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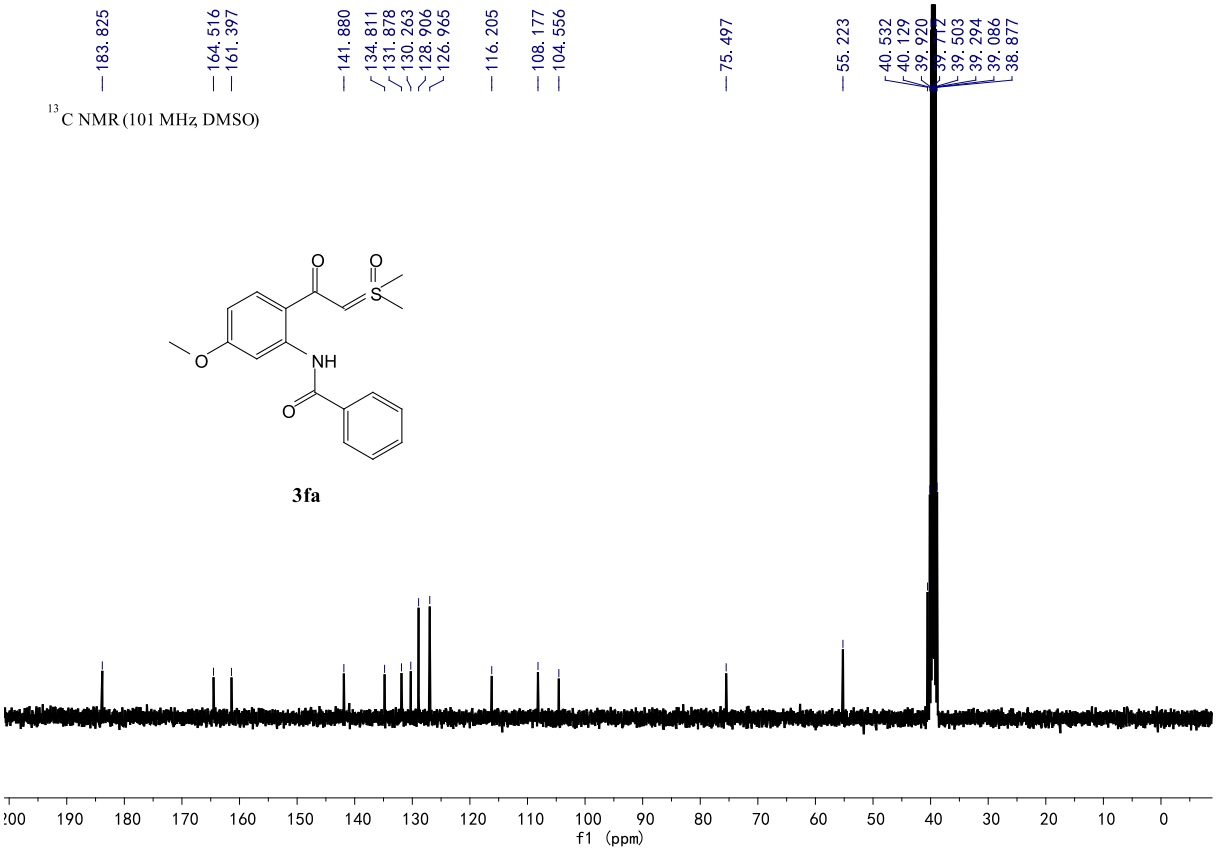
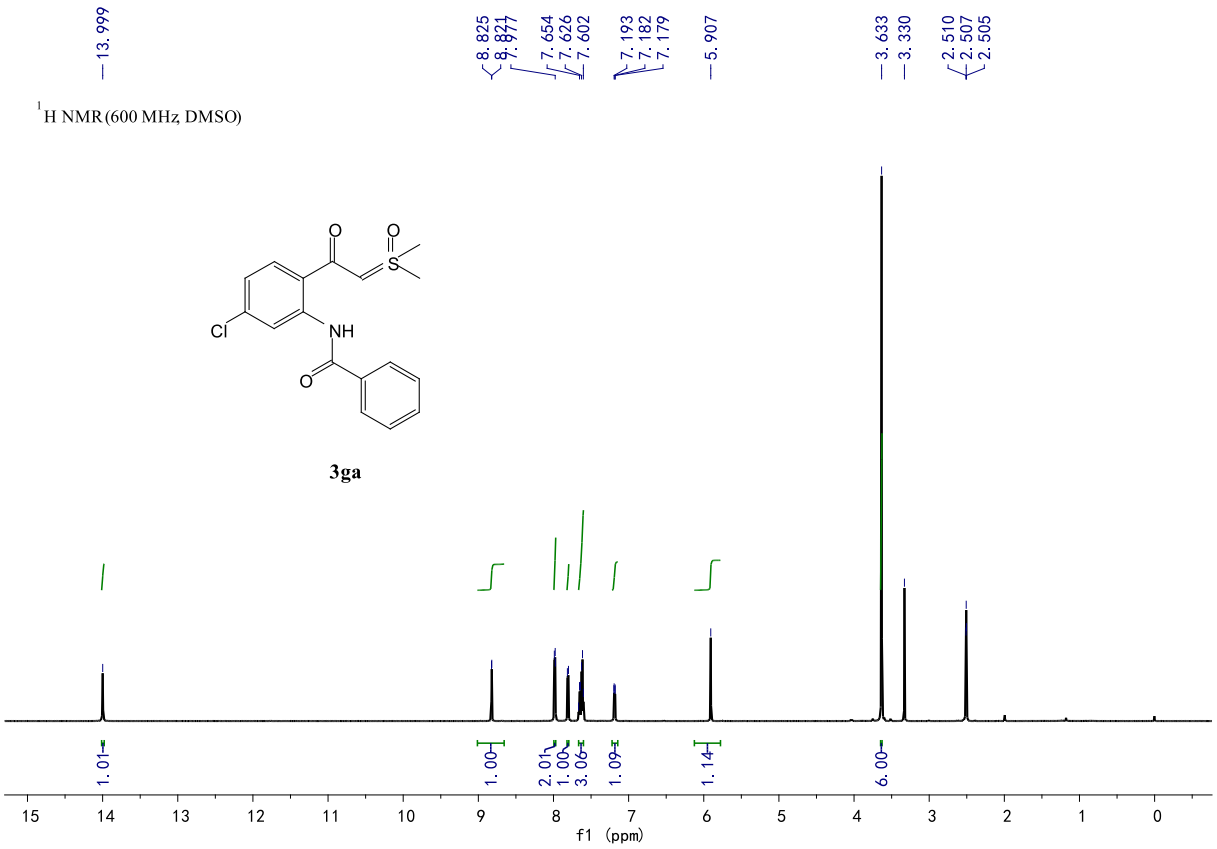
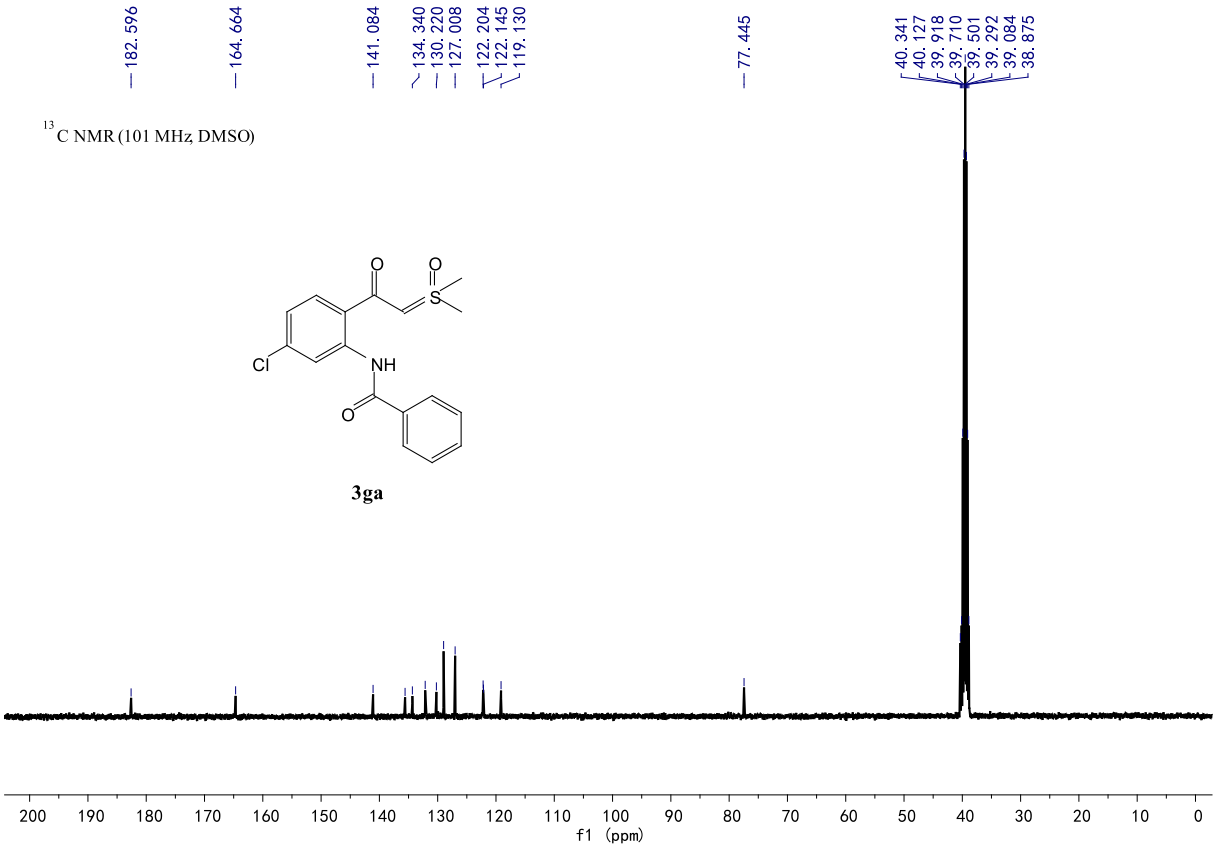
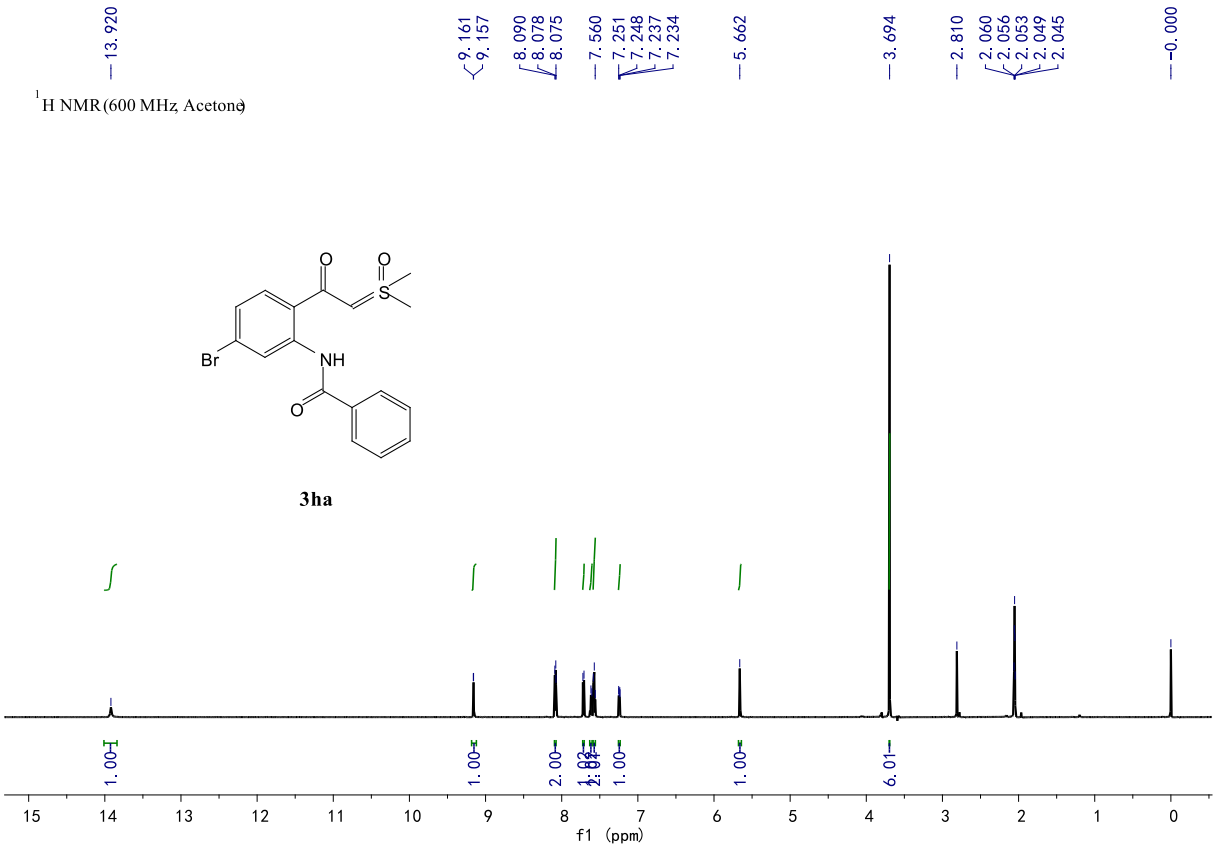
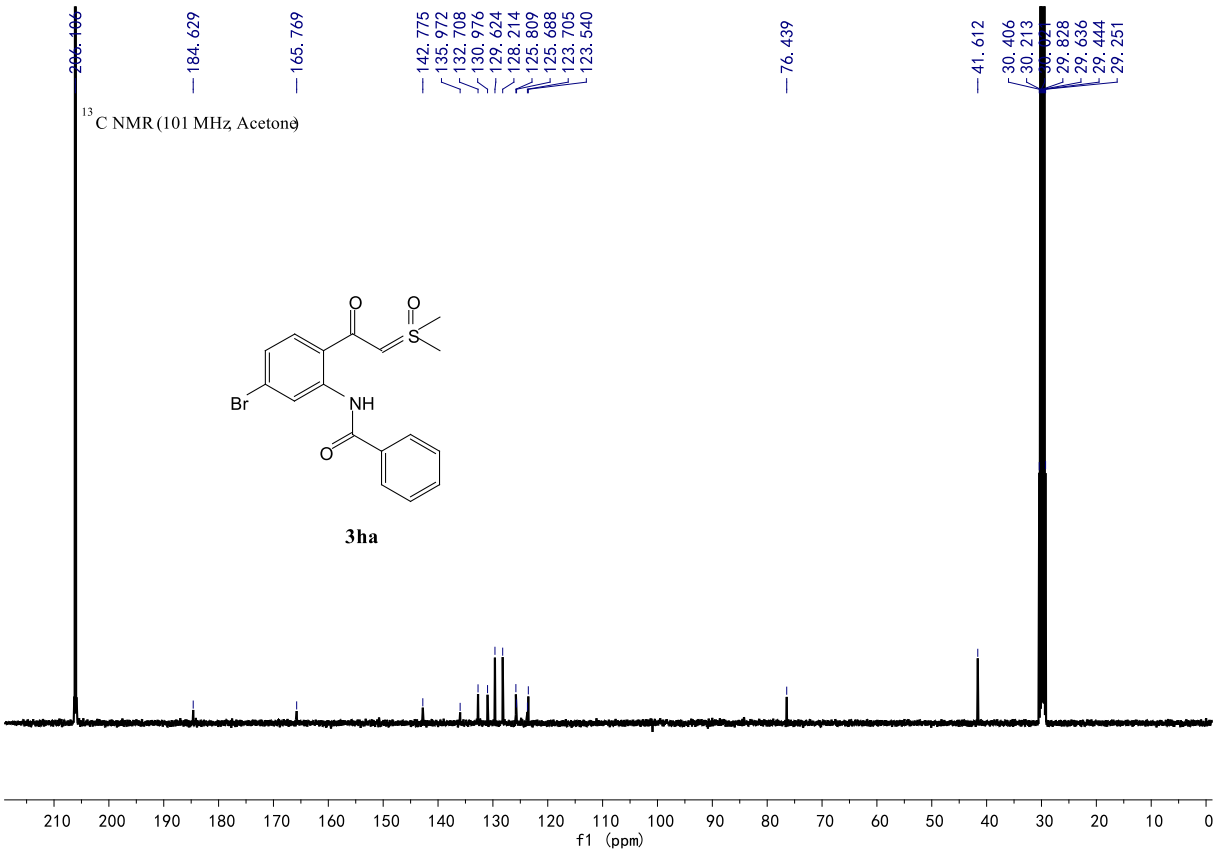
8.410
8.406
7.983
7.735
7.586
6.680
6.675
6.665
6.661
5.766
3.822
3.602
3.320
2.500
1H NMR (600 MHz, DMSO)
3fa
1.00
1.00
2.00
1.00
3.00
1.00
1.00
3.00
6.00
f1 (ppm)

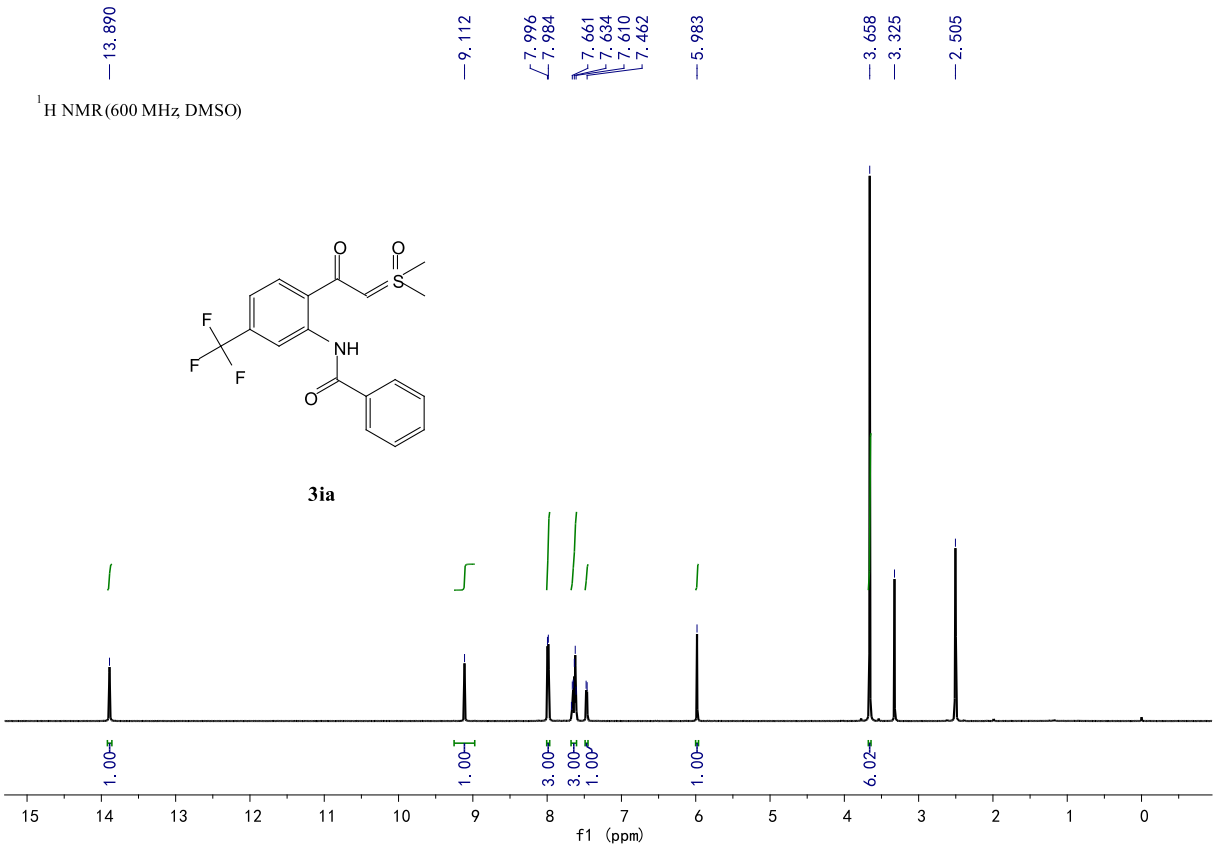

183.825
164.516
161.397
141.880
134.811
131.878
130.263
128.906
126.965
116.205
108.177
104.556
75.497
55.223
40.532
40.129
39.920
39.712
39.503
39.294
39.086
38.877
13C NMR (101 MHz, DMSO)
3fa
f1 (ppm)

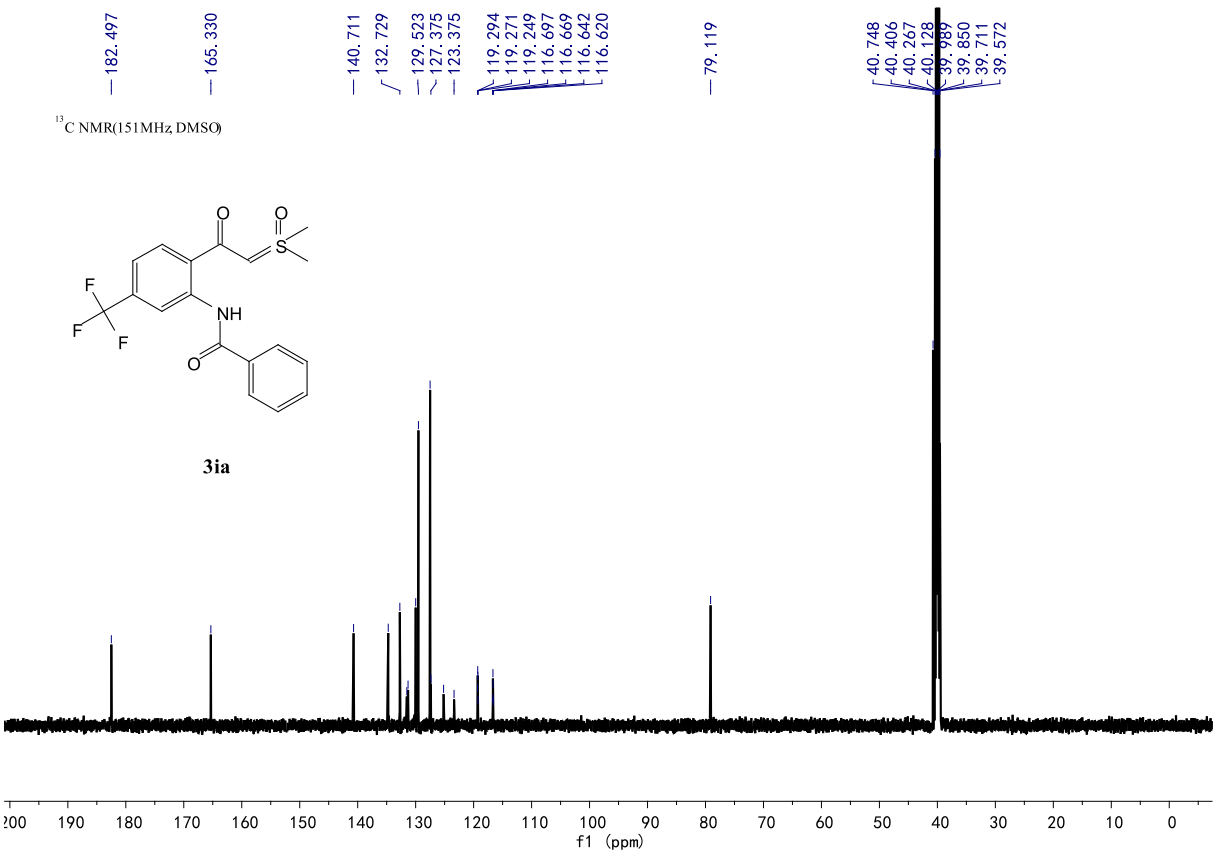

13.999
8.825
8.821
7.654
7.626
7.602
7.193
7.182
7.179
5.907
3.633
3.330
2.510
2.507
2.505
1H NMR (600 MHz, DMSO)
Cl
NH
O
S
3ga
1.01
1.00
2.01
1.00
3.06
1.09
1.14
6.00
f1 (ppm)


182.596
164.664
141.084
134.340
130.220
127.008
122.204
122.145
119.130
77.445
40.341
40.127
39.918
39.710
39.501
39.292
39.084
38.875
13C NMR (101 MHz, DMSO)
Cl
NH
O
S
3ga
f1 (ppm)

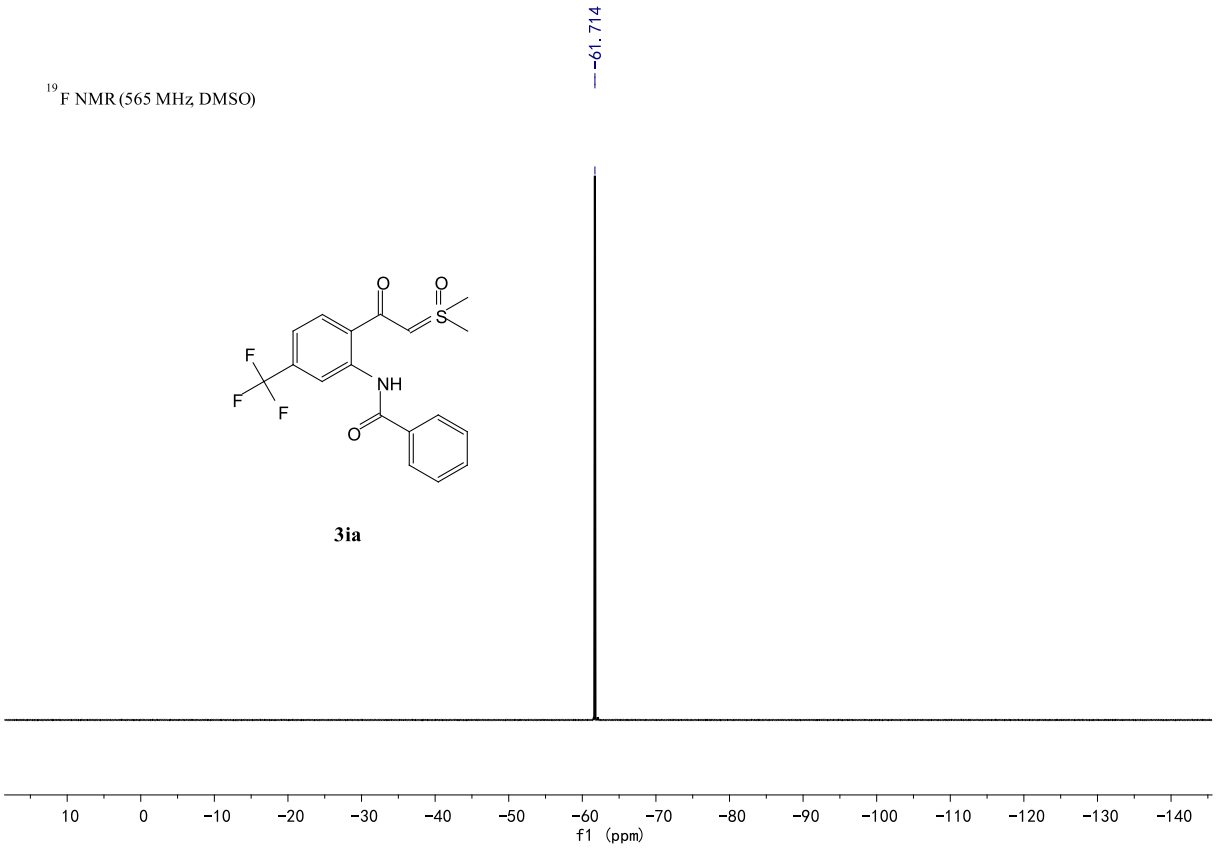

13.920
9.161
9.157
8.090
8.078
8.075
7.560
7.251
7.248
7.237
7.234
5.662
3.694
2.810
2.060
2.056
2.053
2.049
2.045
0.000
1H NMR (600 MHz, Acetone)
O
O
S
Br
NH
O
3ha
1.00
1.00
2.00
1.00
1.00
6.01
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


206.102
184.629
165.769
142.775
135.972
132.708
130.976
129.624
128.214
125.809
125.688
123.705
123.540
76.439
41.612
30.406
30.213
29.828
29.636
29.444
29.251
13C NMR (101 MHz, Acetone)
O
O
S
Br
NH
O
3ha
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


13.890
9.112
7.996
7.984
7.661
7.634
7.610
7.462
5.983
3.658
3.325
2.505
1H NMR (600 MHz, DMSO)
3ia
1.00
1.00
3.00
3.00
1.00
1.00
6.02
f1 (ppm)

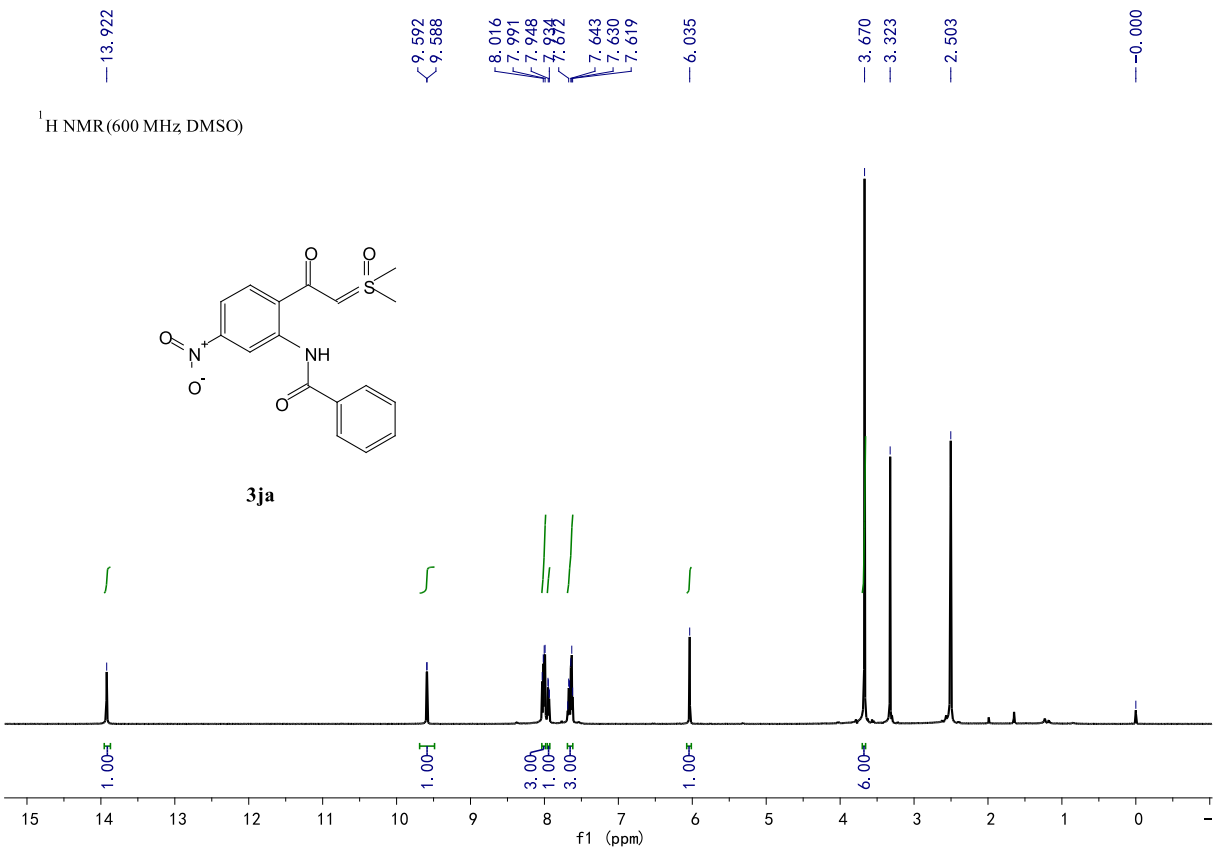

182.497
165.330
140.711
132.729
129.523
127.375
123.375
119.294
119.271
119.249
116.697
116.669
116.642
116.620
79.119
40.748
40.406
40.267
40.128
39.989
39.850
39.711
39.572
13C NMR(151MHz, DMSO)
3ia
f1 (ppm)

^{19}F NMR (565 MHz, DMSO)

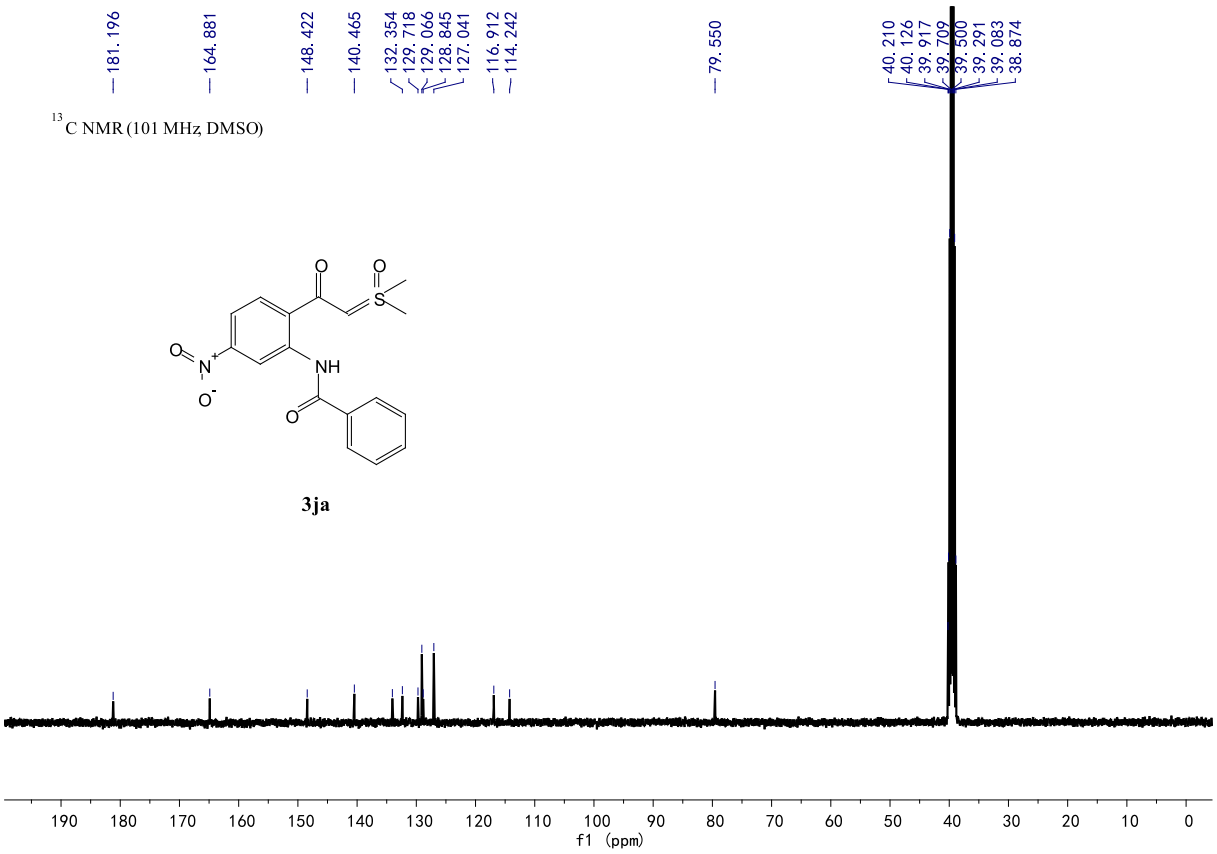


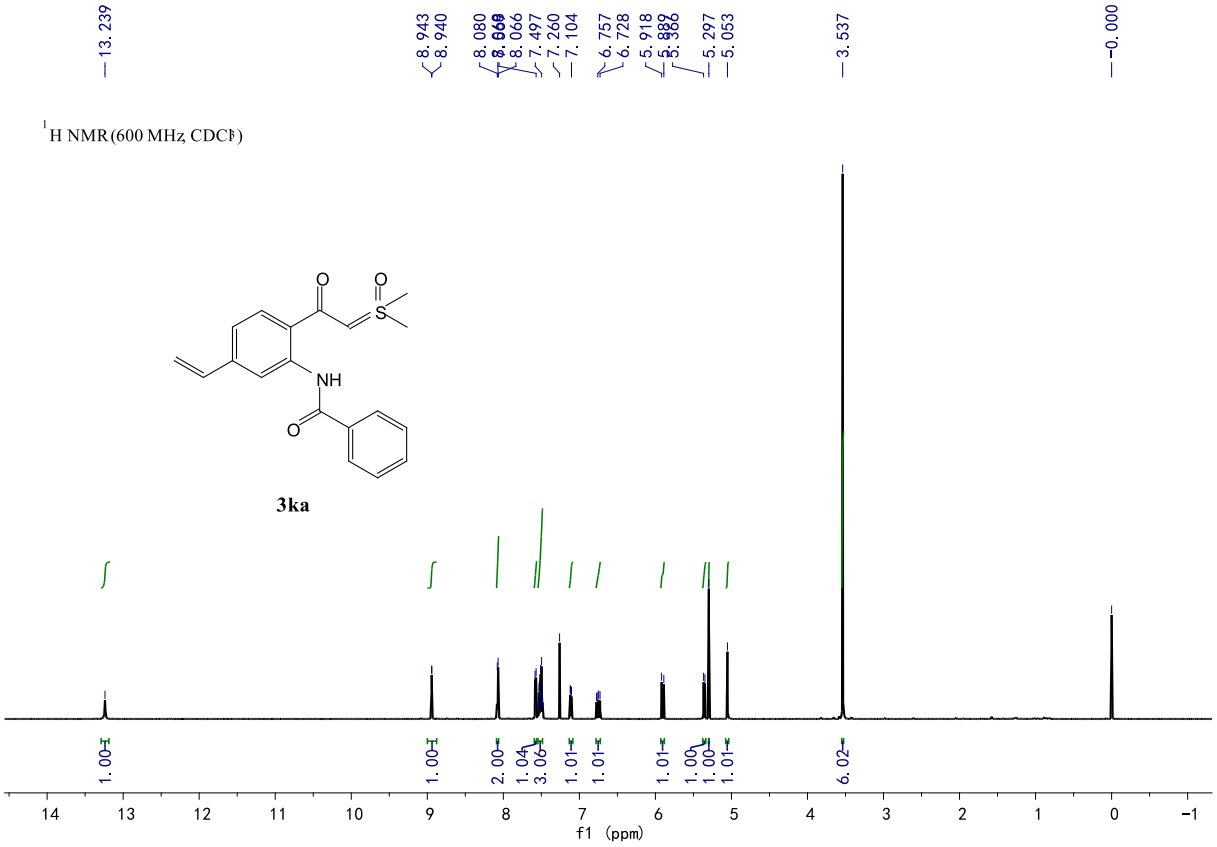
3ia

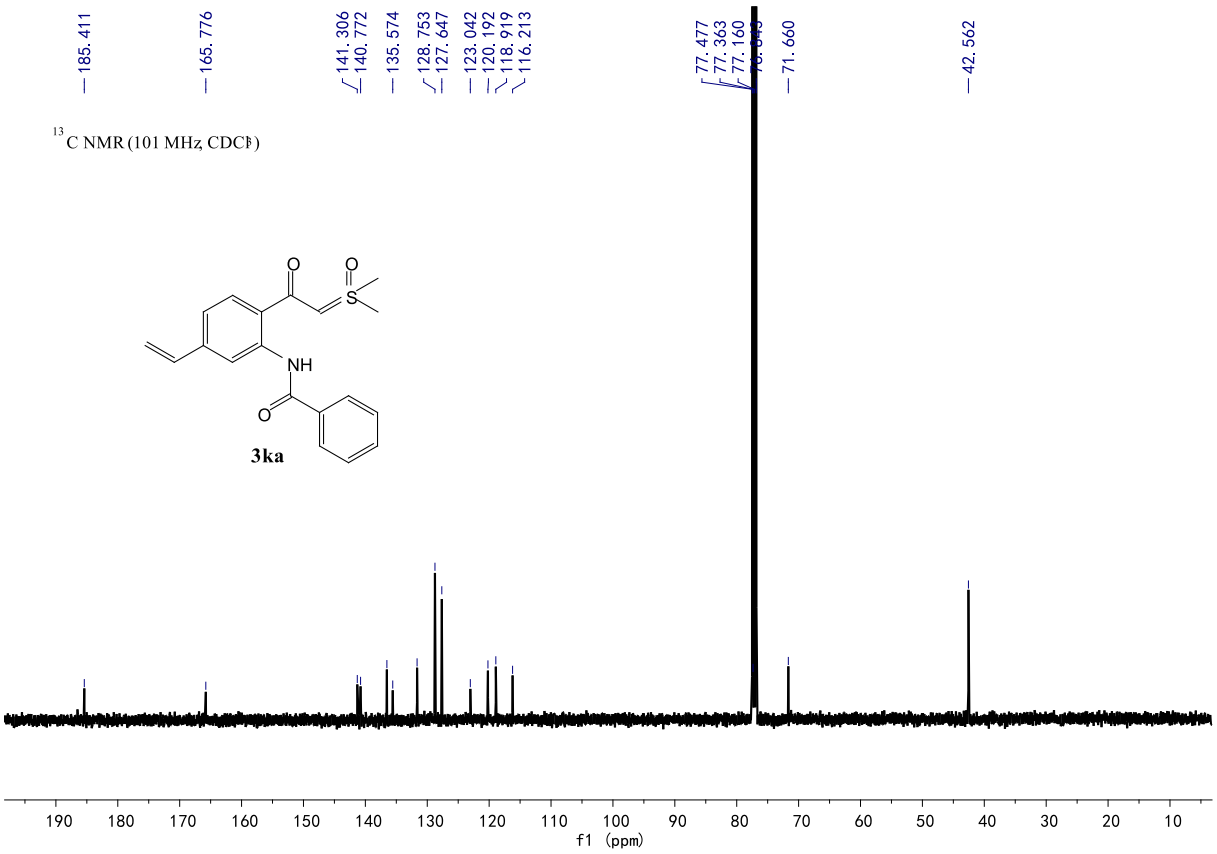
^{1}H NMR (600 MHz, DMSO)

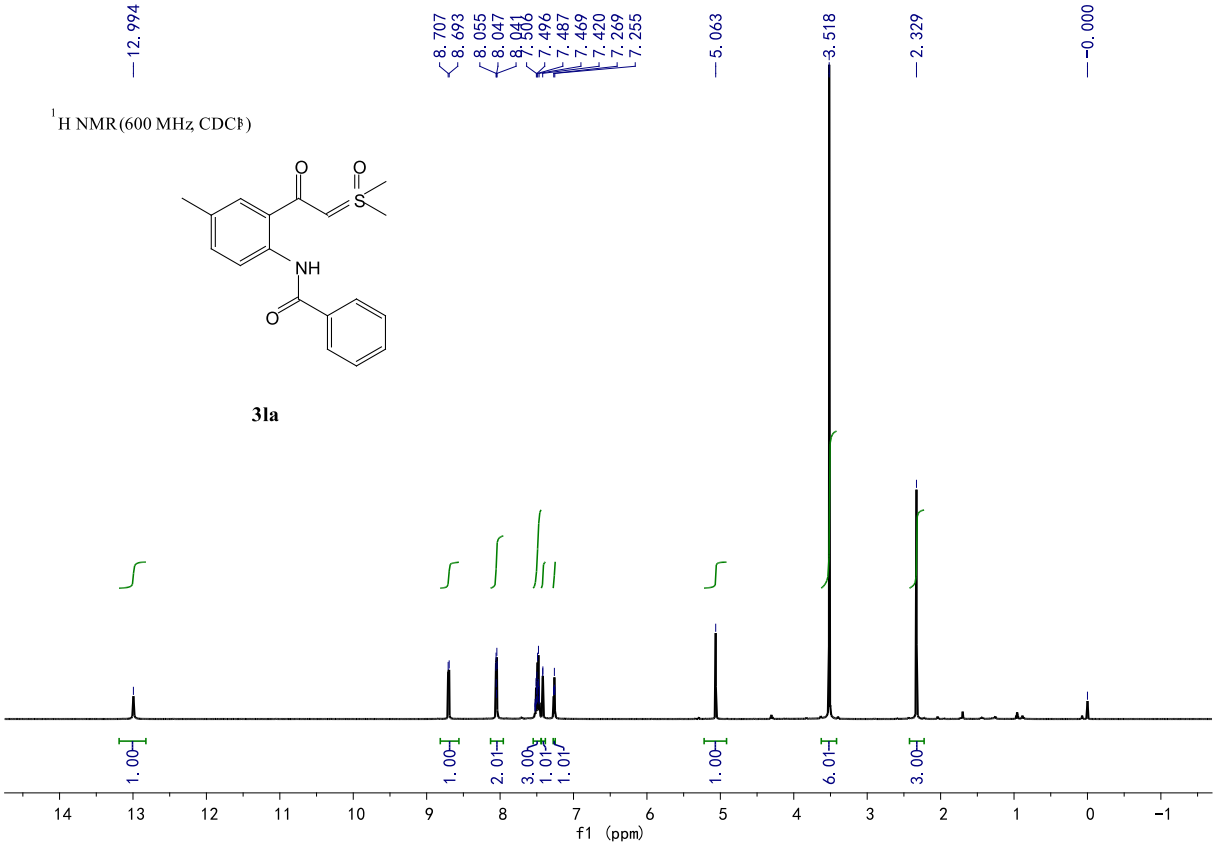


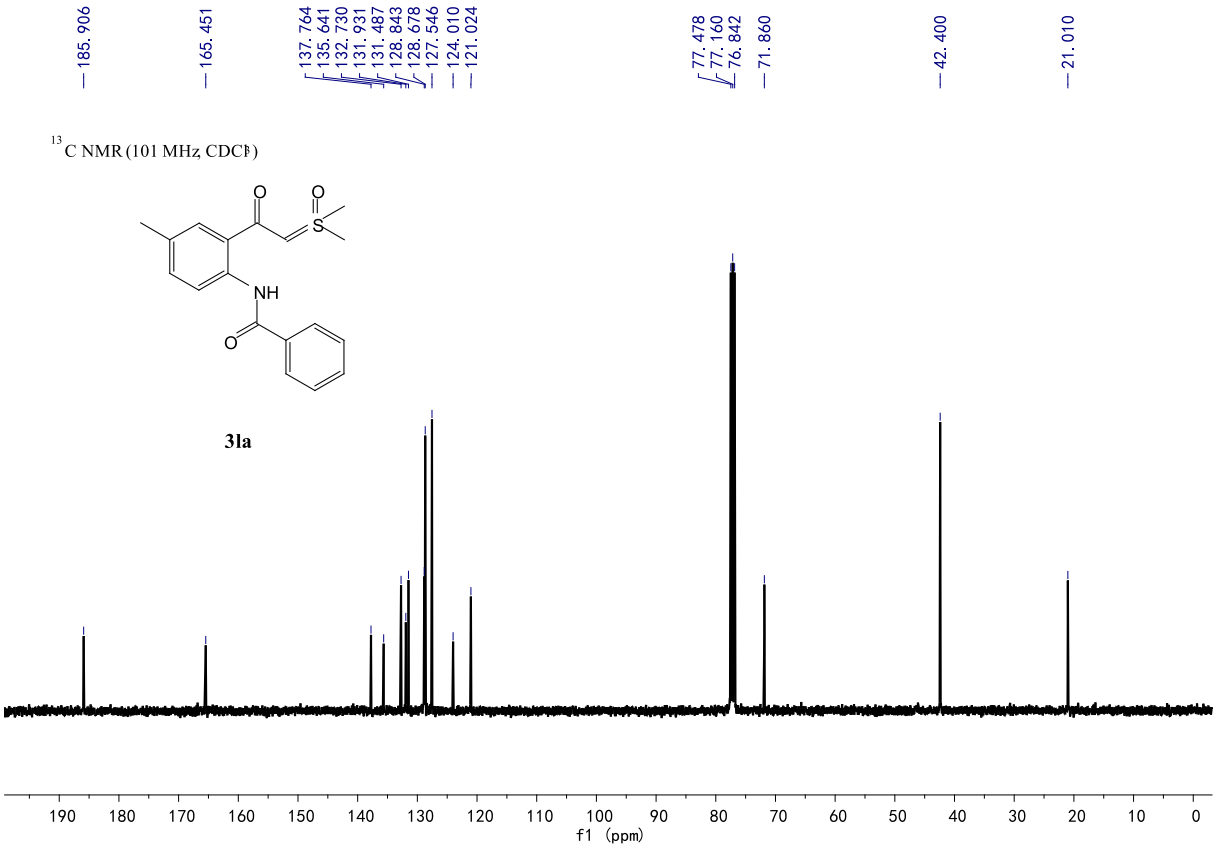
3ja

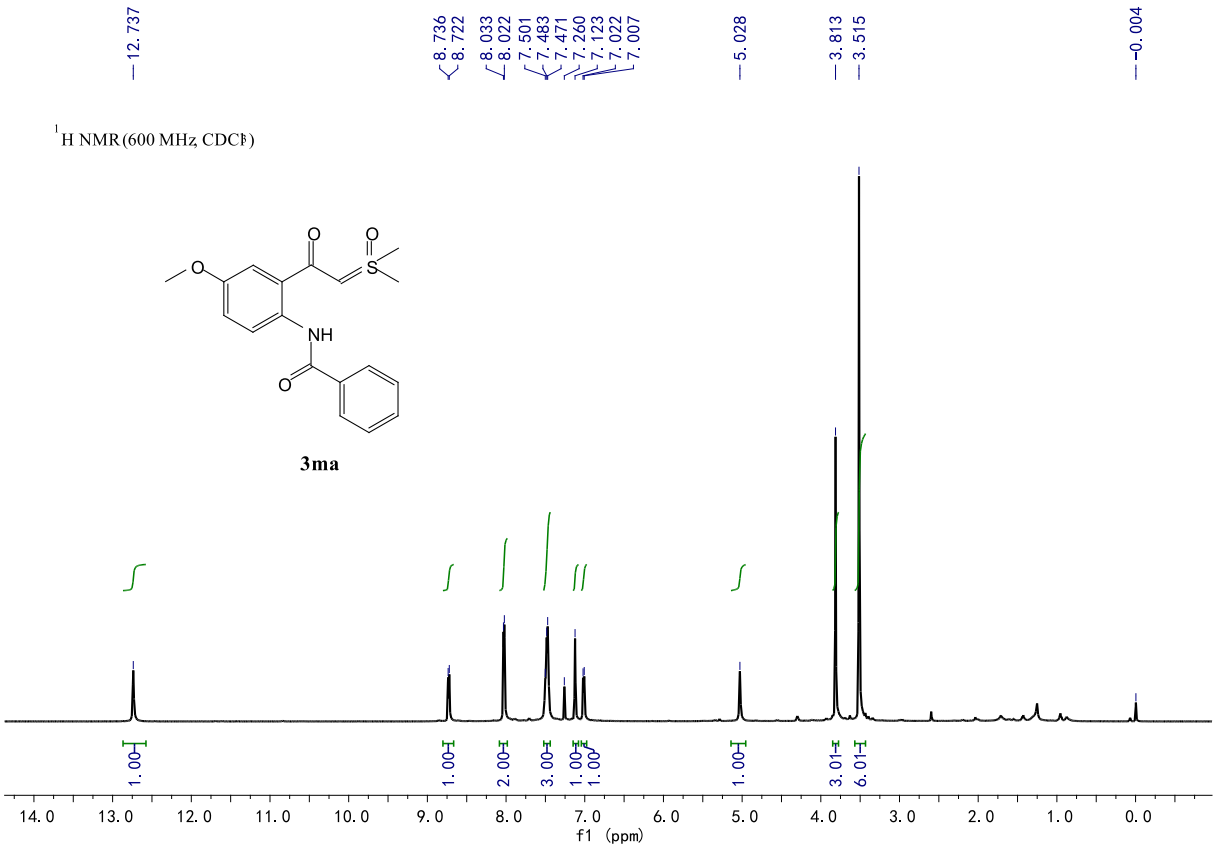

181.196
164.881
148.422
140.465
132.354
129.718
129.066
128.845
127.041
116.912
114.242
79.550
40.210
40.126
39.917
39.709
39.500
39.291
39.083
38.874
13C NMR (101 MHz, DMSO)
3ja
f1 (ppm)

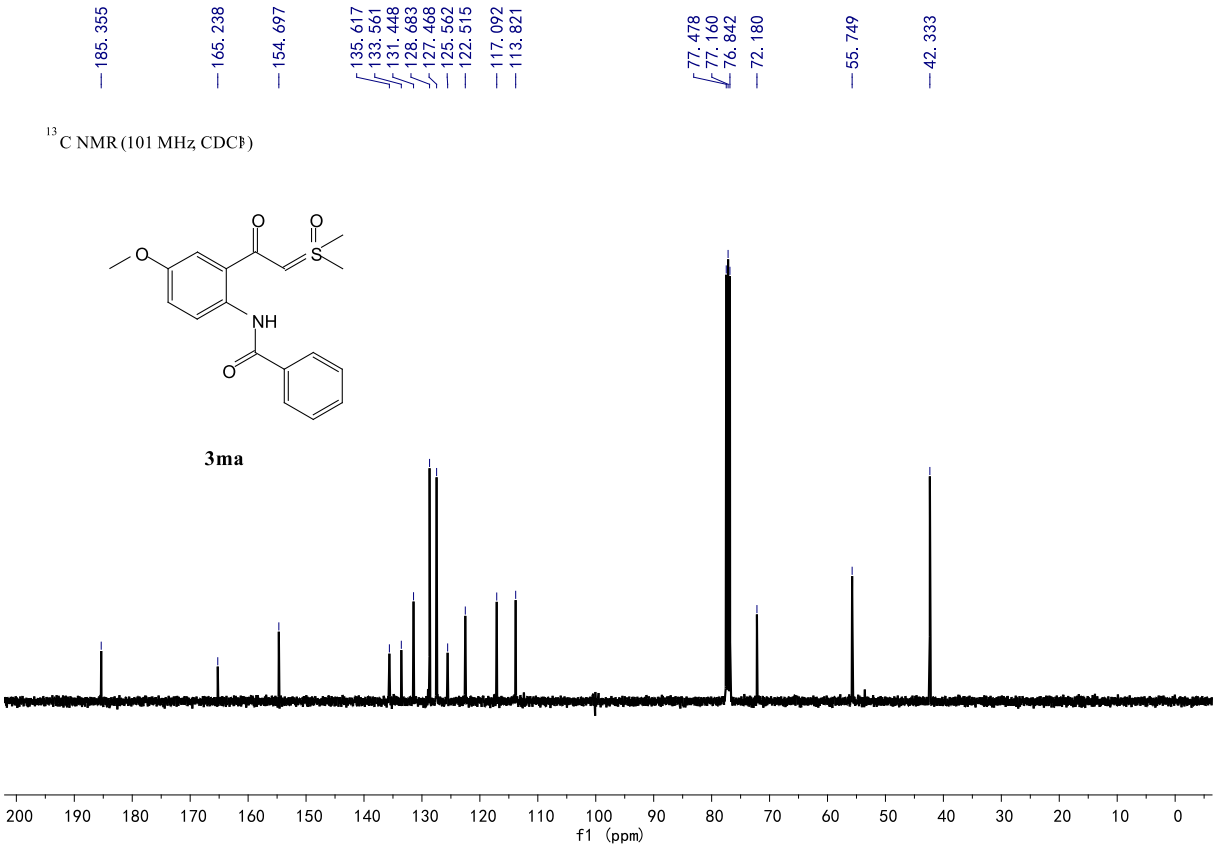

13.239
8.943
8.940
8.080
8.066
7.497
7.260
7.104
6.757
6.728
5.918
5.297
5.053
3.537
-0.000
1H NMR (600 MHz, CDCl3)
3ka
1.00
1.00
2.00
1.04
3.06
1.01
1.01
1.01
1.00
1.01
6.02
f1 (ppm)

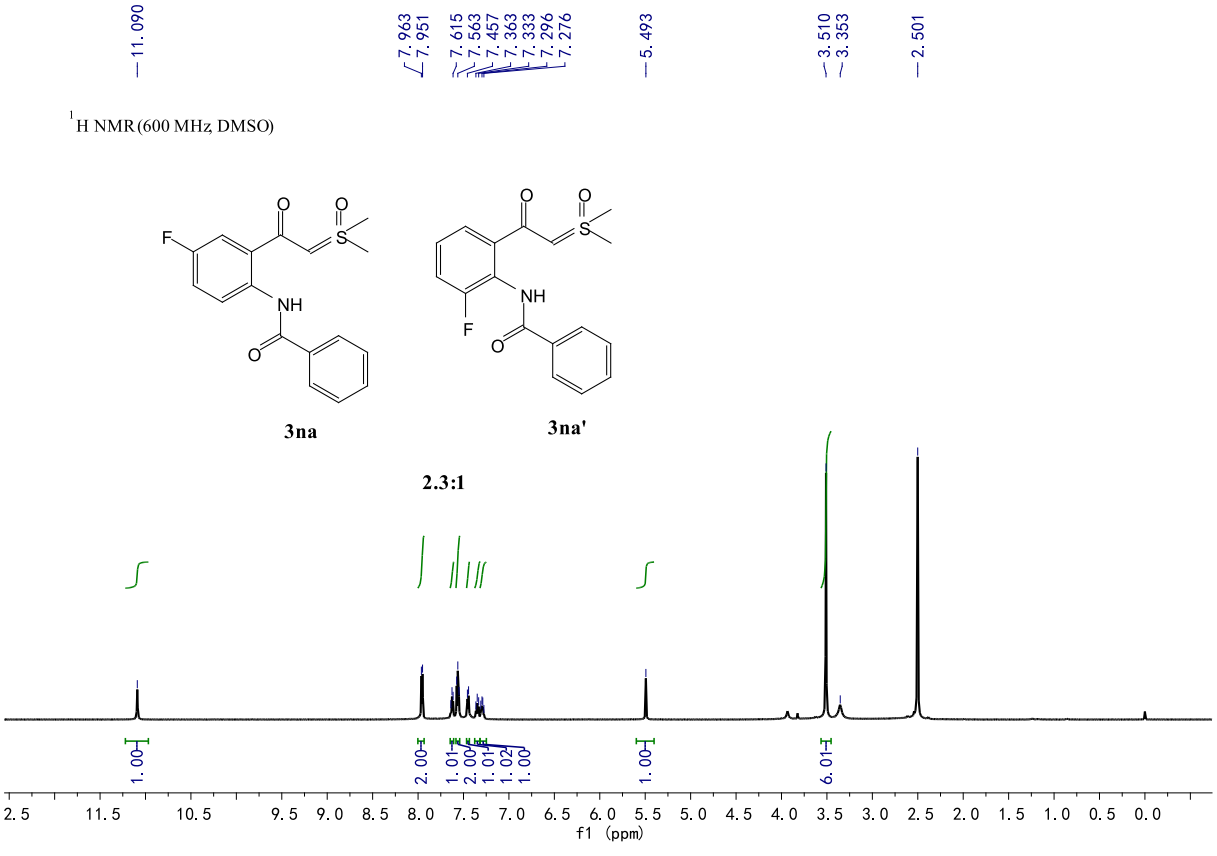

185.411
165.776
141.306
140.772
135.574
128.753
127.647
123.042
120.192
118.919
116.213
77.477
77.363
77.160
71.660
42.562
13C NMR (101 MHz, CDCl3)
O
O
S
NH
O
3ka
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

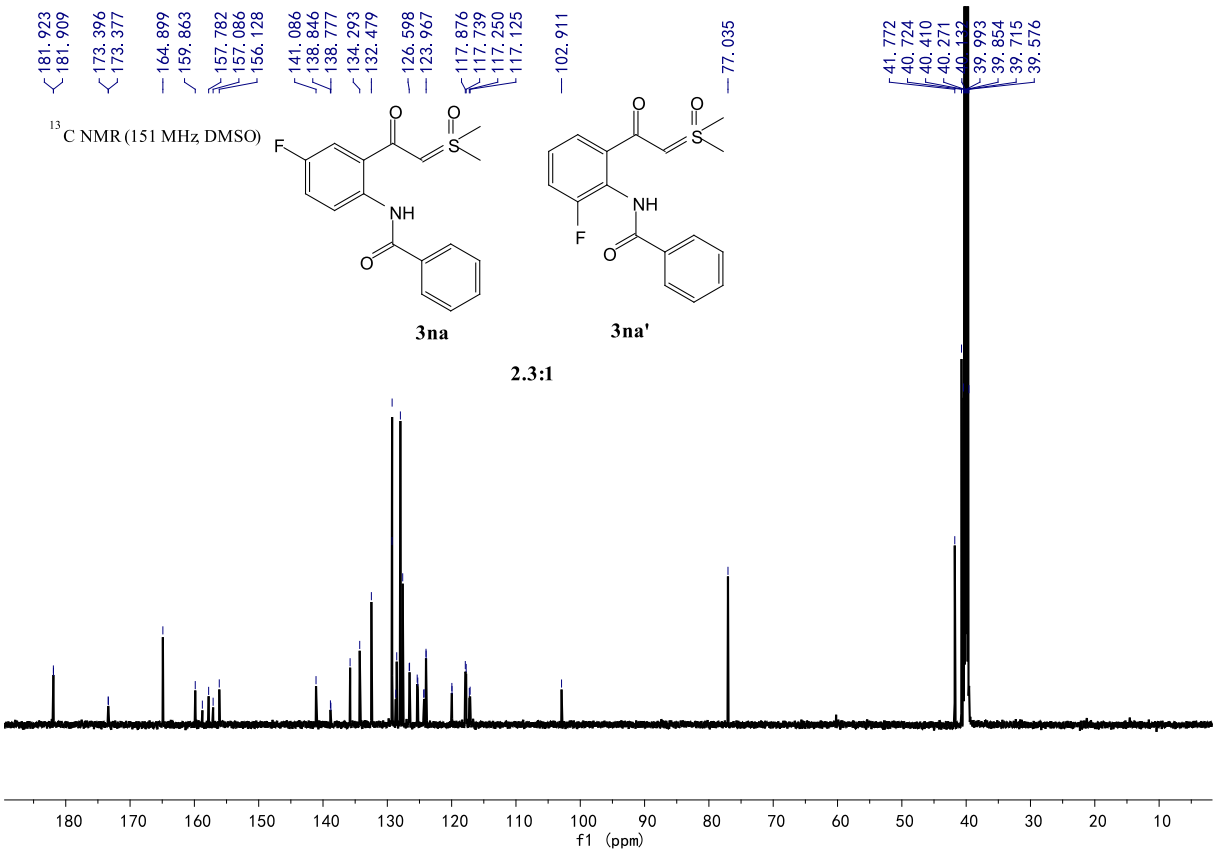

12.994
8.707
8.693
8.055
8.047
8.041
7.506
7.496
7.487
7.469
7.420
7.269
7.255
5.063
3.518
2.329
0.000
1H NMR (600 MHz, CDCl3)
O
O
S
NH
O
3la
1.00
1.00
2.01
3.00
1.01
1.01
1.00
6.01
3.00
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
f1 (ppm)

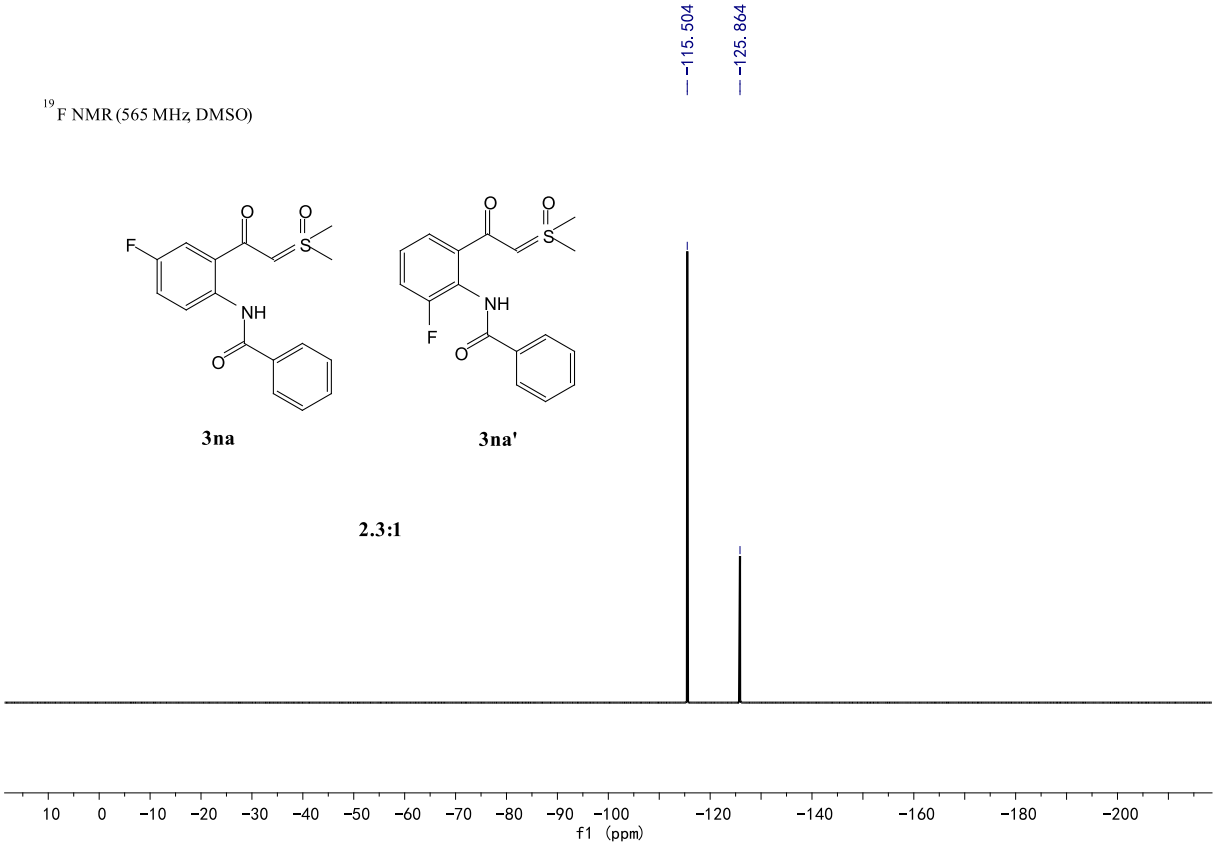

185.906
165.451
137.764
135.641
132.730
131.931
131.487
128.843
128.678
127.546
124.010
121.024
77.478
77.160
76.842
71.860
42.400
21.010
13C NMR (101 MHz, CDCl3)
NH
O
O
O
S
3la
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

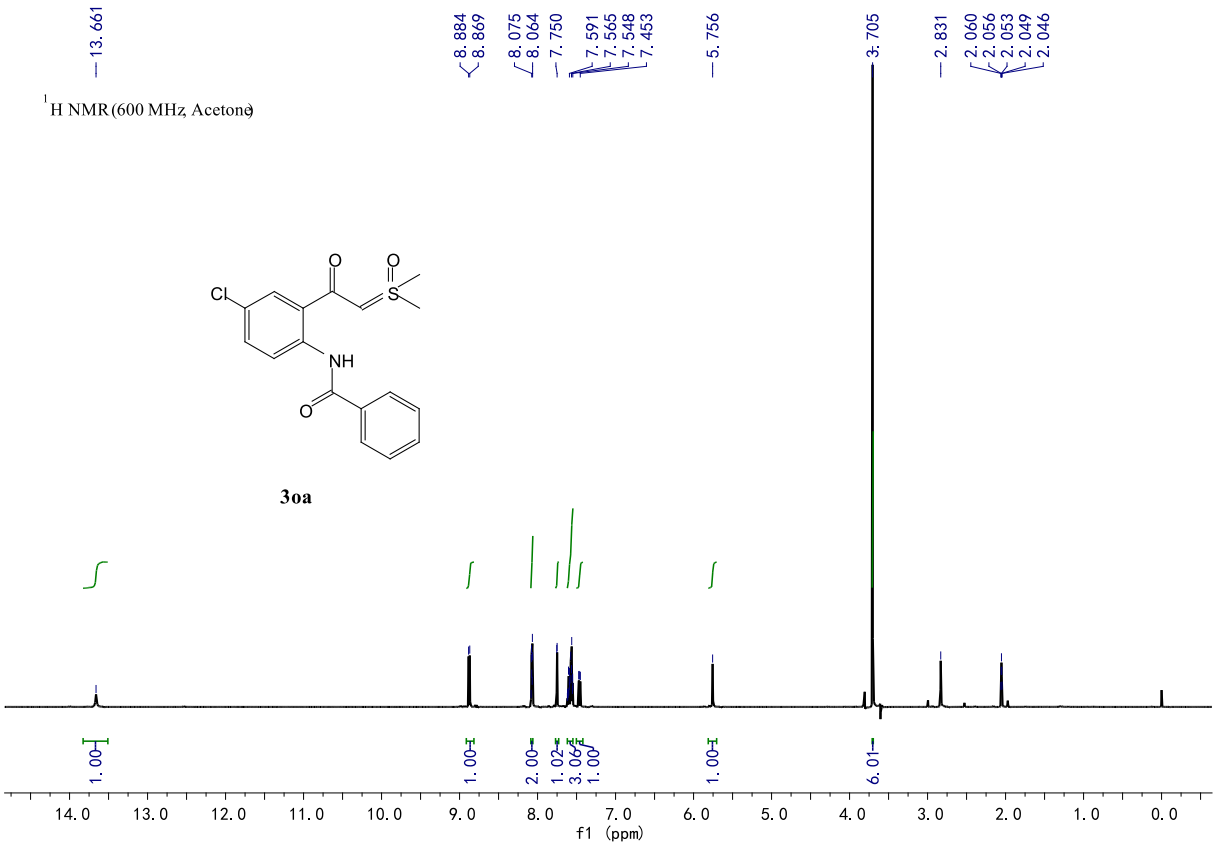

12.737
8.736
8.722
8.033
8.022
7.501
7.483
7.471
7.260
7.123
7.022
7.007
5.028
3.813
3.515
-0.004
1H NMR (600 MHz, CDCl3)
O
O
O
S
NH
O
3ma
1.00
1.00
2.00
3.00
1.00
1.00
1.00
3.01
6.01
14.0 13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

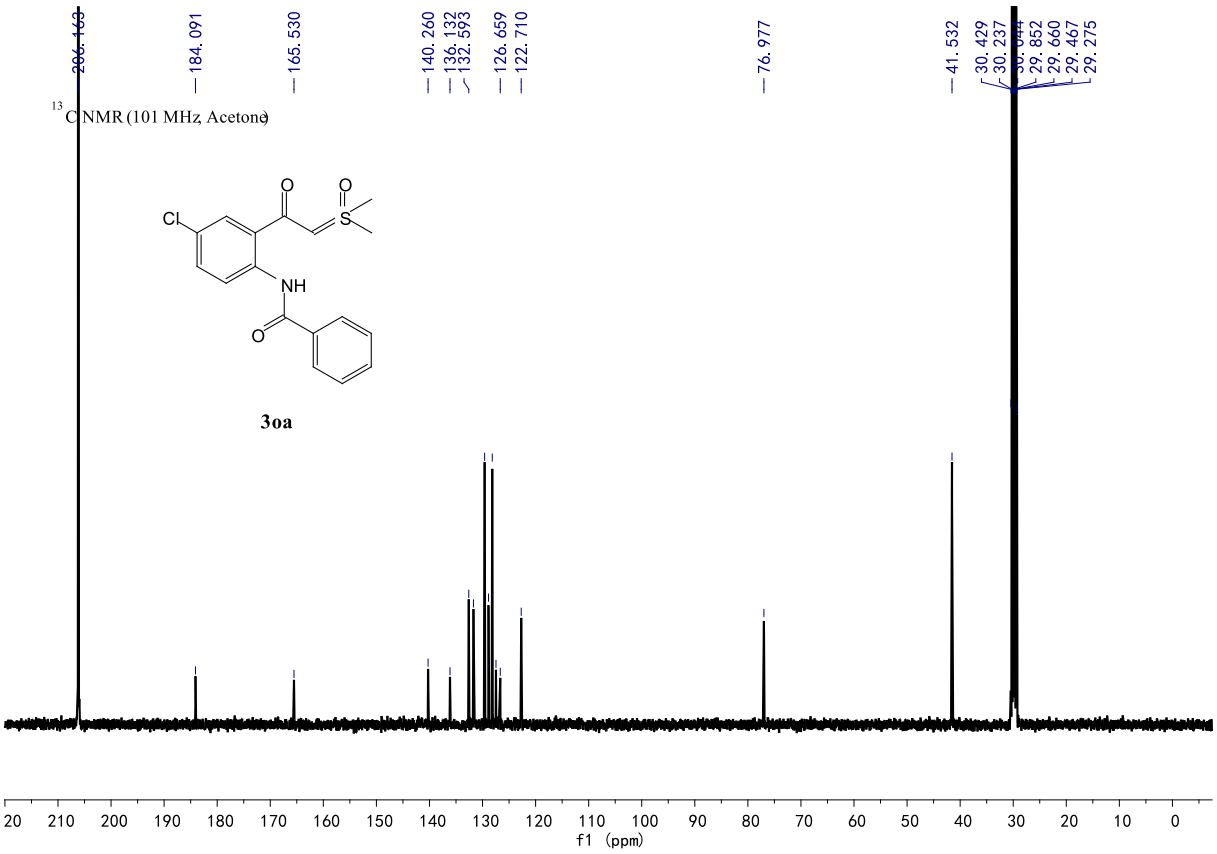

185.355
165.238
154.697
135.617
133.561
131.448
128.683
127.468
125.562
122.515
117.092
113.821
77.478
77.160
76.842
72.180
55.749
42.333
13C NMR (101 MHz, CDCl3)
3ma
f1 (ppm)

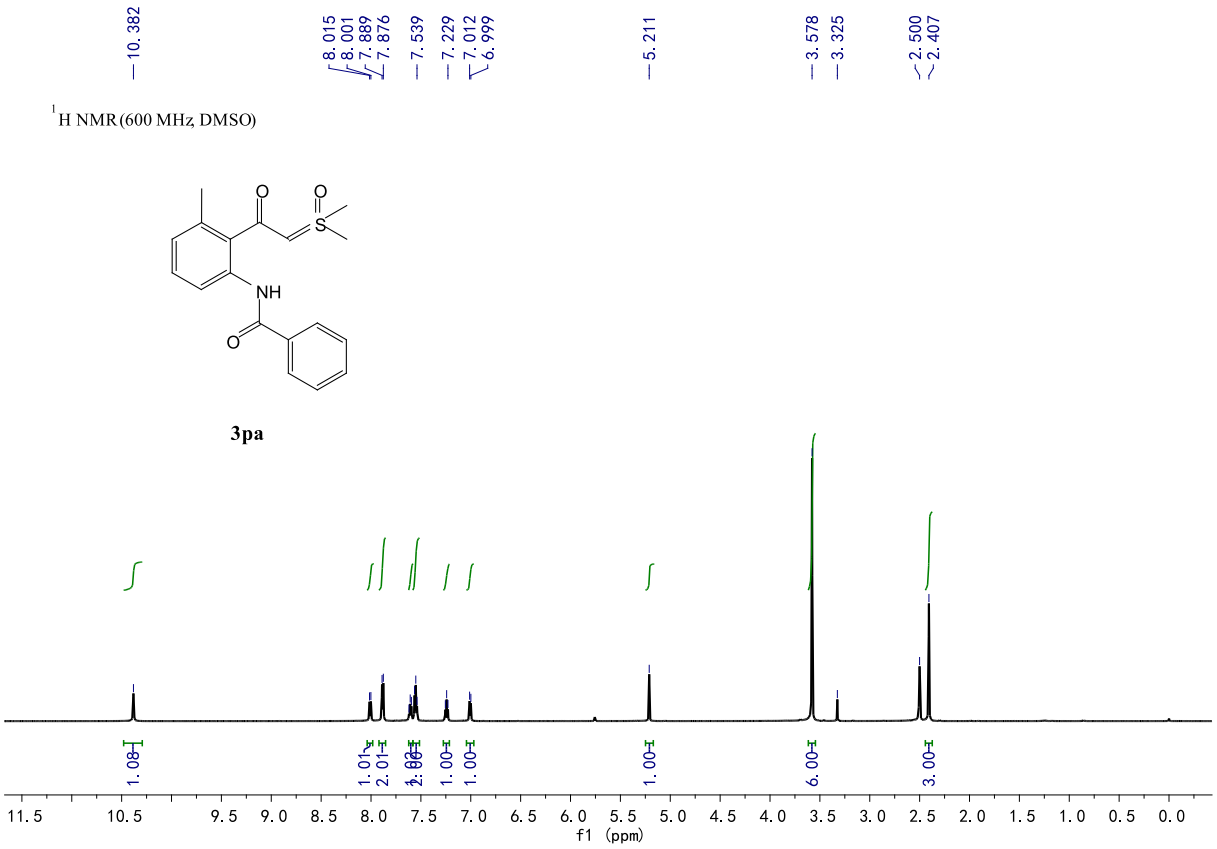

11.090
7.963
7.951
7.615
7.563
7.457
7.363
7.333
7.296
7.276
5.493
3.510
3.353
2.501
1H NMR (600 MHz, DMSO)
3na
3na'
2.3:1
1.00
2.00
1.01
2.00
1.01
1.02
1.00
1.00
6.01
f1 (ppm)

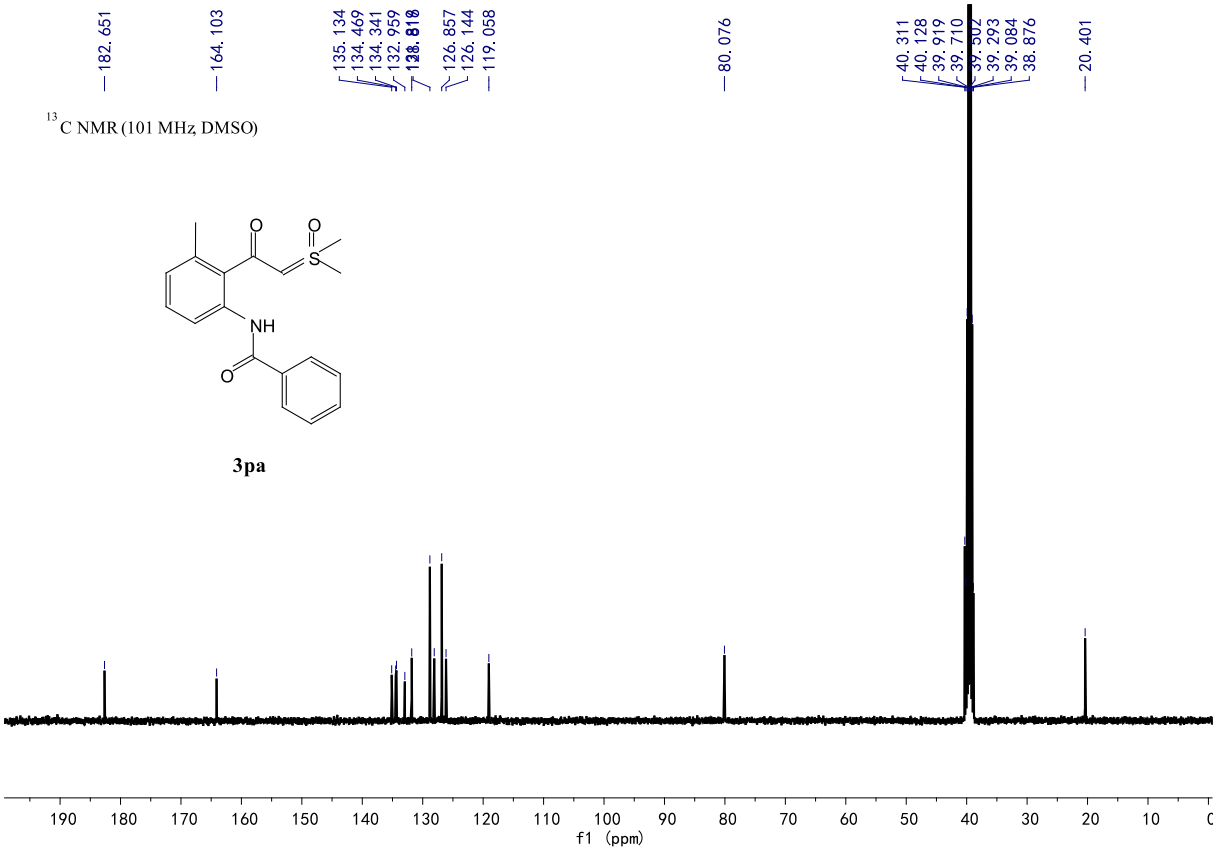

181.923
181.909
173.396
173.377
164.899
159.863
157.782
157.086
156.128
141.086
138.846
138.777
134.293
132.479
126.598
123.967
117.876
117.739
117.250
117.125
102.911
77.035
41.772
40.724
40.410
40.271
40.132
39.993
39.854
39.715
39.576
13C NMR (151 MHz, DMSO)
F
O
O
S
NH
O
3na
3na'
2.3:1
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

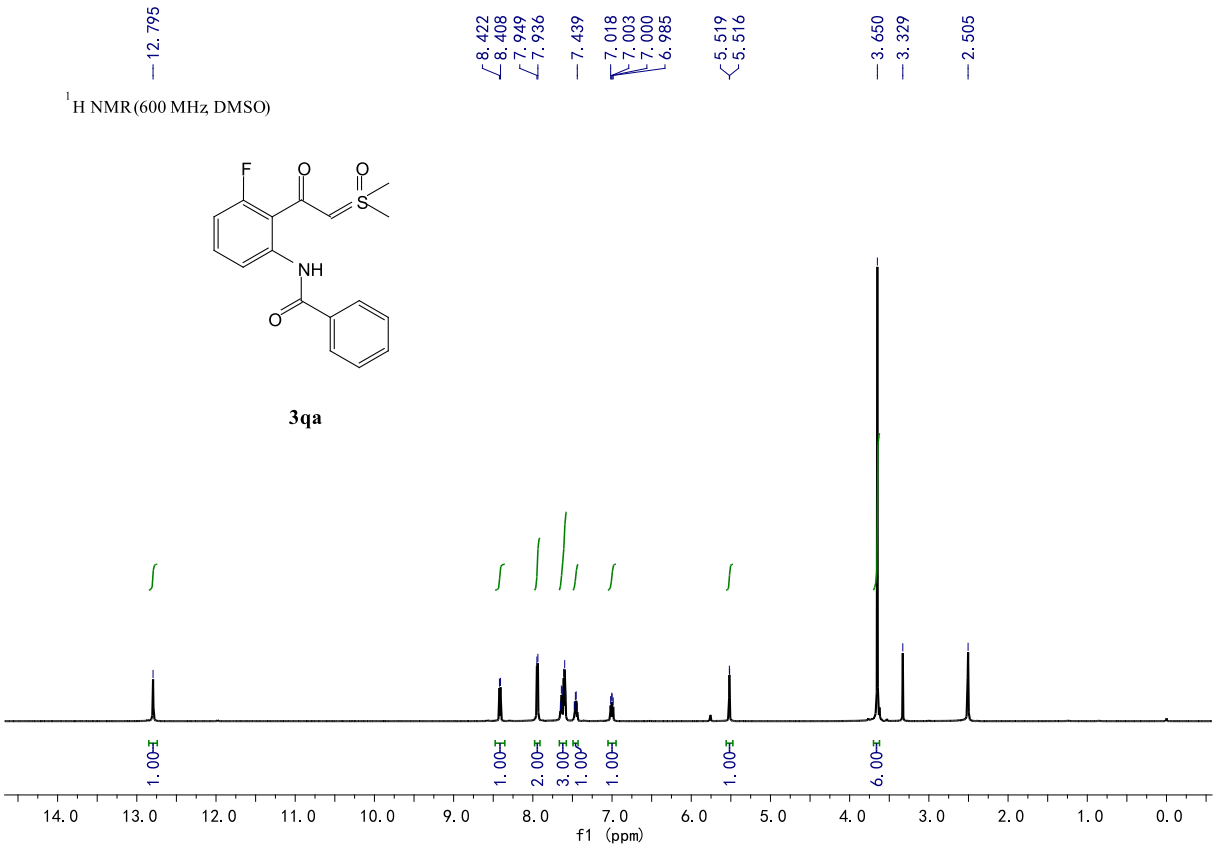

-115.504
-125.864
19F NMR (565 MHz, DMSO)
F
O
O
S
NH
O
3na
3na'
2.3:1
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)


13.661
8.884
8.869
8.075
8.064
7.750
7.591
7.565
7.548
7.453
5.756
3.705
2.831
2.060
2.056
2.053
2.049
2.046
1H NMR (600 MHz, Acetone)
Cl
O
O
S
NH
O
3oa
1.00
1.00
2.00
1.02
3.06
1.00
1.00
6.01
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

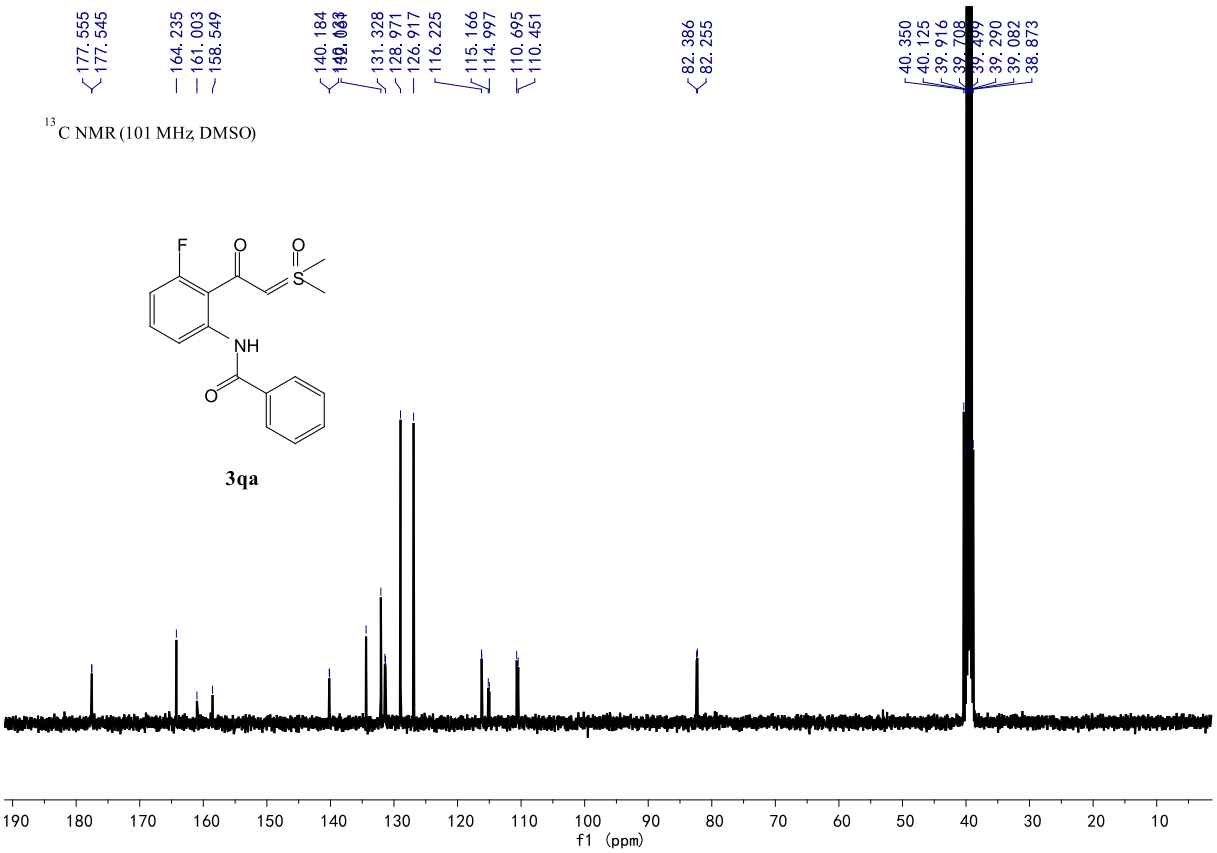

206.163
184.091
165.530
140.260
136.132
132.593
126.659
122.710
76.977
41.532
30.429
30.237
30.044
29.852
29.660
29.467
29.275
13C NMR (101 MHz, Acetone)
Cl
O
O
S
NH
O
3oa
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


10.382
8.015
8.001
7.889
7.876
7.539
7.229
7.012
6.999
5.211
3.578
3.325
2.500
2.407
1H NMR (600 MHz, DMSO)
O
O
S
NH
O
3pa
1.08
1.01
2.01
1.00
1.00
1.00
6.00
3.00
11.5
10.5
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
0.0
f1 (ppm)


182.651
164.103
135.134
134.469
134.341
132.959
126.857
126.144
119.058
80.076
40.311
40.128
39.919
39.710
39.502
39.293
39.084
38.876
20.401
13C NMR (101 MHz, DMSO)
O
O
S
NH
O
3pa
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

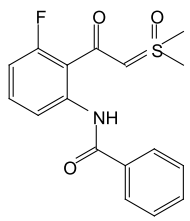

12.795
8.422
8.408
7.949
7.936
7.439
7.018
7.003
7.000
6.985
5.519
5.516
3.650
3.329
2.505
1H NMR (600 MHz, DMSO)
F
O
O
S
NH
O
1.00
1.00
2.00
3.00
1.00
1.00
1.00
6.00
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

3qa


177.555
177.545
164.235
161.003
158.549
140.184
131.328
128.971
126.917
116.225
115.166
114.997
110.695
110.451
82.386
82.255
40.350
40.125
39.916
39.708
39.499
39.290
39.082
38.873
13C NMR (101 MHz, DMSO)
F
O
O
S
NH
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

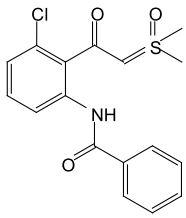
3qa

^{19}F NMR (565 MHz, DMSO)

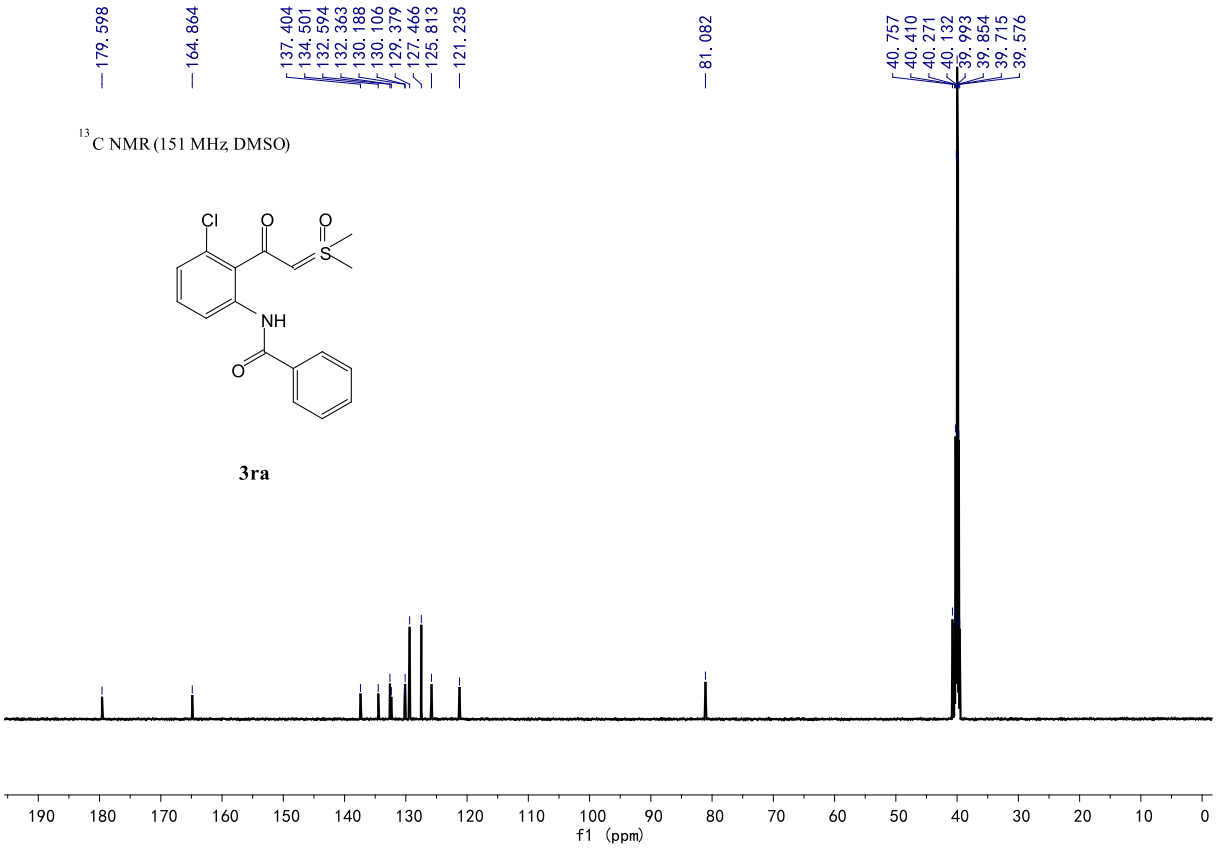


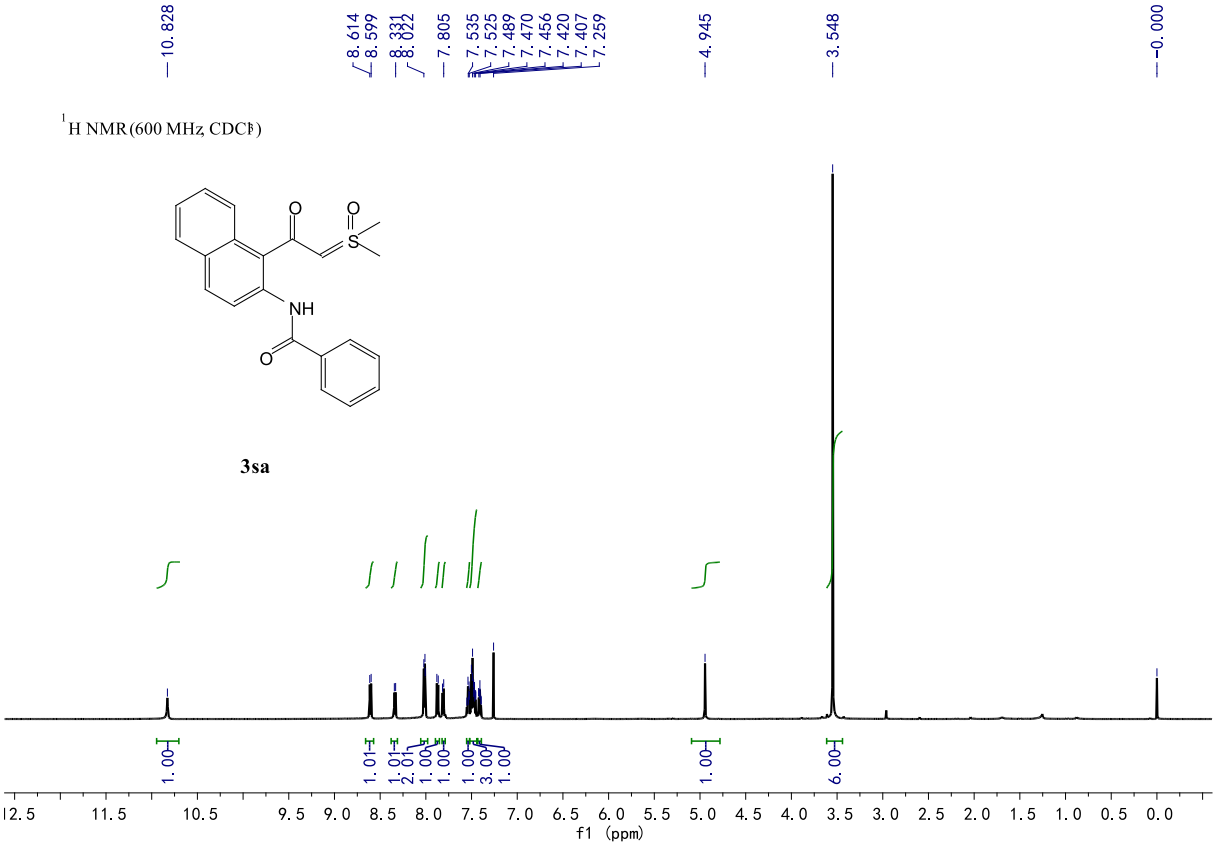
3qa

^{1}H NMR (600 MHz, DMSO)

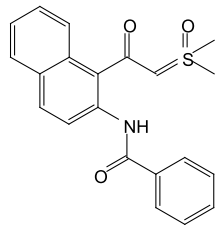


3ra

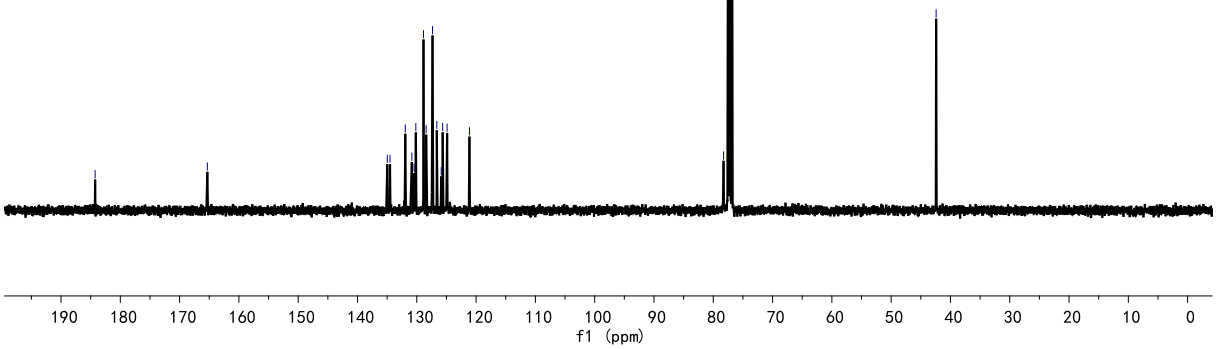

179.598
164.864
137.404
134.501
132.594
132.363
130.188
130.106
129.379
127.466
125.813
121.235
81.082
40.757
40.410
40.271
40.132
39.993
39.854
39.715
39.576
13C NMR (151 MHz, DMSO)
Cl
O
O
S
NH
O
3ra
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


10.828
8.614
8.599
8.331
8.022
7.805
7.535
7.525
7.489
7.470
7.456
7.420
7.407
7.259
4.945
3.548
0.000
1H NMR (600 MHz, CDCl3)
O
O
S
NH
O
3sa
1.00
1.01
1.01
2.01
1.00
1.00
1.00
3.00
1.00
1.00
6.00
12.5 11.5 10.5 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 0.0
f1 (ppm)

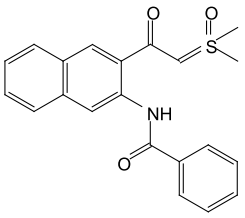
^{13}C NMR (101 MHz, CDCl$_3$)



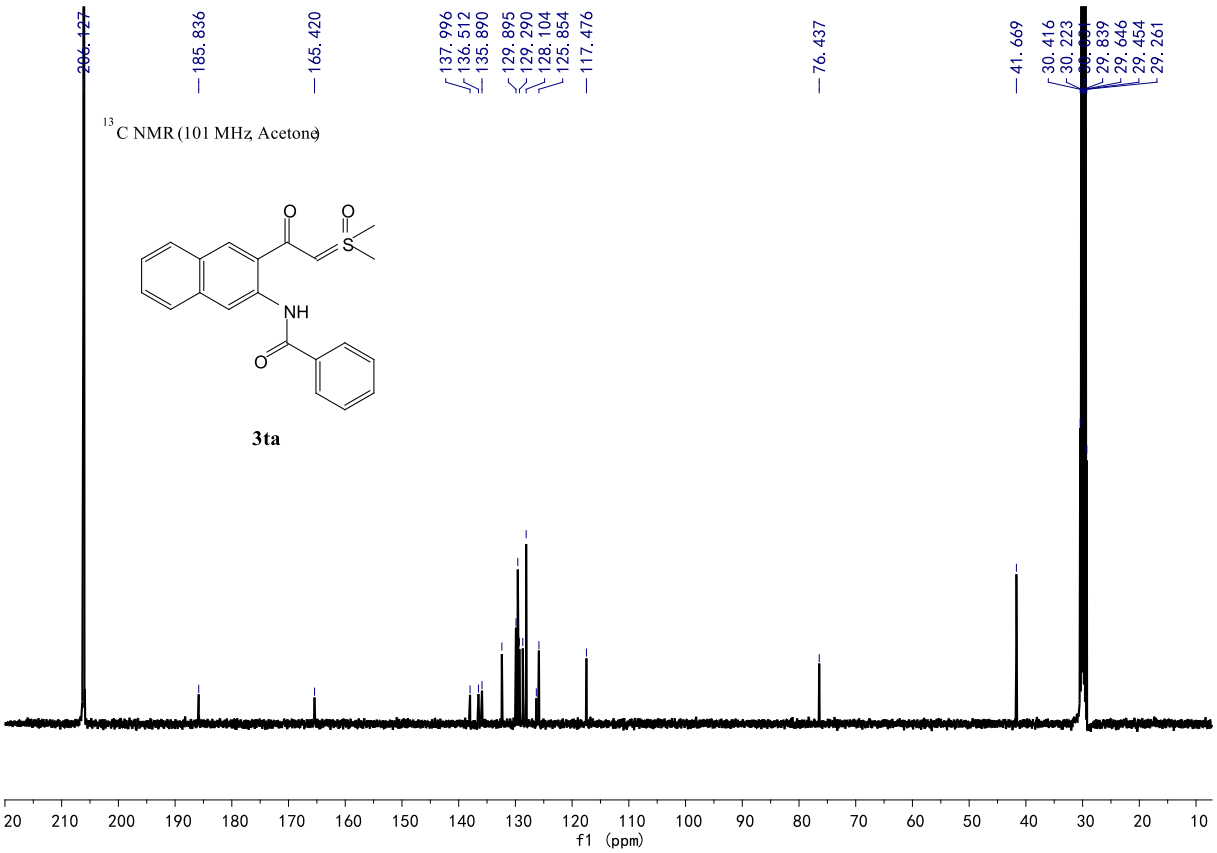
3sa

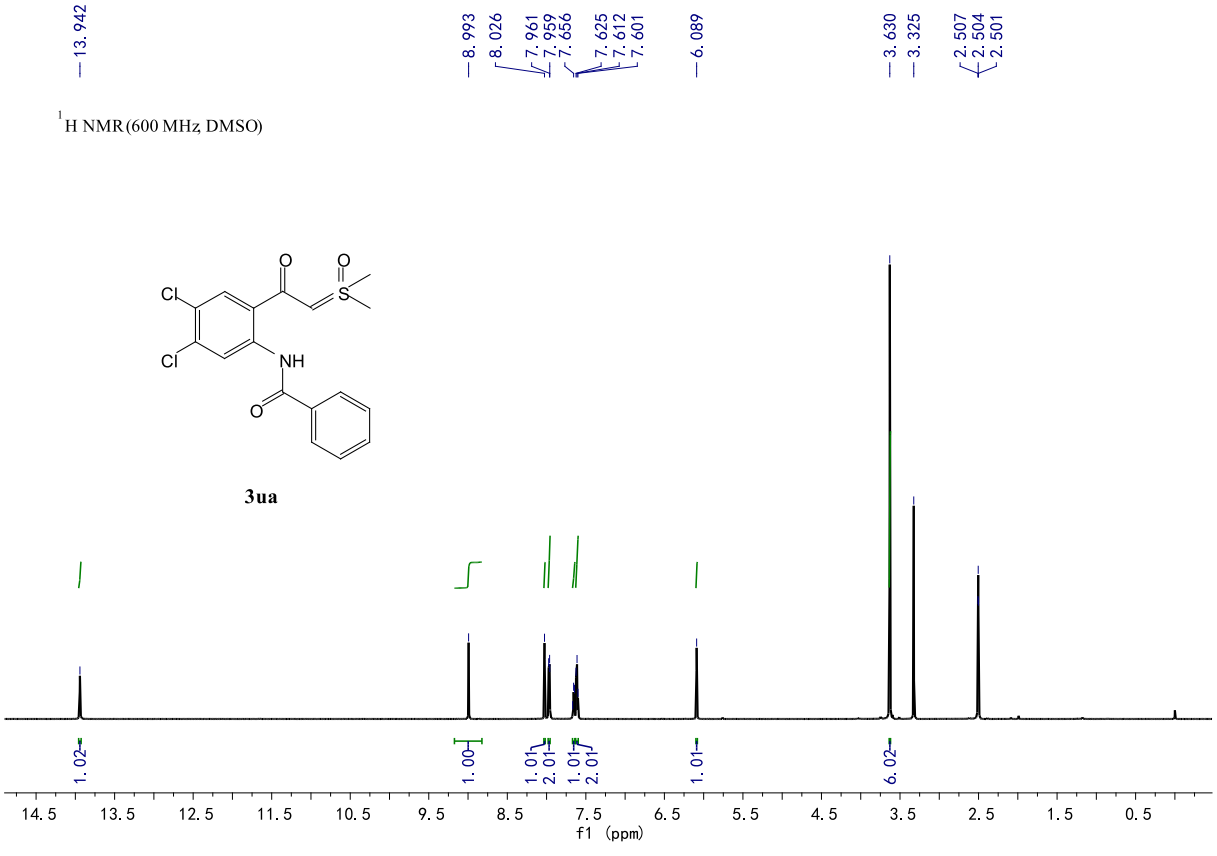


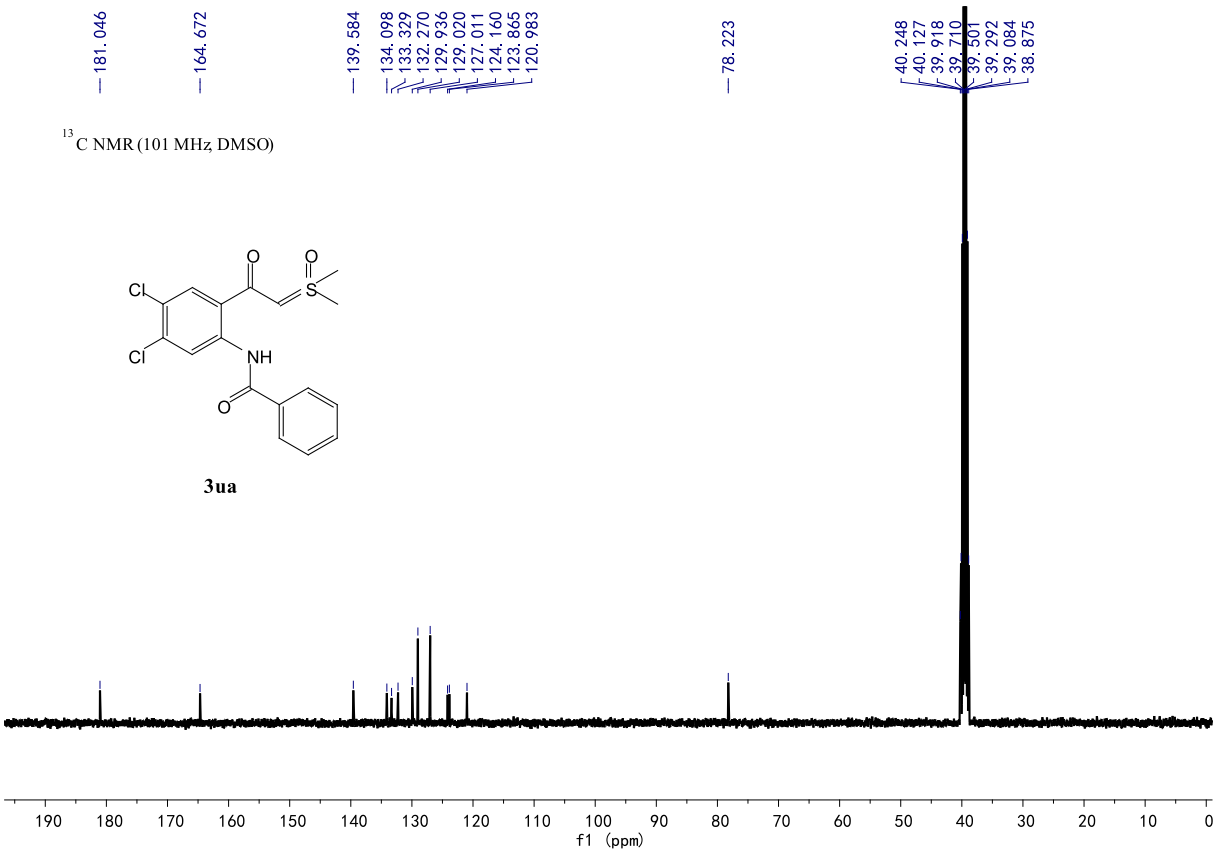
^{1}H NMR (600 MHz, Acetone)



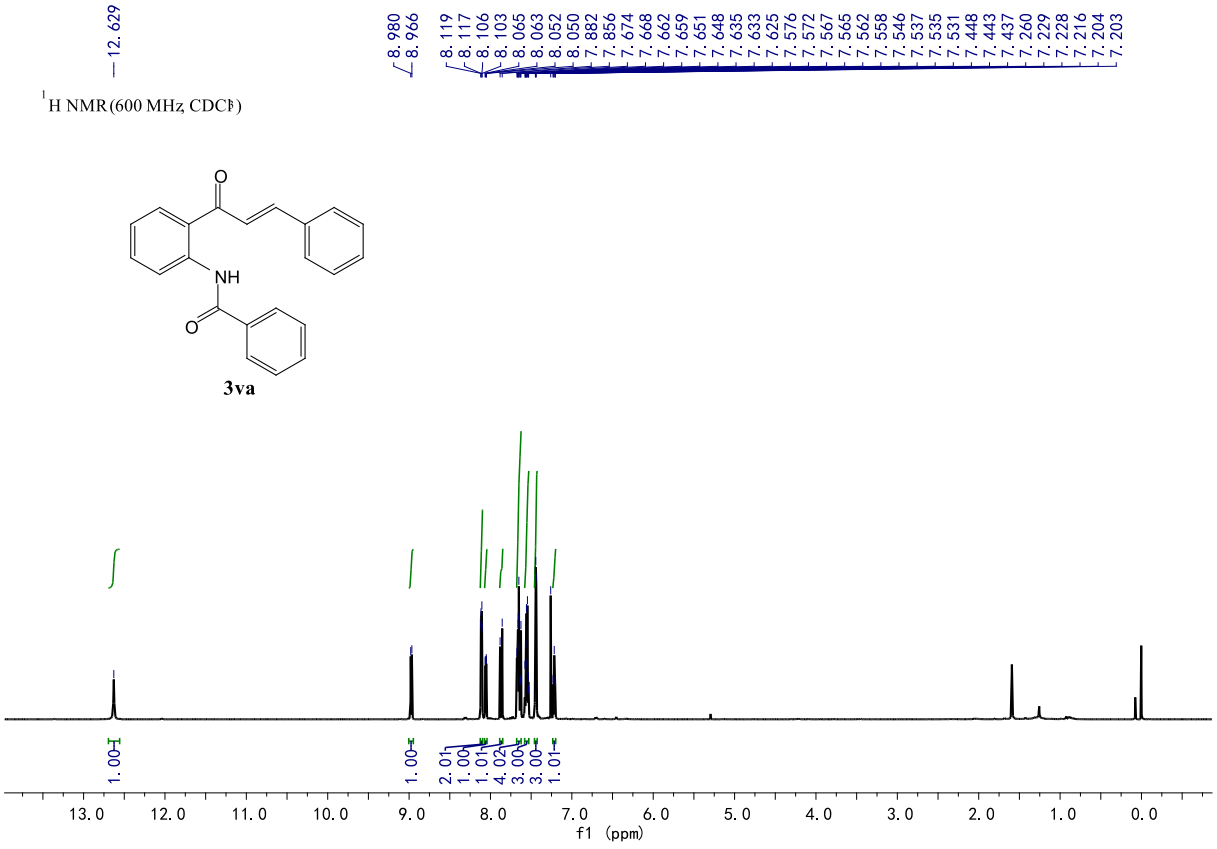
3ta


206.427
185.836
165.420
137.996
136.512
135.890
129.895
129.290
128.104
125.854
117.476
76.437
41.669
30.416
30.223
29.839
29.646
29.454
29.261
13C NMR (101 MHz, Acetone)
O
O
S
NH
O
3ta
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

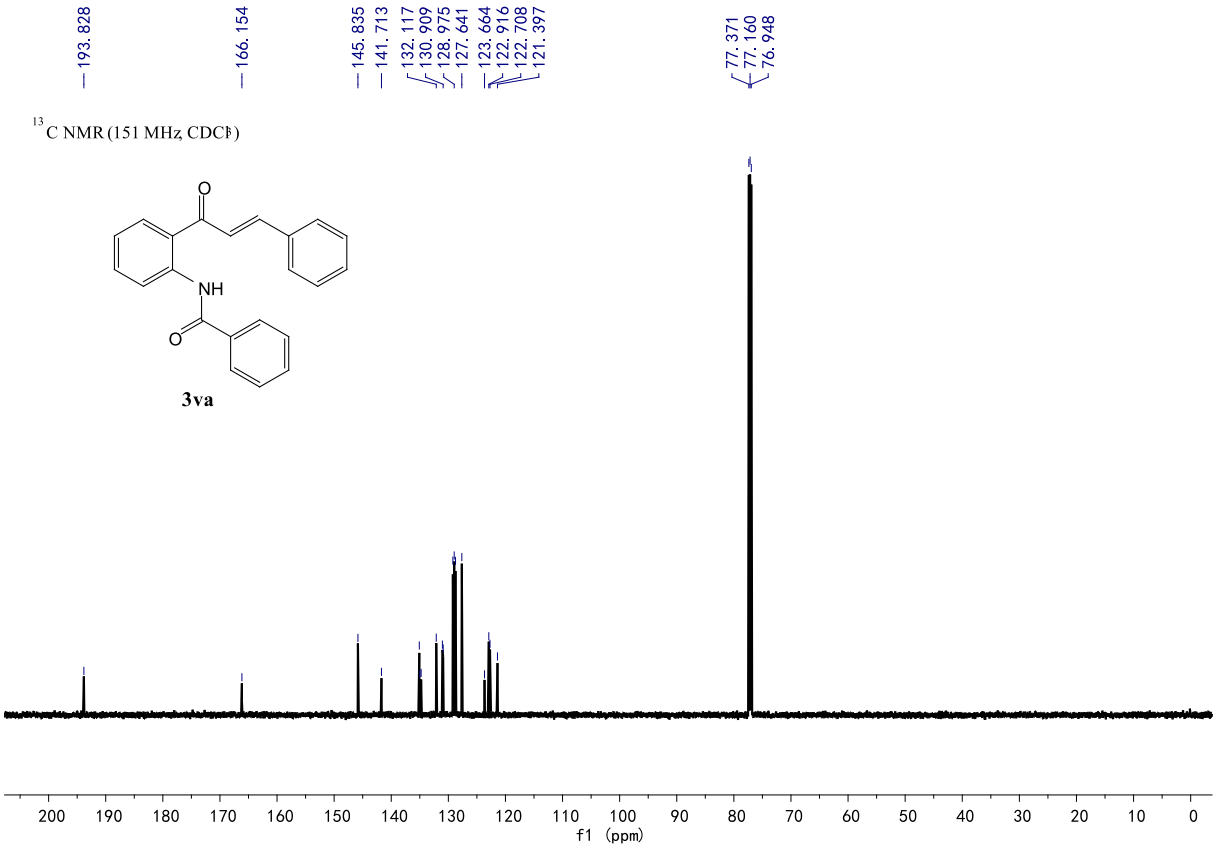

13.942
8.993
8.026
7.961
7.959
7.656
7.625
7.612
7.601
6.089
3.630
3.325
2.507
2.504
2.501
1H NMR (600 MHz, DMSO)
Cl
Cl
O
O
S
NH
O
3ua
1.02
1.00
1.01
2.01
1.01
2.01
1.01
6.02
14.5 13.5 12.5 11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5
f1 (ppm)

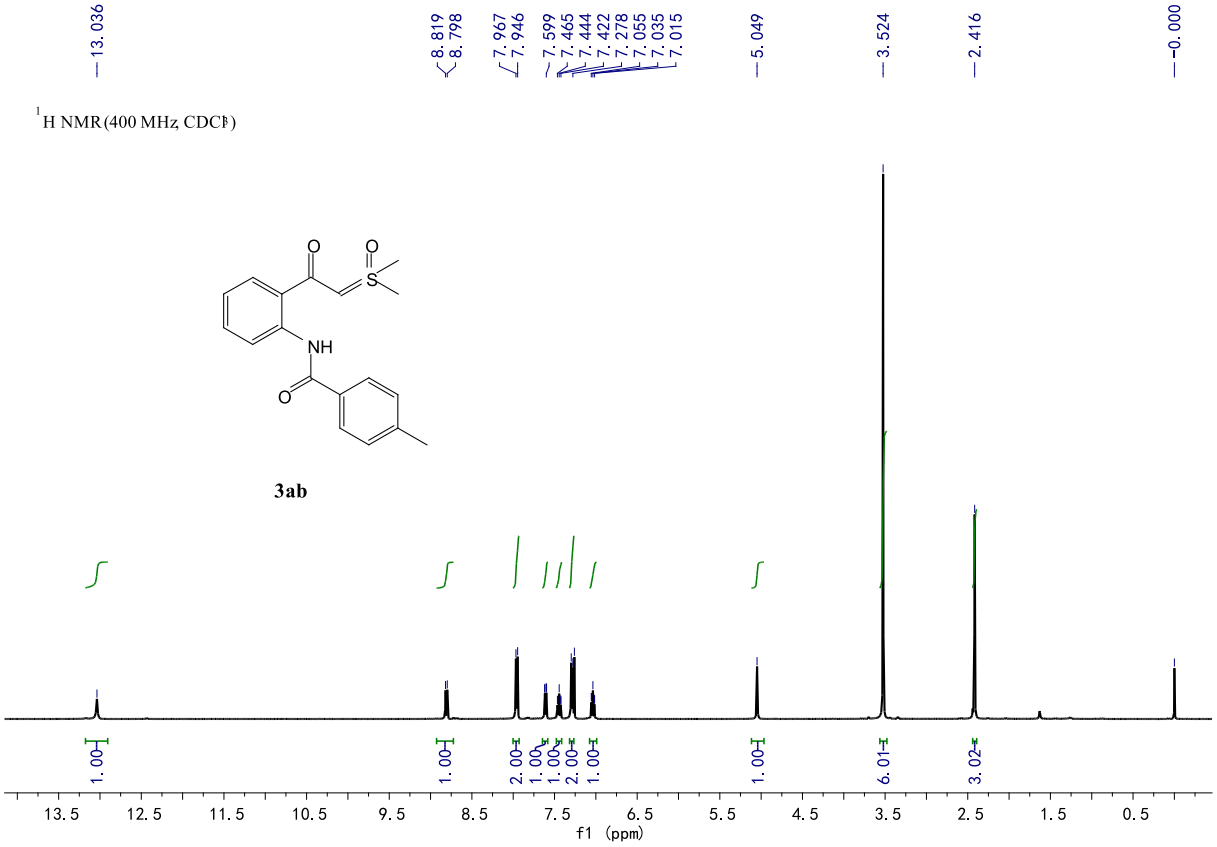

181.046
164.672
139.584
134.098
133.329
132.270
129.936
129.020
127.011
124.160
123.865
120.983
78.223
40.248
40.127
39.918
39.710
39.501
39.292
39.084
38.875
13C NMR (101 MHz, DMSO)
Cl
Cl
NH
O
O
O
S
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

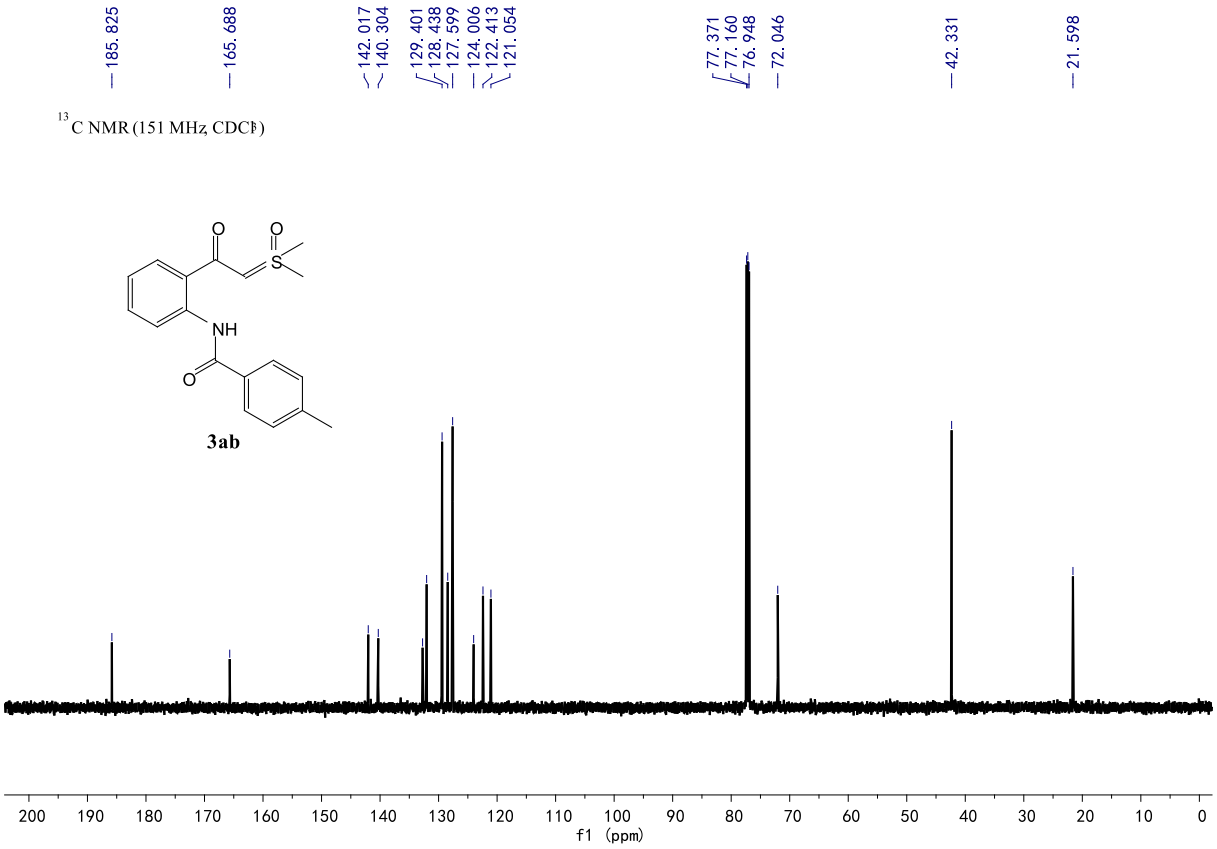
3ua

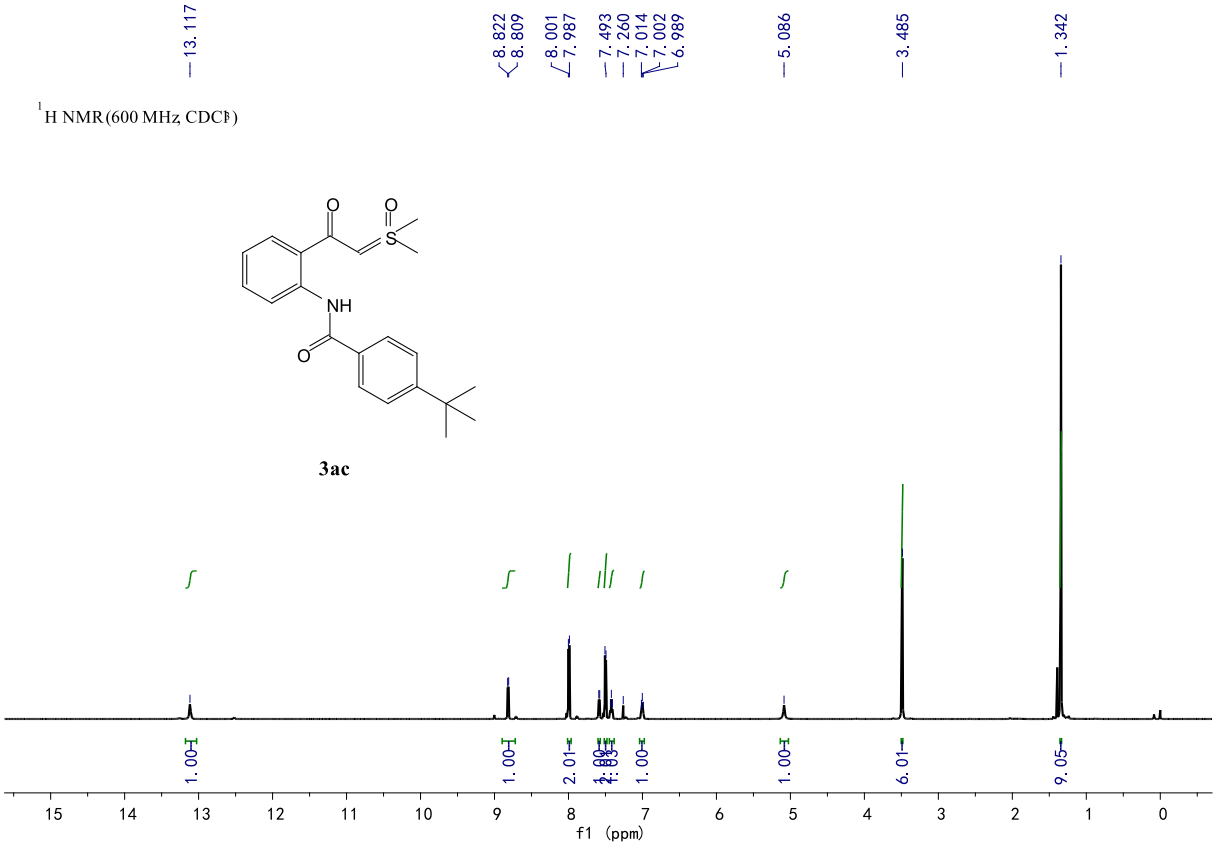

12.629
8.980
8.966
8.119
8.117
8.106
8.103
8.065
8.063
8.052
8.050
7.882
7.856
7.674
7.668
7.662
7.659
7.651
7.648
7.635
7.633
7.625
7.576
7.572
7.567
7.565
7.562
7.558
7.546
7.537
7.535
7.531
7.448
7.443
7.437
7.260
7.229
7.228
7.216
7.204
7.203
1H NMR (600 MHz, CDCl3)
O
NH
O
1.00
1.00
2.01
1.00
1.01
4.02
3.00
3.00
1.01
13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

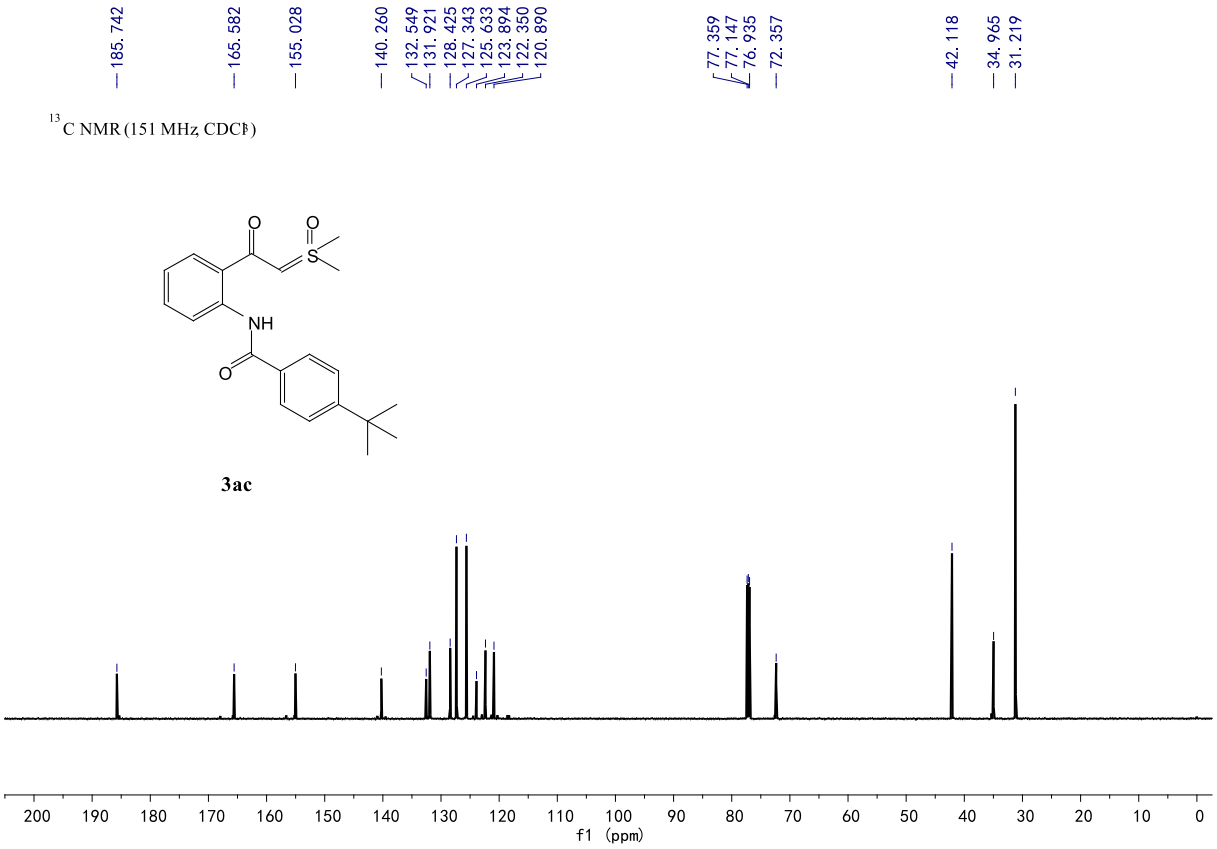
3va

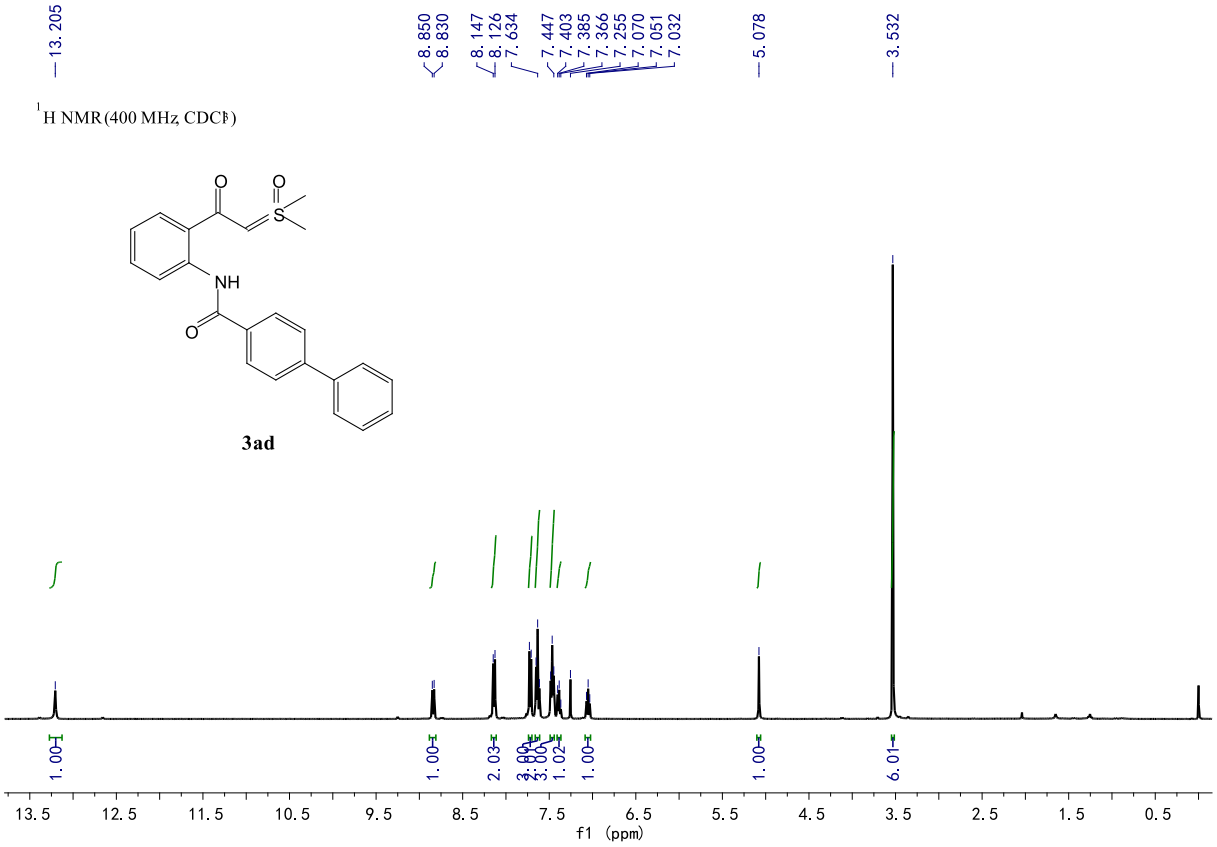

193.828
166.154
145.835
141.713
132.117
130.909
128.975
127.641
123.664
122.916
122.708
121.397
77.371
77.160
76.948
13C NMR (151 MHz, CDCl3)
O
NH
O
3va
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

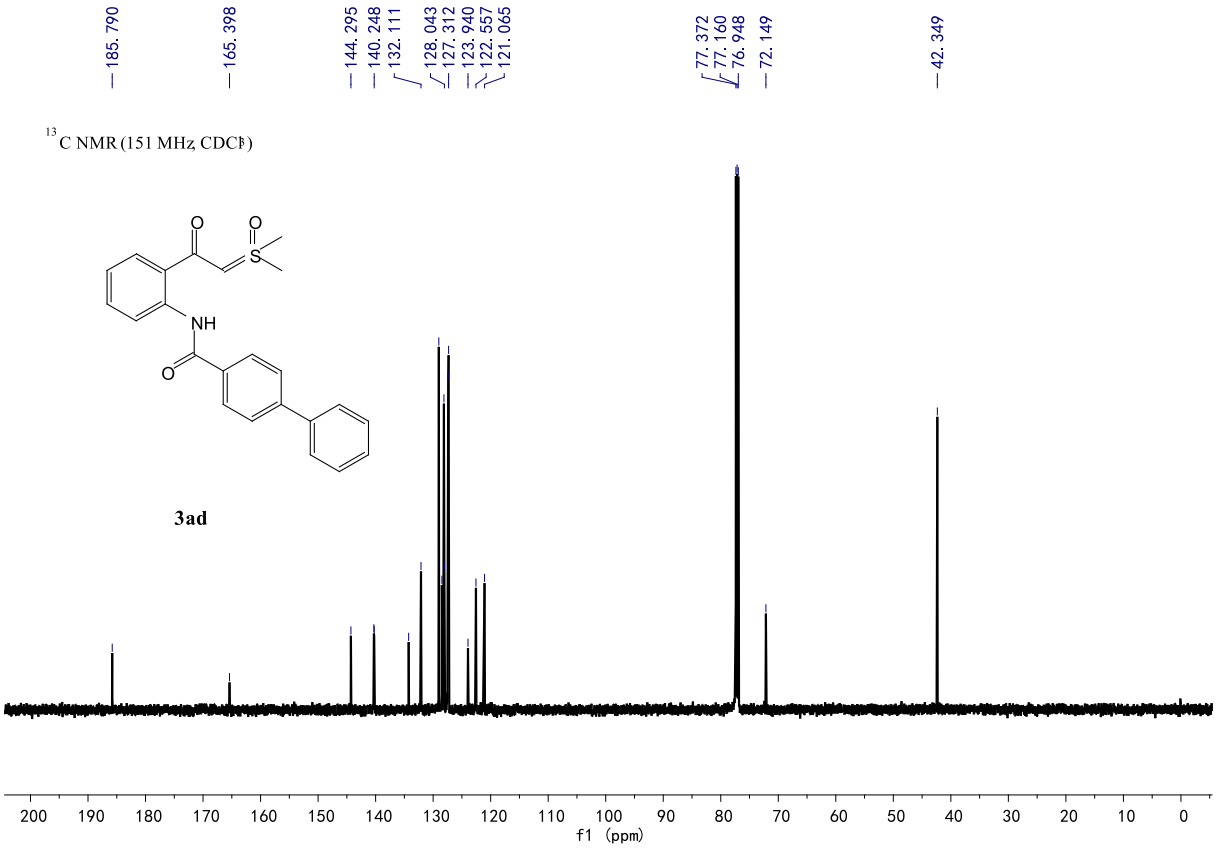

13.036
8.819
8.798
7.967
7.946
7.599
7.465
7.444
7.422
7.278
7.055
7.035
7.015
5.049
3.524
2.416
0.000
1H NMR (400 MHz, CDCl3)
O
O
S
NH
O
3ab
1.00
1.00
2.00
1.00
1.00
2.00
1.00
1.00
6.01
3.02
13.5 12.5 11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5
f1 (ppm)

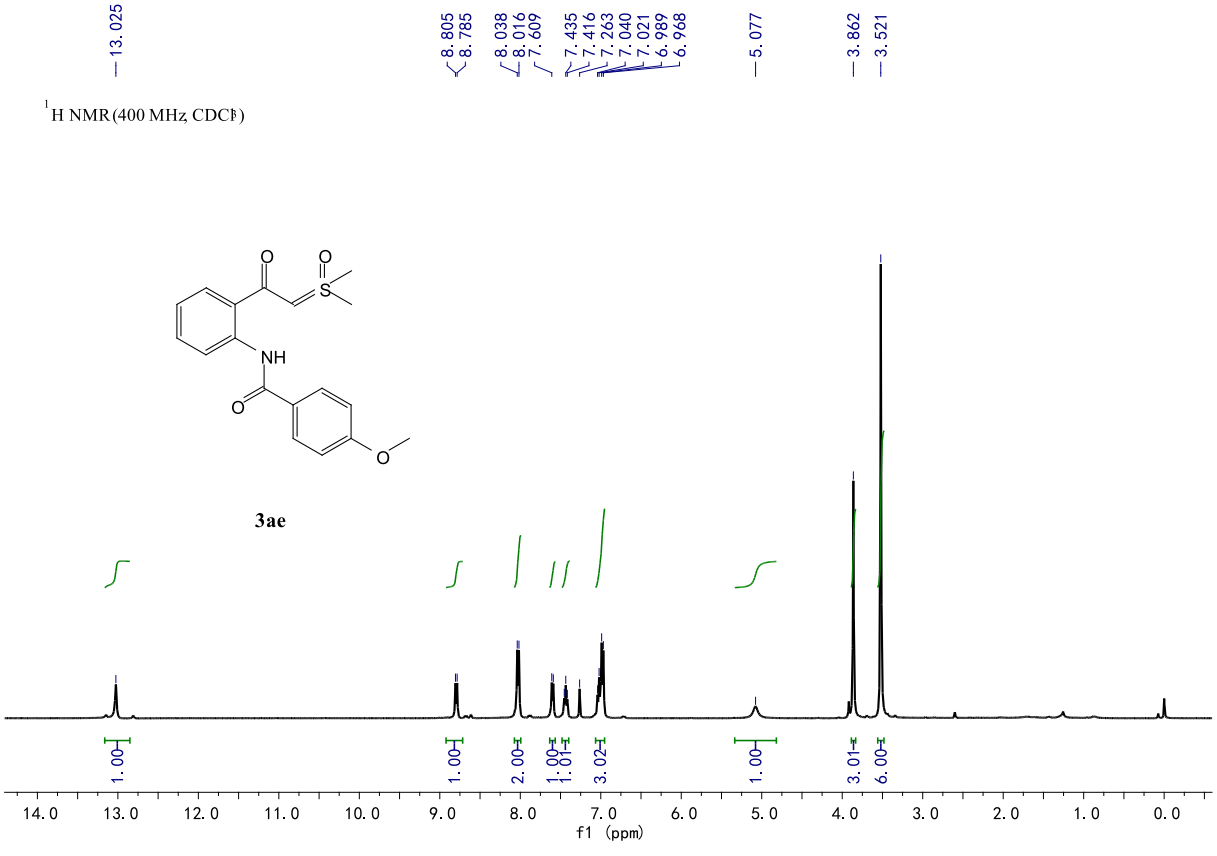

185.825
165.688
142.017
140.304
129.401
128.438
127.599
124.006
122.413
121.054
77.371
77.160
76.948
72.046
42.331
21.598
13C NMR (151 MHz, CDCl3)
O
O
S
NH
O
3ab
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

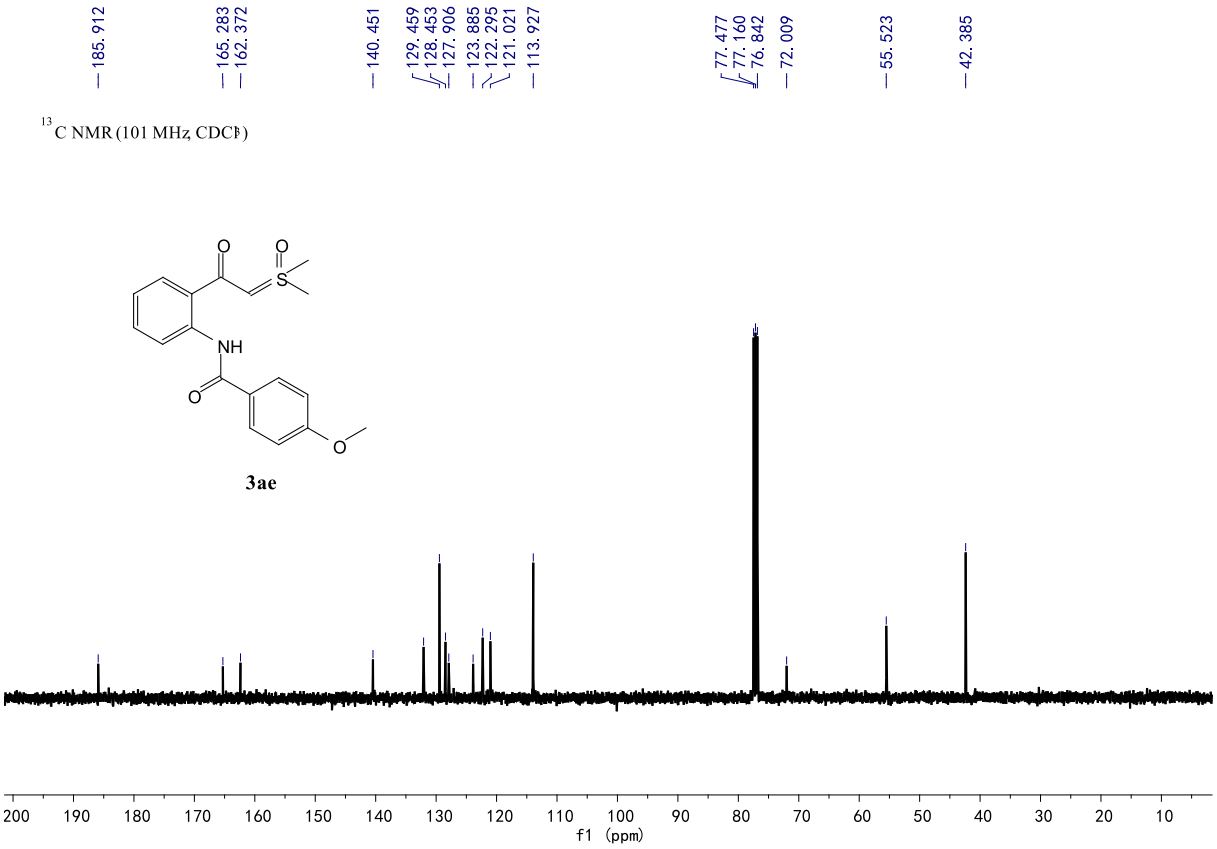

13.117
8.822
8.809
8.001
7.987
7.493
7.260
7.014
7.002
6.989
5.086
3.485
1.342
1H NMR (600 MHz, CDCl3)
O
O
S
NH
O
3ac
1.00
1.00
2.01
1.00
1.00
6.01
9.05
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

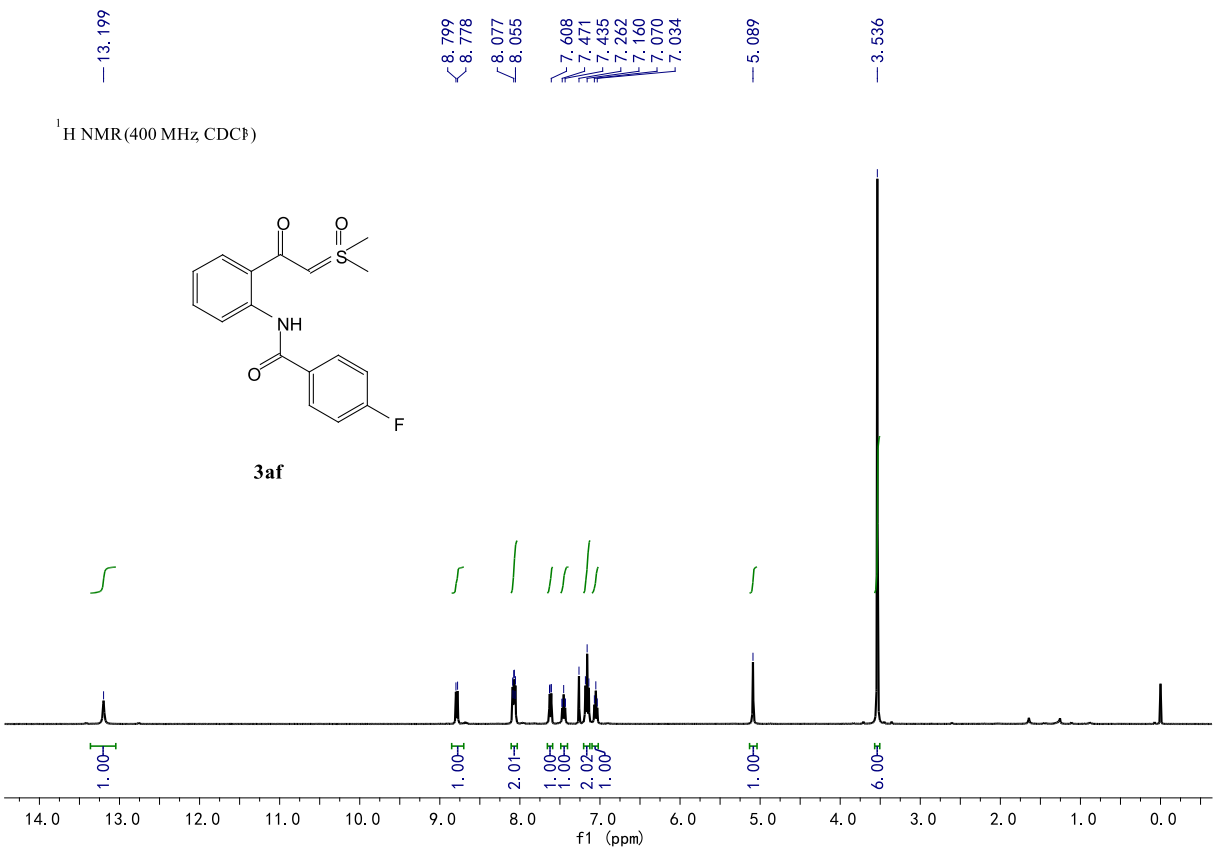

185.742
165.582
155.028
140.260
132.549
131.921
128.425
127.343
125.633
123.894
122.350
120.890
77.359
77.147
76.935
72.357
42.118
34.965
31.219
13C NMR (151 MHz, CDCl3)
O
O
S
NH
O
3ac
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

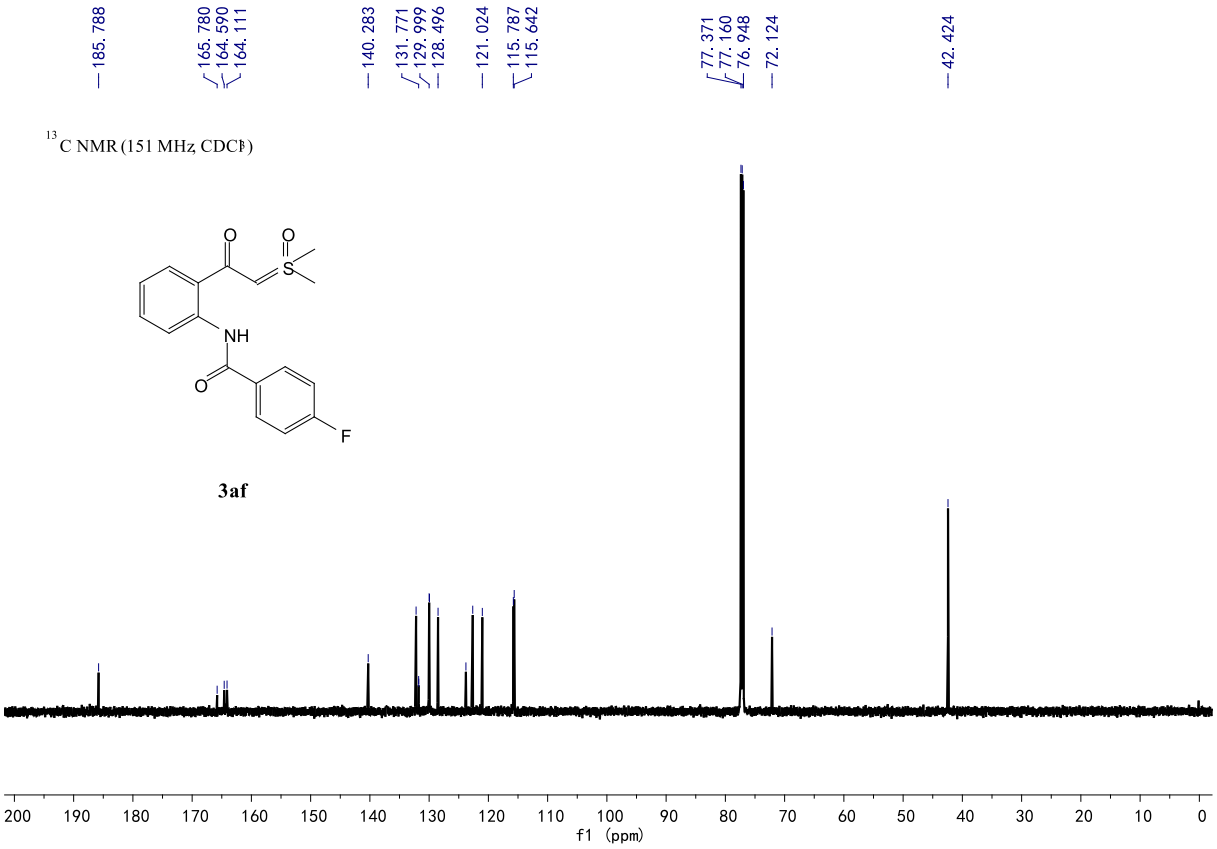

13.205
8.850
8.830
8.147
8.126
7.634
7.447
7.403
7.385
7.366
7.255
7.070
7.051
7.032
5.078
3.532
1H NMR (400 MHz, CDCl3)
O
O
S
NH
O
3ad
1.00
1.00
2.03
3.00
3.05
1.02
1.00
1.00
6.01
13.5 12.5 11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5
f1 (ppm)

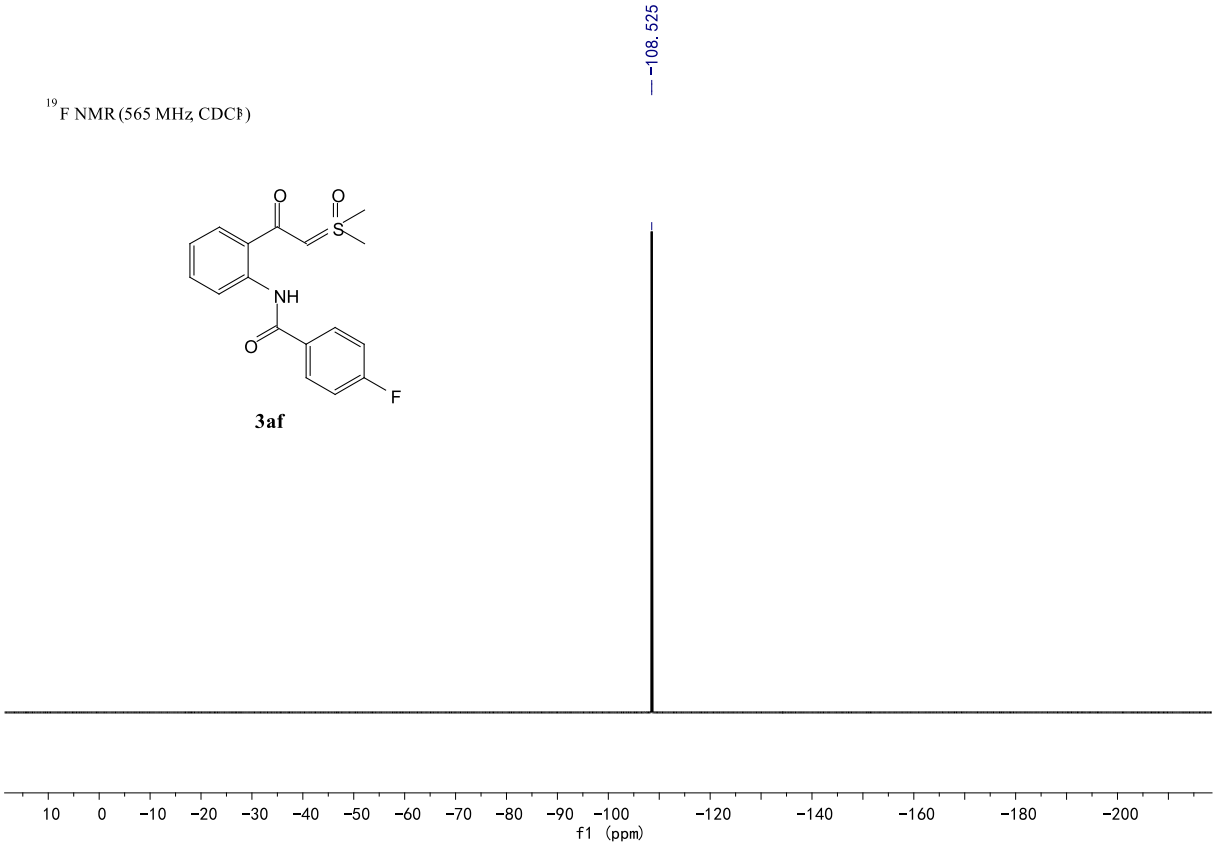

185.790
165.398
144.295
140.248
132.111
128.043
127.312
123.940
122.557
121.065
77.372
77.160
76.948
72.149
42.349
13C NMR (151 MHz, CDCl3)
O
O
S
NH
O
3ad
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

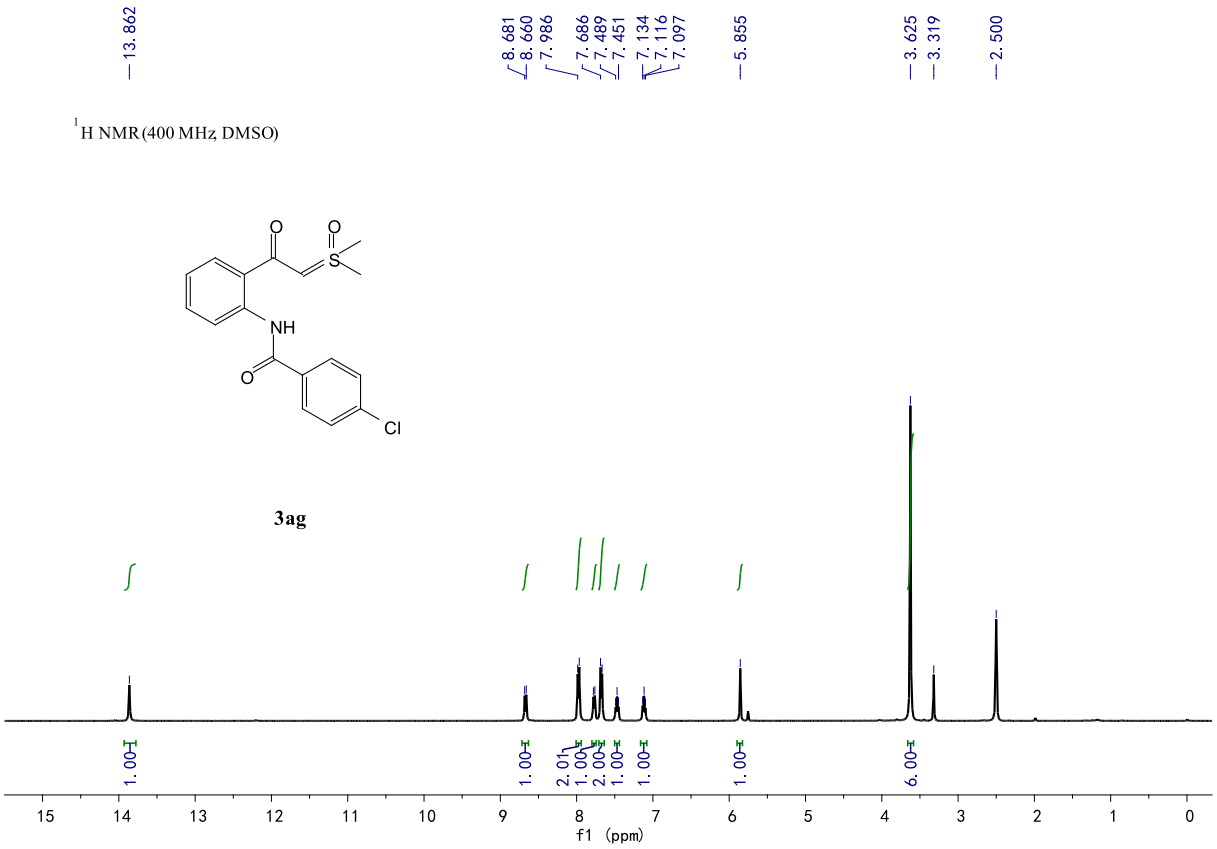

13.025
8.805
8.785
8.038
8.016
7.609
7.435
7.416
7.263
7.040
7.021
6.989
6.968
5.077
3.862
3.521
1H NMR (400 MHz, CDCl3)
O
O
S
NH
O
O
3ae
1.00
1.00
2.00
1.00
1.01
3.02
1.00
3.01
6.00
14.0 13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

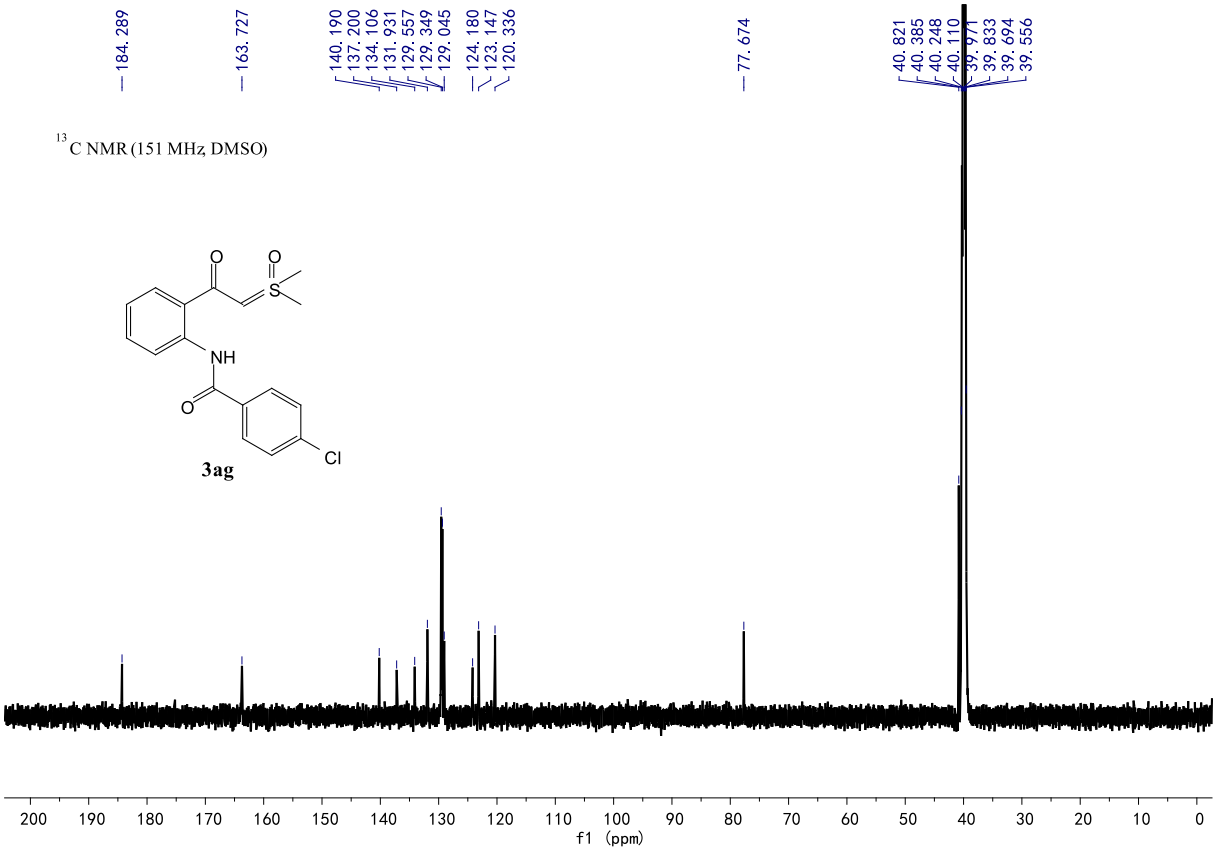

185.912
165.283
162.372
140.451
129.459
128.453
127.906
123.885
122.295
121.021
113.927
77.477
77.160
76.842
72.009
55.523
42.385
13C NMR (101 MHz, CDCl3)
O
O
S
NH
O
O
3ae
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

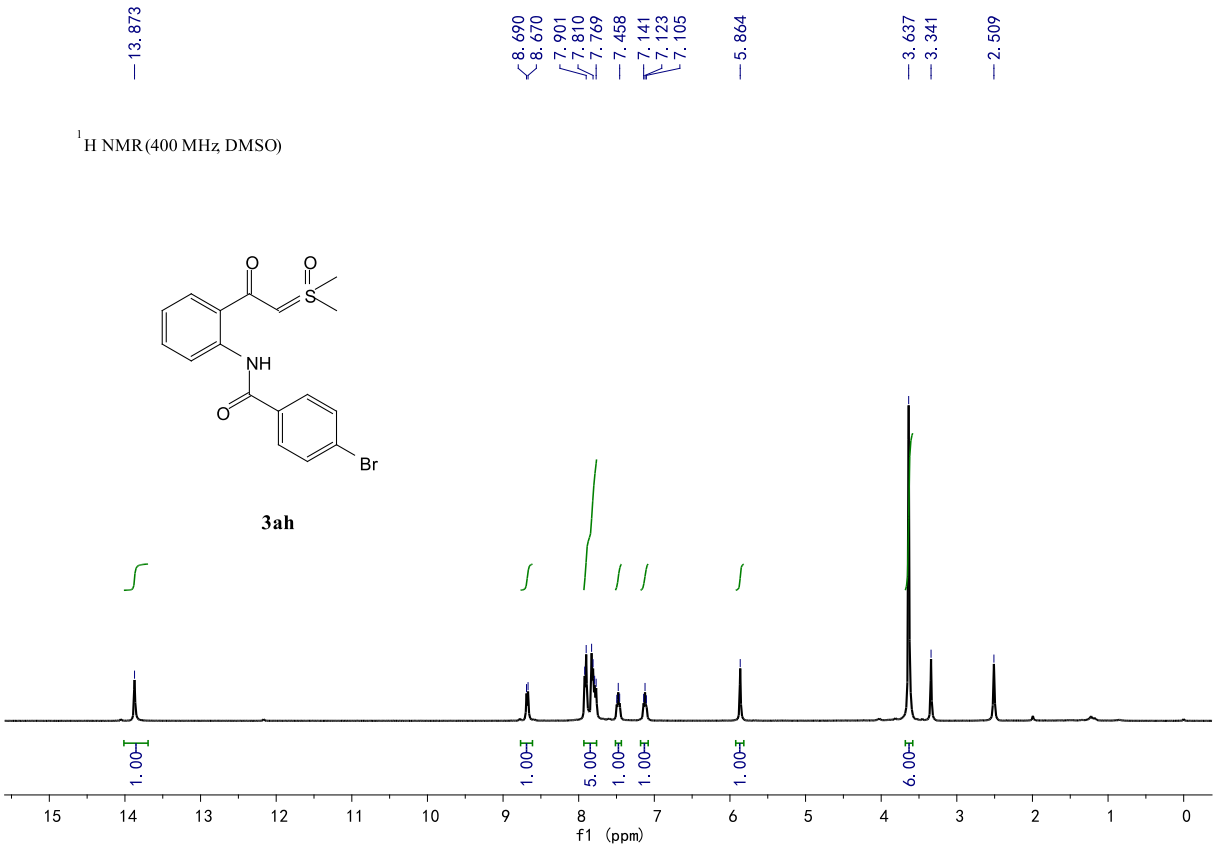

13.199
8.799
8.778
8.077
8.055
7.608
7.471
7.435
7.262
7.160
7.070
7.034
5.089
3.536
1H NMR (400 MHz, CDCl3)
O
O
S
NH
O
F
3af
1.00
1.00
2.01
1.00
1.00
2.02
1.00
1.00
6.00
14.0 13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)


185.788
165.780
164.590
164.111
140.283
131.771
129.999
128.496
121.024
115.787
115.642
77.371
77.160
76.948
72.124
42.424
13C NMR (151 MHz, CDCl3)
O
O
S
NH
O
F
3af
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-108.525
19F NMR (565 MHz, CDCl3)
O
O
S
NH
O
F
3af
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

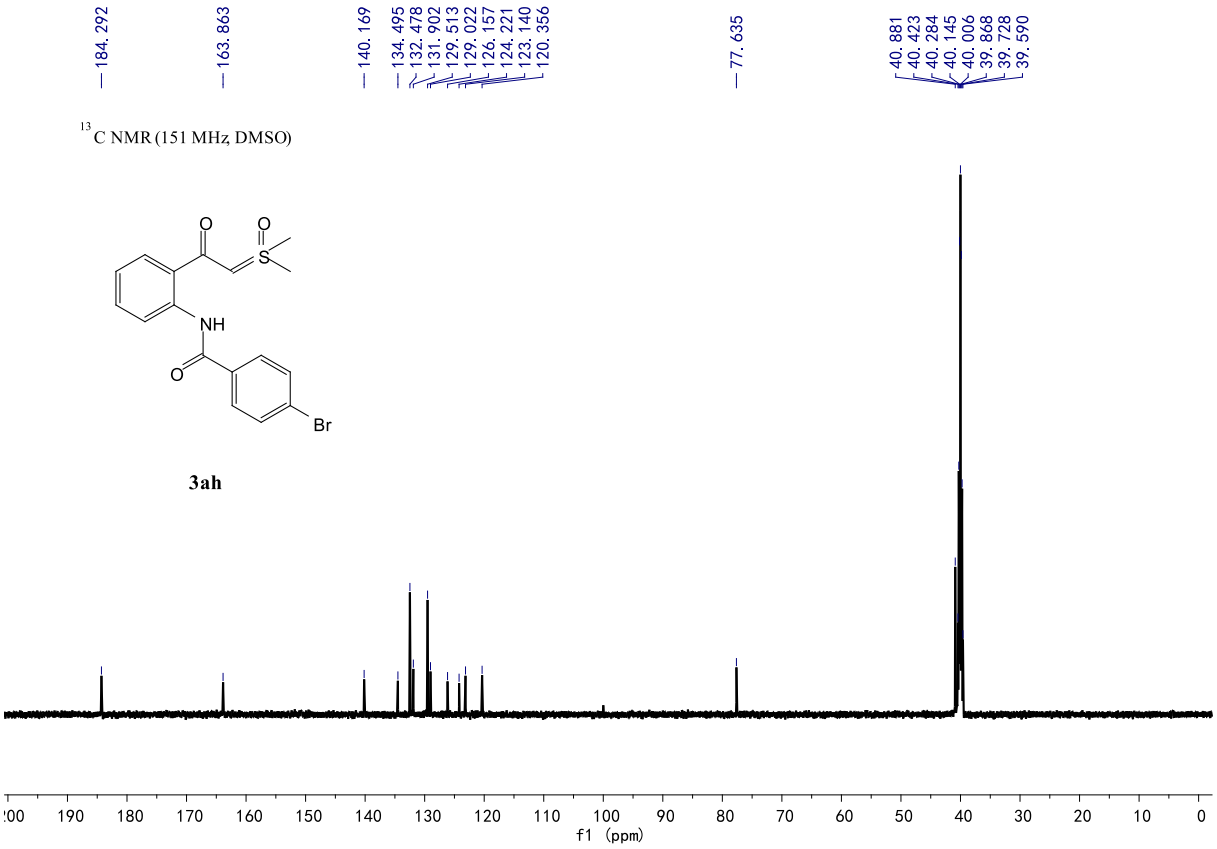

13.862
8.681
8.660
7.986
7.686
7.489
7.451
7.134
7.116
7.097
5.855
3.625
3.319
2.500
1H NMR (400 MHz, DMSO)
O
O
S
NH
O
Cl
3ag
1.00
1.00
2.01
1.00
2.00
1.00
1.00
1.00
6.00
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


184.289
163.727
140.190
137.200
134.106
131.931
129.557
129.349
129.045
124.180
123.147
120.336
77.674
40.821
40.385
40.248
40.110
39.971
39.833
39.694
39.556
13C NMR (151 MHz, DMSO)
O
O
S
NH
O
Cl
3ag
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



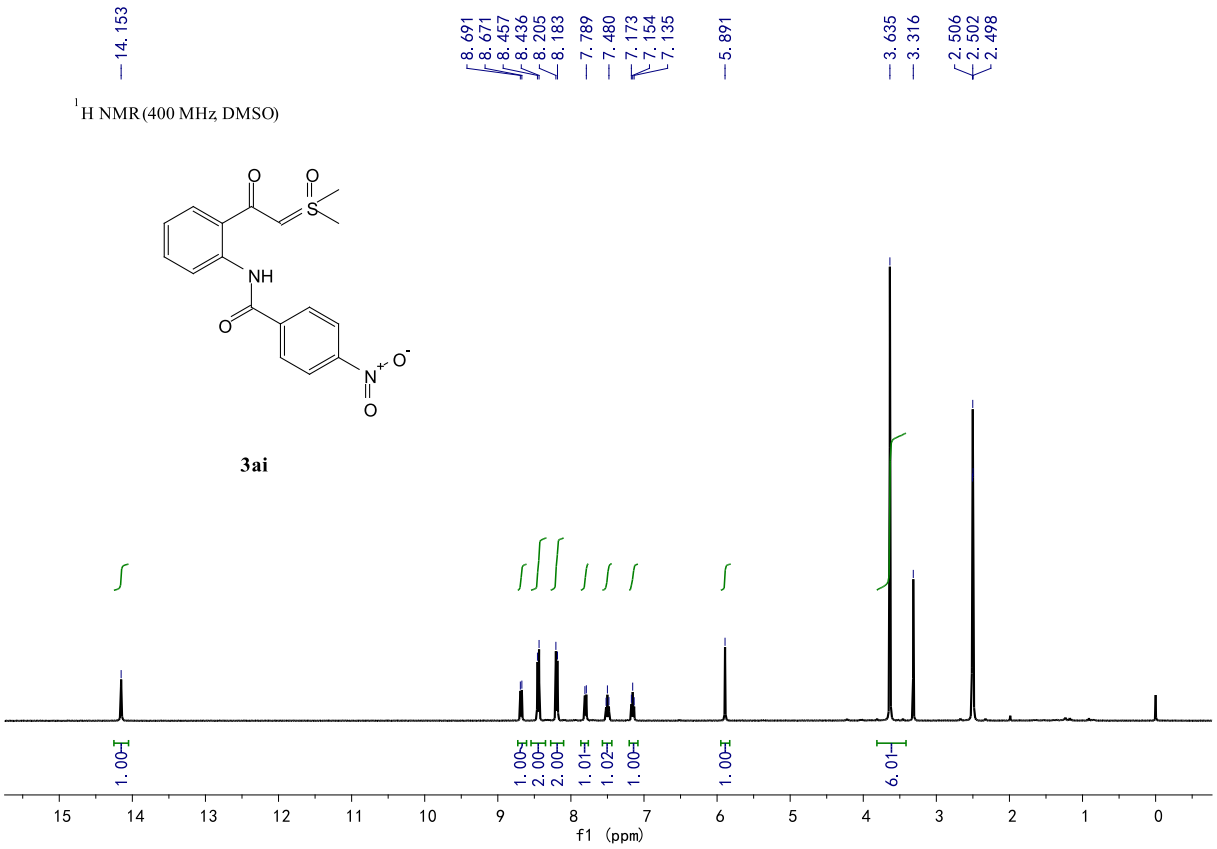
^{1}H NMR (400 MHz, DMSO)

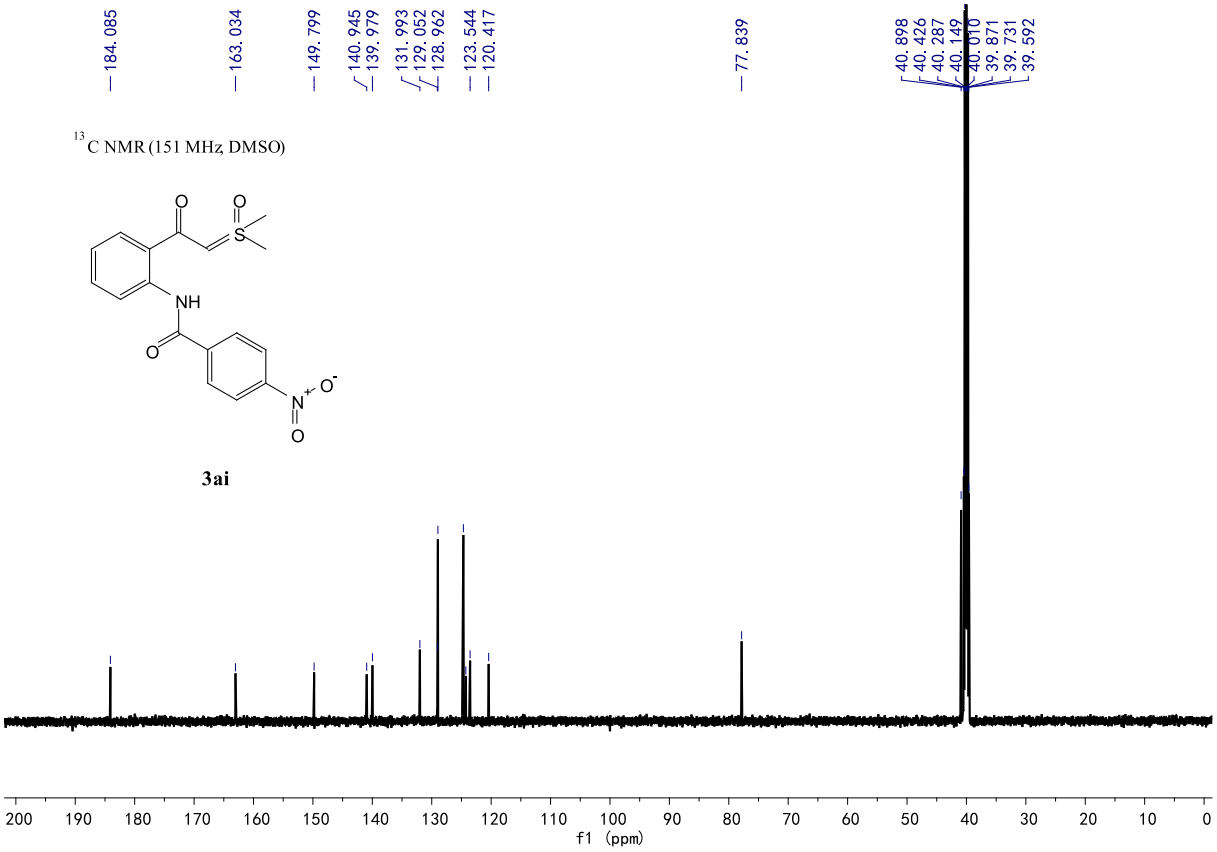
3ah

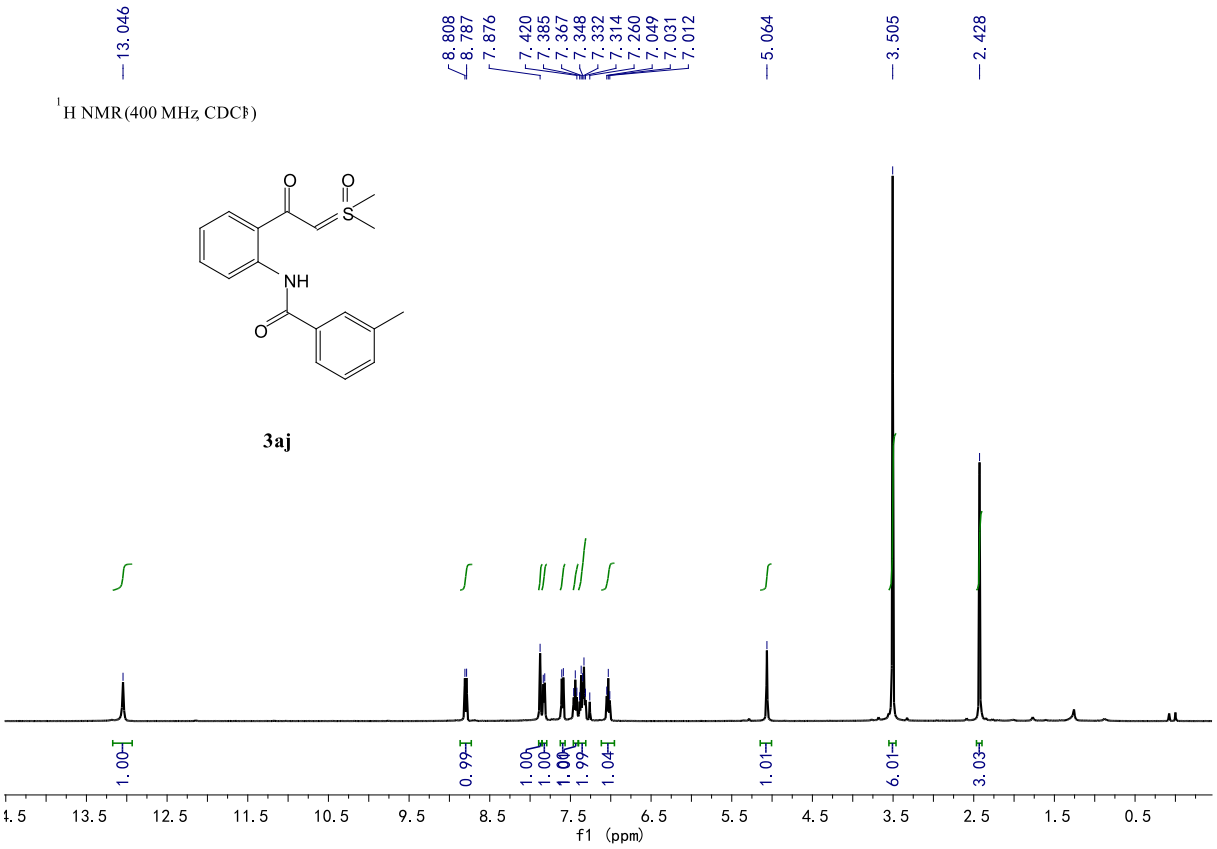


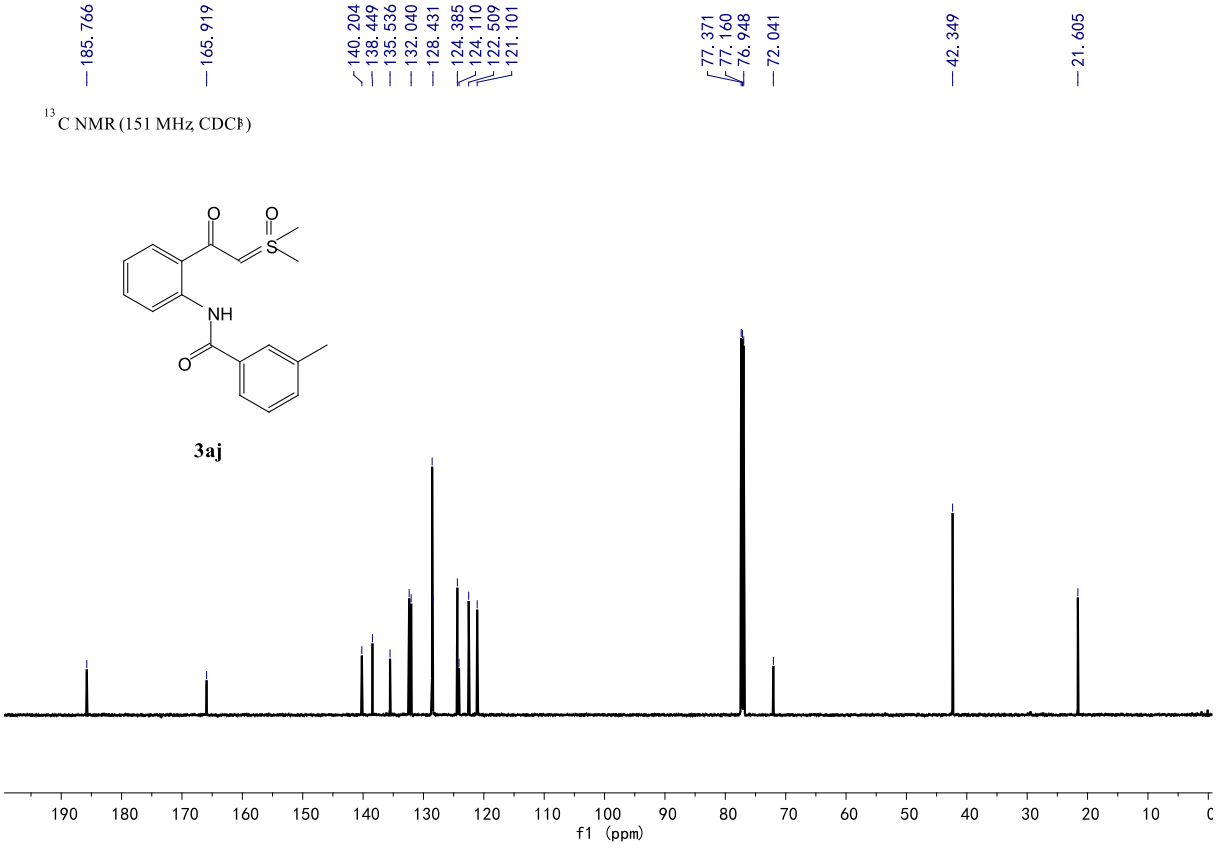
^{13}C NMR (151 MHz, DMSO)

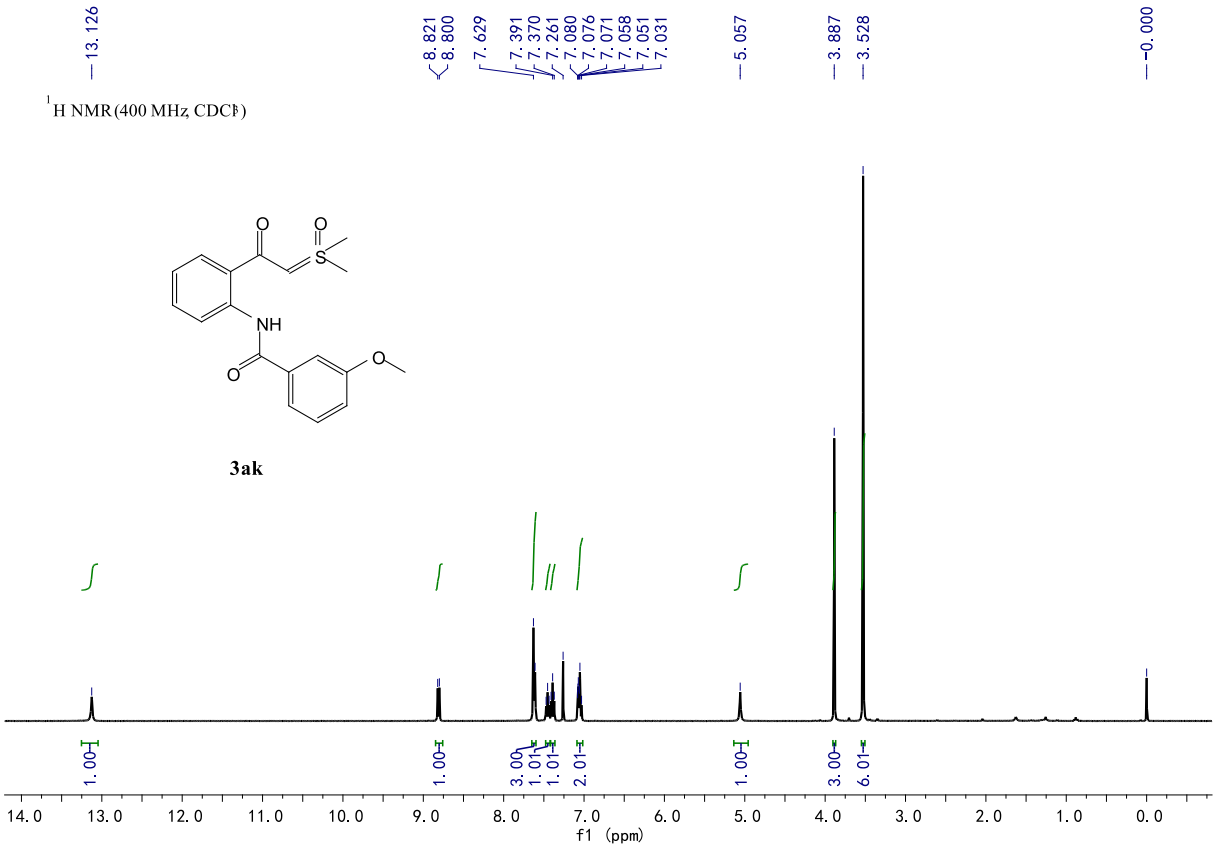
3ah

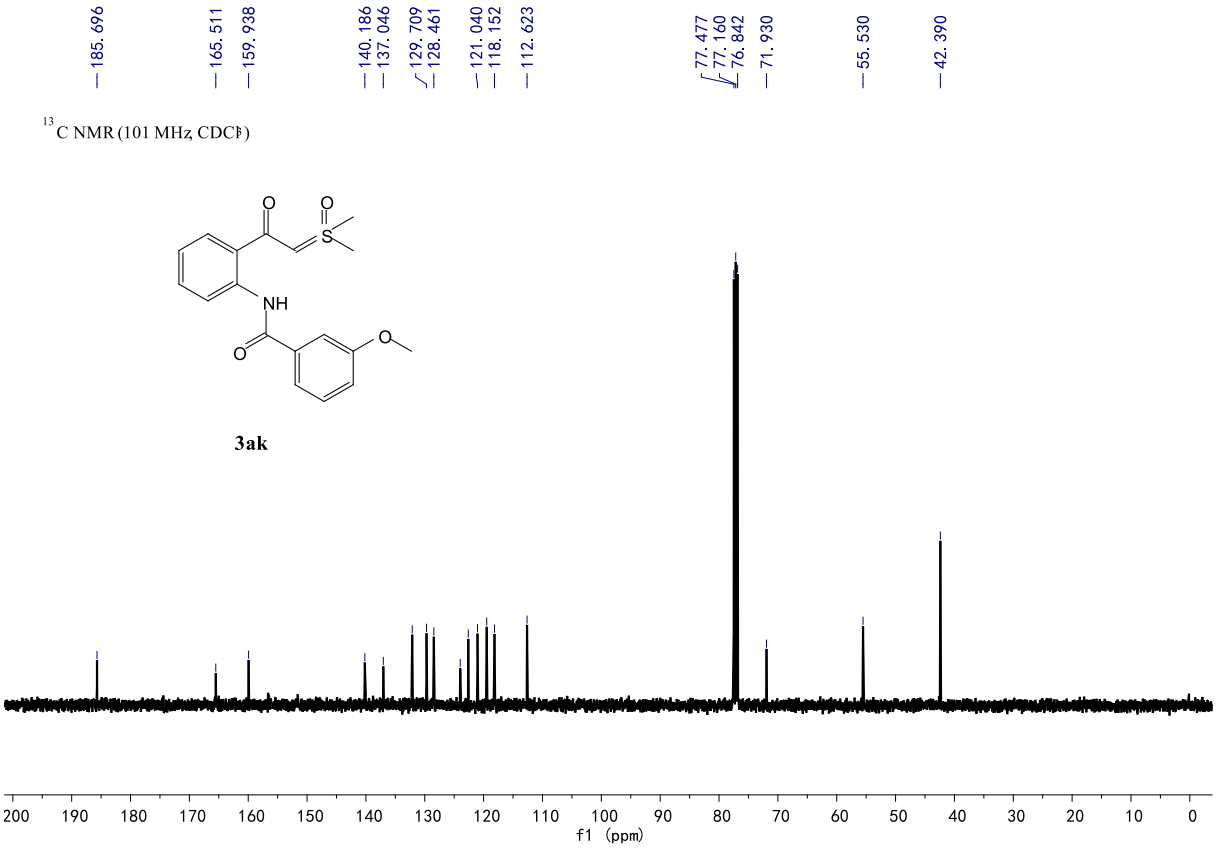

14.153
8.691
8.671
8.457
8.436
8.205
8.183
7.789
7.480
7.173
7.154
7.135
5.891
3.635
3.316
2.506
2.502
2.498
1H NMR (400 MHz, DMSO)
3ai
1.00
1.00
2.00
2.00
1.01
1.02
1.00
1.00
6.01
f1 (ppm)

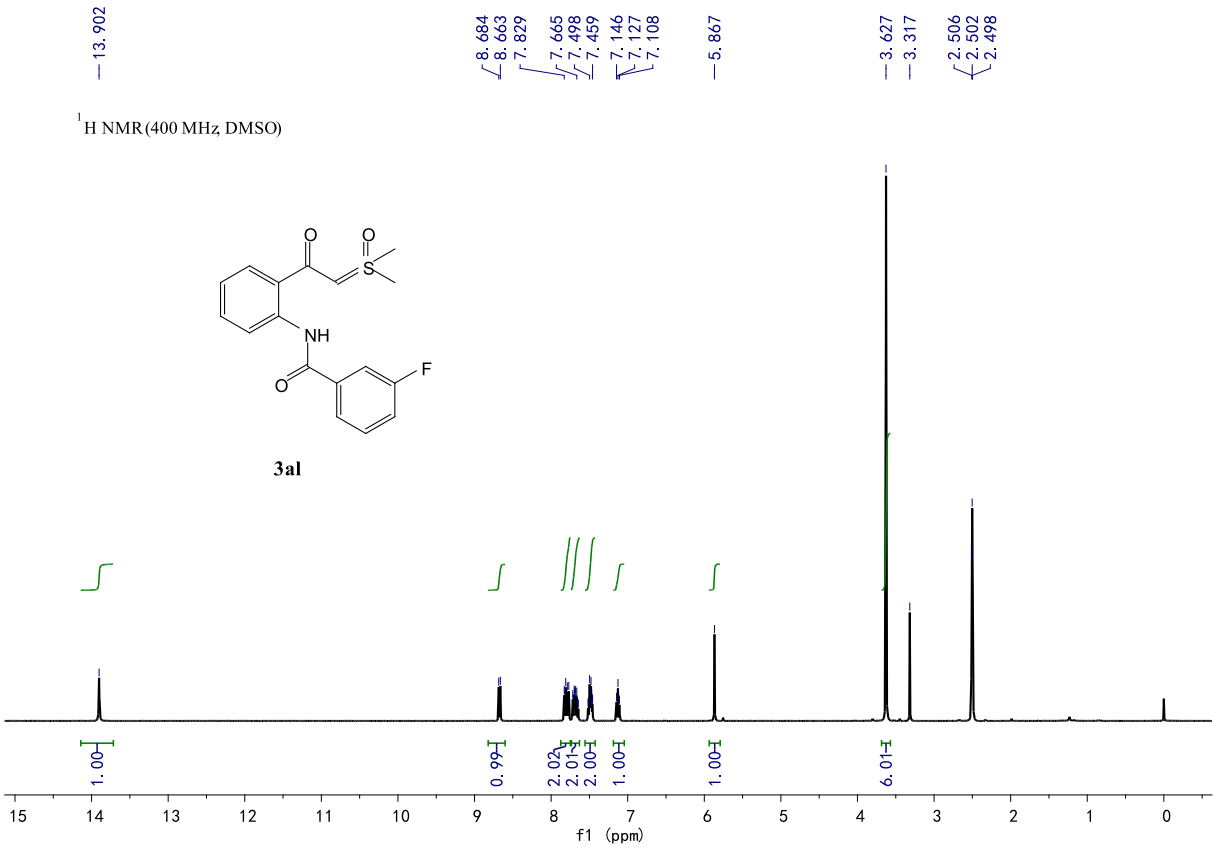

184.085
163.034
149.799
140.945
139.979
131.993
129.052
128.962
123.544
120.417
77.839
40.898
40.426
40.287
40.149
40.010
39.871
39.731
39.592
13C NMR (151 MHz, DMSO)
3ai
f1 (ppm)

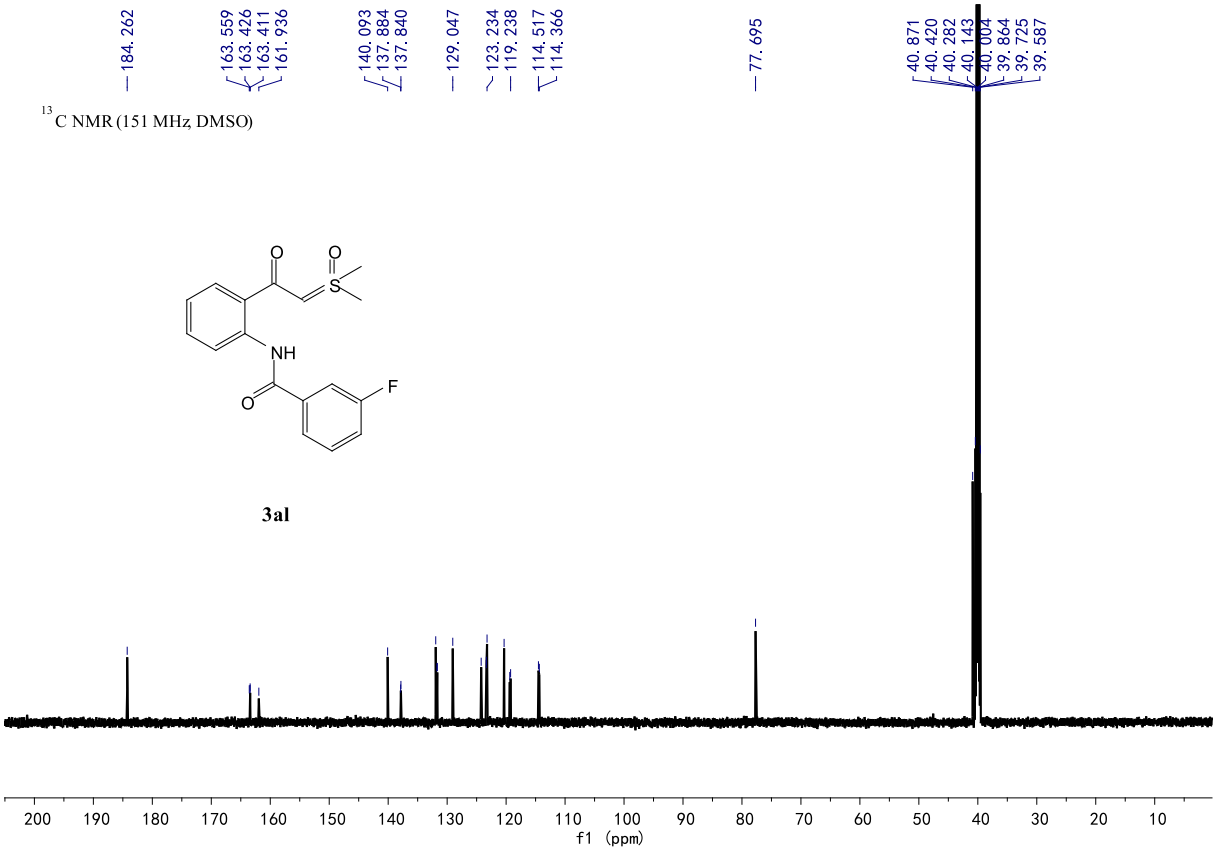

13.046
8.808
8.787
7.876
7.420
7.385
7.367
7.348
7.332
7.314
7.260
7.049
7.031
7.012
5.064
3.505
2.428
1H NMR (400 MHz, CDCl3)
O
O
S
NH
O
3aj
1.00
0.99
1.00
1.00
1.00
1.99
1.04
1.01
6.01
3.03
4.5
13.5
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


185.766
165.919
140.204
138.449
135.536
132.040
128.431
124.385
124.110
122.509
121.101
77.371
77.160
76.948
72.041
42.349
21.605
13C NMR (151 MHz, CDCl3)
O
O
S
NH
O
3aj
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

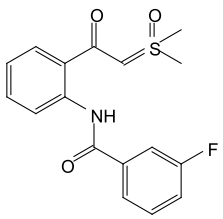

13.126
8.821
8.800
7.629
7.391
7.370
7.261
7.080
7.076
7.071
7.058
7.051
7.031
5.057
3.887
3.528
0.000
1H NMR (400 MHz, CDCl3)
NH
O
O
O
O
S
O
3ak
1.00
1.00
3.00
1.01
1.01
2.01
1.00
3.00
6.01
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


185.696
165.511
159.938
140.186
137.046
129.709
128.461
121.040
118.152
112.623
77.477
77.160
76.842
71.930
55.530
42.390
13C NMR (101 MHz, CDCl3)
NH
O
O
O
O
S
O
3ak
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


13.902
8.684
8.663
7.829
7.665
7.498
7.459
7.146
7.127
7.108
5.867
3.627
3.317
2.506
2.502
2.498
1H NMR (400 MHz, DMSO)
O
O
S
NH
O
F
3al
1.00
0.99
2.02
2.01
2.00
1.00
1.00
6.01
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

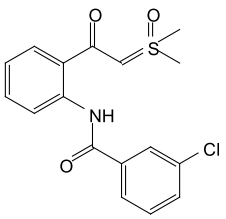

184.262
163.559
163.426
163.411
161.936
140.093
137.884
137.840
129.047
123.234
119.238
114.517
114.366
77.695
40.871
40.420
40.282
40.143
40.004
39.864
39.725
39.587
13C NMR (151 MHz, DMSO)
O
O
S
NH
O
F
3al
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

^{19}F NMR (565 MHz, DMSO)

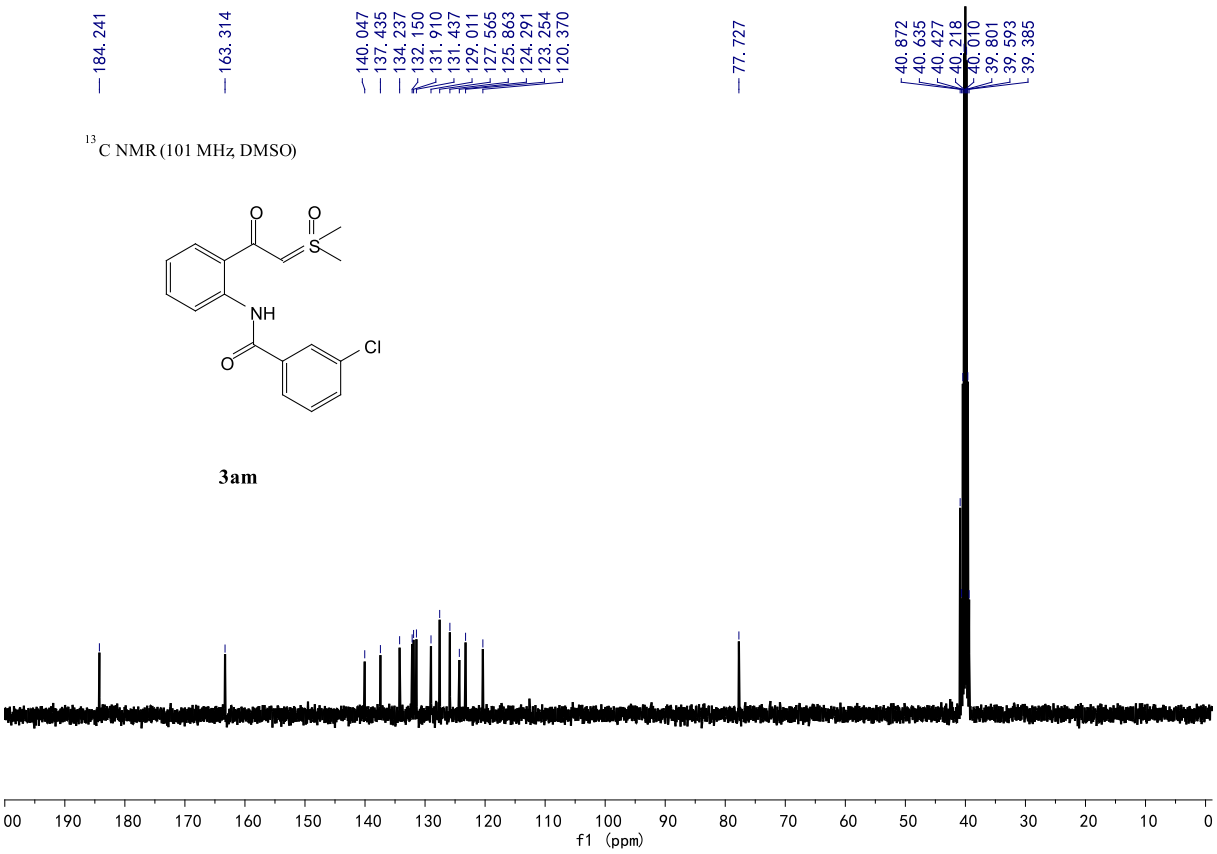


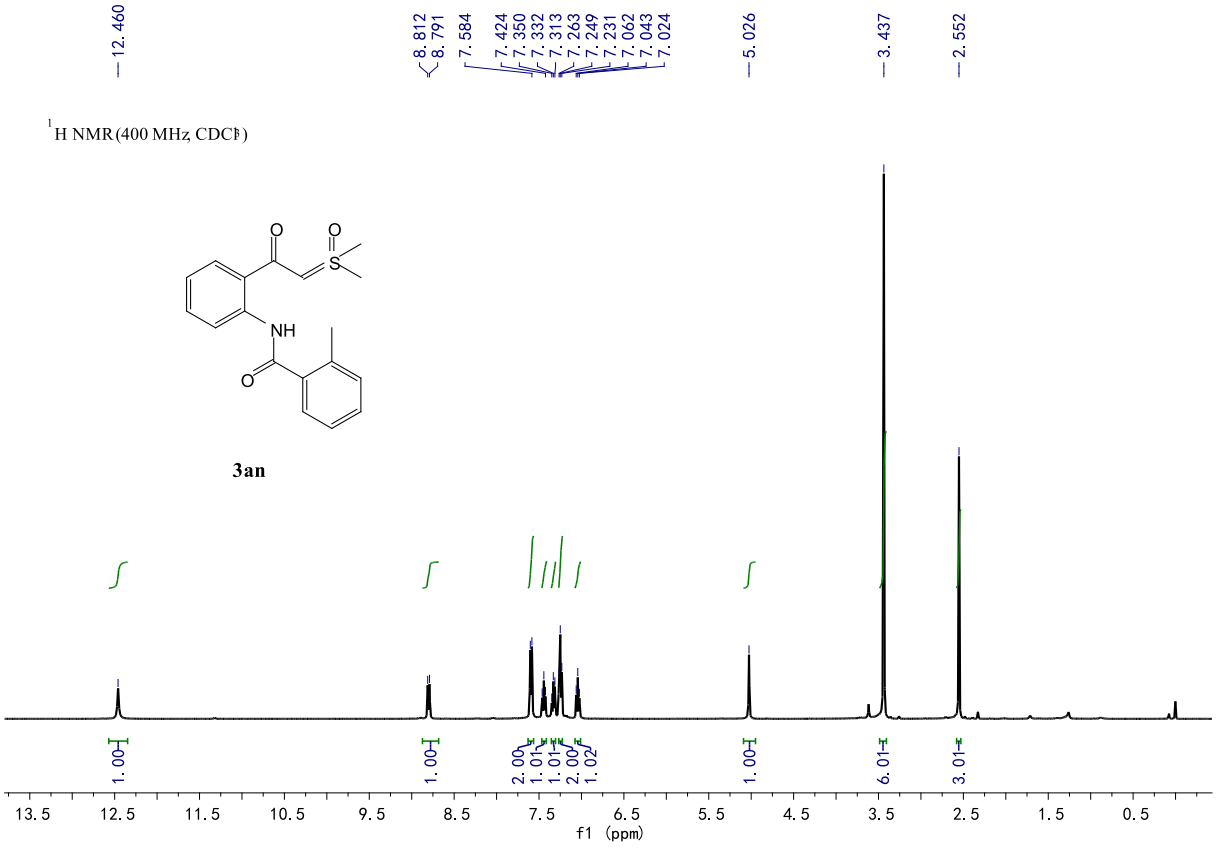
3al

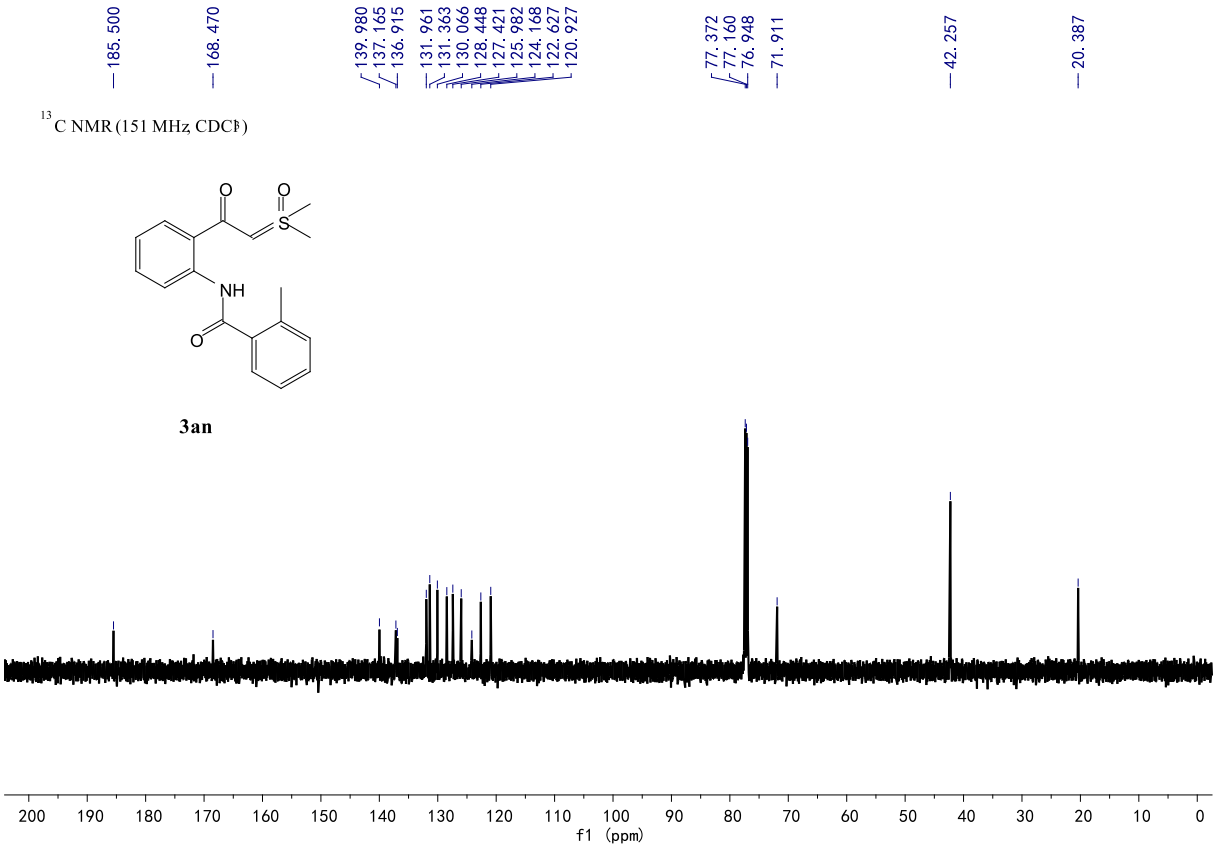
^{1}H NMR (400 MHz, DMSO)

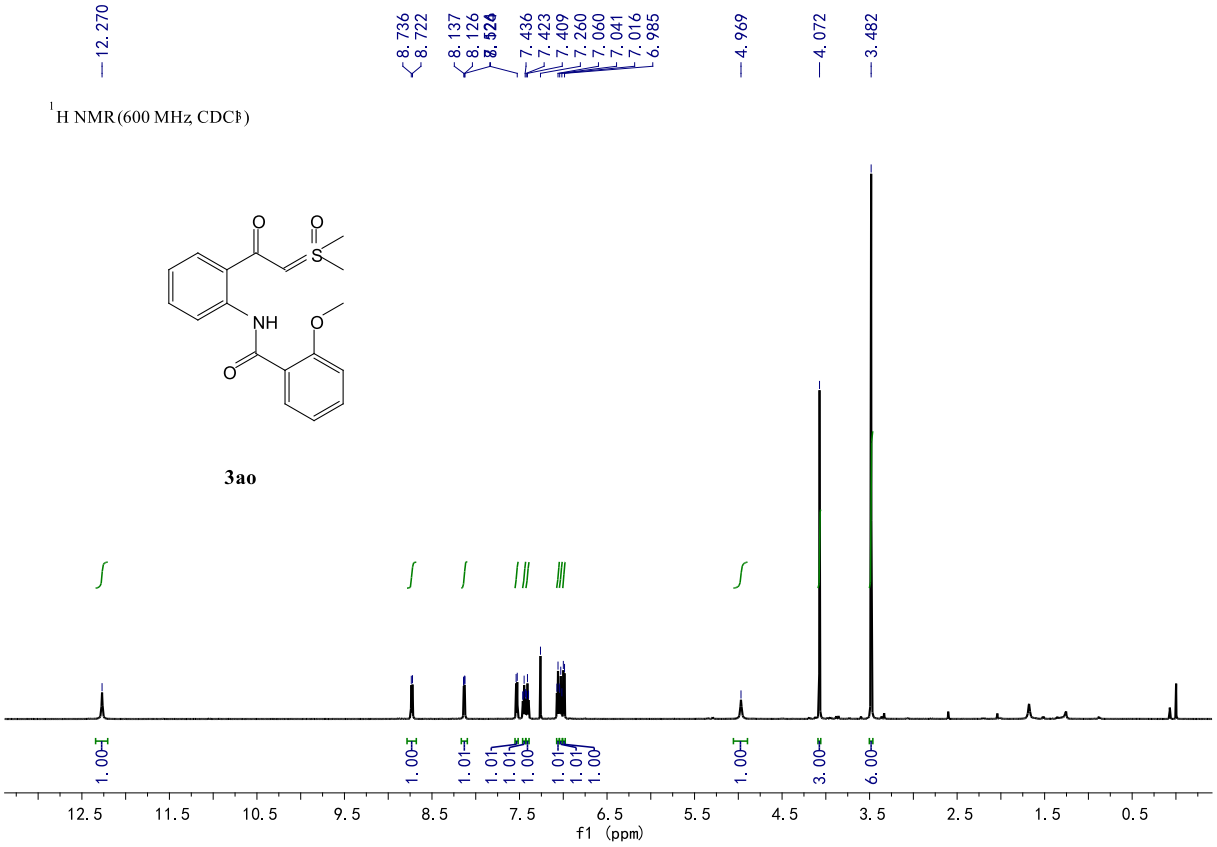


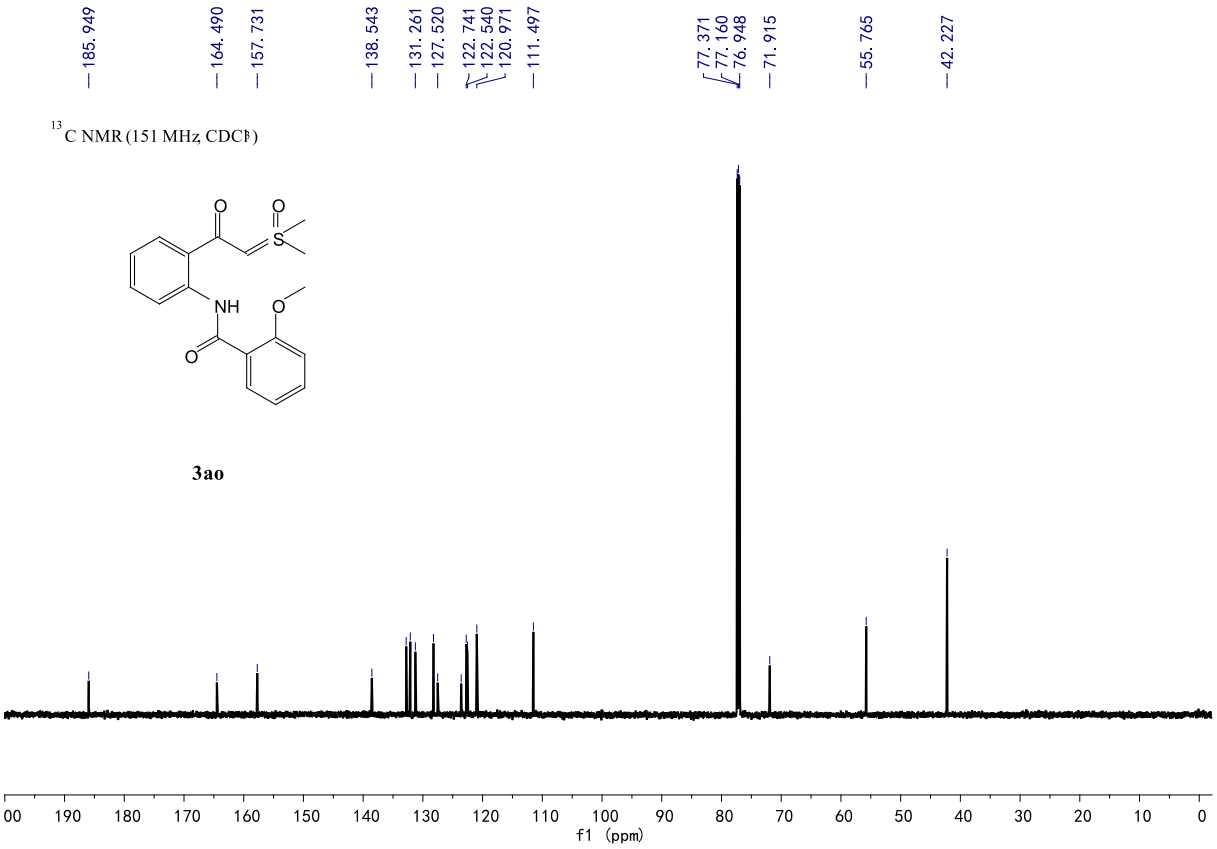
3am


184.241
163.314
140.047
137.435
134.237
132.150
131.910
131.437
129.011
127.565
125.863
124.291
123.254
120.370
77.727
40.872
40.635
40.427
40.218
40.010
39.801
39.593
39.385
13C NMR (101 MHz, DMSO)
O
O
S
NH
O
Cl
3am
f1 (ppm)

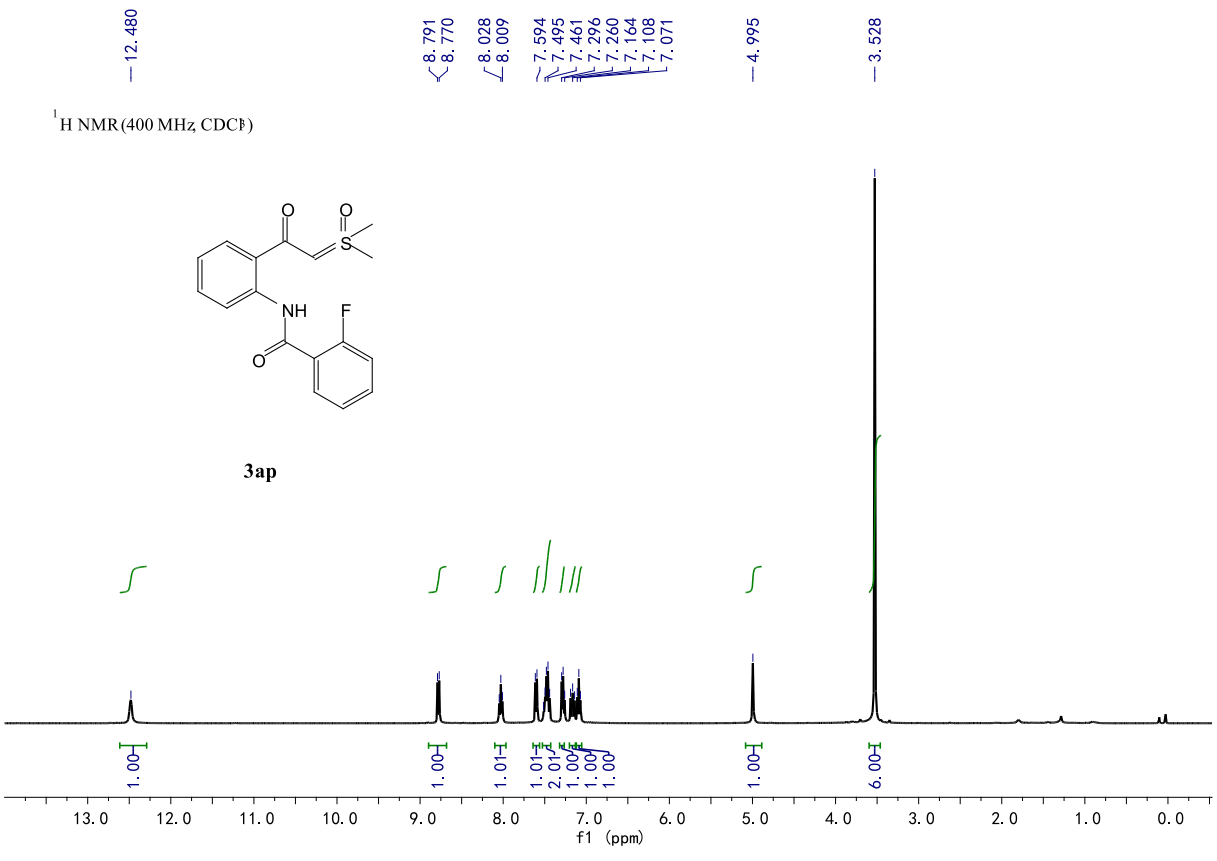

12.460
8.812
8.791
7.584
7.424
7.350
7.332
7.313
7.263
7.249
7.231
7.062
7.043
7.024
5.026
3.437
2.552
1H NMR (400 MHz, CDCl3)
O
O
S
NH
O
3an
1.00
1.00
2.00
1.01
1.01
2.00
1.02
1.00
6.01
3.01
f1 (ppm)


185.500
168.470
139.980
137.165
136.915
131.961
131.363
130.066
128.448
127.421
125.982
124.168
122.627
120.927
77.372
77.160
76.948
71.911
42.257
20.387
13C NMR (151 MHz, CDCl3)
O
O
S
NH
O
3an
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

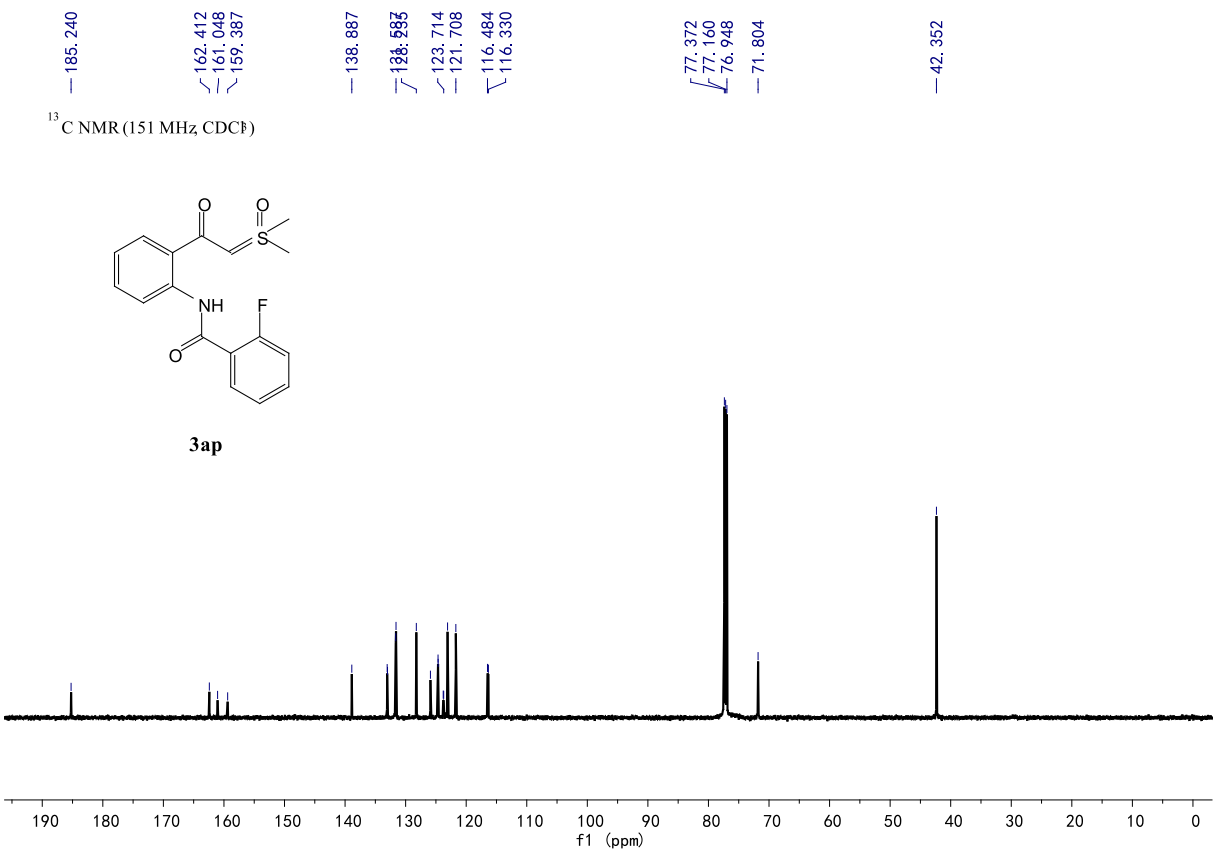

12.270
8.736
8.722
8.137
8.126
7.436
7.423
7.409
7.260
7.060
7.041
7.016
6.985
4.969
4.072
3.482
1H NMR (600 MHz, CDCl3)
O
O
S
NH
O
O
3ao
1.00
1.00
1.01
1.01
1.01
1.00
1.01
1.01
1.00
1.00
3.00
6.00
12.5 11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5
f1 (ppm)

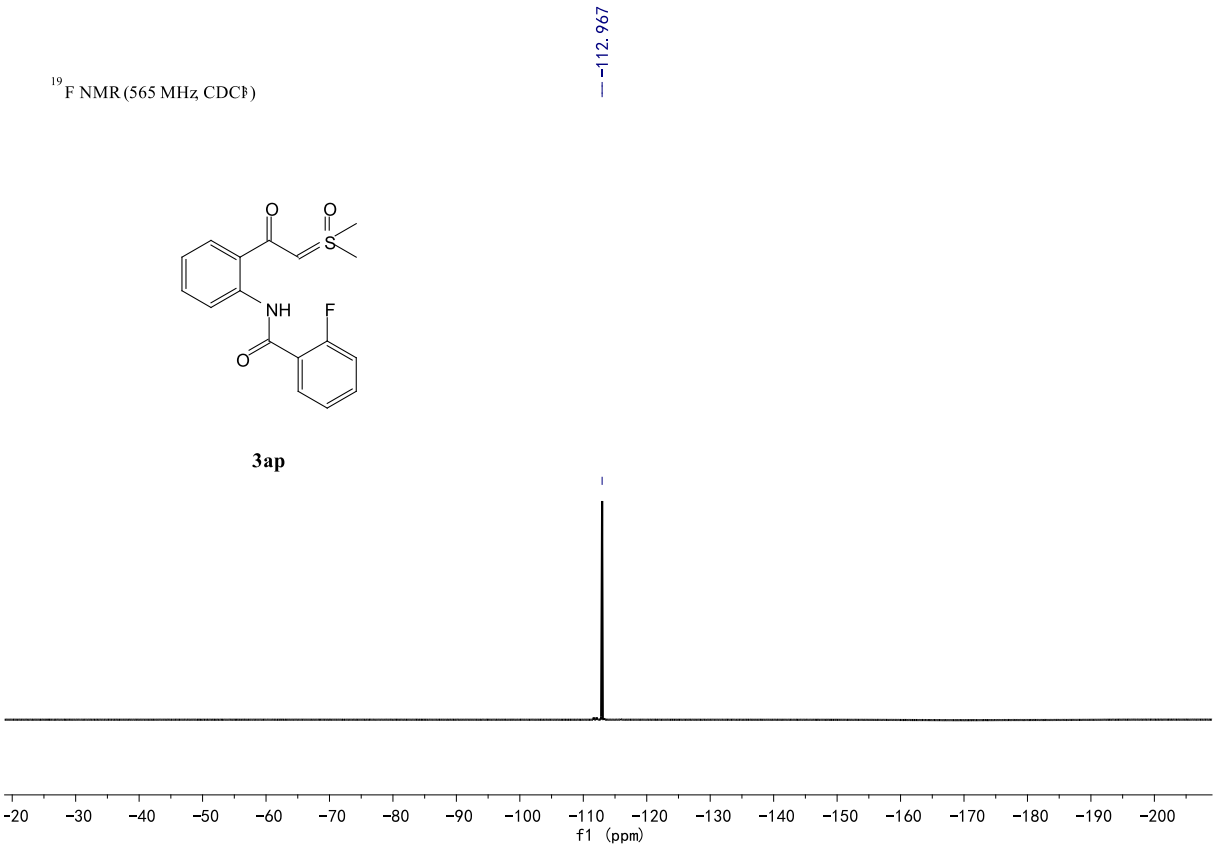

185.949
164.490
157.731
138.543
131.261
127.520
122.741
122.540
120.971
111.497
77.371
77.160
76.948
71.915
55.765
42.227
13C NMR (151 MHz, CDCl3)
NH
O
f1 (ppm)

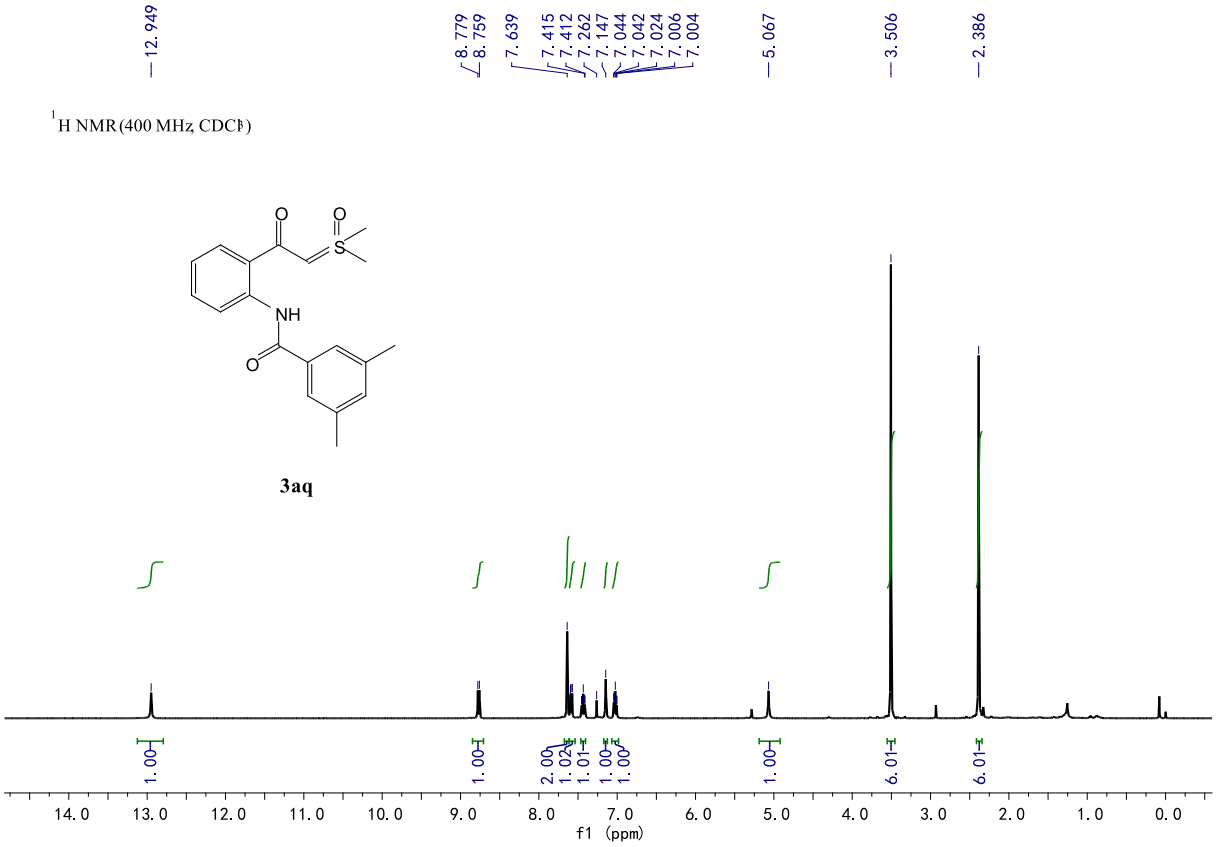
3ao


12.480
8.791
8.770
8.028
8.009
7.594
7.495
7.461
7.296
7.260
7.164
7.108
7.071
4.995
3.528
1H NMR (400 MHz, CDCl3)
NH
F
O
f1 (ppm)

3ap

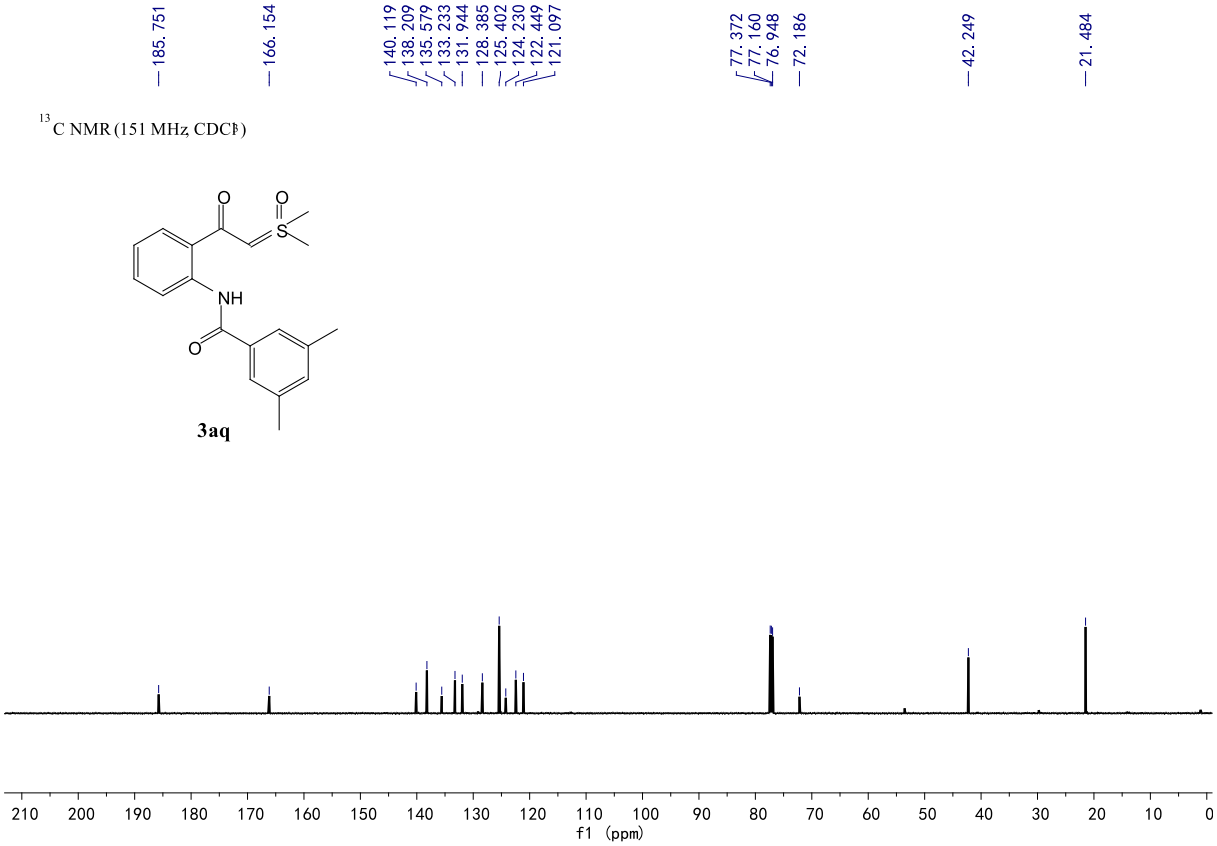

185.240
162.412
161.048
159.387
138.887
123.714
121.708
116.484
116.330
77.372
77.160
76.948
71.804
42.352
13C NMR (151 MHz, CDCl3)
O
O
S
NH
F
O
3ap
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-112.967
19F NMR (565 MHz, CDCl3)
O
O
S
NH
F
O
3ap
-20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)



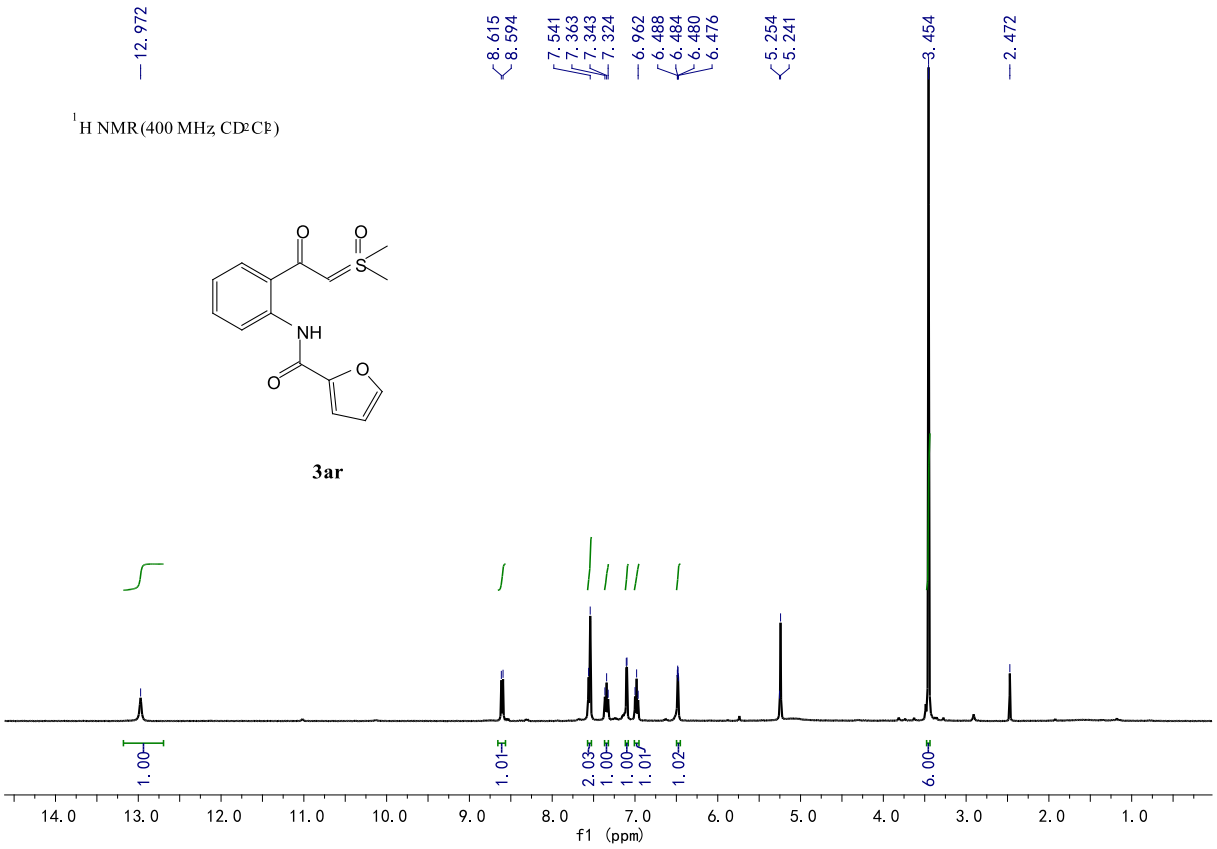
^{1}H NMR (400 MHz, CDCl$_3$)

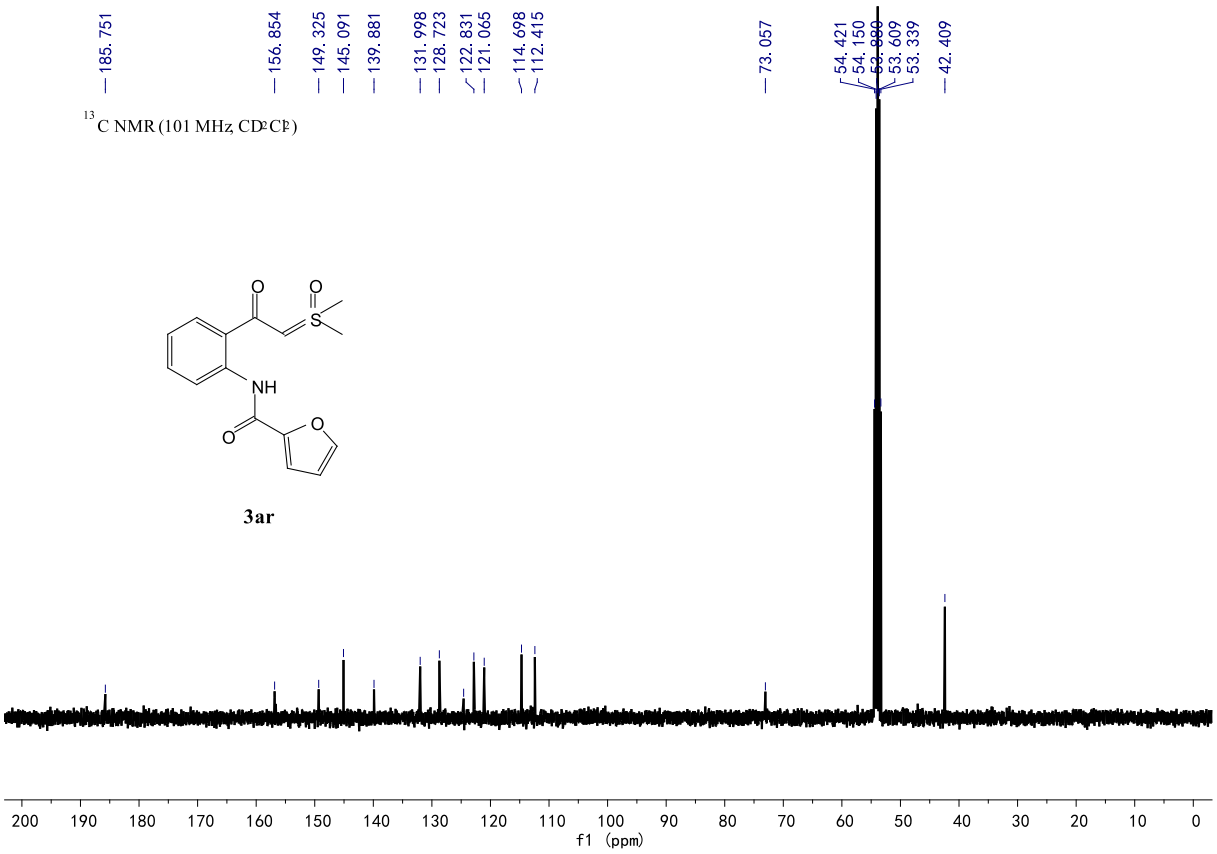
3aq

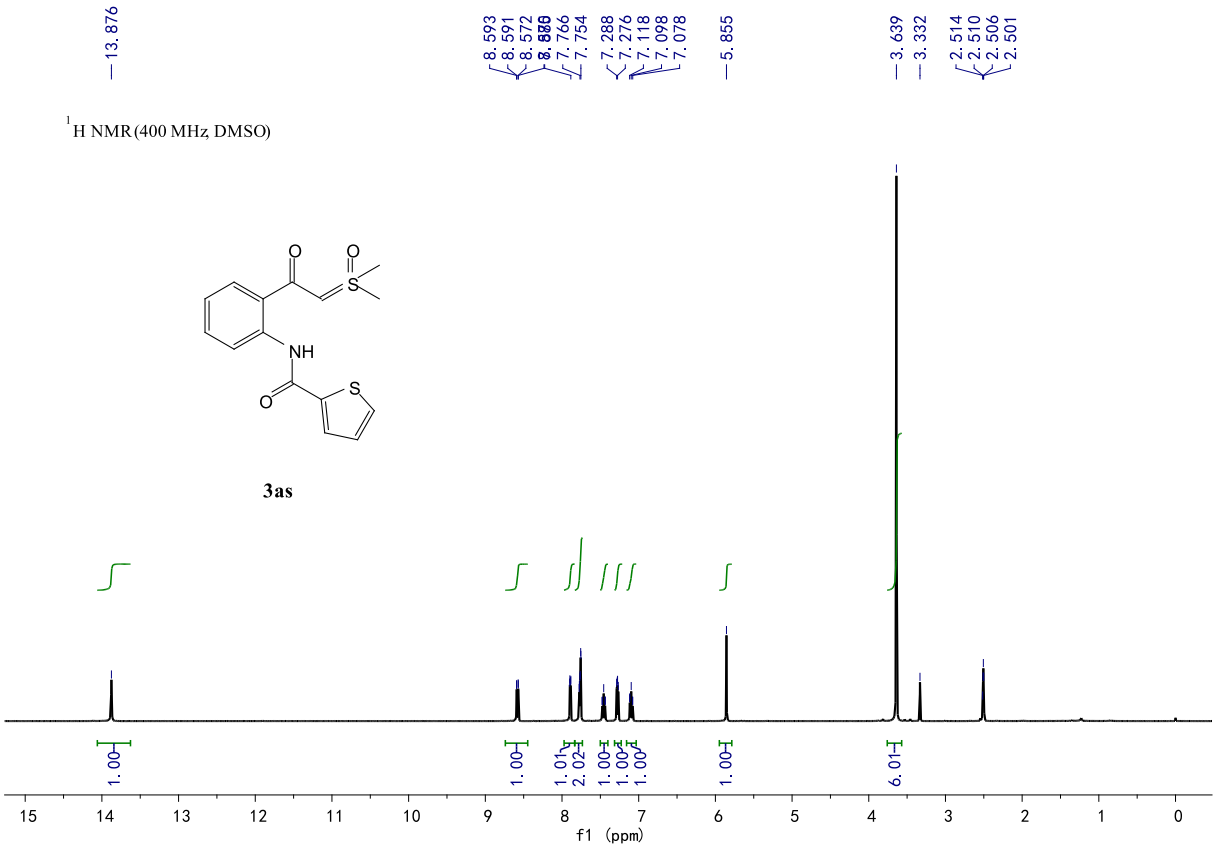


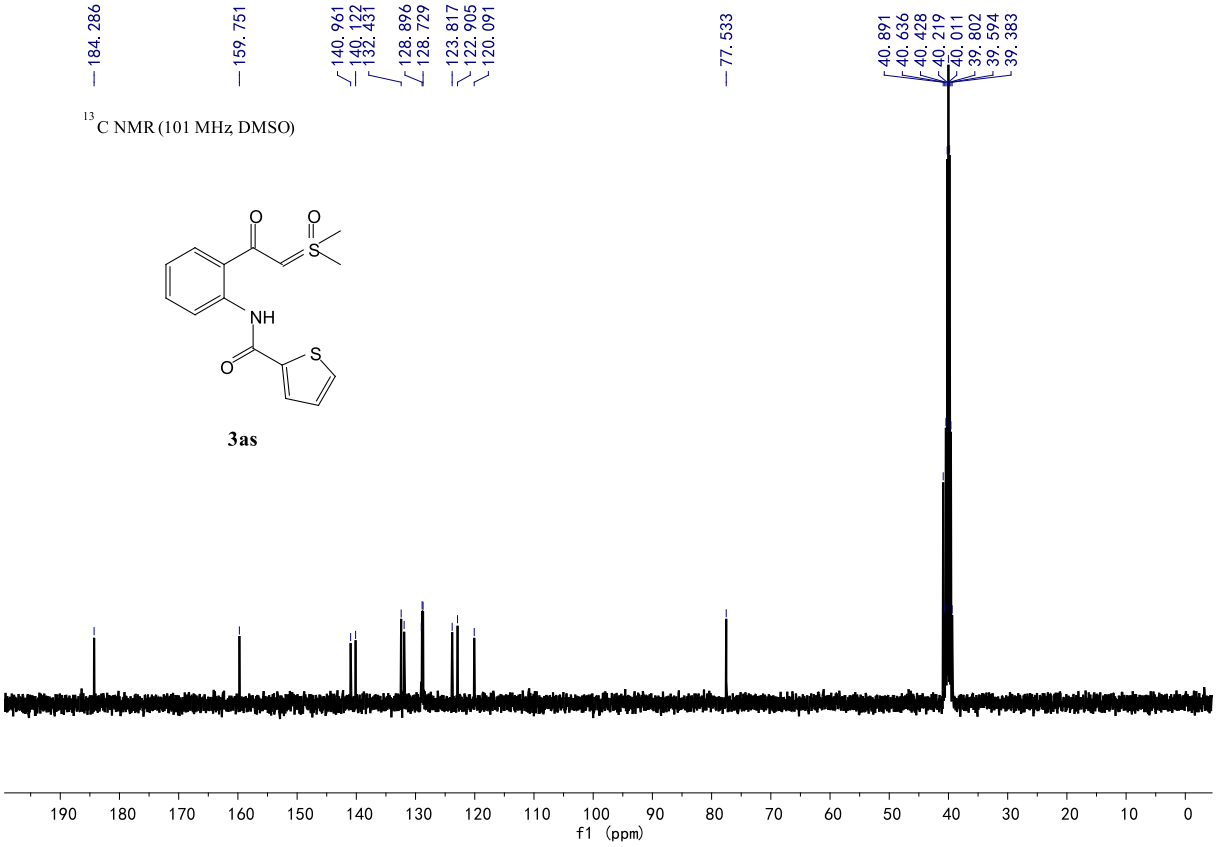
^{13}C NMR (151 MHz, CDCl$_3$)

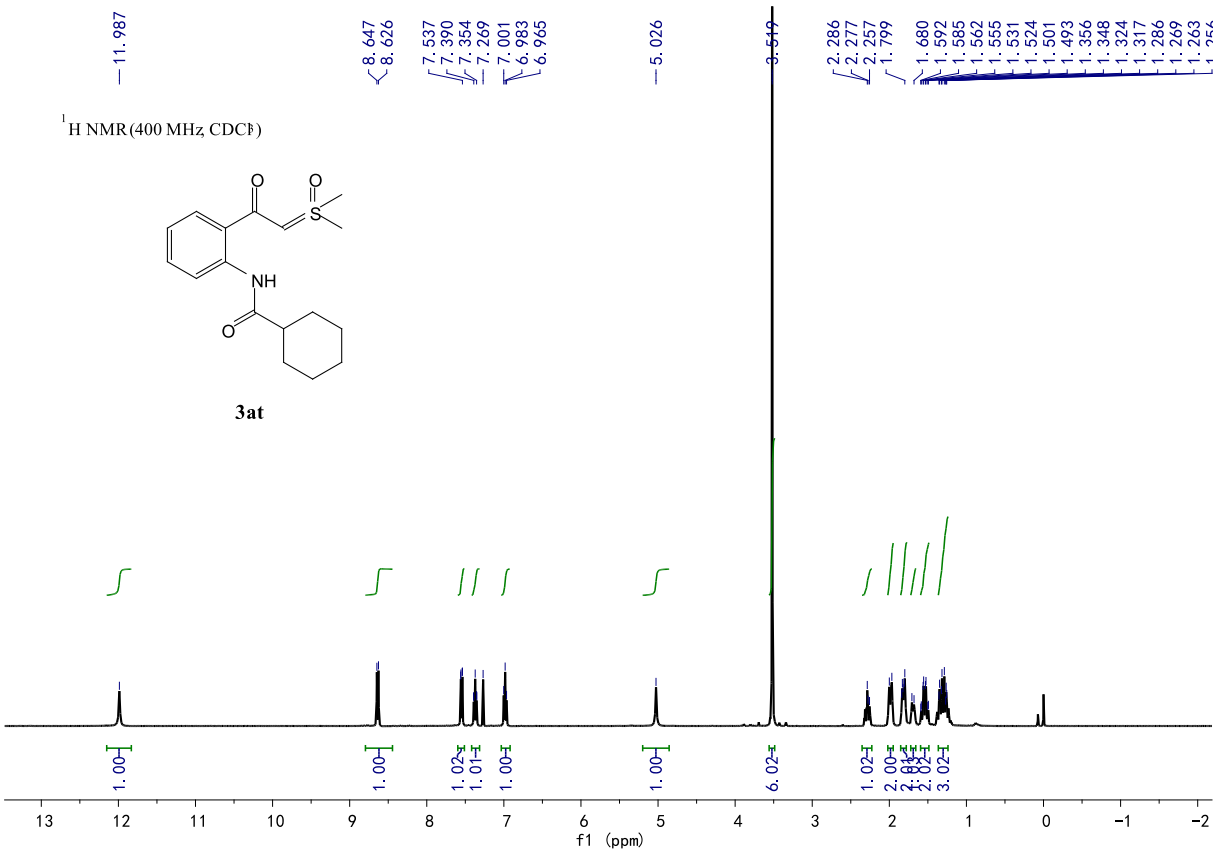
3aq


12.972
8.615
8.594
7.541
7.363
7.343
7.324
6.962
6.488
6.484
6.480
6.476
5.254
5.241
3.454
2.472
1H NMR (400 MHz, CD2Cl2)
NH
3ar
1.00
1.01
2.03
1.00
1.00
1.01
1.02
6.00
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
f1 (ppm)


185.751
156.854
149.325
145.091
139.881
131.998
128.723
122.831
121.065
114.698
112.415
73.057
54.421
54.150
53.880
53.609
53.339
42.409
13C NMR (101 MHz, CD2Cl2)
NH
3ar
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

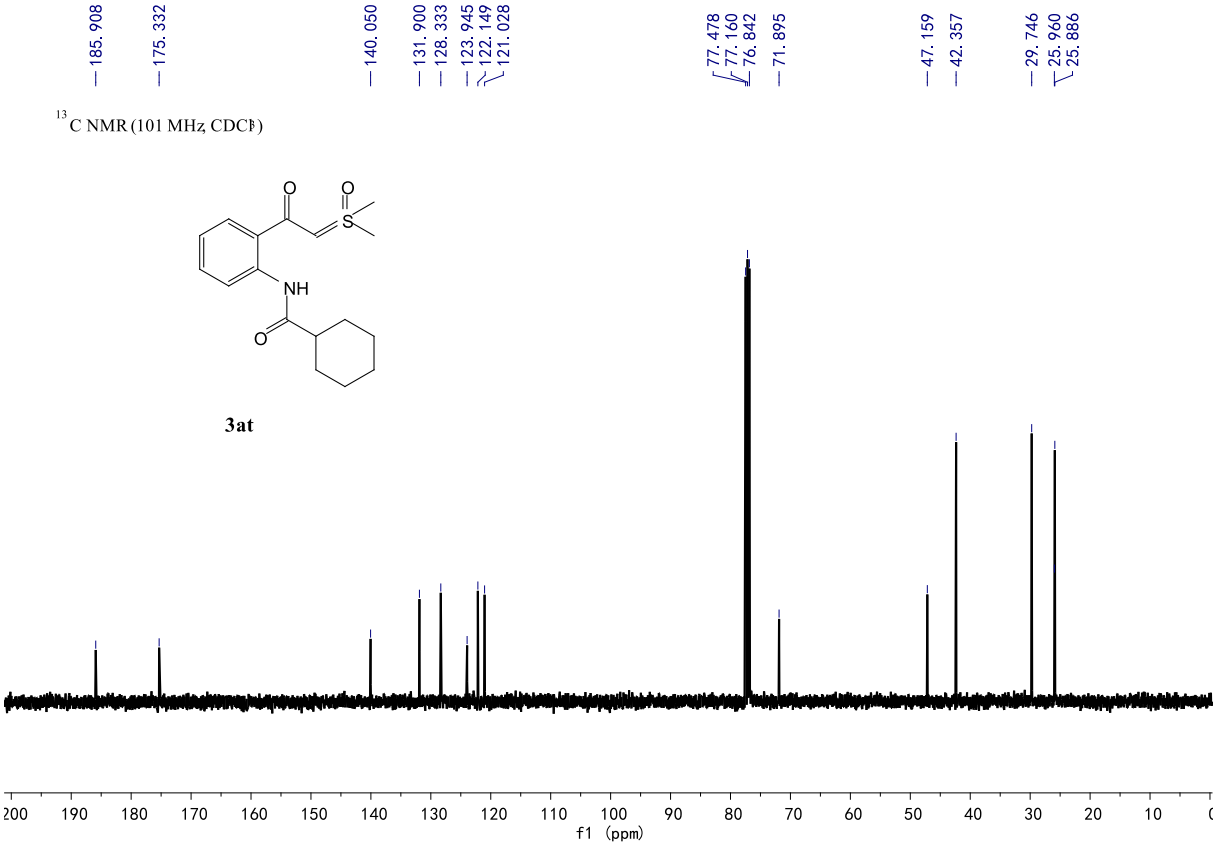

13.876
8.593
8.591
8.572
7.766
7.754
7.288
7.276
7.118
7.098
7.078
5.855
3.639
3.332
2.514
2.510
2.506
2.501
1H NMR (400 MHz, DMSO)
3as
1.00
1.00
1.01
2.02
1.00
1.00
1.00
1.00
6.01
f1 (ppm)


184.286
159.751
140.961
140.122
132.431
128.896
128.729
123.817
122.905
120.091
77.533
40.891
40.636
40.428
40.219
40.011
39.802
39.594
39.383
13C NMR (101 MHz, DMSO)
3as
f1 (ppm)



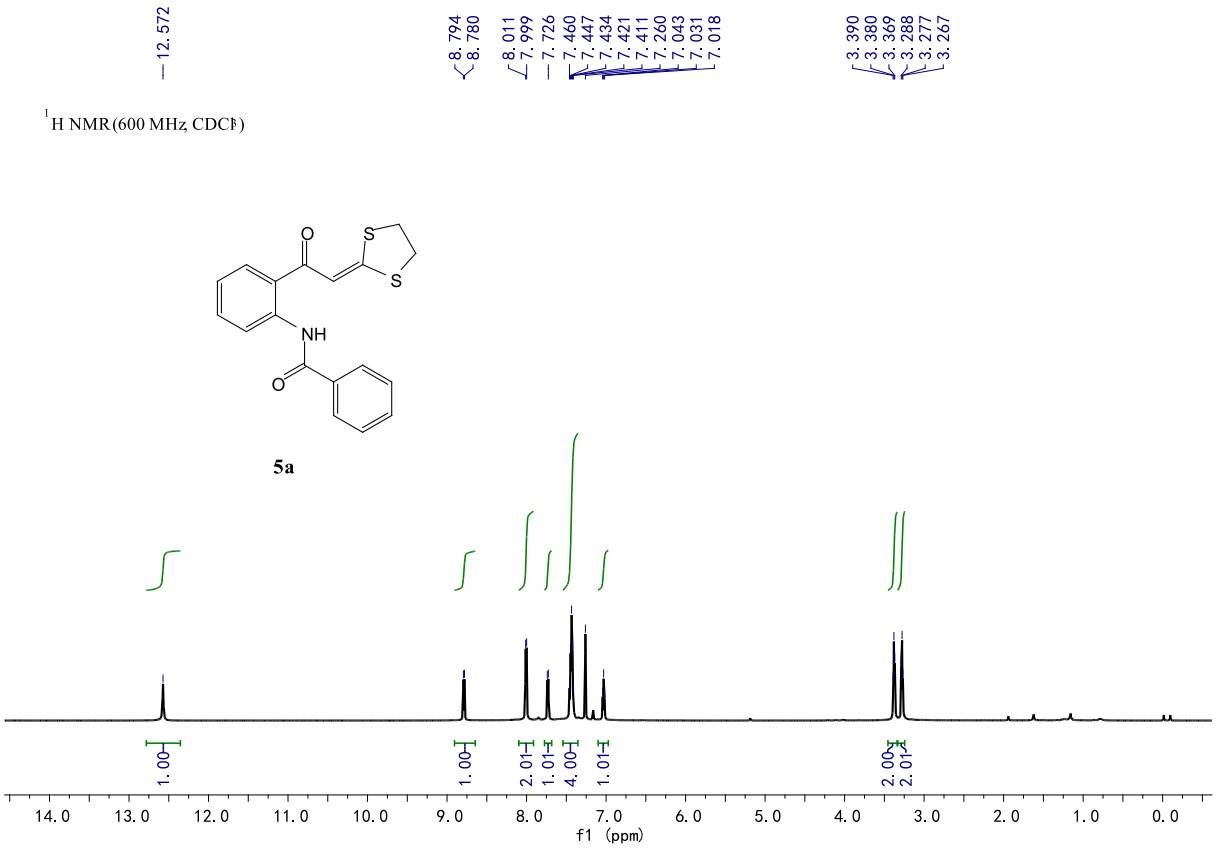
^{1}H NMR (400 MHz, CDCl$_3$)

3at

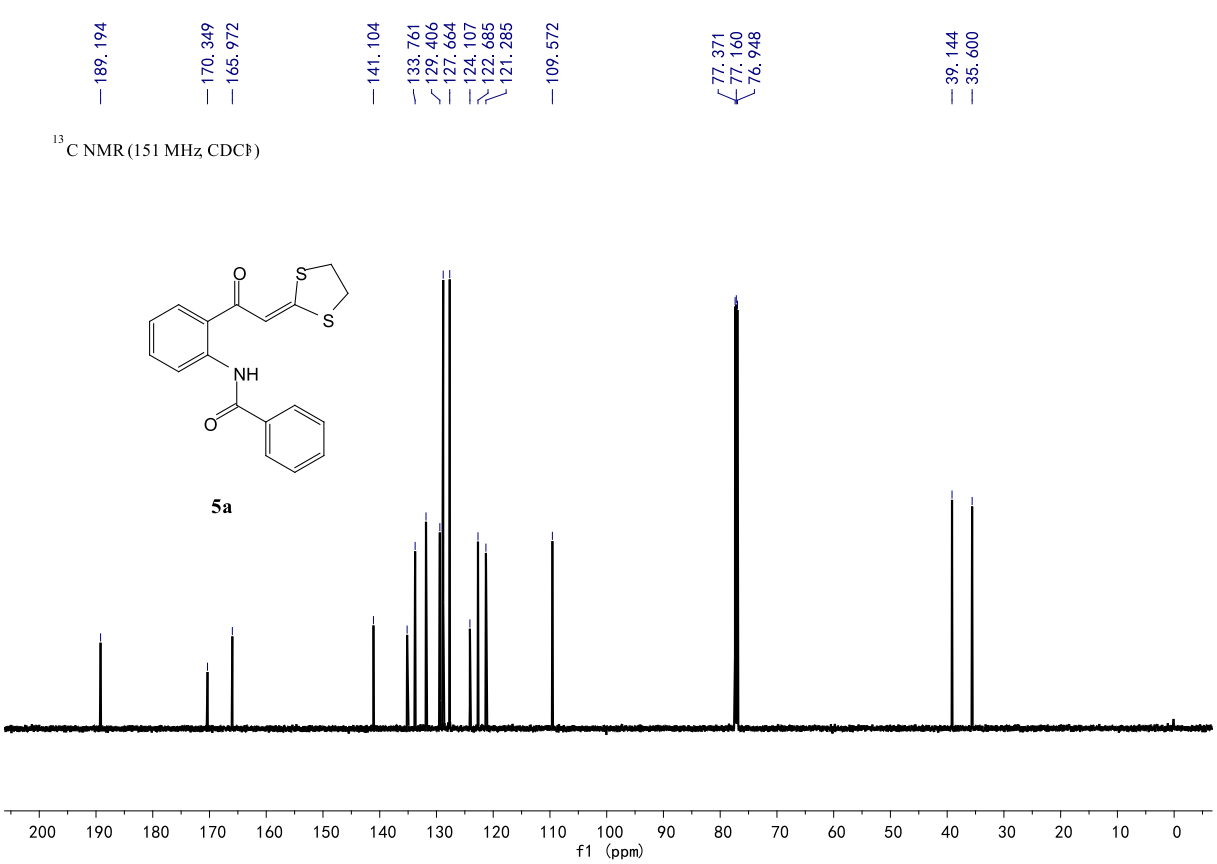


^{13}C NMR (101 MHz, CDCl$_3$)

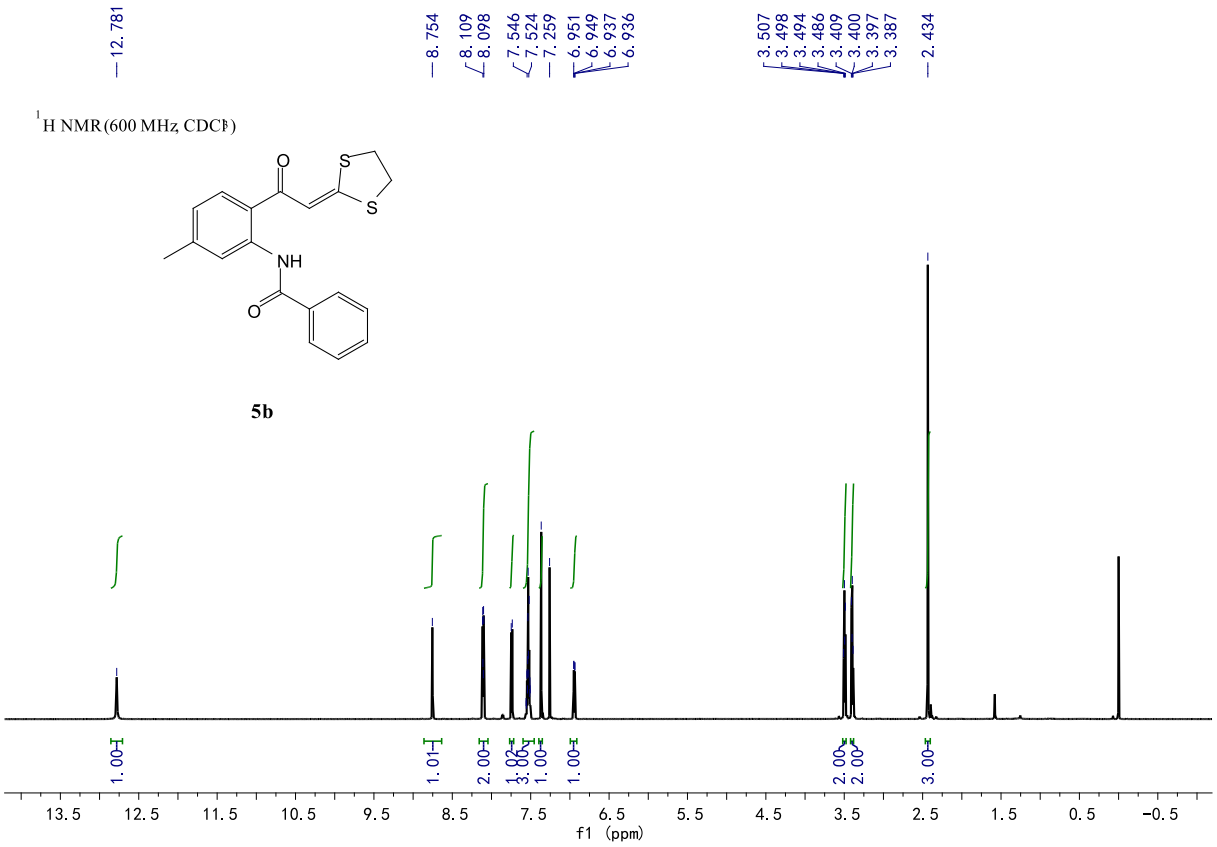
3at

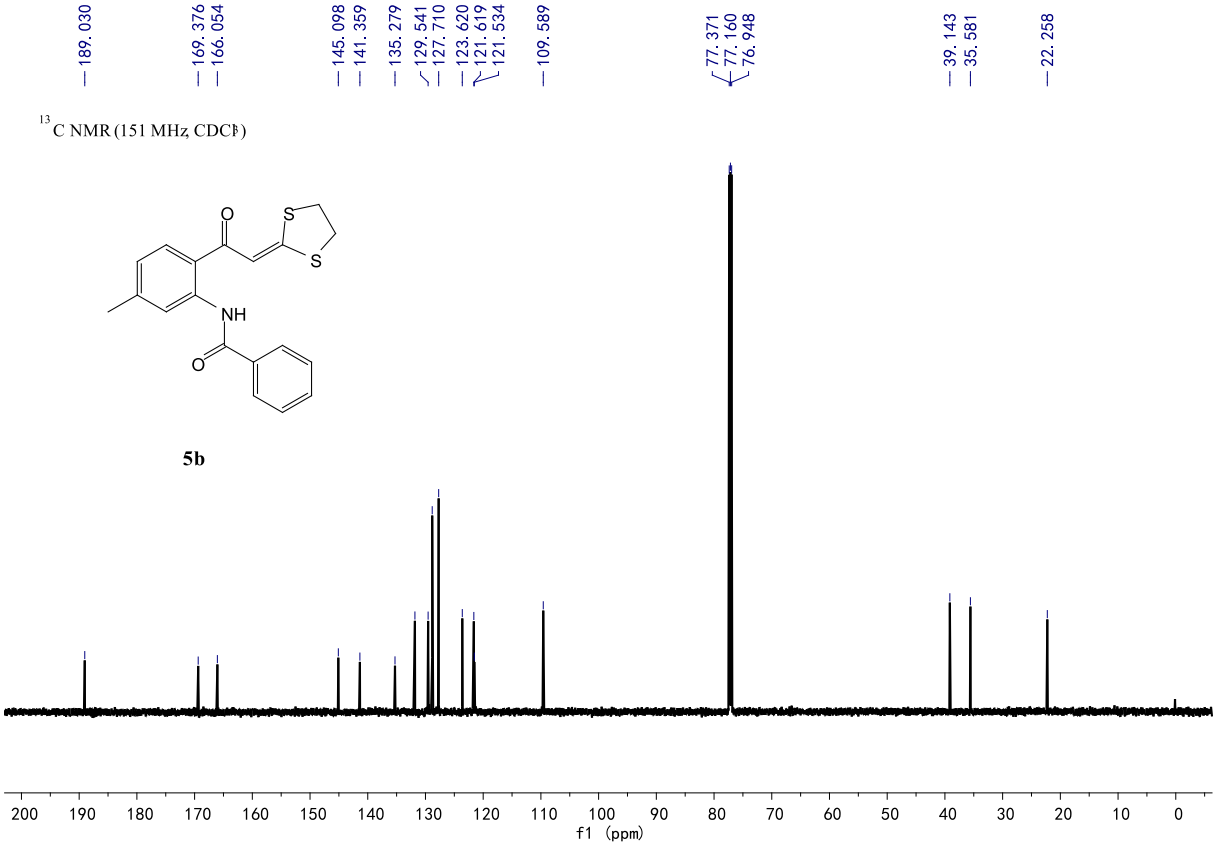


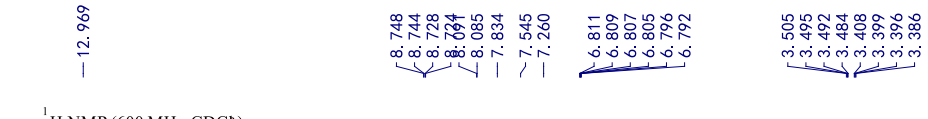
^{1}H NMR (600 MHz, CDCl$_3$)



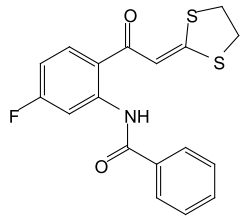
^{13}C NMR (151 MHz, CDCl$_3$)


12.781
8.754
8.109
8.098
7.546
7.524
7.259
6.951
6.949
6.937
6.936
3.507
3.498
3.494
3.486
3.409
3.400
3.397
3.387
2.434
1H NMR (600 MHz, CDCl3)
O
S
S
NH
O
5b
1.00
1.01
2.00
1.02
3.00
1.00
1.00
2.00
2.00
3.00
13.5
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
−0.5
f1 (ppm)

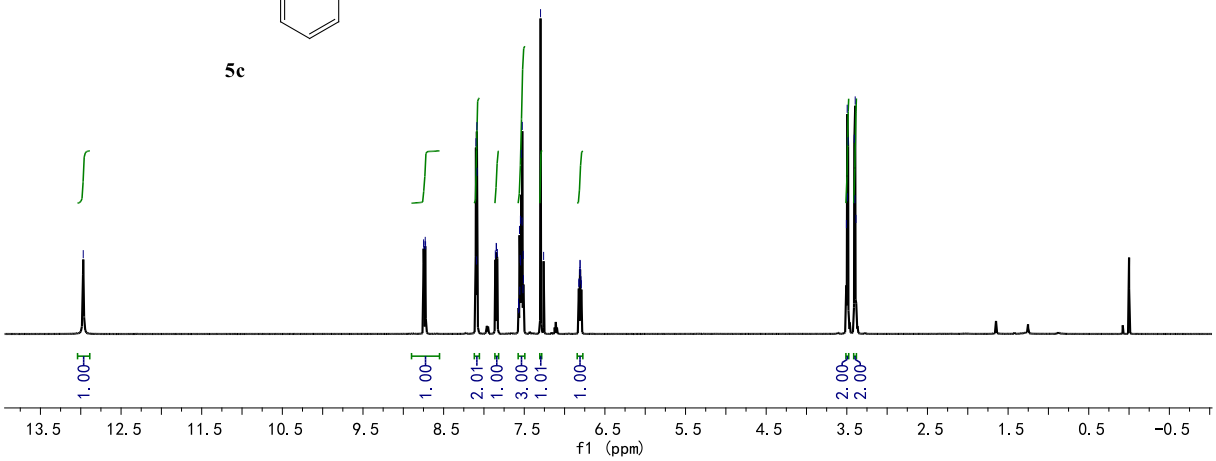

189.030
169.376
166.054
145.098
141.359
135.279
129.541
127.710
123.620
121.619
121.534
109.589
77.371
77.160
76.948
39.143
35.581
22.258
13C NMR (151 MHz, CDCl3)
O
S
S
NH
O
5b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

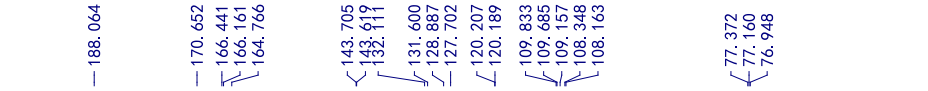


^{1}H NMR (600 MHz, CDCl$_3$)

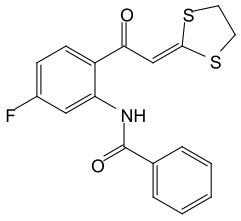


5c

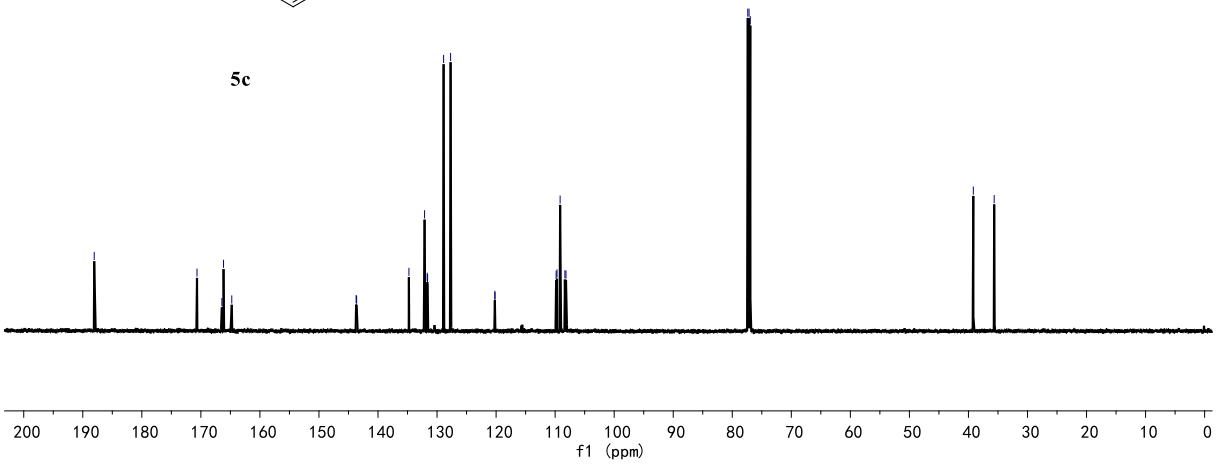




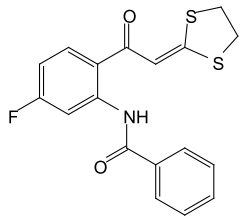
^{13}C NMR (151 MHz, CDCl$_3$)



5c

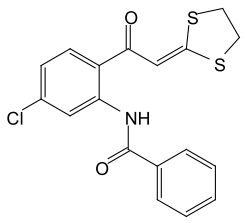


^{19}F NMR (565 MHz, CDCl$_3$)

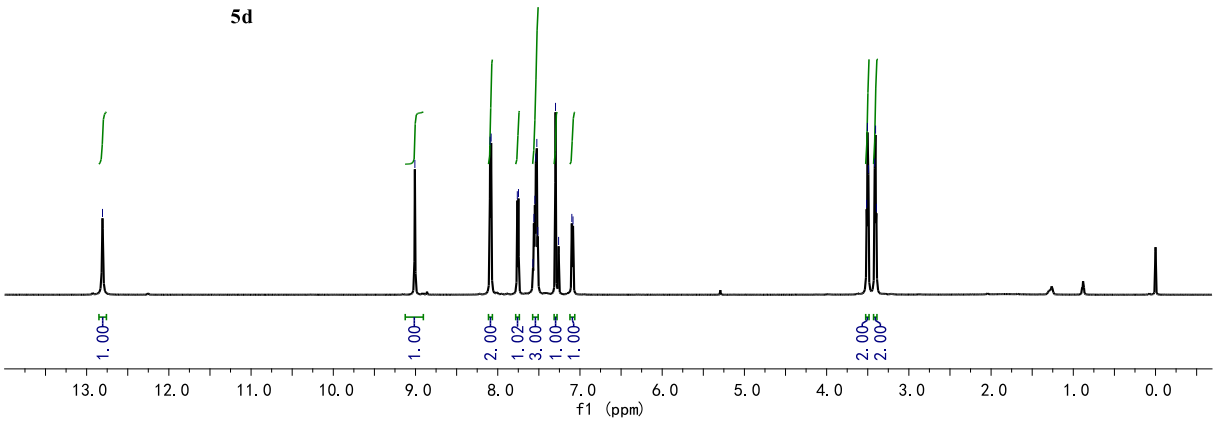


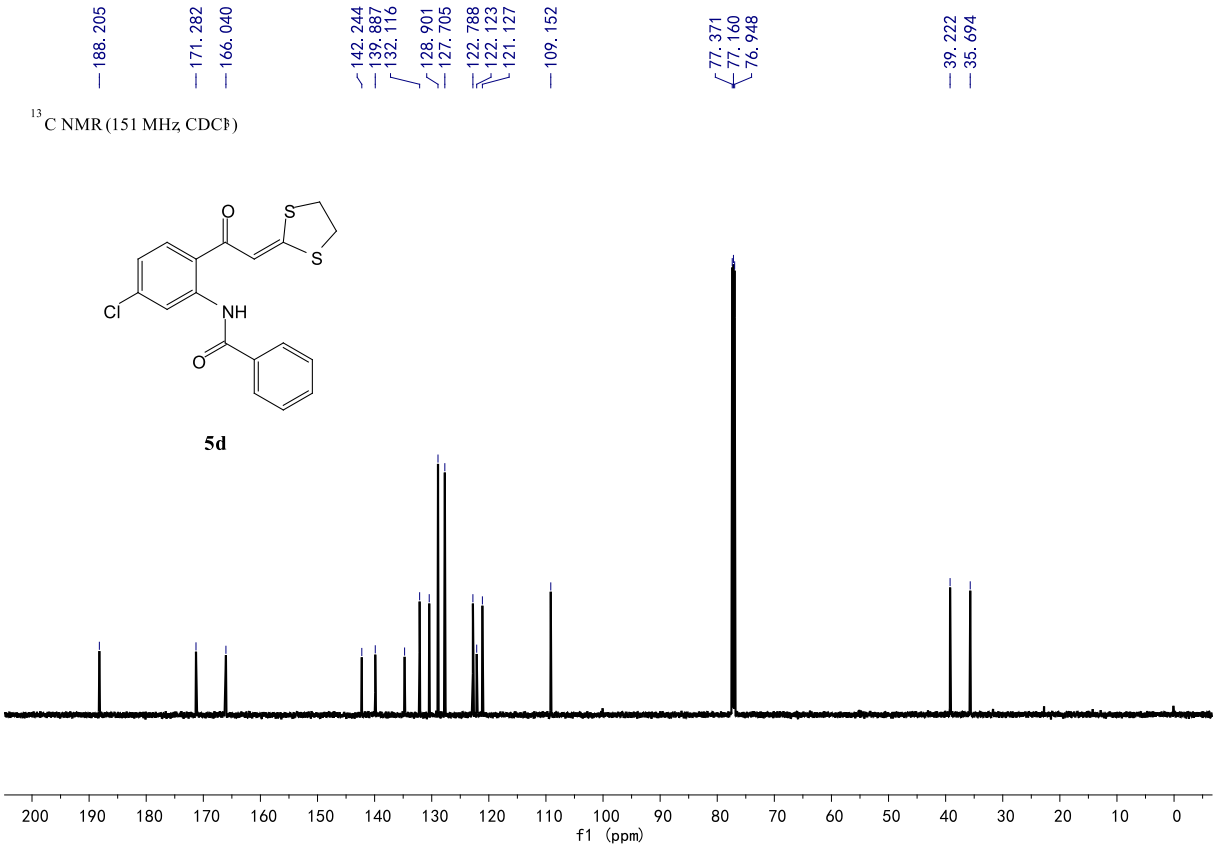
5c

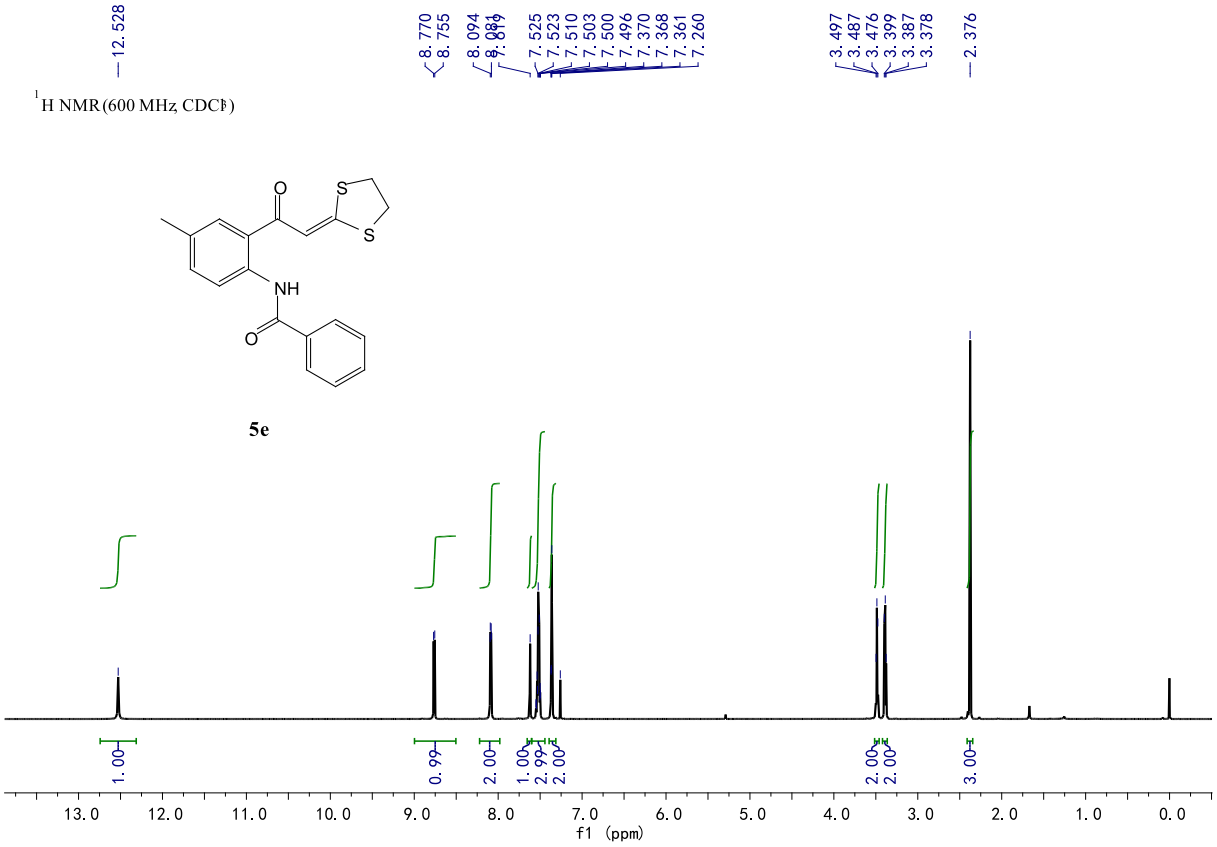
^{1}H NMR (600 MHz, CDCl$_3$)

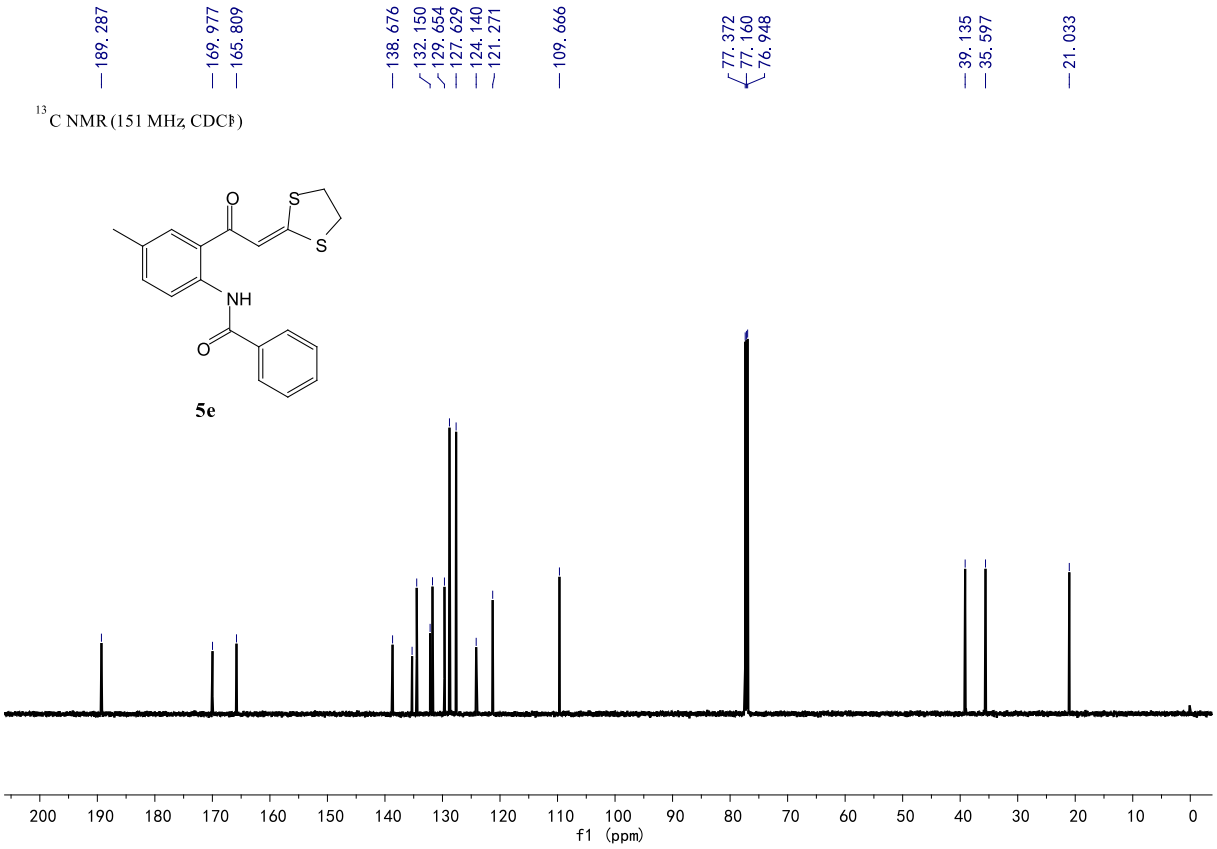


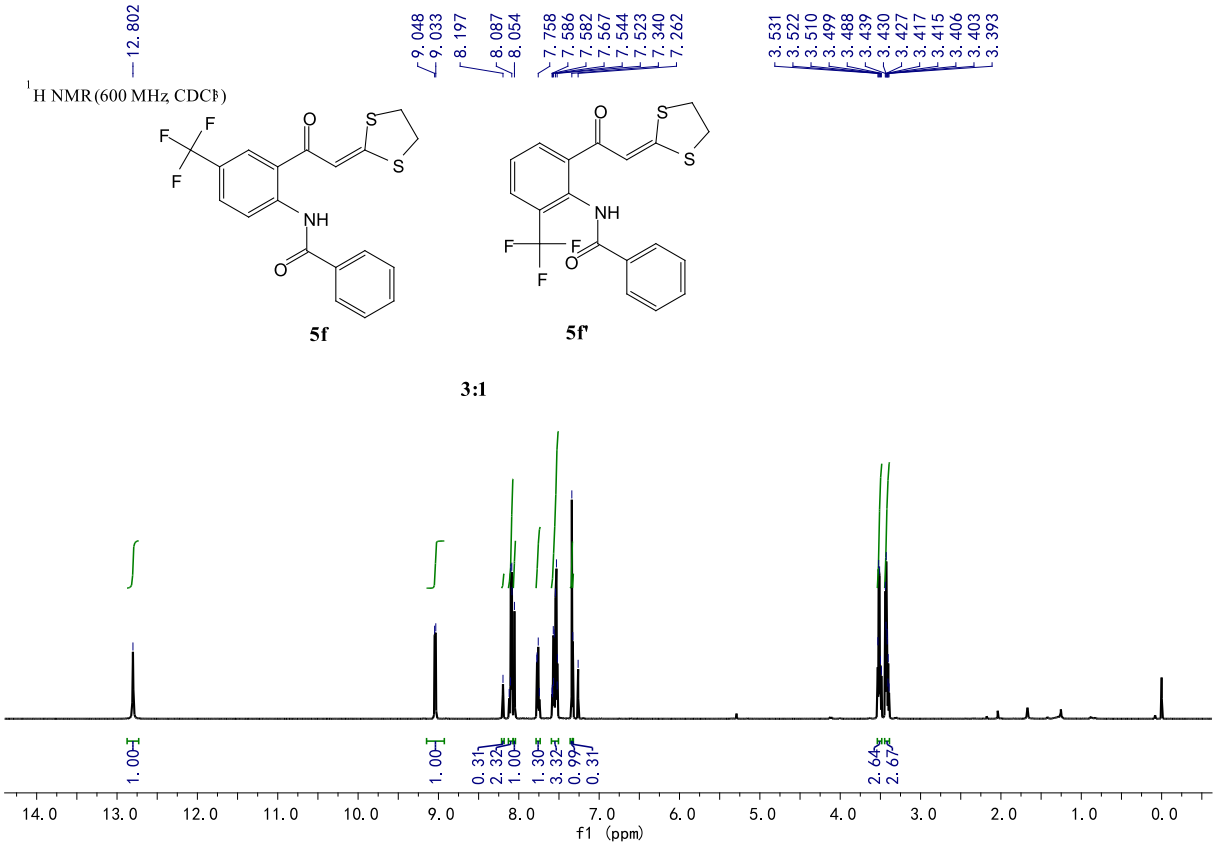
5d

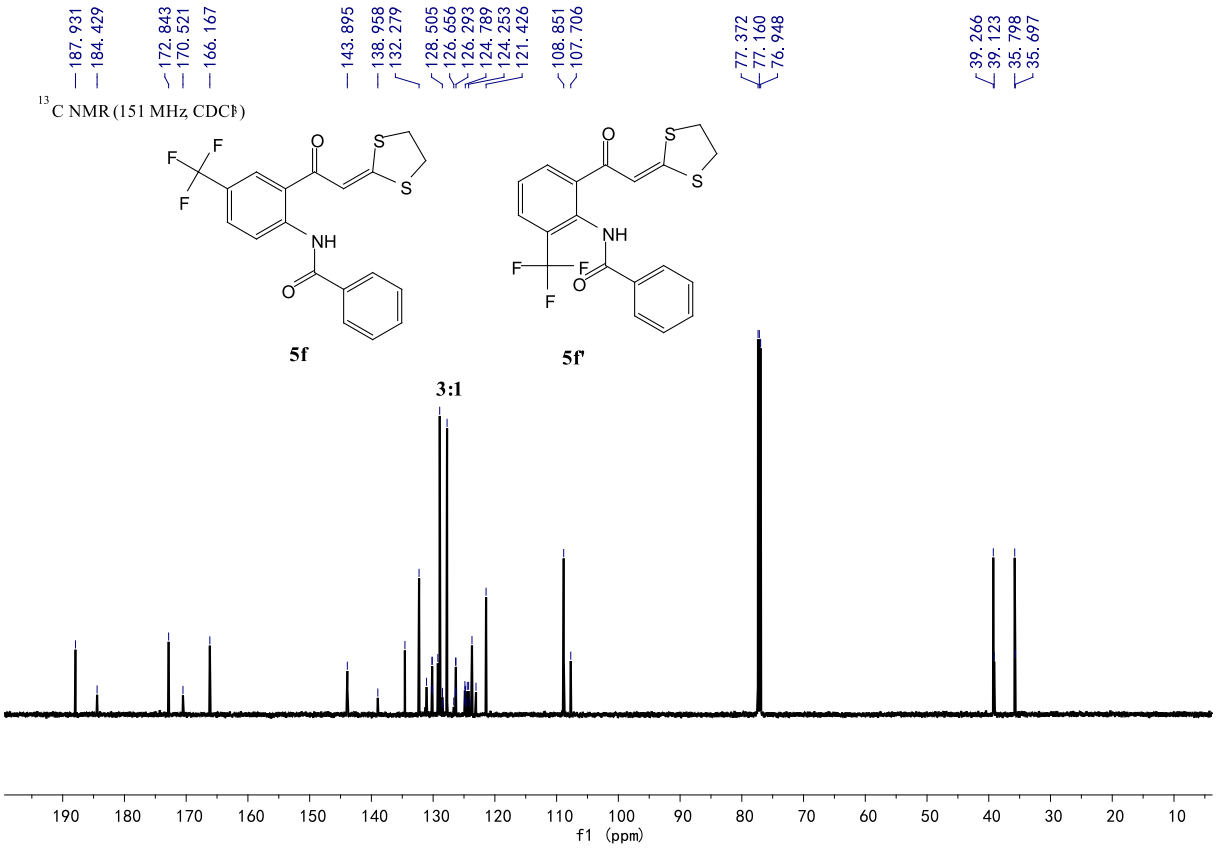


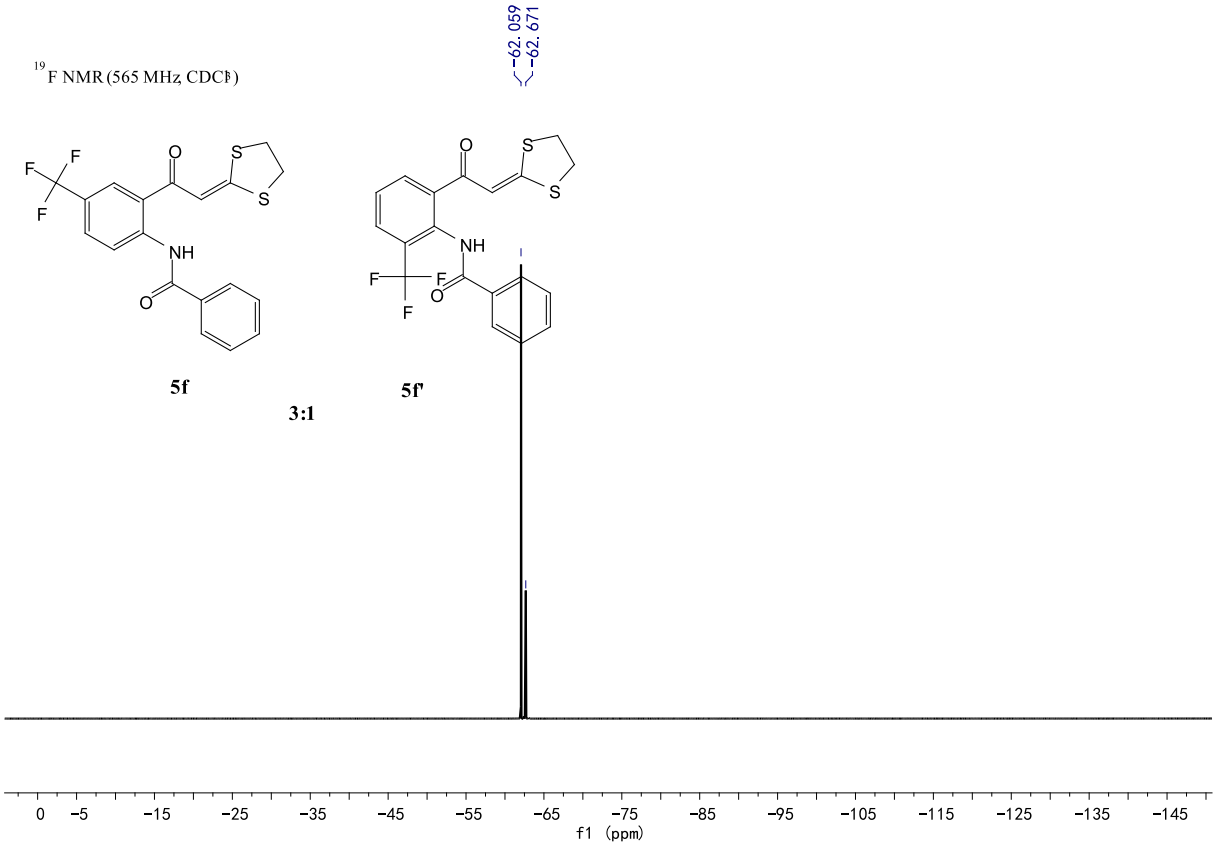

188.205
171.282
166.040
142.244
139.887
132.116
128.901
127.705
122.788
122.123
121.127
109.152
77.371
77.160
76.948
39.222
35.694
13C NMR (151 MHz, CDCl3)
O
S
S
Cl
NH
O
5d
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

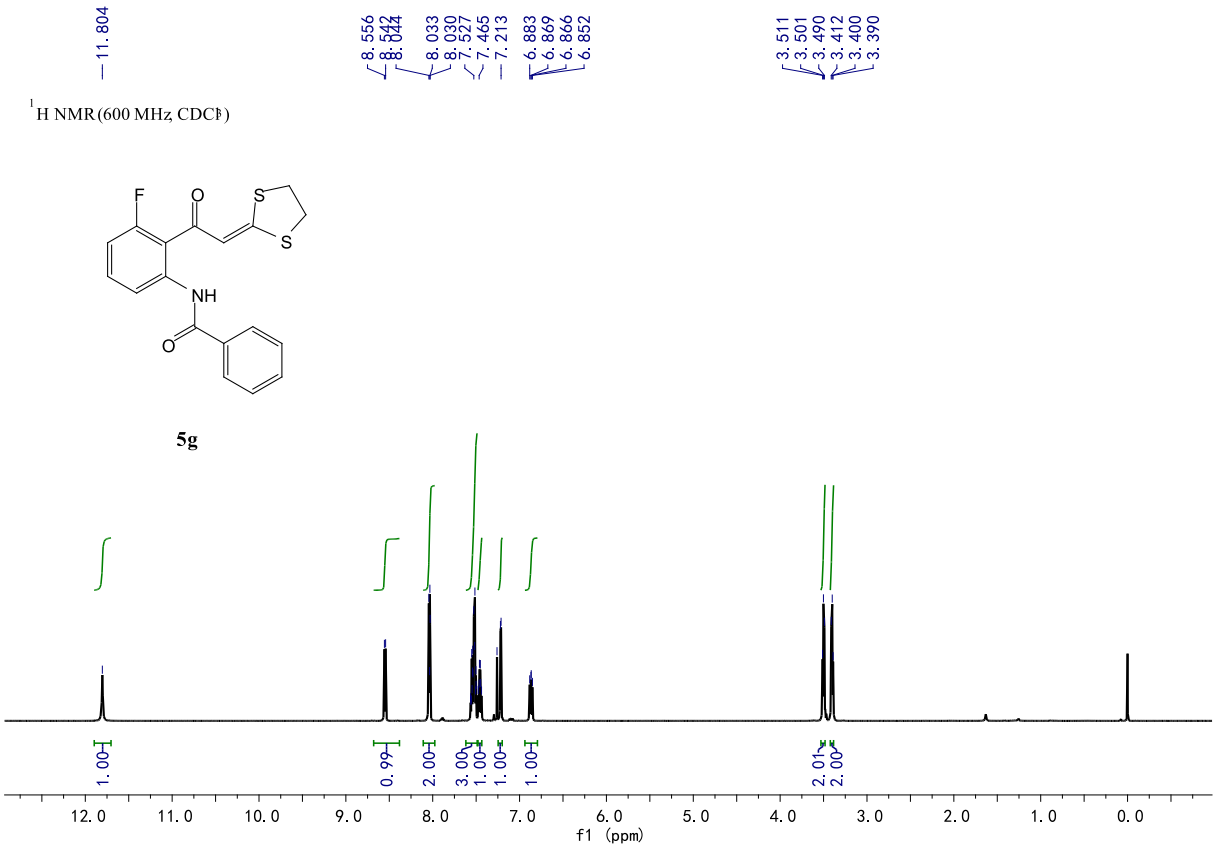

12.528
8.770
8.755
8.094
8.079
7.819
7.525
7.523
7.510
7.503
7.500
7.496
7.370
7.368
7.361
7.260
3.497
3.487
3.476
3.399
3.387
3.378
2.376
1H NMR (600 MHz, CDCl3)
O
S
S
NH
O
5e
1.00
0.99
2.00
1.00
2.99
2.00
2.00
2.00
3.00
13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

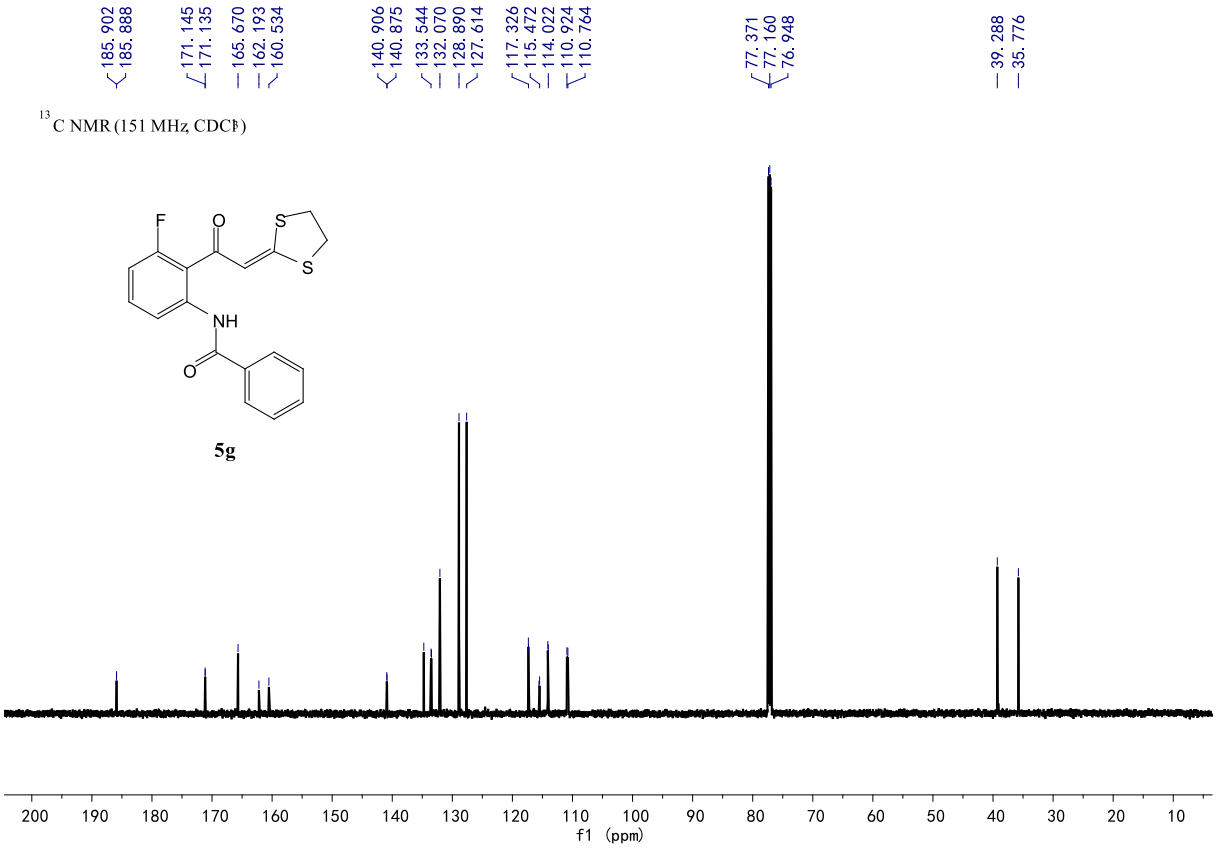

189.287
169.977
165.809
138.676
132.150
129.654
127.629
124.140
121.271
109.666
77.372
77.160
76.948
39.135
35.597
21.033
13C NMR (151 MHz, CDCl3)
O
S
S
NH
O
5e
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


12.802
9.048
9.033
8.197
8.087
8.054
7.758
7.586
7.582
7.567
7.544
7.523
7.340
7.262
3.531
3.522
3.510
3.499
3.488
3.439
3.430
3.427
3.417
3.415
3.406
3.403
3.393
1H NMR (600 MHz, CDCl3)
F
F
F
O
S
S
NH
O
5f
5f'
3:1
1.00
1.00
0.31
2.32
1.00
1.30
3.32
0.99
0.31
2.64
2.67
14.0 13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

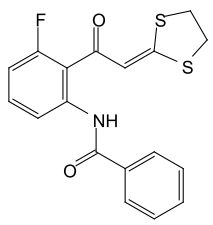

187.931
184.429
172.843
170.521
166.167
143.895
138.958
132.279
128.505
126.656
126.293
124.789
124.253
121.426
108.851
107.706
77.372
77.160
76.948
39.266
39.123
35.798
35.697
13C NMR (151 MHz, CDCl3)
5f
5f'
3:1
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


-62.059
-62.671
19F NMR (565 MHz, CDCl3)
5f
5f'
3:1
0 -5 -15 -25 -35 -45 -55 -65 -75 -85 -95 -105 -115 -125 -135 -145
f1 (ppm)


11.804
8.556
8.542
8.044
8.033
8.030
7.527
7.465
7.213
6.883
6.869
6.866
6.852
3.511
3.501
3.490
3.412
3.400
3.390
1H NMR (600 MHz, CDCl3)
F
O
S
S
NH
O
5g
1.00
0.99
2.00
3.00
1.00
1.00
1.00
2.01
2.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

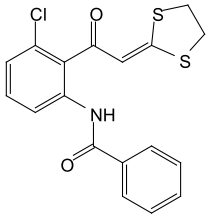

185.902
185.888
171.145
171.135
165.670
162.193
160.534
140.906
140.875
133.544
132.070
128.890
127.614
117.326
115.472
114.022
110.924
110.764
77.371
77.160
76.948
39.288
35.776
13C NMR (151 MHz, CDCl3)
F
O
S
S
NH
O
5g
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

^{19}F NMR (376 MHz, CDCl$_3$)

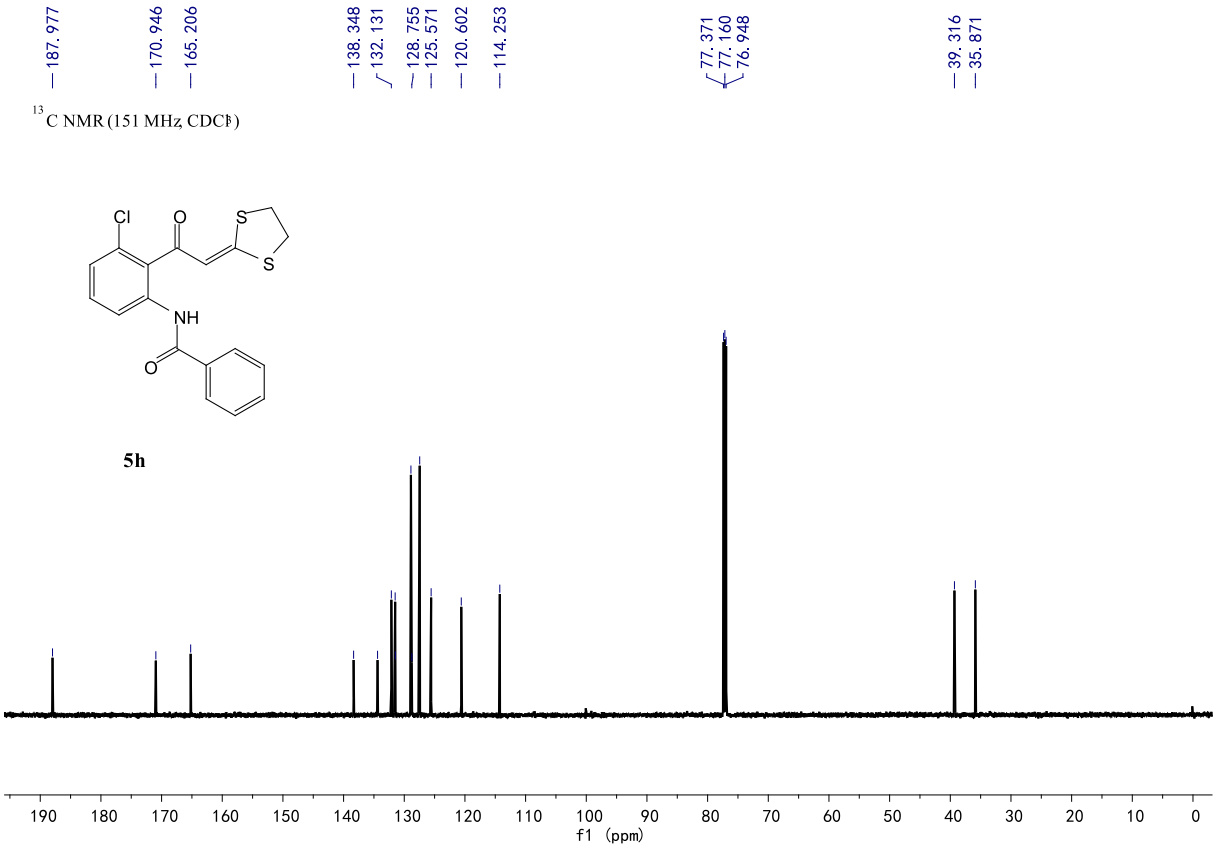


5g

^{1}H NMR (600 MHz, CDCl$_3$)

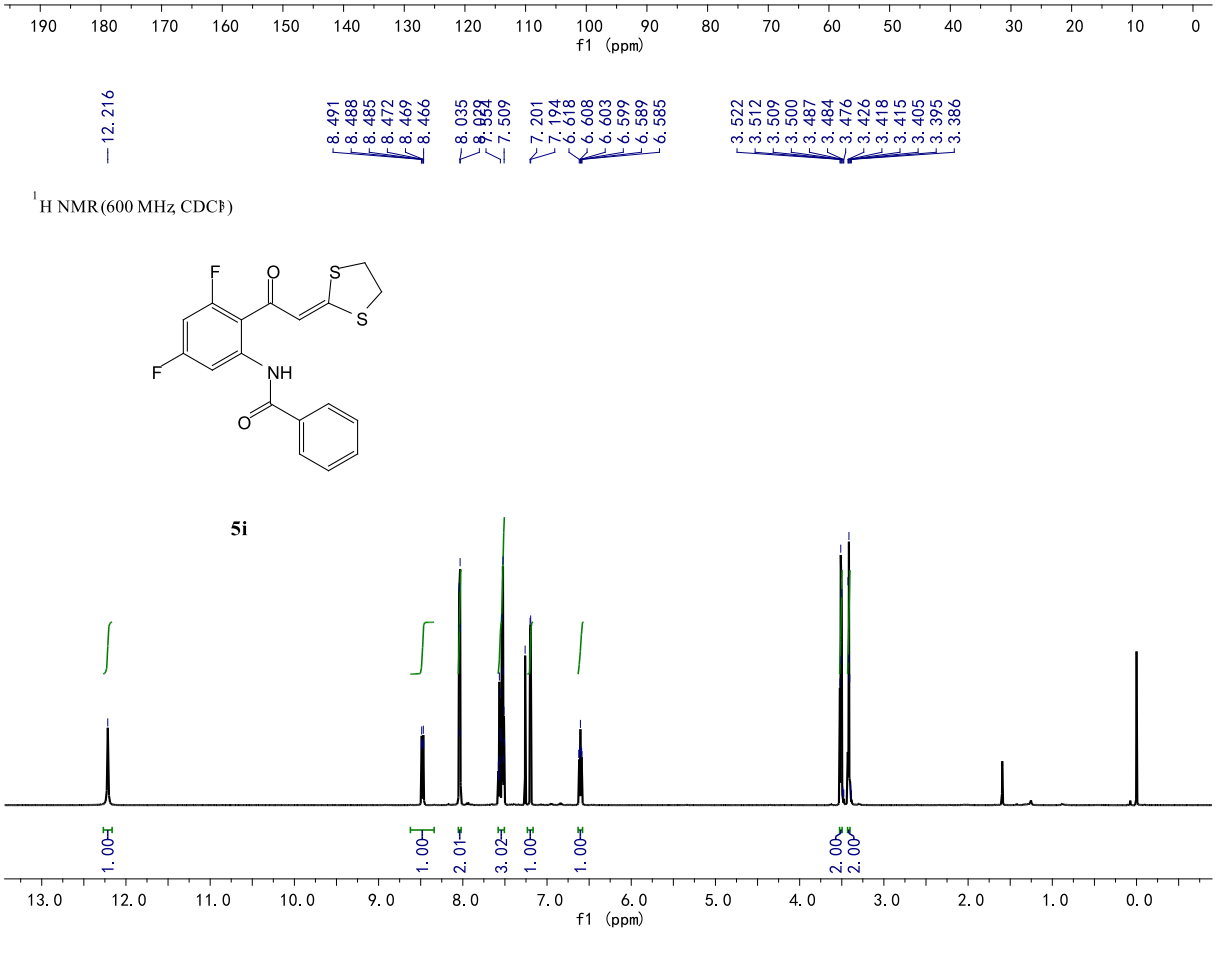


5h



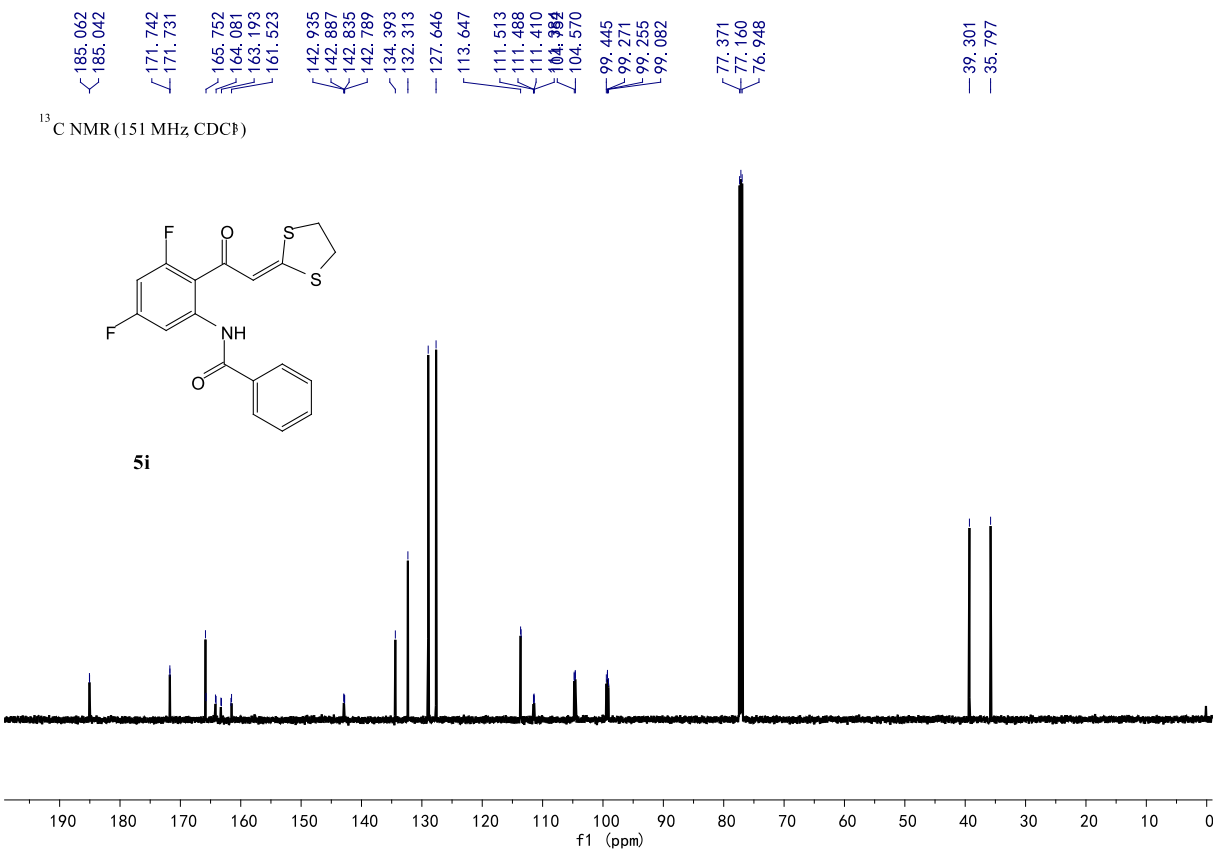
^{13}C NMR (151 MHz, CDCl$_3$)

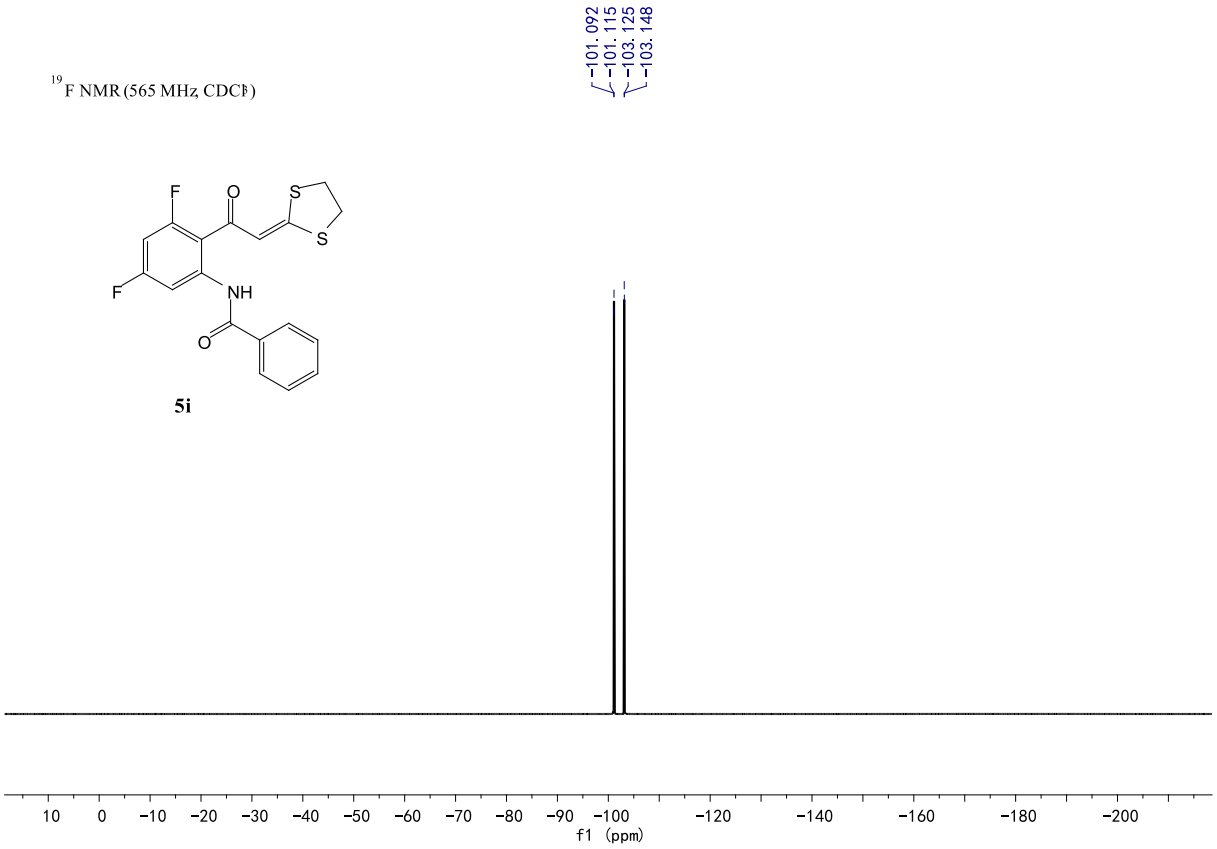
5h

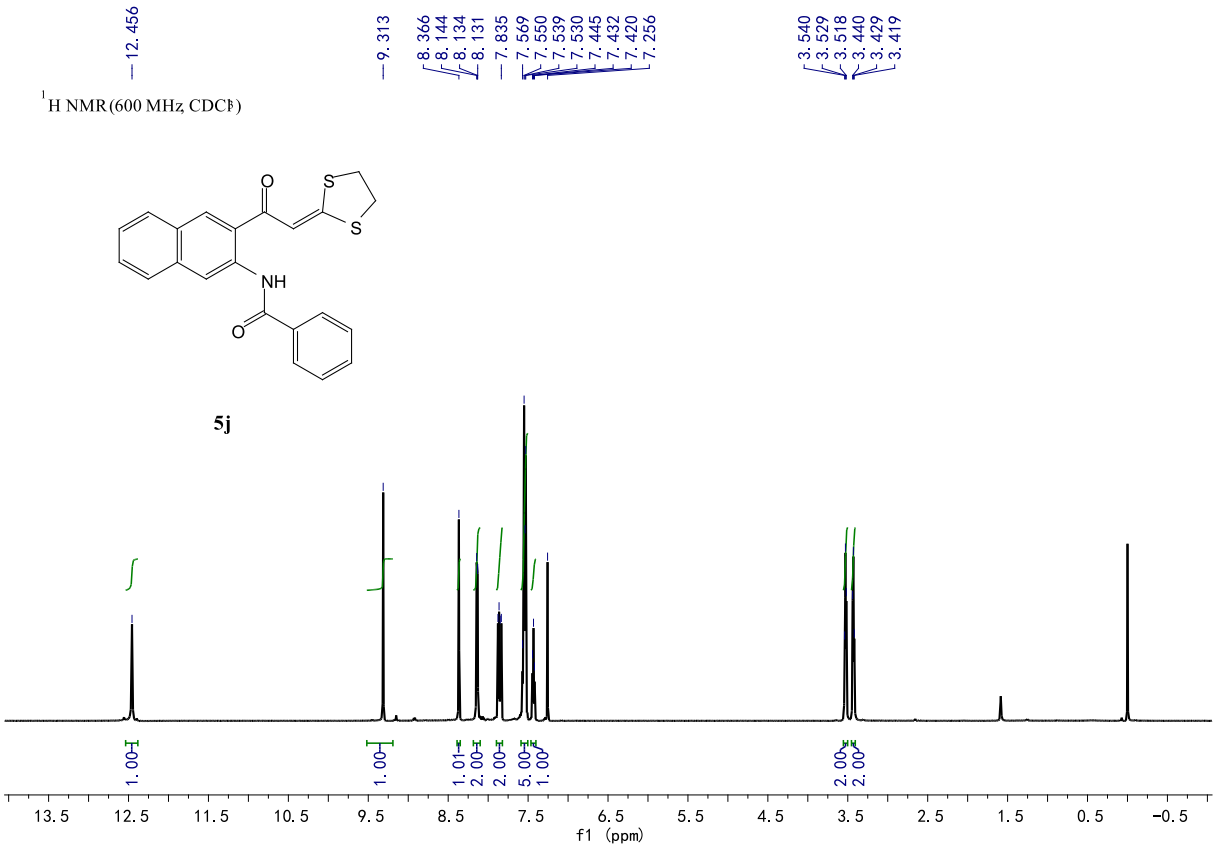


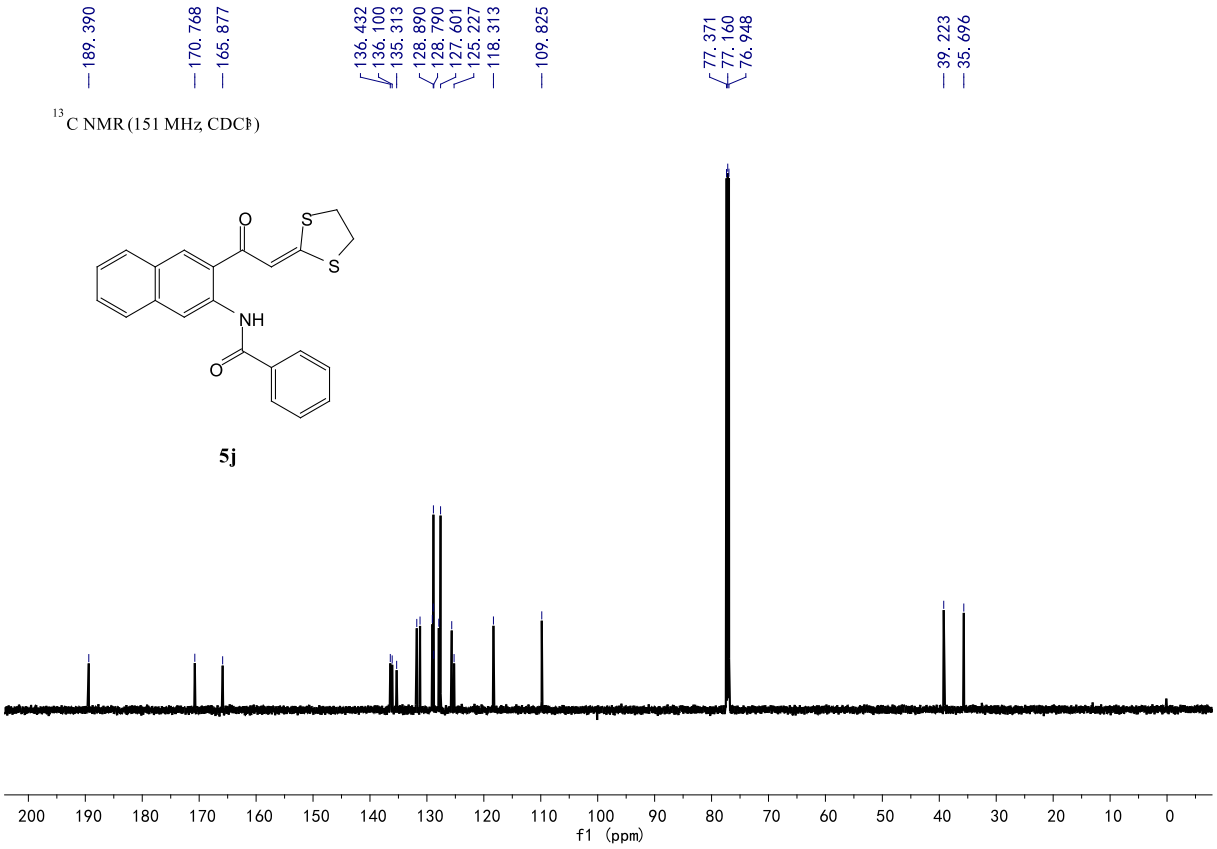
^{1}H NMR (600 MHz, CDCl$_3$)

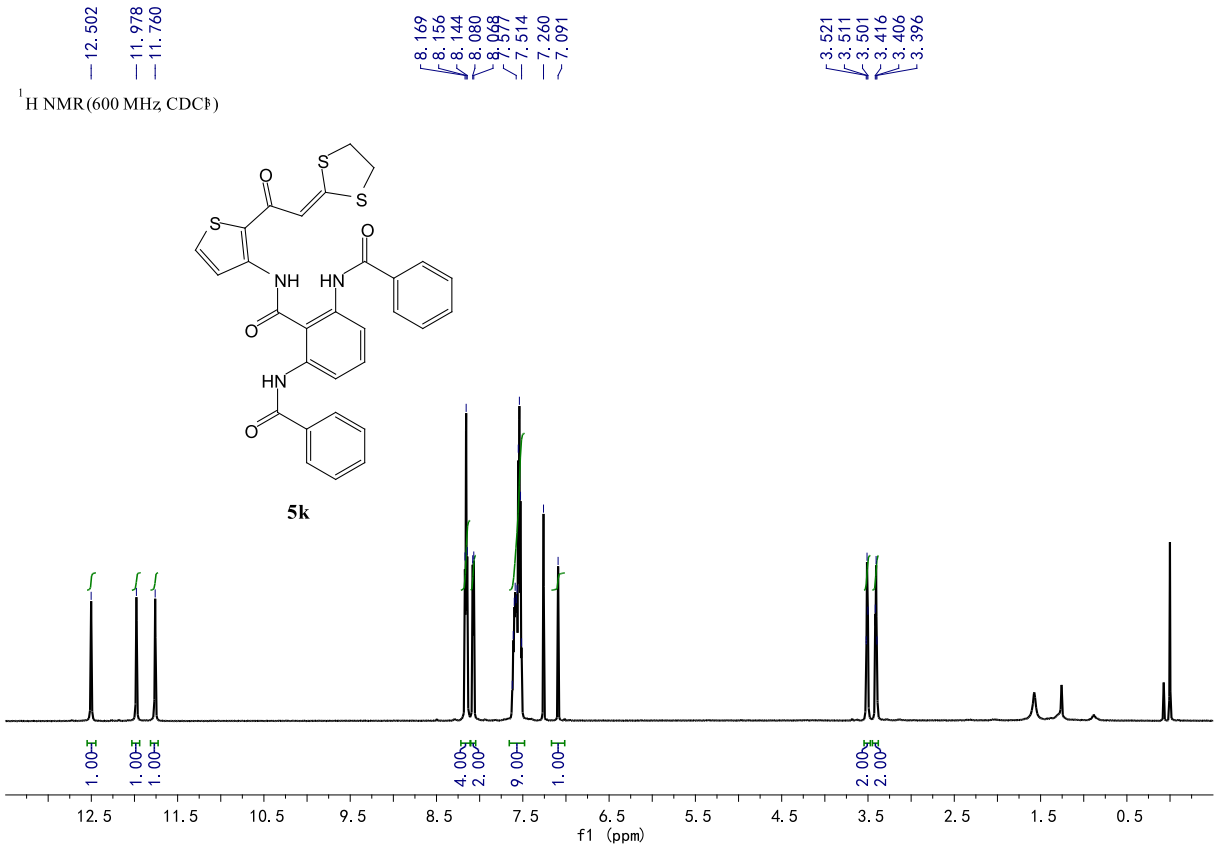
5i

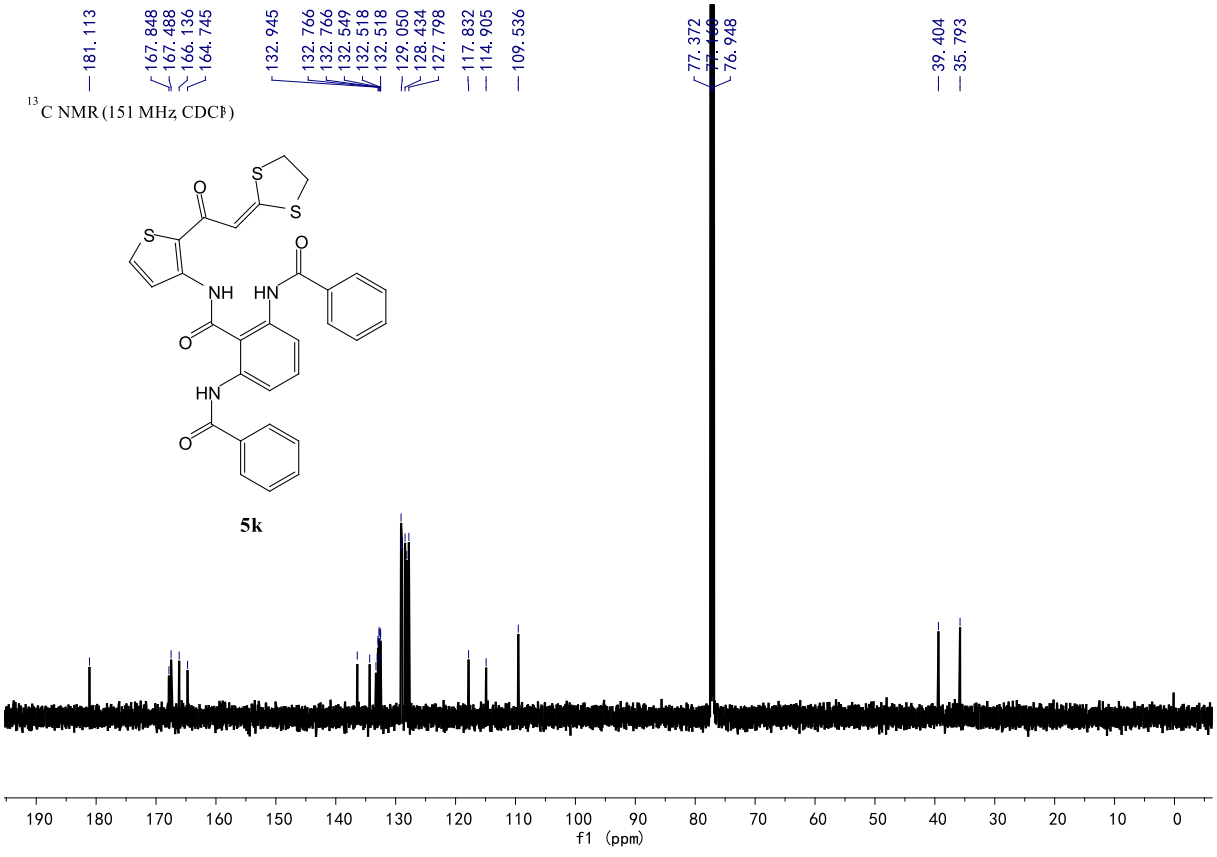

185.062
185.042
171.742
171.731
165.752
164.081
163.193
161.523
142.935
142.887
142.835
142.789
134.393
132.313
127.646
113.647
111.513
111.488
111.410
104.570
99.445
99.271
99.255
99.082
77.371
77.160
76.948
39.301
35.797
13C NMR (151 MHz, CDCl3)
F
O
S
S
F
NH
O
5i
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

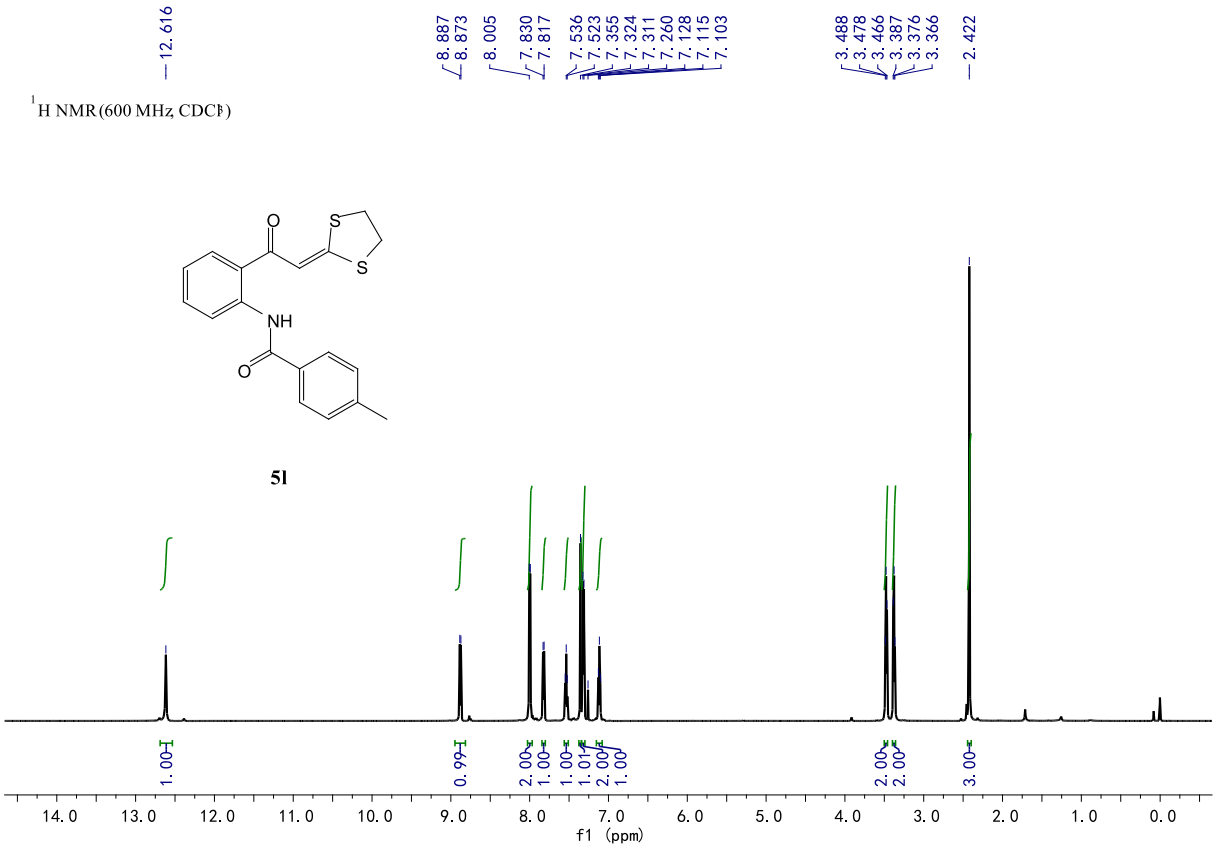

-101.092
-101.115
-103.125
-103.148
19F NMR (565 MHz, CDCl3)
F
O
S
S
F
NH
O
5i
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)


12.456
9.313
8.366
8.144
8.134
8.131
7.835
7.569
7.550
7.539
7.530
7.445
7.432
7.420
7.256
3.540
3.529
3.518
3.440
3.429
3.419
1H NMR (600 MHz, CDCl3)
O
S
S
NH
O
5j
1.00
1.00
1.01
2.00
2.00
5.00
1.00
2.00
2.00
13.5
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)


189.390
170.768
165.877
136.432
136.100
135.313
128.890
128.790
127.601
125.227
118.313
109.825
77.371
77.160
76.948
39.223
35.696
13C NMR (151 MHz, CDCl3)
O
S
S
NH
O
5j
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

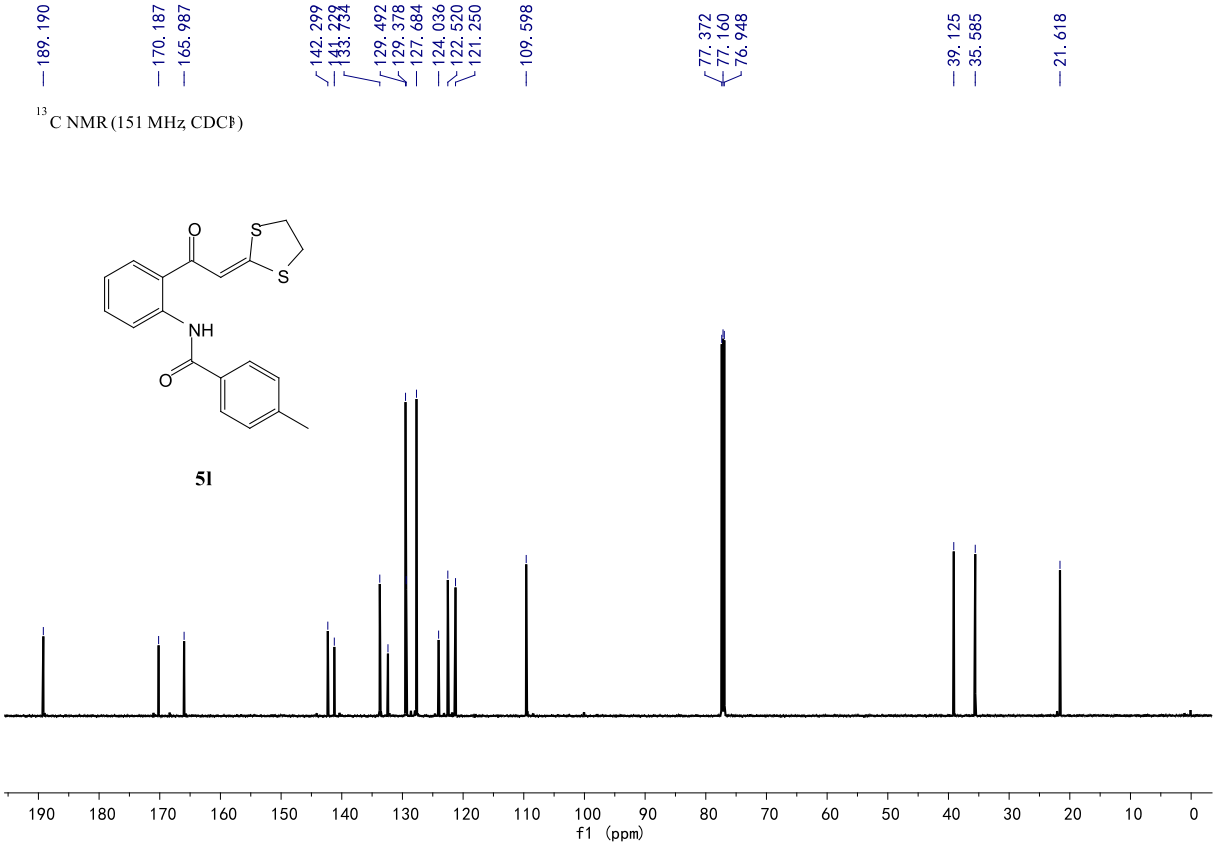

12.502
11.978
11.760
8.169
8.156
8.144
8.080
8.068
7.577
7.514
7.260
7.091
3.521
3.511
3.501
3.416
3.406
3.396
1H NMR (600 MHz, CDCl3)
5k
1.00
1.00
1.00
4.00
2.00
9.00
1.00
2.00
2.00
f1 (ppm)


181.113
167.848
167.488
166.136
164.745
132.945
132.766
132.766
132.549
132.518
132.518
129.050
128.434
127.798
117.832
114.905
109.536
77.372
77.160
76.948
39.404
35.793
13C NMR (151 MHz, CDCl3)
5k
f1 (ppm)



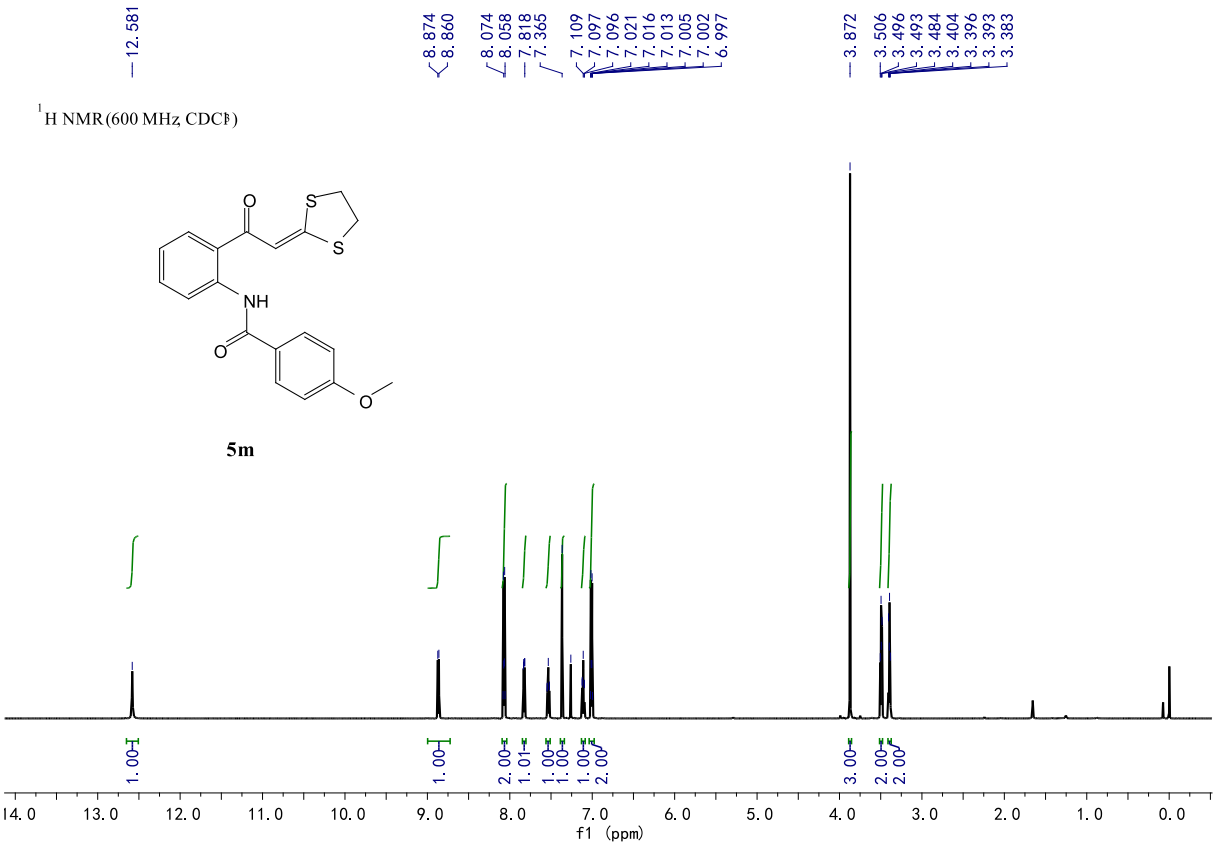
^{1}H NMR (600 MHz, CDCl$_3$)

5l



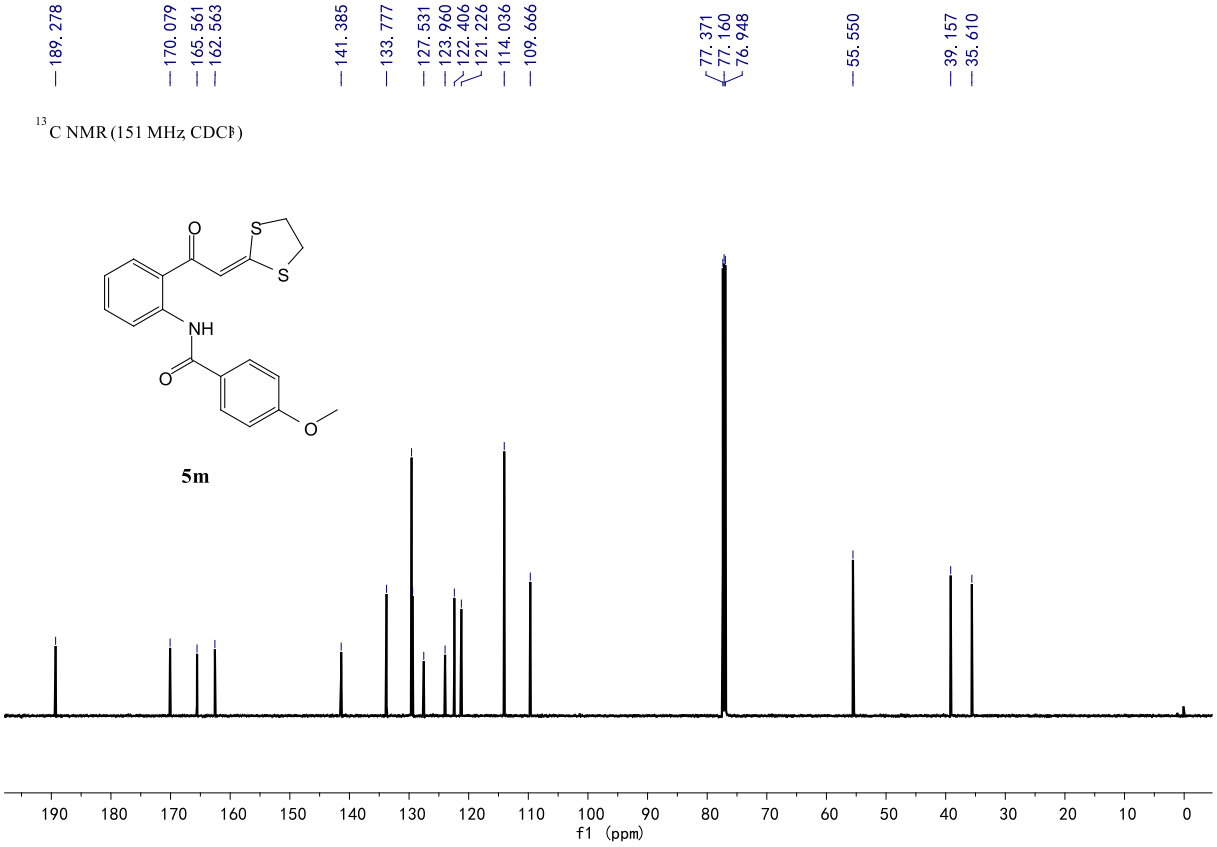
^{13}C NMR (151 MHz, CDCl$_3$)

5l



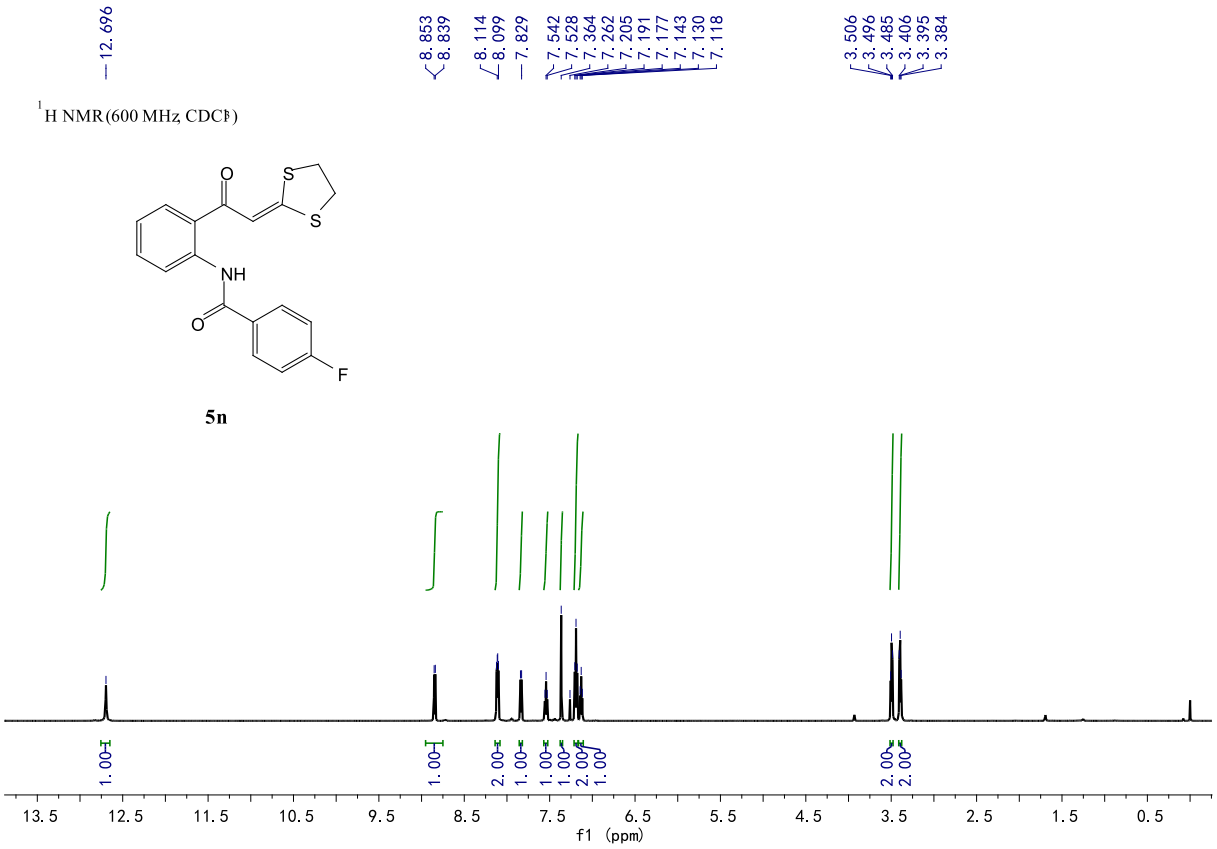
^{1}H NMR (600 MHz, CDCl$_3$)

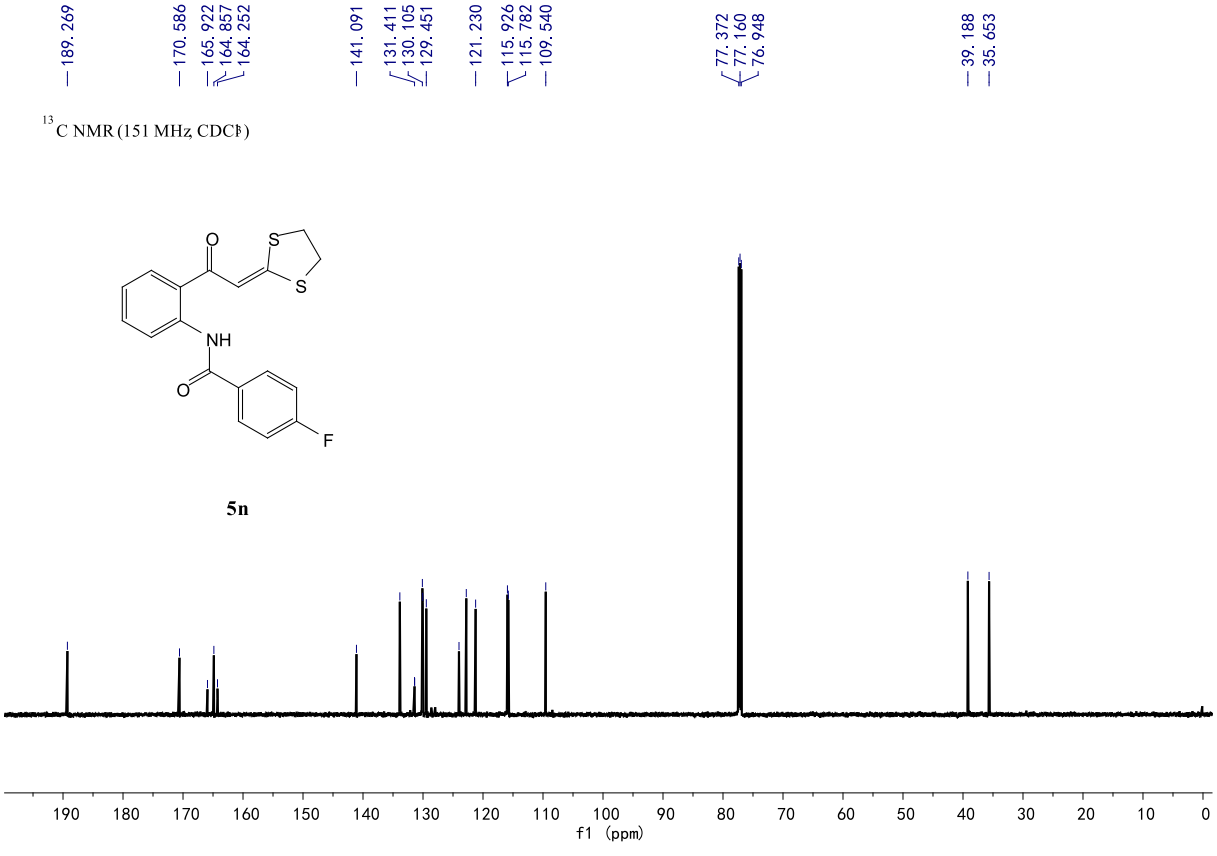
5m



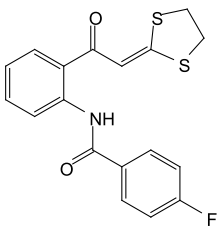
^{13}C NMR (151 MHz, CDCl$_3$)

5m


12.696
8.853
8.839
8.114
8.099
7.829
7.542
7.528
7.364
7.262
7.205
7.191
7.177
7.143
7.130
7.118
3.506
3.496
3.485
3.406
3.395
3.384
1H NMR (600 MHz, CDCl3)
O
S
S
NH
O
F
5n
1.00
1.00
2.00
1.00
1.00
2.00
1.00
2.00
2.00
13.5
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

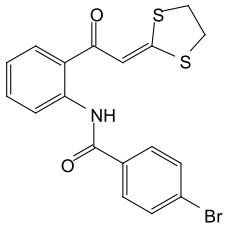

189.269
170.586
165.922
164.857
164.252
141.091
131.411
130.105
129.451
121.230
115.926
115.782
109.540
77.372
77.160
76.948
39.188
35.653
13C NMR (151 MHz, CDCl3)
O
S
S
NH
O
F
5n
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{19}F NMR (565 MHz, CDCl$_3$)

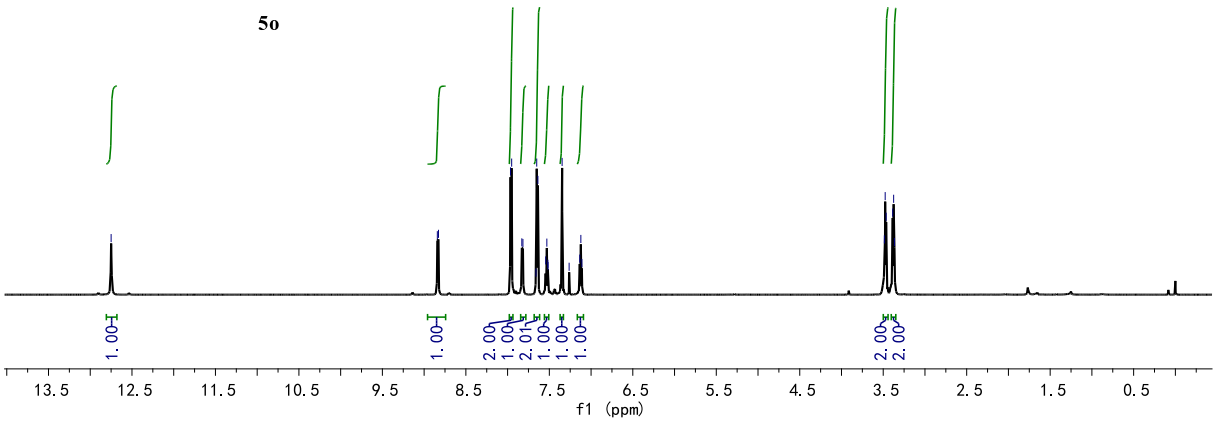


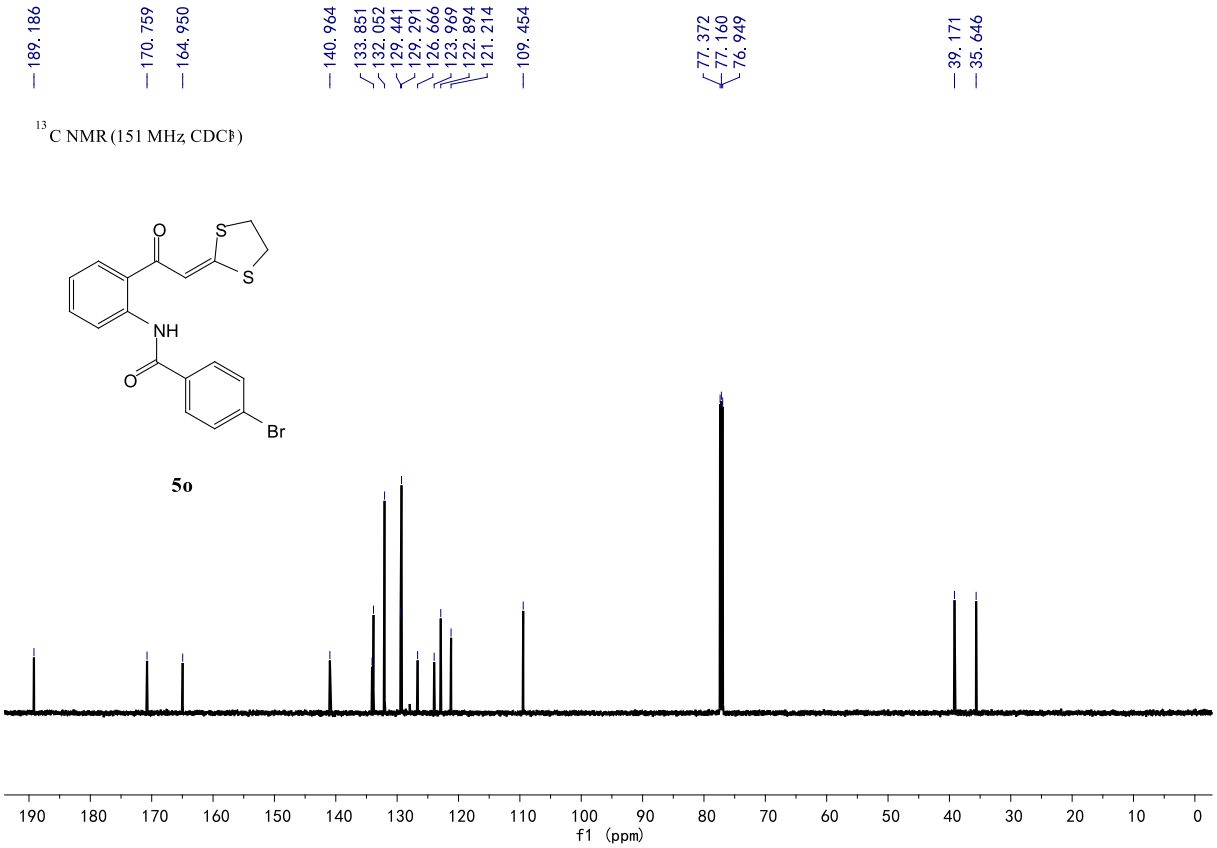
5n

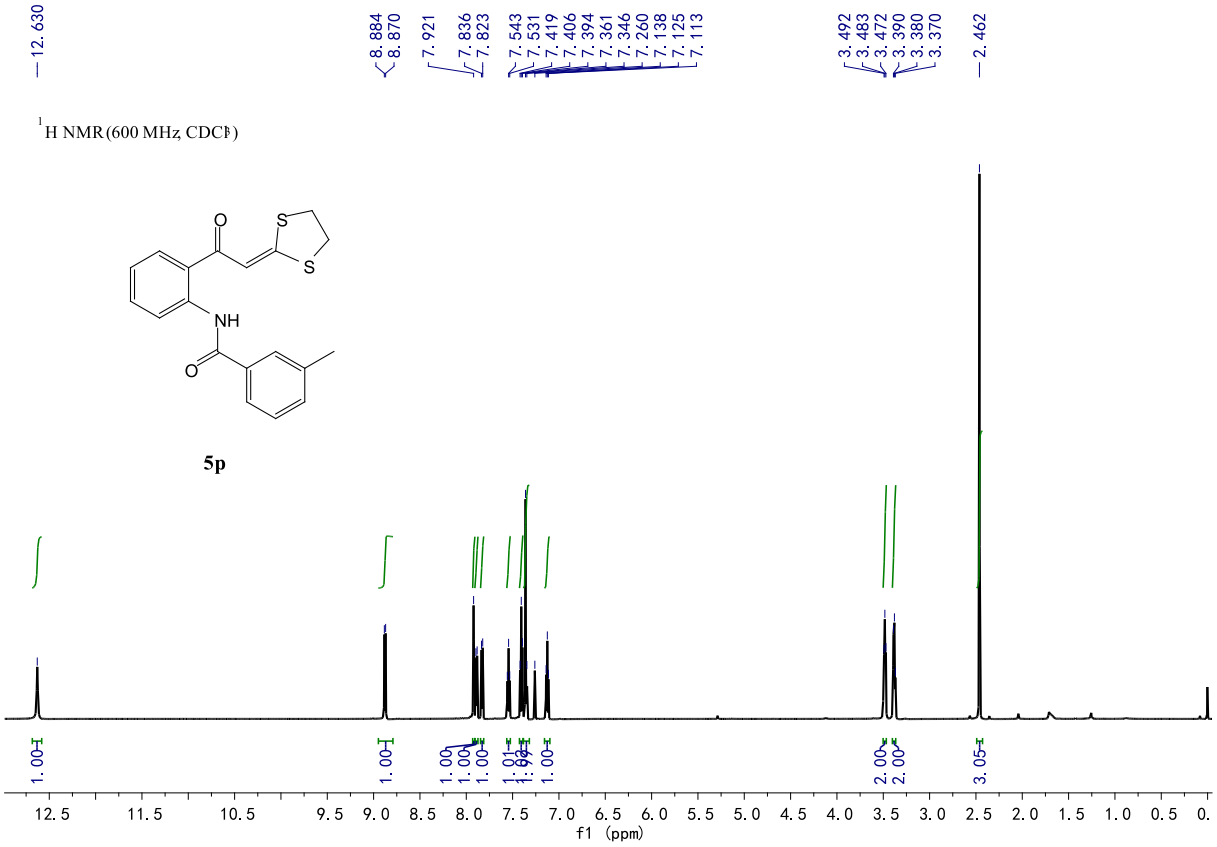
^{1}H NMR (600 MHz, CDCl$_3$)

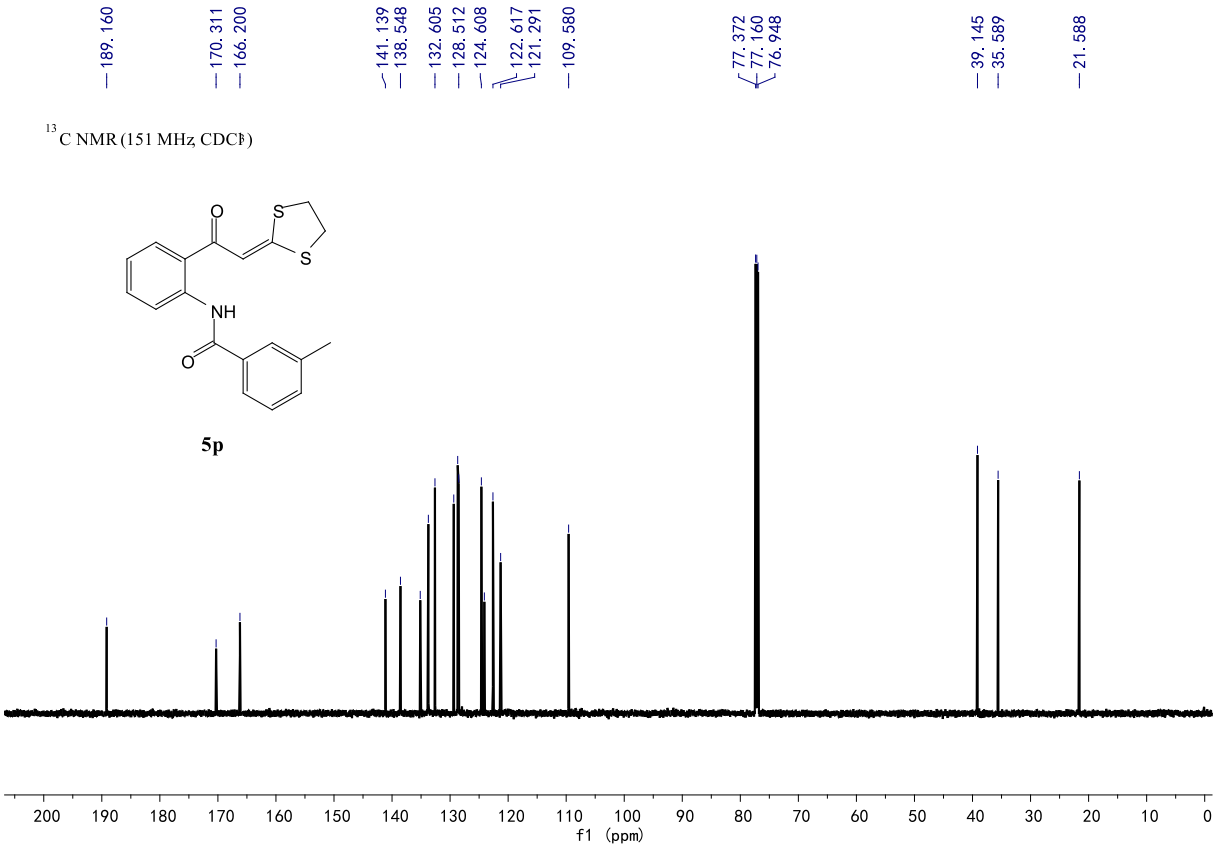


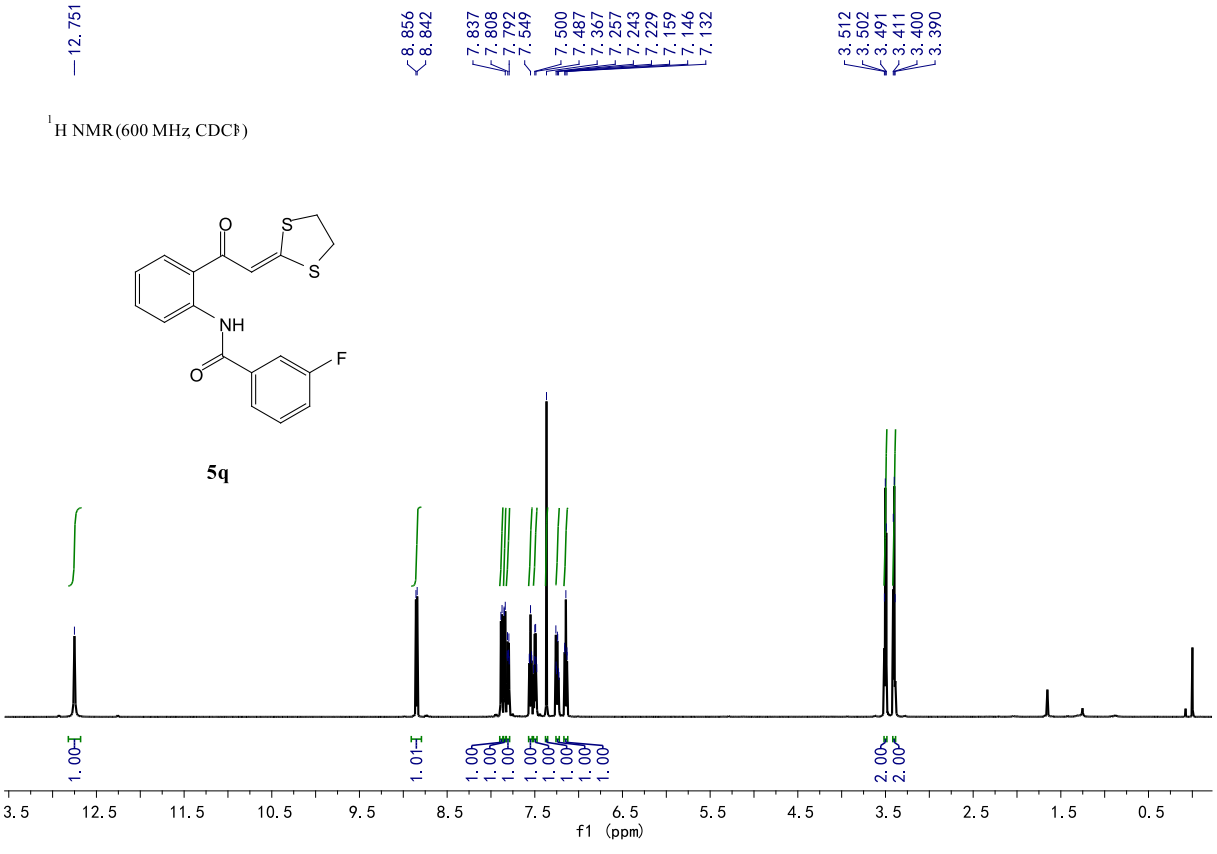
5o

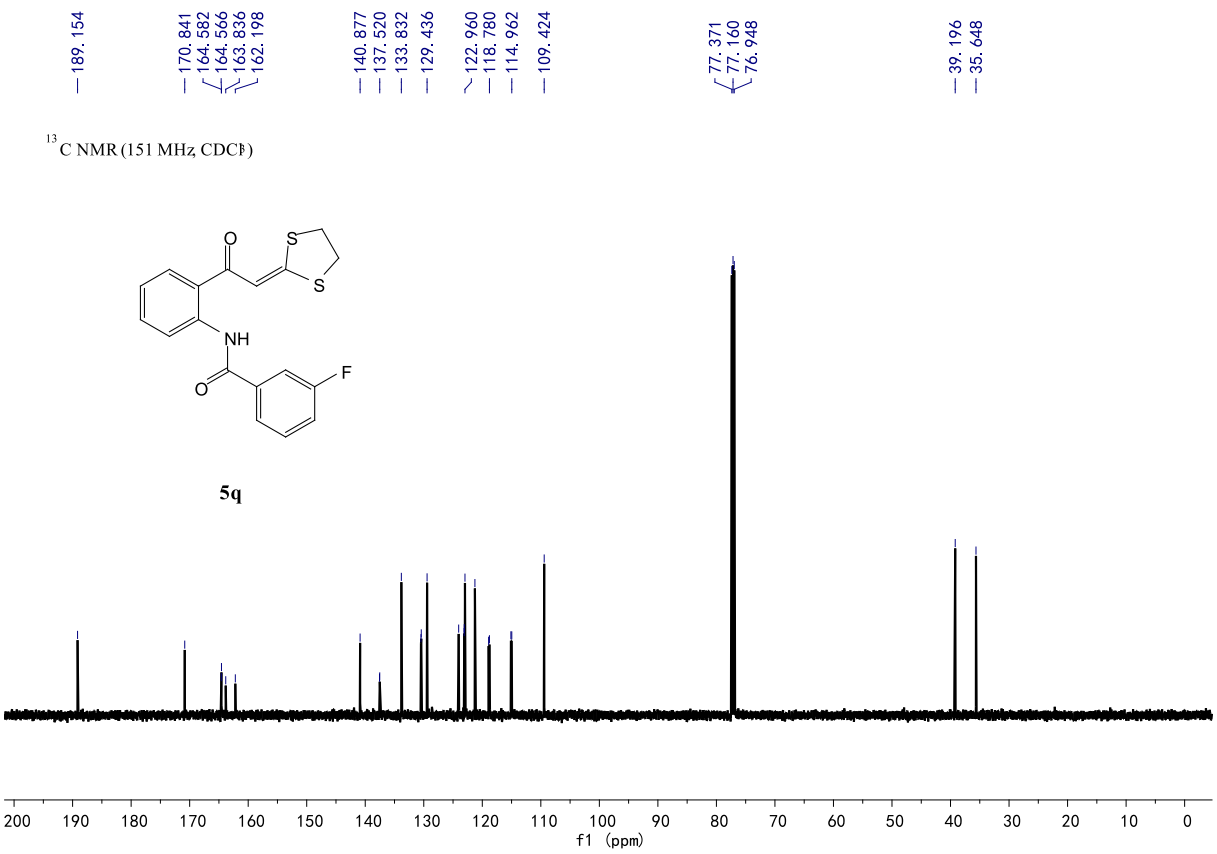


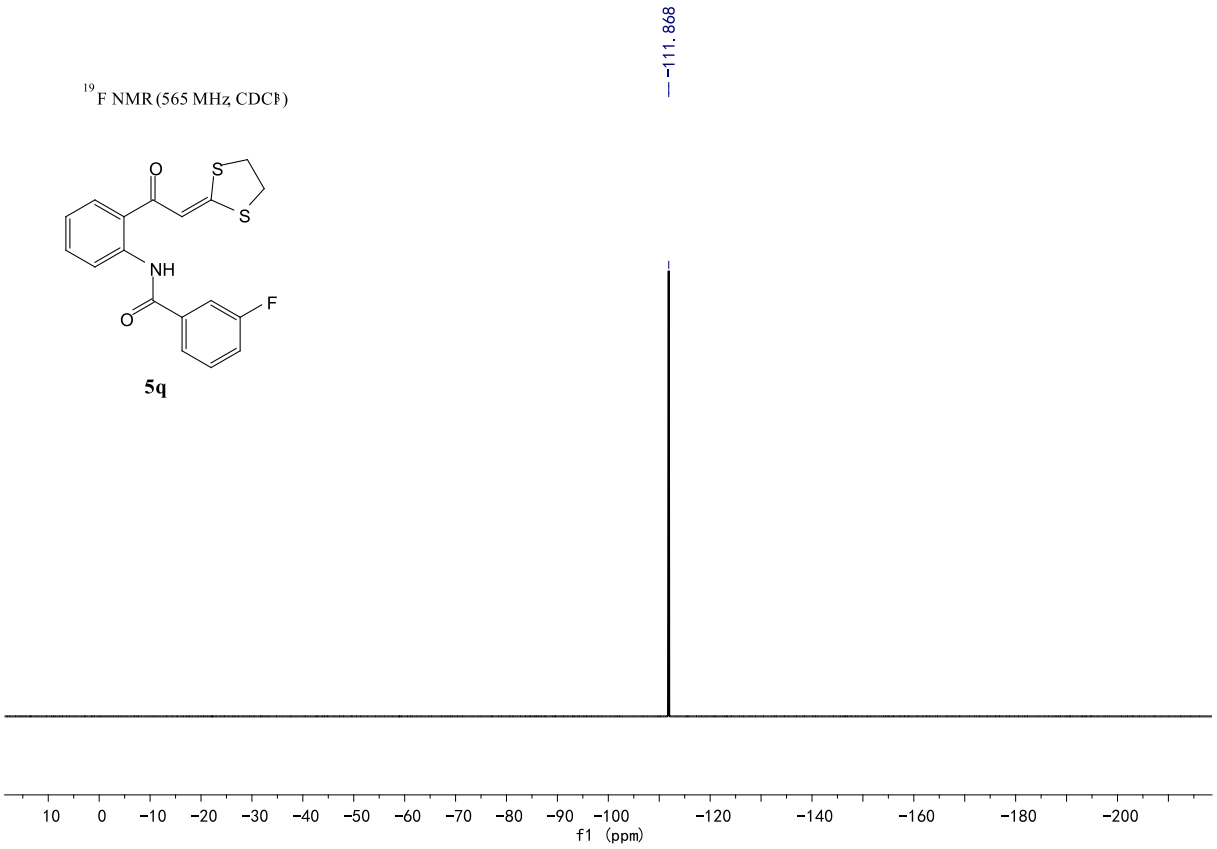

189.186
170.759
164.950
140.964
133.851
132.052
129.441
129.291
126.666
123.969
122.894
121.214
109.454
77.372
77.160
76.949
39.171
35.646
13C NMR (151 MHz, CDCl3)
O
S
S
NH
O
Br
5o
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

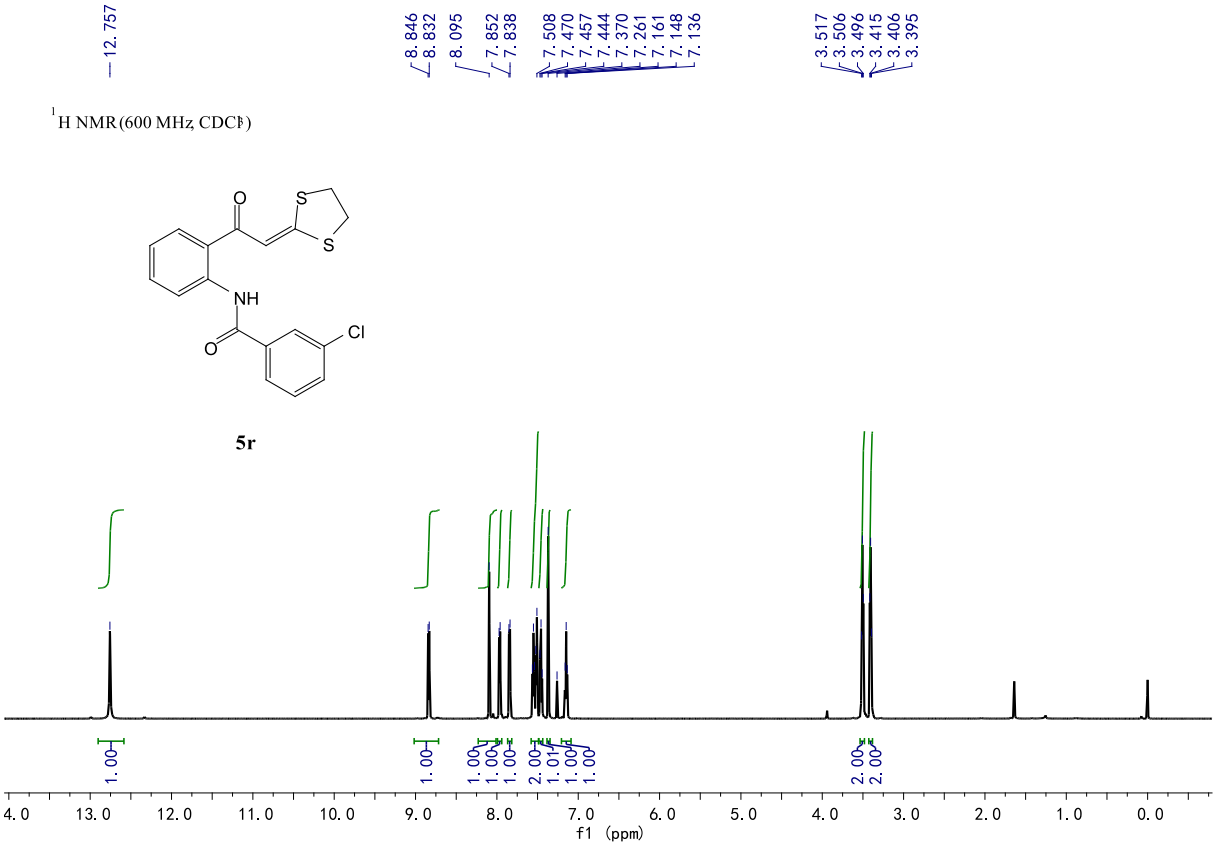

12.630
8.884
8.870
7.921
7.836
7.823
7.543
7.531
7.419
7.406
7.394
7.361
7.346
7.260
7.138
7.125
7.113
3.492
3.483
3.472
3.390
3.380
3.370
2.462
1H NMR (600 MHz, CDCl3)
O
S
S
NH
O
5p
1.00
1.00
1.00
1.00
1.00
1.01
1.00
1.00
2.00
2.00
3.05
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)

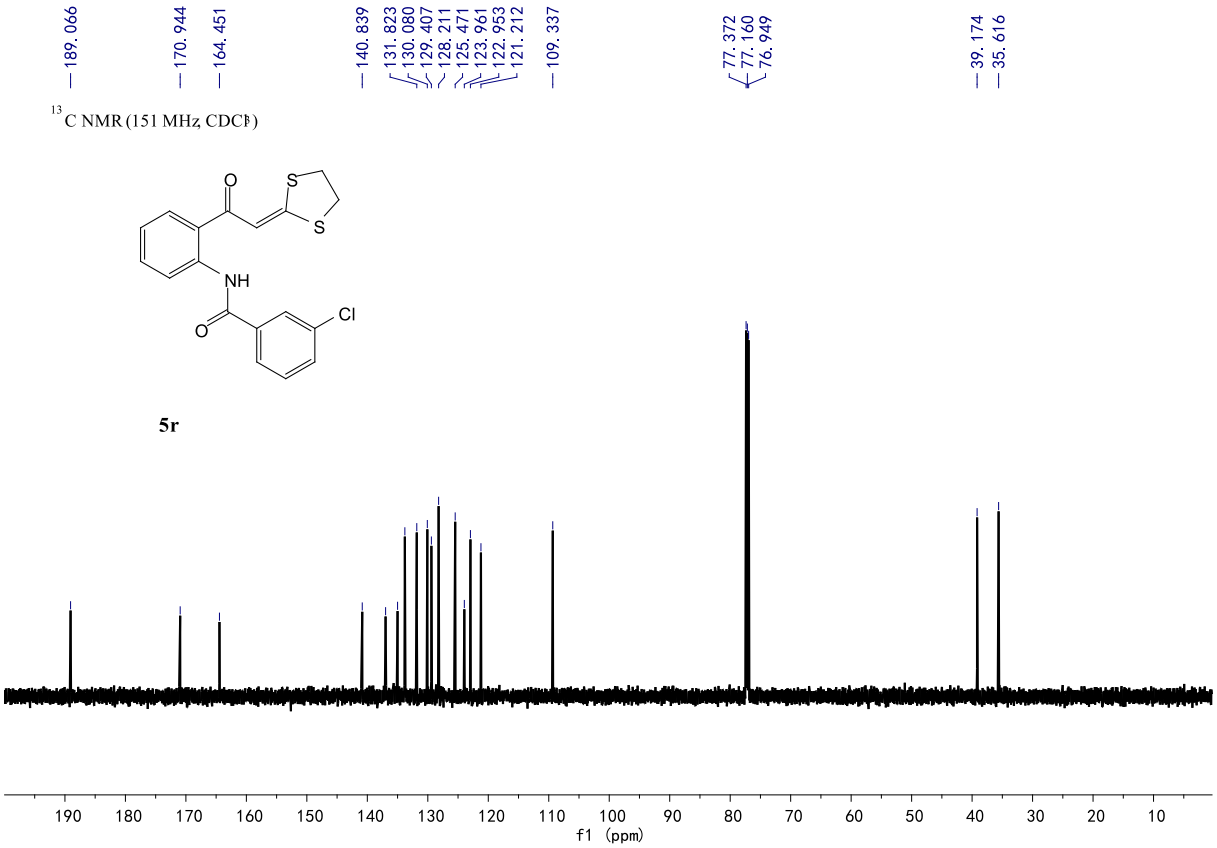

189.160
170.311
166.200
141.139
138.548
132.605
128.512
124.608
122.617
121.291
109.580
77.372
77.160
76.948
39.145
35.589
21.588
13C NMR (151 MHz, CDCl3)
O
S
S
NH
O
5p
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

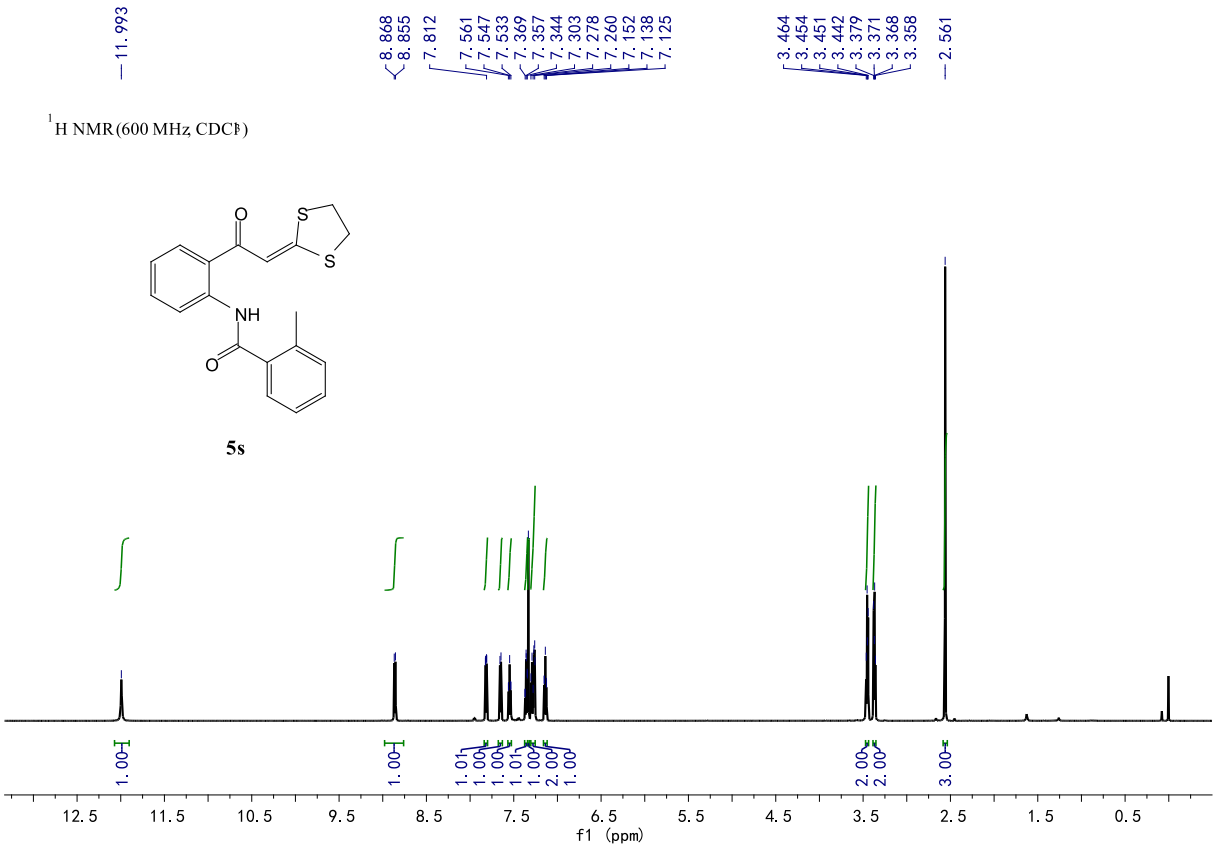

12.751
8.856
8.842
7.837
7.808
7.792
7.549
7.500
7.487
7.367
7.257
7.243
7.229
7.159
7.146
7.132
3.512
3.502
3.491
3.411
3.400
3.390
1H NMR (600 MHz, CDCl3)
O
S
S
NH
O
F
5q
1.00
1.01
1.00
1.00
1.00
1.00
1.00
1.00
1.00
2.00
2.00
3.5 12.5 11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5
f1 (ppm)


189.154
170.841
164.582
164.566
163.836
162.198
140.877
137.520
133.832
129.436
122.960
118.780
114.962
109.424
77.371
77.160
76.948
39.196
35.648
13C NMR (151 MHz, CDCl3)
O
S
S
NH
O
F
5q
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-111.868
19F NMR (565 MHz, CDCl3)
O
S
S
NH
O
F
5q
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

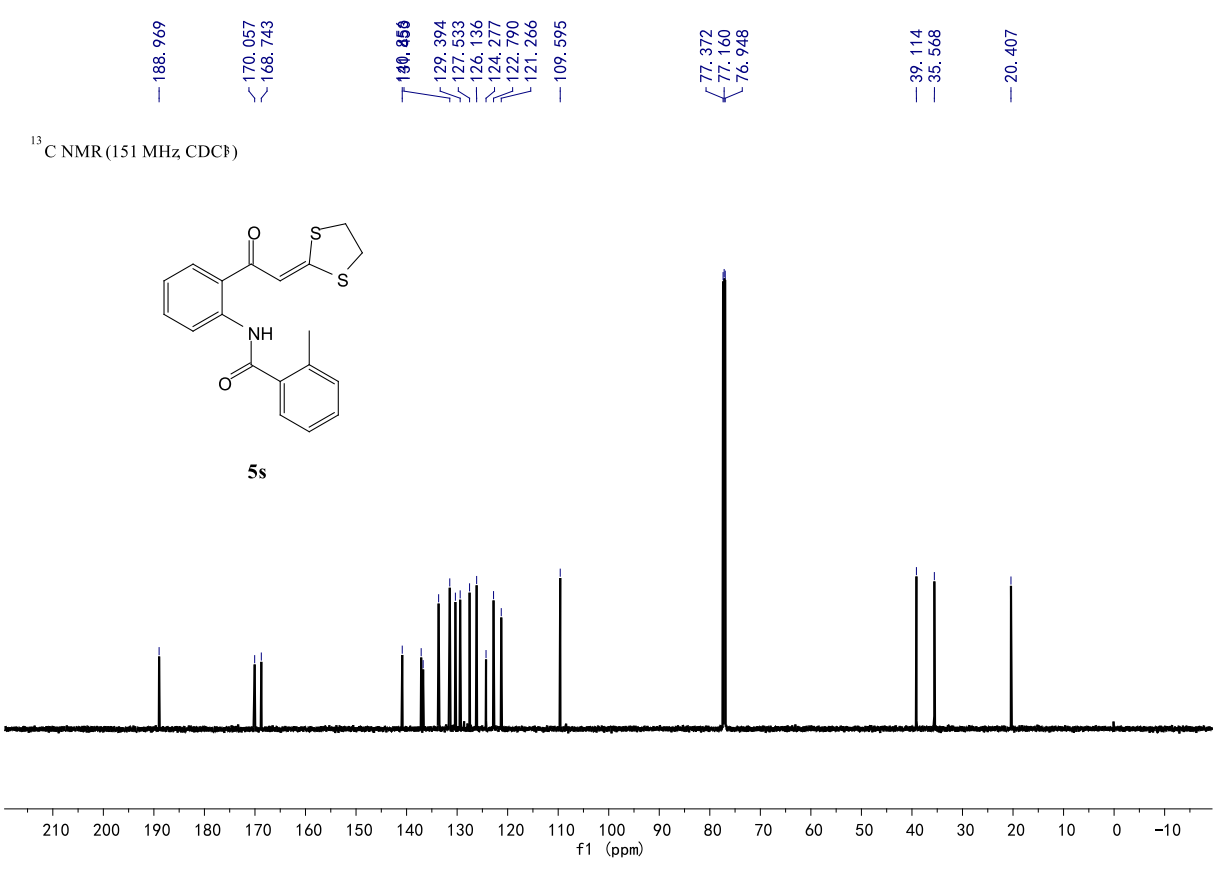

12.757
8.846
8.832
8.095
7.852
7.838
7.508
7.470
7.457
7.444
7.370
7.261
7.161
7.148
7.136
3.517
3.506
3.496
3.415
3.406
3.395
1H NMR (600 MHz, CDCl3)
O
S
S
NH
O
Cl
5r
1.00
1.00
1.00
1.00
1.00
2.00
1.01
1.00
1.00
2.00
2.00
4.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


189.066
170.944
164.451
140.839
131.823
130.080
129.407
128.211
125.471
123.961
122.953
121.212
109.337
77.372
77.160
76.949
39.174
35.616
13C NMR (151 MHz, CDCl3)
O
S
S
NH
O
Cl
5r
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



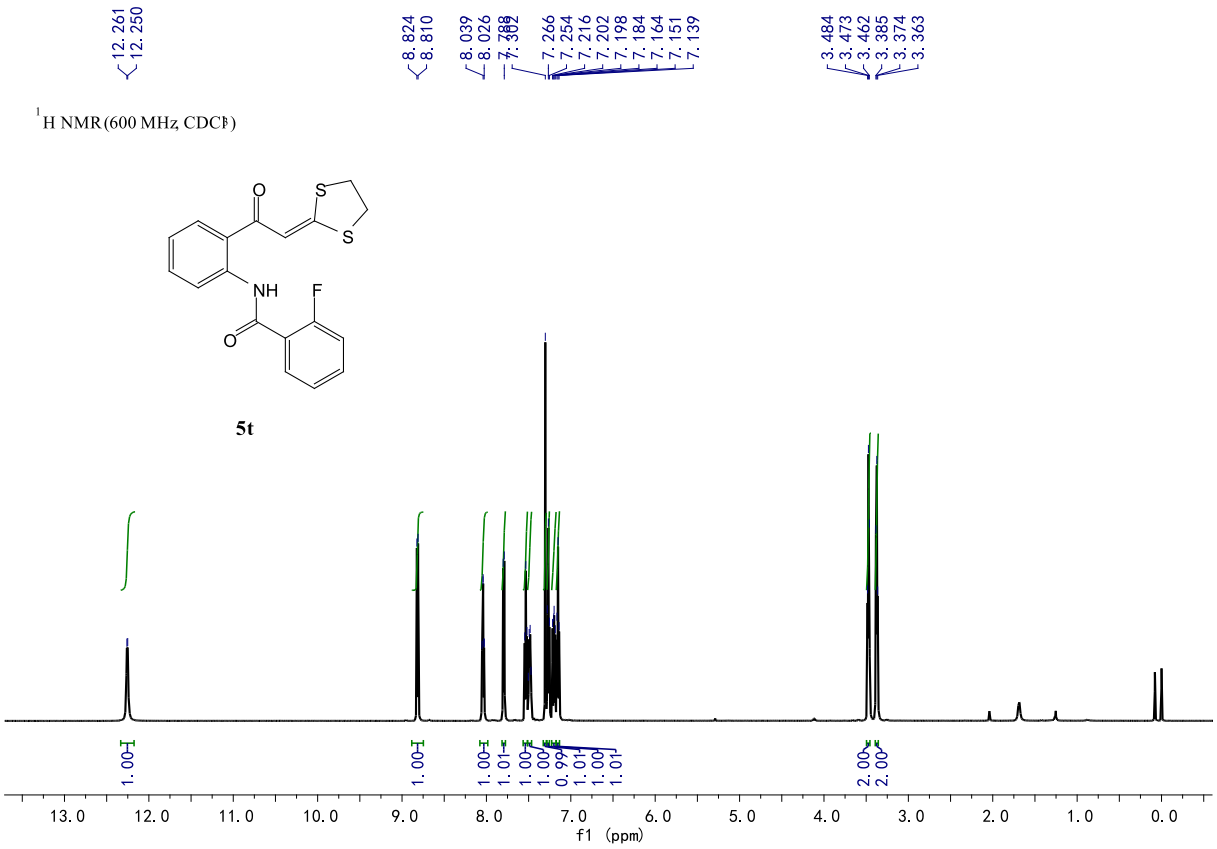
^{1}H NMR (600 MHz, CDCl$_3$)

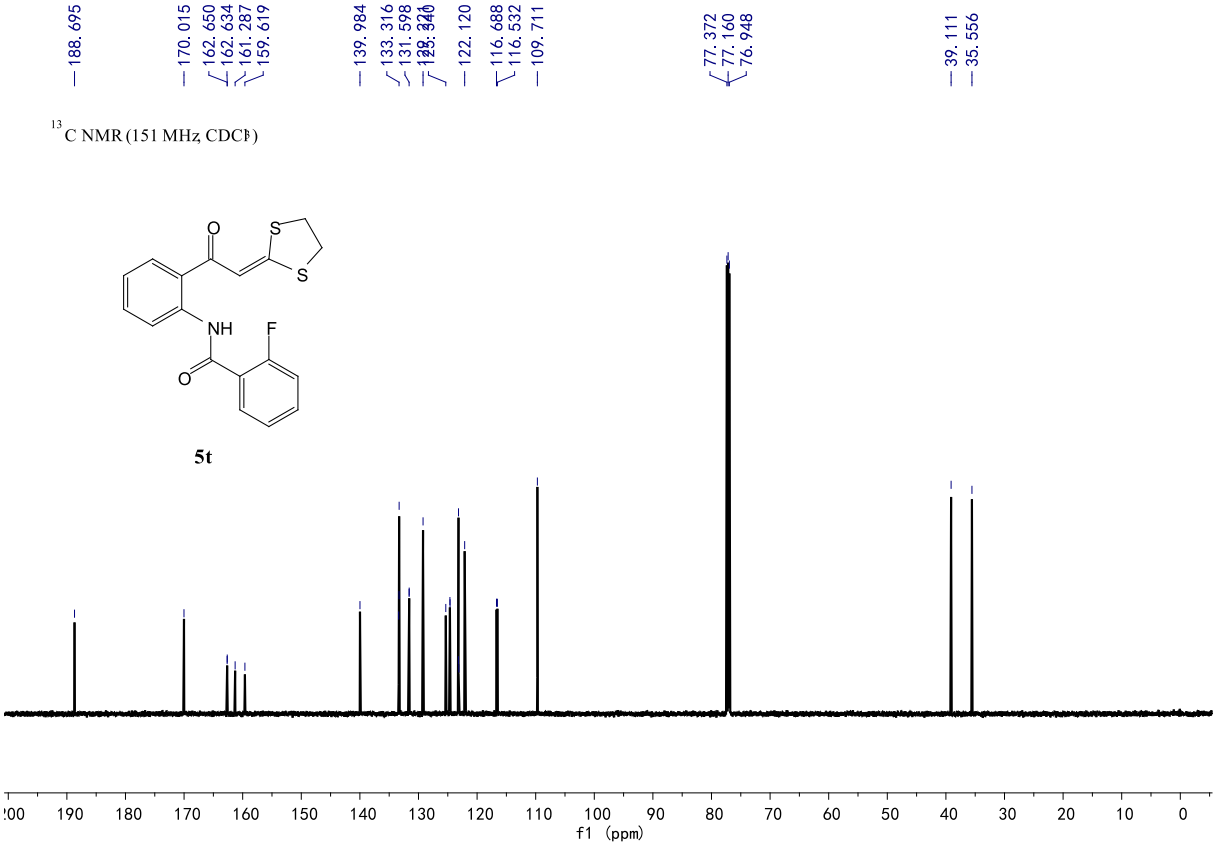
5s



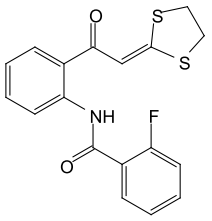
^{13}C NMR (151 MHz, CDCl$_3$)

5s


12.261
12.250
8.824
8.810
8.039
8.026
7.266
7.254
7.216
7.202
7.198
7.184
7.164
7.151
7.139
3.484
3.473
3.462
3.385
3.374
3.363
1H NMR (600 MHz, CDCl3)
O
S
S
NH
F
O
5t
1.00
1.00
1.00
1.01
1.00
0.99
1.01
1.00
1.01
2.00
2.00
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

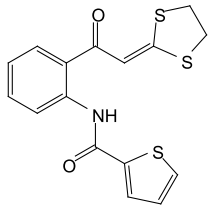

188.695
170.015
162.650
162.634
161.287
159.619
139.984
133.316
131.598
122.120
116.688
116.532
109.711
77.372
77.160
76.948
39.111
35.556
13C NMR (151 MHz, CDCl3)
O
S
S
NH
F
O
5t
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{19}F NMR (565 MHz, CDCl$_3$)

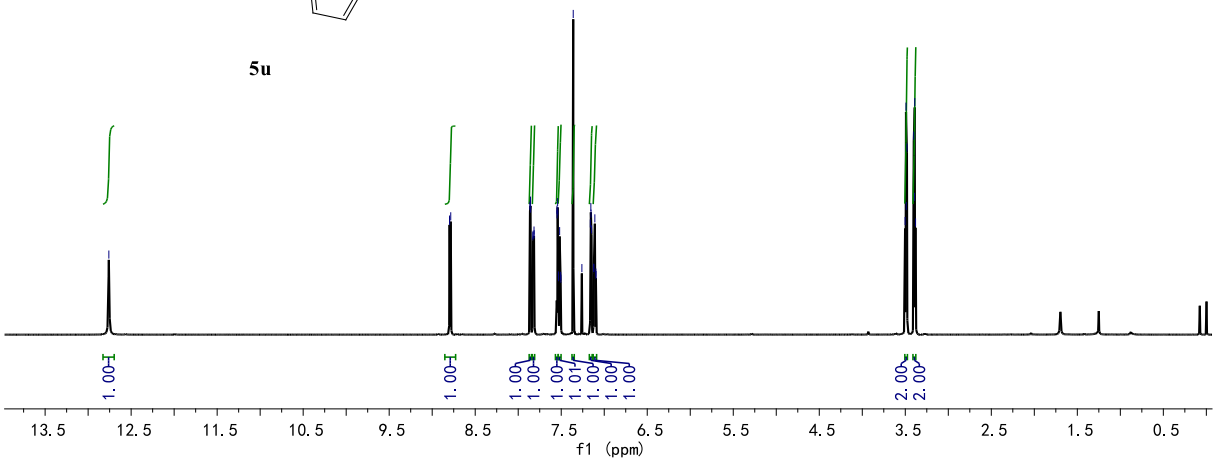


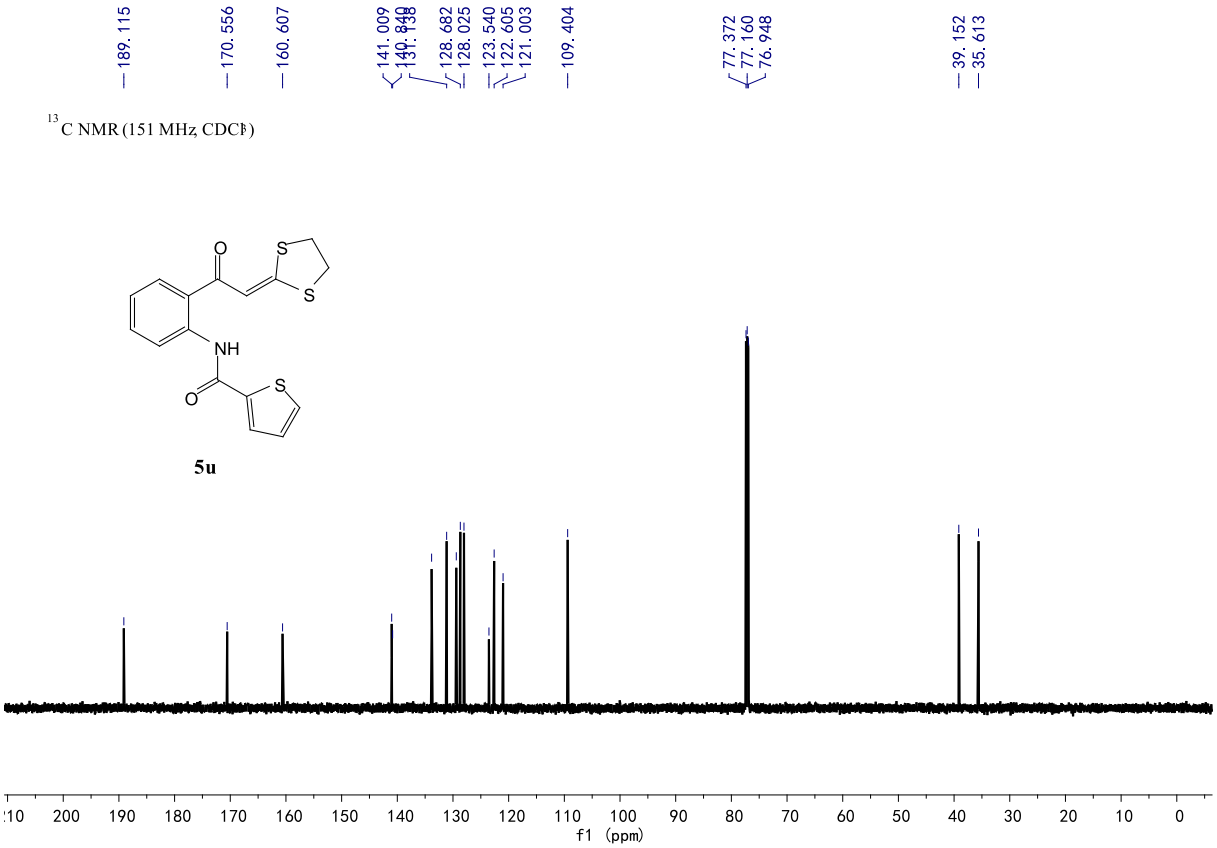
5t

^{1}H NMR (600 MHz, CDCl$_3$)

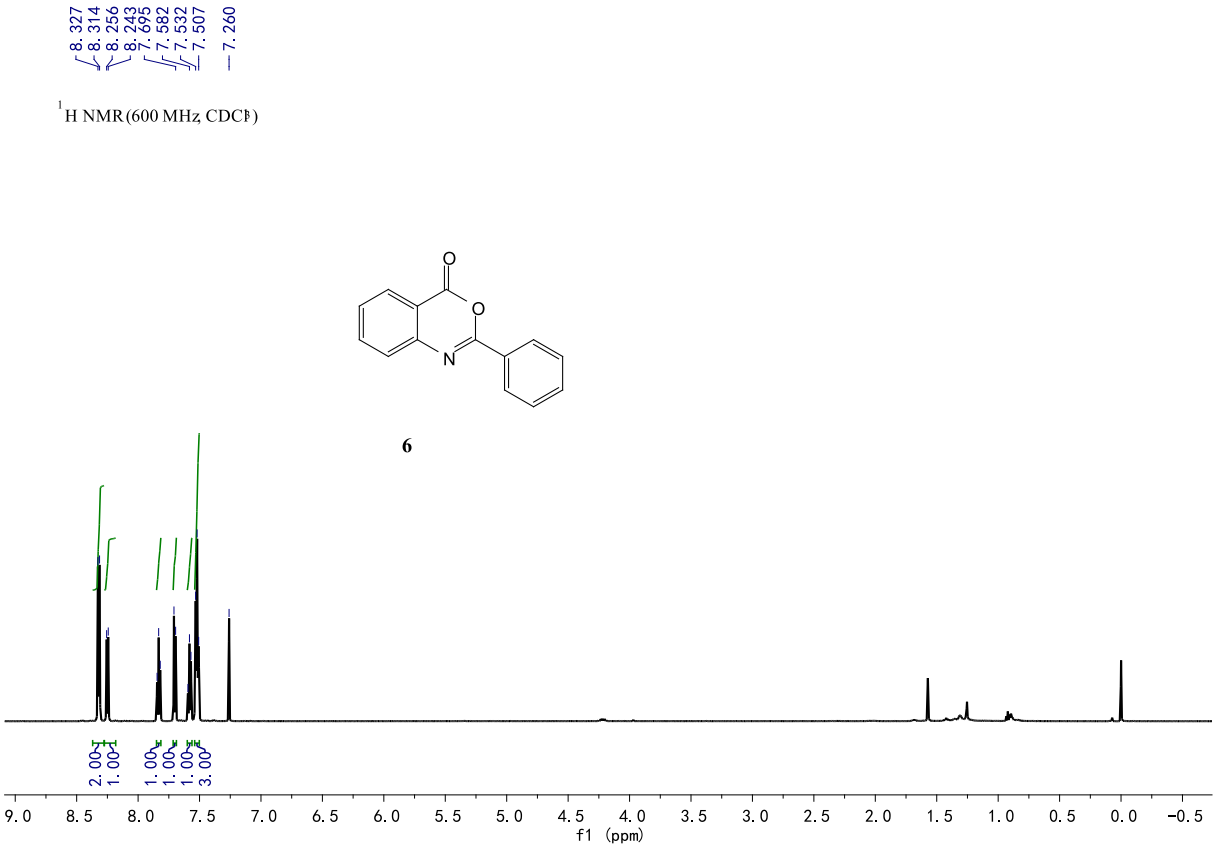


5u

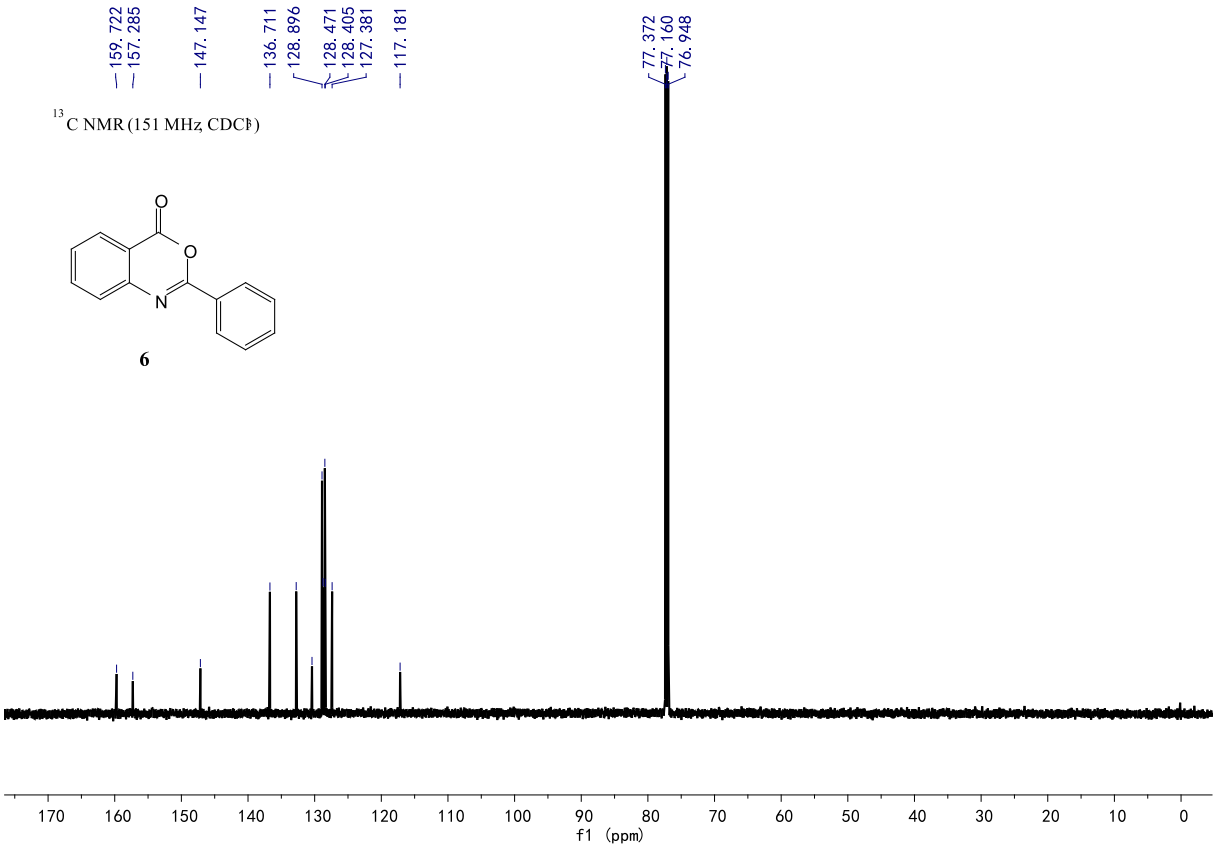


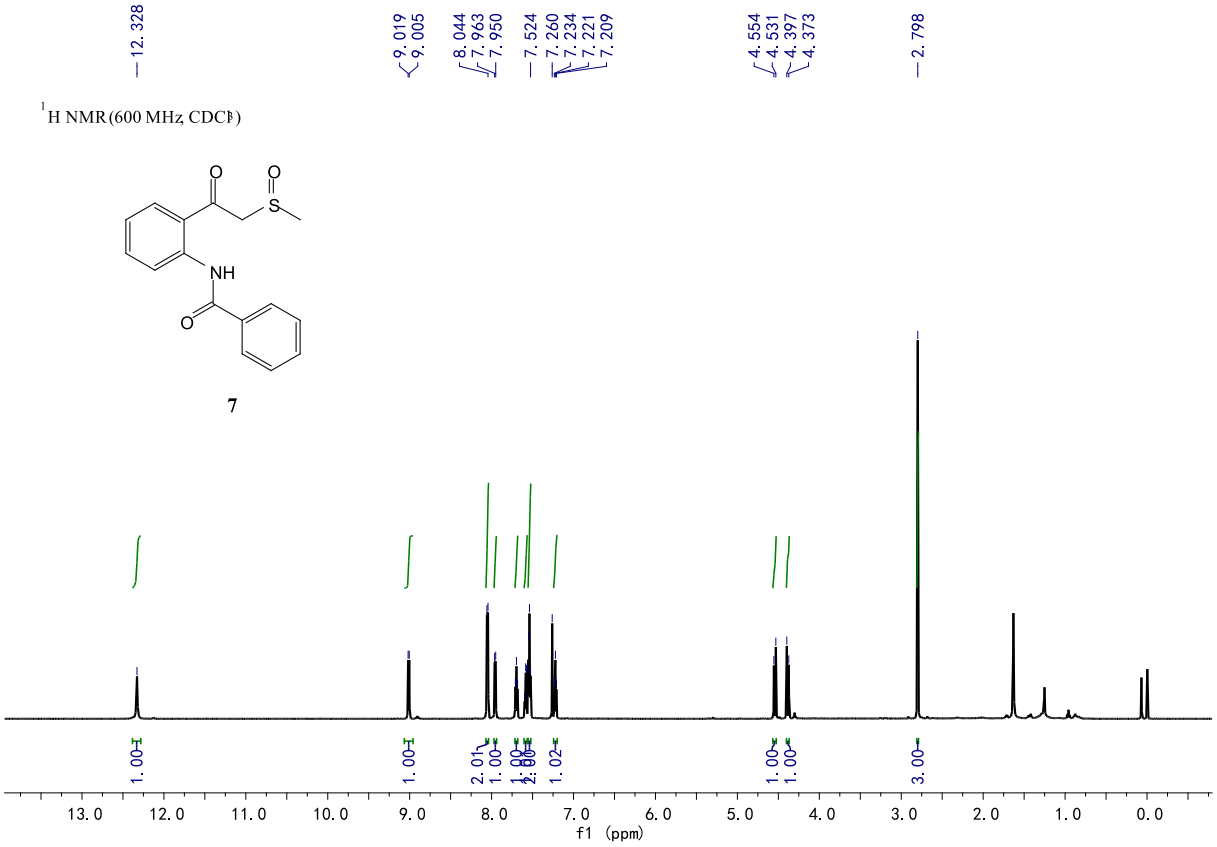


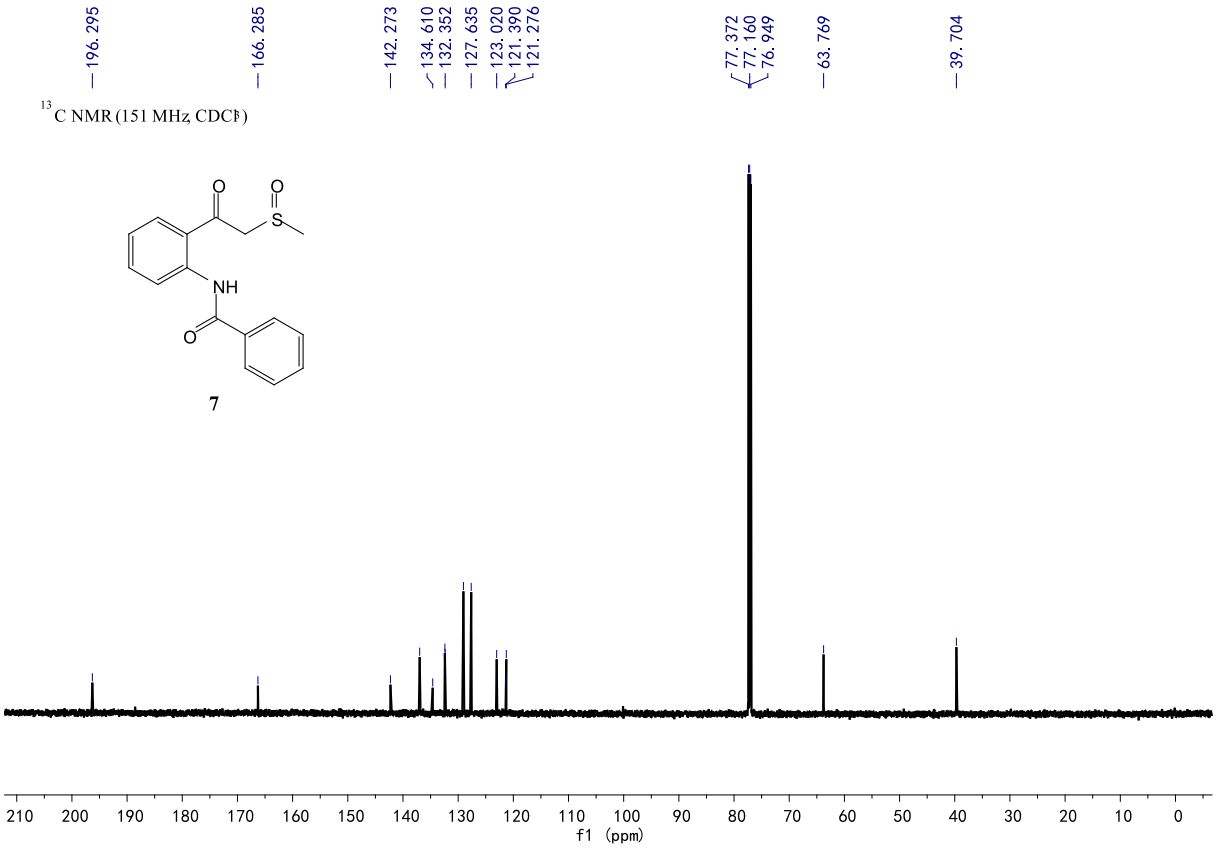
^{13}C NMR (151 MHz, CDCl$_3$)

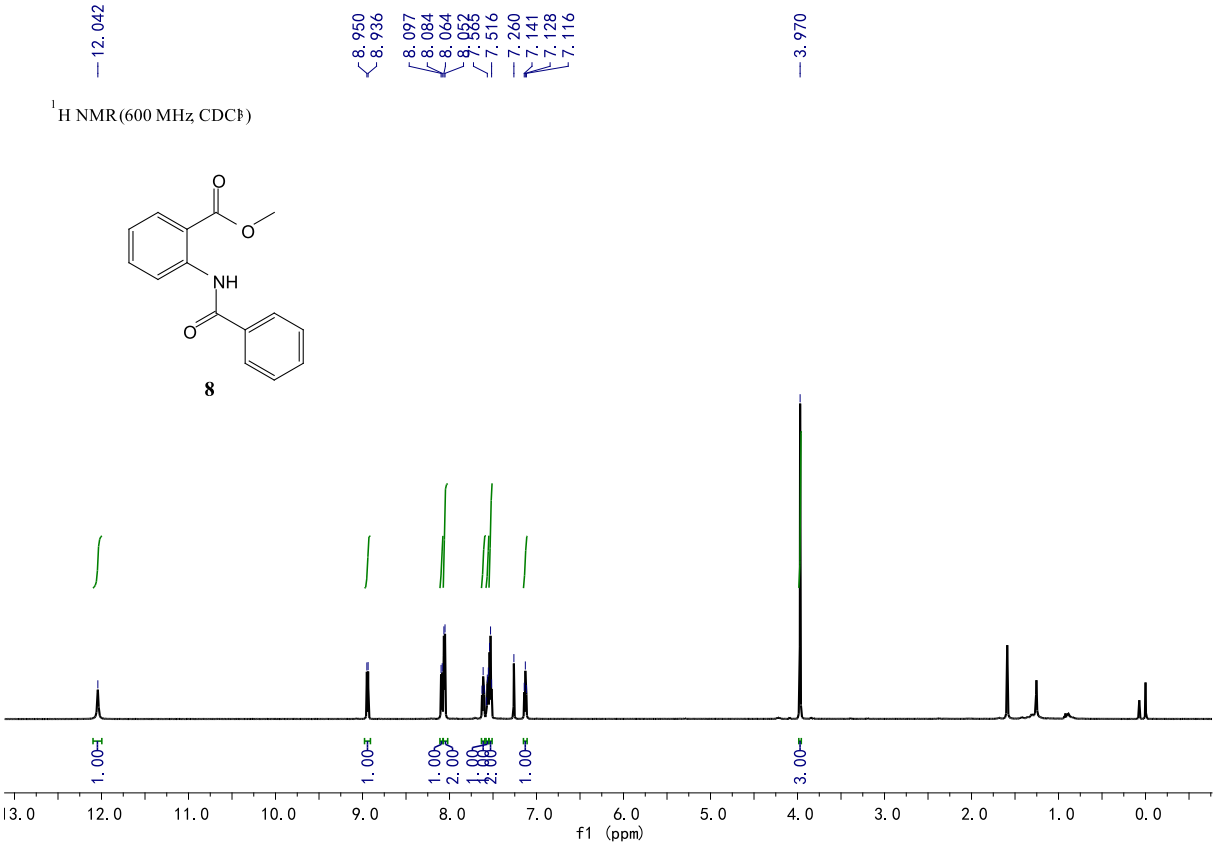


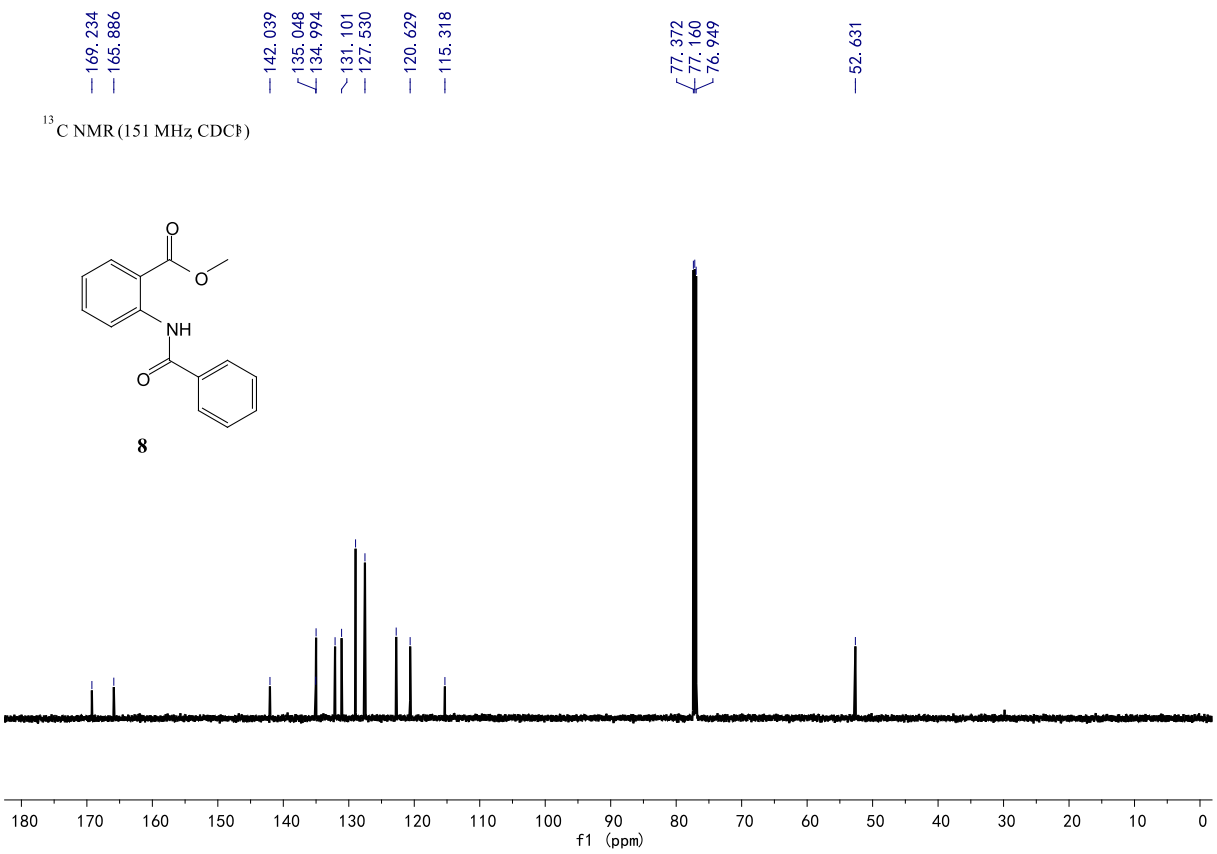
^{1}H NMR (600 MHz, CDCl$_3$)


159.722
157.285
147.147
136.711
128.896
128.471
128.405
127.381
117.181
77.372
77.160
76.948
13C NMR (151 MHz, CDCl3)
O
O
N
6
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


12.328
9.019
9.005
8.044
7.963
7.950
7.524
7.260
7.234
7.221
7.209
4.554
4.531
4.397
4.373
2.798
1H NMR (600 MHz, CDCl3)
O
O
S
NH
O
7
1.00
1.00
2.01
1.00
1.00
1.02
1.00
1.00
3.00
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


196.295
166.285
142.273
134.610
132.352
127.635
123.020
121.390
121.276
77.372
77.160
76.949
63.769
39.704
13C NMR (151 MHz, CDCl3)
O
O
S
NH
O
7
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


12.042
8.950
8.936
8.097
8.084
8.064
8.052
7.585
7.516
7.260
7.141
7.128
7.116
3.970
1H NMR (600 MHz, CDCl3)
O
O
NH
O
8
1.00
1.00
1.00
2.00
1.00
1.00
1.00
3.00
13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)



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[1] C. Zhou, F. Fang, Y. Cheng, Y. Li. H. Liu, Y. Zhou, *Adv. Synth. Catal.*, 2018, ***360(13)***, 2546.

[2] V. Bizet, L. Buglioni, C. Bolm, *Angew. Chem. Int. Ed.*, 2014, ***53(22)***, 5639.

[3] M. Wang, L. Kong, Q. Wu, X. Li, *Org. Lett.*, 2018, ***20(15)***, 4597.