

Supporting Information

Rhodium(III)-catalyzed C–H alkylation of arylhydrophthalazinediones with α -Cl ketones as a sp^3 -carbon alkylated agent

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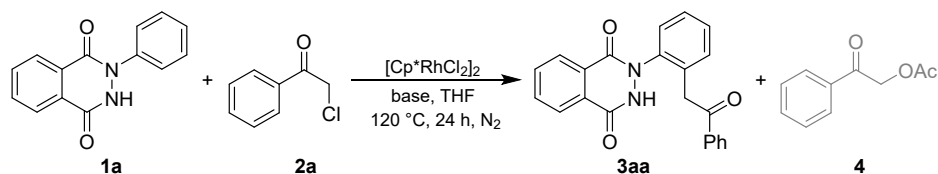
1. General Information

All reactions were carried out under air atmosphere unless otherwise noted. An aluminum heating block placed on a stirring plate was used as the heating source. Solvents were purified by standard techniques without special instructions. ^1H and ^{13}C NMR spectra were recorded on a Bruker AscendTM 500 M NMR Spectrometer (500 MHz for ^1H , 125 MHz for ^{13}C); DMSO- d_6 was used as the solvents. The chemical shifts are reported in ppm down field (δ), the coupling constants J are given in Hz. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. IR spectra were recorded on a SHIMADZU IRTracer-100 spectrometer. HRESIMS data were recorded on a Thermo Scientific Q Exactive (Thermo Fisher Scientific) mass spectrometry. TLC was carried out on SiO_2 (silica gel 60F₂₅₄, Merck), and the spots were located with UV light. Flash chromatography was carried out on SiO_2 (silica gel 60, 200-300 meth).

The starting materials **1**, **2** were synthesized according the previous literatures.^[1-2] **2d-2l**, and **2p** are commercially available.

2. Synthesis of Phthalazinediones

2.1 Optimized Bases of Reaction Conditions

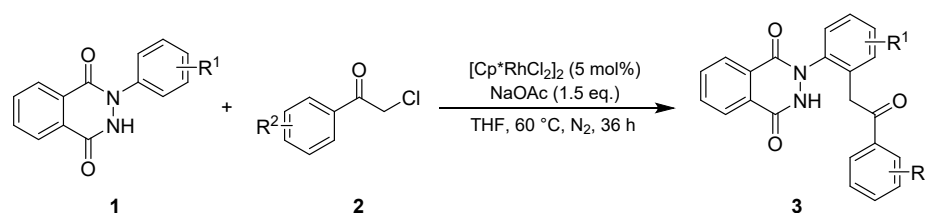


Entry	Base	3aa (%)	4 (%)
1	Na_2CO_3	nd	79
2	K_2CO_3	nd	85
3	NaHCO_3	nd	71
4	KHCO_3	nd	76
5	Na_3PO_4	nd	81
6	K_3PO_4	nd	86

7	K ₂ HPO ₄	nd	72
8	KH ₂ PO ₄	nd	75

^aReaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), [Cp*RhCl₂]₂ (5 mol%) and base (0.3 mmol, 1.5 eq.) in THF (1.0 mL) at 120 °C under N₂ for 24 h. Isolated yields. nd = not detected.

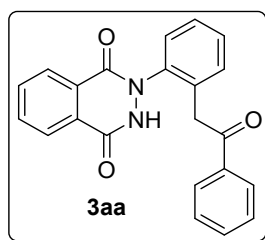
2.2 General Procedure for the Rh(III)-Catalyzed C–H Alkylation Reaction



A reaction flask was charged with a mixture of *N*-aryl phthalazinone (**1**) (0.2 mmol), α-Cl ketones (**2**) (0.4 mmol, 2.0 equiv.), [Cp*RhCl₂]₂ (6.2 mg, 0.01 mmol, 5 mol%), NaOAc (24.6 mg, 0.3 mmol, 1.5 equiv.), and THF (1.0 mL). The reaction mixture was stirred at 60 °C under N₂ atmosphere for 36 h. After the reaction mixture was cooled to room temperature, the solvent was removed under reduced pressure, and the residue was purified via silica gel chromatography (eluent: dichloromethane/ethyl acetate to petroleum ether/ethyl acetate) to give product **3**.

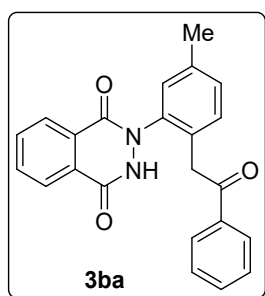
3. Characterization Data of Products

2-(2-(2-oxo-2-phenylethyl)phenyl)-2,3-dihydrophthalazine-1,4-dione (**3aa**)^[3]



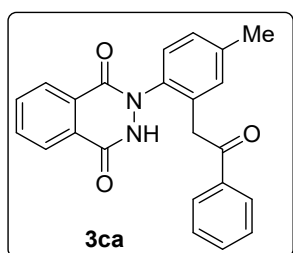
White solid (68.4 mg, 96% yield). Eluents for column chromatography: dichloromethane/ethyl acetate (24:1 v/v) to petroleum ether/ethyl acetate (10:1 v/v). ¹H NMR (DMSO-*d*₆, 500 MHz) δ 11.78 (s, 1H), 8.17 (d, *J* = 5.0 Hz, 1H), 7.91-7.90 (m, 2H), 7.87-7.83 (m, 1H), 7.73 (d, *J* = 10.0 Hz, 2H), 7.45-7.41 (m, 5H), 7.31-7.28 (m, 2H), 4.28 (s, 2H); ¹³C NMR (DMSO-*d*₆, 125 MHz) δ 197.0, 157.5, 136.6, 133.6, 133.1, 132.5, 131.6, 129.1, 128.6, 128.5, 128.1, 127.8, 126.8, 124.3, 41.2.

2-(5-methyl-2-(2-oxo-2-phenylethyl)phenyl)-2,3-dihydrophthalazine-1,4-dione (**3ba**)



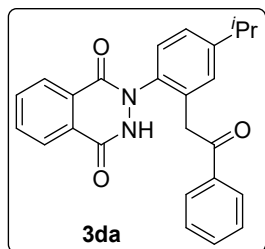
White solid (39.8 mg, 54% yield). Eluents for column chromatography: dichloromethane/ethyl acetate (45:1 v/v) to petroleum ether/ethyl acetate (10:1 v/v). ^1H NMR (DMSO- d_6 , 500 MHz) δ 11.79 (s, 1H), 8.19 (d, $J = 10.0$ Hz, 1H), 7.94-7.88 (m, 2H), 7.86-7.83 (m, 1H), 7.74 (d, $J = 10.0$ Hz, 2H), 7.44-7.41 (m, 1H), 7.32-7.27 (m, 3H), 7.23-7.21 (m, 2H), 4.24 (s, 2H), 2.32 (s, 3H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ 197.2, 157.4, 137.2, 136.6, 133.5, 133.0, 132.5, 131.3, 130.4, 129.2, 129.1, 128.9, 128.5, 128.2, 126.8, 124.3, 40.9, 20.6; IR (KBr): 3126, 3067, 1676, 1639, 1559, 1503, 1324, 1254, 1092, 692 (cm^{-1}); HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{18}\text{N}_2\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 393.1210; found: 393.1193.

2-(4-methyl-2-(2-oxo-2-phenylethyl)phenyl)-2,3-dihydrophthalazine-1,4-dione (3ca)^[3]



White solid (48.5 mg, 66% yield). Eluents for column chromatography: dichloromethane/ethyl acetate (24:1 v/v) to petroleum ether/ethyl acetate (10:1 v/v). ^1H NMR (DMSO- d_6 , 500 MHz) δ 11.76 (s, 1H), 8.16 (d, $J = 5.0$ Hz, 1H), 7.90-7.88 (m, 2H), 7.87-7.81 (m, 1H), 7.73-7.71 (m, 2H), 7.43-7.41 (m, 1H), 7.30-7.27 (m, 3H), 7.22-7.18 (m, 2H), 4.22 (s, 2H), 2.35 (s, 3H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ 197.1, 157.5, 150.6, 137.7, 136.6, 133.5, 133.2, 133.0, 132.4, 131.9, 129.1, 129.0, 128.5, 128.3, 128.3, 128.1, 126.8, 125.9, 124.3, 41.1, 20.9.

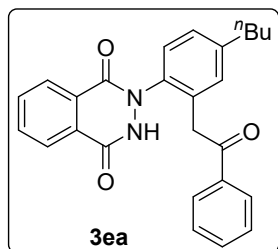
2-(4-isopropyl-2-(2-oxo-2-phenylethyl)phenyl)-2,3-dihydrophthalazine-1,4-dione (3da)



White solid (56.3 mg, 71% yield). Eluents for column chromatography: dichloromethane/ethyl acetate (45:1 v/v) to petroleum ether/ethyl acetate (10:1 v/v). ^1H NMR (DMSO- d_6 , 500 MHz) δ 11.74 (s, 1H), 8.16 (d, $J = 5.0$ Hz, 1H), 7.90-7.86 (m, 2H), 7.84-7.81 (m, 1H), 7.72-7.71 (m, 2H), 7.42-7.39 (m, 1H), 7.31-7.24 (m, 5H), 4.26 (s, 2H), 3.00-2.88 (m, 1H), 1.23 (d, $J = 5.0$ Hz, 6H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ 197.1, 157.5, 148.6, 136.7, 133.5, 133.3, 133.0, 132.4, 129.6, 129.2,

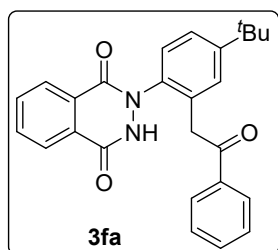
128.5, 128.4, 128.1, 126.8, 125.5, 124.3, 41.3, 33.4, 24.1; IR (KBr): 3064, 2958, 1680, 1643, 1588, 1500, 1327, 1269, 1210, 688 (cm⁻¹); HRMS (ESI) m/z calcd for C₂₅H₂₂N₂O₃Na [M+Na]⁺: 421.1523; found: 421.1508.

2-(4-butyl-2-(2-oxo-2-phenylethyl)phenyl)-2,3-dihydrophthalazine-1,4-dione (3ea)



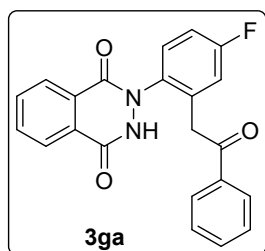
White solid (64.2 mg, 78% yield). Eluents for column chromatography: dichloromethane/ethyl acetate (24:1 v/v) to petroleum ether/ethyl acetate (10:1 v/v). ¹H NMR (DMSO-*d*₆, 500 MHz) δ 11.76 (s, 1H), 8.17 (d, *J* = 5.0 Hz, 1H), 7.92-7.86 (m, 2H), 7.85-7.82 (m, 1H), 7.72 (d, *J* = 10.0 Hz, 2H), 7.43-7.40 (m, 1H), 7.29-7.26 (m, 3H), 7.23 (s, 1H), 7.20 (d, *J* = 5.0 Hz, 1H), 4.24 (s, 2H), 2.62 (t, *J* = 5.0 Hz, 2H), 1.59-1.53 (m, 2H), 1.32-1.24 (m, 2H), 0.89 (t, *J* = 10.0 Hz, 3H); ¹³C NMR (DMSO-*d*₆, 125 MHz) δ 197.1, 157.5, 142.5, 136.6, 133.5, 133.2, 133.0, 132.4, 131.4, 129.2, 128.5, 128.4, 128.3, 128.1, 127.6, 126.8, 125.9, 124.3, 41.3, 34.6, 33.2, 21.8, 14.0; IR (KBr): 3134, 2961, 2928, 1683, 1639, 1573, 1364, 1324, 1254, 692 (cm⁻¹); HRMS (ESI) m/z calcd for C₂₆H₂₄N₂O₃Na [M+Na]⁺: 435.1679; found: 435.1665.

2-(4-(tert-butyl)-2-(2-oxo-2-phenylethyl)phenyl)-2,3-dihydrophthalazine-1,4-dione (3fa)



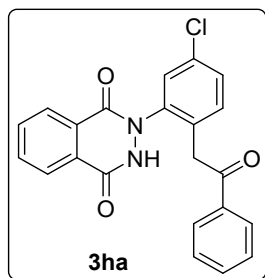
White solid (63.8 mg, 77% yield). Eluents for column chromatography: dichloromethane/ethyl acetate (24:1 v/v) to petroleum ether/ethyl acetate (10:1 v/v). ¹H NMR (DMSO-*d*₆, 500 MHz) δ 11.69 (s, 1H), 8.16 (d, *J* = 10.0 Hz, 1H), 7.93-7.89 (m, 2H), 7.86-7.82 (m, 1H), 7.73 (d, *J* = 5.0 Hz, 2H), 7.47-7.40 (m, 3H), 7.31-7.27 (m, 3H), 4.29 (s, 2H), 1.32 (s, 9H); ¹³C NMR (DMSO-*d*₆, 125 MHz) δ 197.1, 136.7, 133.4, 133.0, 132.4, 129.1, 128.6, 128.5, 128.1, 128.0, 126.8, 124.5, 41.5, 34.6, 31.3; IR (KBr): 3310, 2958, 1676, 1654, 1592, 1500, 1349, 1254, 1221, 692 (cm⁻¹); HRMS (ESI) m/z calcd for C₂₆H₂₄N₂O₃Na [M+Na]⁺: 435.1679; found: 435.1667.

2-(4-fluoro-2-(2-oxo-2-phenylethyl)phenyl)-2,3-dihydrophthalazine-1,4-dione (3ga)^[3]



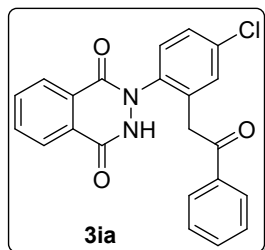
White solid (54.0 mg, 72% yield). Eluents for column chromatography: dichloromethane/ethyl acetate (45:1 v/v) to petroleum ether/ethyl acetate (10:1 v/v). ^1H NMR (DMSO- d_6 , 500 MHz) δ 11.80 (s, 1H), 8.15 (d, $J = 10.0$ Hz, 1H), 7.92-7.89 (m, 2H), 7.86-7.83 (m, 1H), 7.75 (d, $J = 5.0$ Hz, 2H), 7.49-7.44 (m, 2H), 7.35-7.24 (m, 4H), 4.32 (s, 2H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ 196.3, 161.0 (d, $^1J_{\text{C-F}} = 243.8$ Hz), 157.6, 150.7, 136.5, 136.2 (d, $^3J_{\text{C-F}} = 8.8$ Hz), 133.6, 133.2, 132.5, 130.5 (d, $^3J_{\text{C-F}} = 7.5$ Hz), 129.0, 128.6, 128.1, 126.8, 124.3 (d, $^4J_{\text{C-F}} = 2.5$ Hz), 118.3 (d, $^2J_{\text{C-F}} = 22.5$ Hz), 114.5 (d, $^2J_{\text{C-F}} = 22.5$ Hz), 40.9.

2-(3-chloro-2-(2-oxo-2-phenylethyl)phenyl)-2,3-dihydrophthalazine-1,4-dione (3ha)



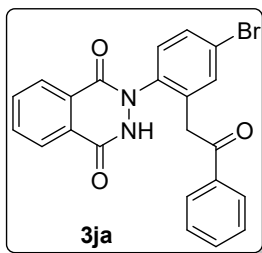
White solid (67.6 mg, 86% yield). Eluents for column chromatography: dichloromethane/ethyl acetate (45:1 v/v) to petroleum ether/ethyl acetate (10:1 v/v). ^1H NMR (DMSO- d_6 , 500 MHz) δ 11.82 (s, 1H), 8.16 (d, $J = 10.0$ Hz, 1H), 7.91-7.82 (m, 3H), 7.74 (d, $J = 5.0$ Hz, 2H), 7.57 (s, 1H), 7.51-7.43 (m, 3H), 7.32-7.29 (m, 2H), 4.33 (s, 2H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ 196.6, 157.6, 150.9, 142.2, 136.5, 133.7, 133.4, 133.2, 132.7, 132.5, 131.6, 129.0, 128.6, 128.6, 128.3, 128.1, 126.8, 125.0, 124.4, 40.7; IR (KBr): 3064, 2961, 1694, 1588, 1489, 1320, 1276, 993, 784, 692 (cm^{-1}); HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{14}\text{ClN}_2\text{O}_3^-$ [M-H^-]: 389.0698; found: 389.0699.

2-(4-chloro-2-(2-oxo-2-phenylethyl)phenyl)-2,3-dihydrophthalazine-1,4-dione (3ia)^[3]



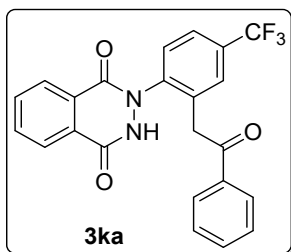
White solid (54.9 mg, 70% yield). Eluents for column chromatography: dichloromethane/ethyl acetate (45:1 v/v) to petroleum ether/ethyl acetate (10:1 v/v). ^1H NMR (DMSO- d_6 , 500 MHz) δ 8.14 (d, $J = 5.0$ Hz, 1H), 7.91-7.89 (m, 2H), 7.86-7.82 (m, 1H), 7.74 (d, $J = 5.0$ Hz, 2H), 7.56 (s, 1H), 7.49-7.44 (m, 3H), 7.32-7.29 (m, 2H), 4.33 (s, 2H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ 196.3, 136.5, 133.6, 133.2, 132.5, 131.5, 130.3, 128.9, 128.6, 128.0, 127.7, 126.8, 40.7.

2-(4-bromo-2-(2-oxo-2-phenylethyl)phenyl)-2,3-dihydrophthalazine-1,4-dione (3ja)^[3]



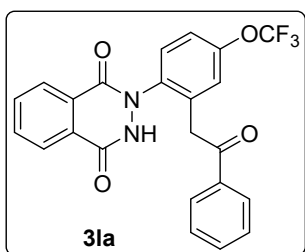
White solid (83.1 mg, 95% yield). Eluents for column chromatography: dichloromethane/ethyl acetate (24:1 v/v) to petroleum ether/ethyl acetate (10:1 v/v). ^1H NMR (DMSO- d_6 , 500 MHz) δ 11.84 (s, 1H), 8.14 (d, $J = 10.0$ Hz, 1H), 7.88-7.82 (m, 3H), 7.74-7.70 (m, 3H), 7.61 (d, $J = 5.0$ Hz, 1H), 7.45-7.40 (m, 2H), 7.31-7.28 (m, 2H), 4.35 (s, 2H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ 196.7, 157.8, 151.1, 140.8, 136.8, 136.5, 134.8, 133.9, 133.5, 132.8, 130.9, 129.3, 128.9, 128.3, 127.1, 125.2, 124.6, 121.3, 41.0.

2-(2-(2-oxo-2-phenylethyl)-4-(trifluoromethyl)phenyl)-2,3-dihydrophthalazine-1,4-dione (3ka)



White solid (77.8 mg, 92% yield). Eluents for column chromatography: dichloromethane/ethyl acetate (45:1 v/v) to petroleum ether/ethyl acetate (10:1 v/v). ^1H NMR (DMSO- d_6 , 500 MHz) δ 11.93 (s, 1H), 8.14 (d, $J = 5.0$ Hz, 1H), 7.97-7.94 (m, 1H), 7.90-7.89 (m, 3H), 7.86-7.82 (m, 1H), 7.80-7.78 (m, 1H), 7.75-7.74 (m, 1H), 7.69-7.68 (m, 1H), 7.51-7.43 (m, 1H), 7.32-7.29 (m, 2H), 4.47 (s, 2H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ 196.3, 167.6, 157.5, 151.0, 144.5, 136.5, 135.0, 133.8, 133.2, 133.1, 132.6, 129.6, 129.5, 129.1 (d, $^4J_{\text{C-F}} = 3.8$ Hz), 128.9, 128.8, 128.6, 128.0, 126.8, 124.7 (d, $^4J_{\text{C-F}} = 3.8$ Hz), 124.4, 123.2, 40.9; IR (KBr): 3189, 1661, 1592, 1423, 1334, 1294, 1155, 1118, 920, 688 (cm^{-1}); HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{15}\text{F}_3\text{N}_2\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 447.0927; found: 447.0916.

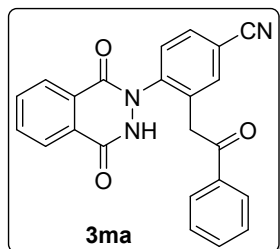
2-(2-(2-oxo-2-phenylethyl)-4-(trifluoromethoxy)phenyl)-2,3-dihydrophthalazine-1,4-dione (3la)



White solid (77.1 mg, 88% yield). Eluents for column chromatography: dichloromethane/ethyl acetate (45:1 v/v) to petroleum ether/ethyl acetate (10:1 v/v). ^1H NMR (DMSO- d_6 , 500 MHz) δ 11.83 (s, 1H), 8.15 (d, $J = 10.0$ Hz, 1H), 7.90-7.82 (m, 3H), 7.75 (d, $J = 10.0$ Hz, 2H), 7.59 (d, $J = 5.0$ Hz, 1H), 7.53 (s, 1H), 7.47-7.42 (m, 2H), 7.32-7.29 (m, 2H), 4.40 (s, 2H); ^{13}C NMR (125 MHz,

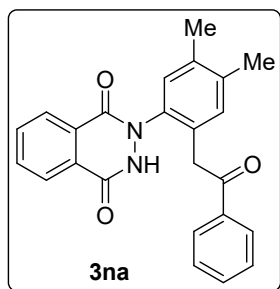
DMSO-*d*₆) δ 196.3, 157.7, 151.0, 147.6, 140.2, 136.5, 136.2, 133.7, 133.3, 132.6, 130.5, 129.5, 129.0, 128.8, 128.6, 128.1, 126.8, 125.0, 124.4 (d, $^3J_{C-F}$ = 3.8 Hz), 121.4, 120.3, 119.3, 40.9; IR (KBr): 3200, 2954, 2924, 1658, 1595, 1496, 1283, 1199, 1155, 688 (cm⁻¹); HRMS (ESI) *m/z* calcd for C₂₃H₁₅F₃N₂O₄Na [M+Na]⁺: 463.0876; found: 463.0864.

4-(1,4-dioxo-3,4-dihydrophthalazin-2(1H)-yl)-3-(2-oxo-2-phenylethyl)benzonitrile (3ma)



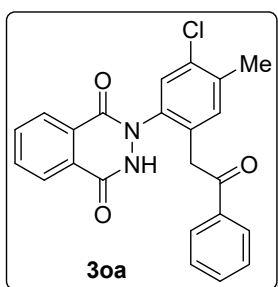
White solid (55.3 mg, 73% yield). Eluents for column chromatography: dichloromethane/ethyl acetate (24:1 v/v) to petroleum ether/ethyl acetate (10:1 v/v). ¹H NMR (DMSO-*d*₆, 500 MHz) δ 11.91 (s, 1H), 8.13 (d, J = 10.0 Hz, 1H), 7.99 (s, 1H), 7.92-7.89 (m, 3H), 7.85-7.81 (m, 1H), 7.76 (d, J = 5.0 Hz, 2H), 7.69 (d, J = 5.0 Hz, 1H), 7.47-7.44 (m, 1H), 7.33-7.30 (m, 2H), 4.44 (s, 2H); ¹³C NMR (DMSO-*d*₆, 125 MHz) δ 196.1, 157.5, 151.1, 145.2, 136.4, 136.1, 135.3, 133.8, 133.3, 132.6, 131.7, 129.9, 128.9, 128.6, 128.0, 126.8, 124.9, 124.4, 118.6, 110.9, 40.8; IR (KBr): 3064, 2234, 1691, 1588, 1551, 1493, 1364, 1338, 1217, 688 (cm⁻¹); HRMS (ESI) *m/z* calcd for C₂₃H₁₅N₃O₃Na [M+Na]⁺: 404.1006; found: 404.0992.

2-(3,4-dimethyl-2-(2-oxo-2-phenylethyl)phenyl)-2,3-dihydrophthalazine-1,4-dione (3na)^[3]



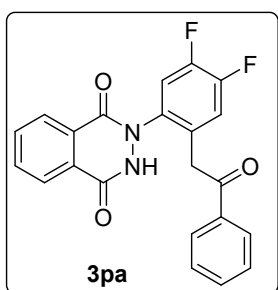
White solid (36.8 mg, 48% yield). Eluents for column chromatography: dichloromethane/ethyl acetate (45:1 v/v) to petroleum ether/ethyl acetate (10:1 v/v). ¹H NMR (DMSO-*d*₆, 500 MHz) δ 11.71 (s, 1H), 8.16 (d, J = 10.0 Hz, 1H), 7.91-7.90 (m, 2H), 7.86-7.83 (m, 1H), 7.73 (d, J = 5.0 Hz, 2H), 7.45-7.42 (m, 1H), 7.31-7.28 (m, 2H), 7.17 (s, 2H), 4.18 (s, 2H), 2.26 (s, 3H), 2.23 (s, 3H); ¹³C NMR (DMSO-*d*₆, 125 MHz) δ 197.2, 157.5, 136.6, 136.4, 135.7, 133.4, 133.0, 132.4, 132.2, 130.4, 129.5, 129.2, 129.2, 128.8, 128.5, 128.1, 126.8, 124.3, 40.8, 19.3, 19.0.

2-(3-chloro-4-methyl-2-(2-oxo-2-phenylethyl)phenyl)-2,3-dihydrophthalazine-1,4-dione (3oa)^[3]



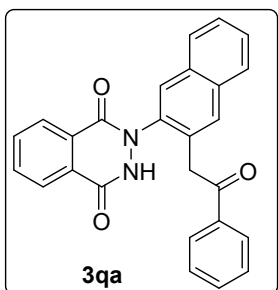
White solid (73.1 mg, 90% yield). Eluents for column chromatography: dichloromethane/ethyl acetate (45:1 v/v) to petroleum ether/ethyl acetate (10:1 v/v). ^1H NMR (DMSO- d_6 , 500 MHz) δ 11.80 (s, 1H), 8.14 (d, $J = 5.0$ Hz, 1H), 7.89-7.88 (m, 2H), 7.85-7.81 (m, 1H), 7.73-7.72 (m, 2H), 7.52-7.48 (m, 1H), 7.45-7.42 (m, 2H), 7.31-7.28 (m, 2H), 4.26 (s, 2H), 2.38 (s, 3H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ 196.7, 167.5, 157.5, 150.7, 139.8, 136.5, 135.5, 134.0, 133.6, 133.2, 133.1, 132.5, 131.6, 129.5, 129.0, 128.8, 128.7, 128.6, 128.1, 126.8, 124.4, 40.6, 19.5.

2-(3,4-difluoro-2-(2-oxo-2-phenylethyl)phenyl)-2,3-dihydrophthalazine-1,4-dione (3pa)



White solid (46.5 mg, 62% yield). Eluents for column chromatography: dichloromethane/ethyl acetate (45:1 v/v) to petroleum ether/ethyl acetate (10:1 v/v). ^1H NMR (DMSO- d_6 , 500 MHz) δ 11.86 (s, 1H), 8.13 (d, $J = 10.0$ Hz, 1H), 7.91 (d, $J = 5.0$ Hz, 2H), 7.86-7.82 (m, 3H), 7.56-7.49 (m, 2H), 7.38-7.35 (m, 3H), 4.39 (s, 2H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ 194.8, 157.8, 136.3, 133.8, 133.4, 132.6, 129.0, 128.7, 128.2, 126.8, 125.1, 124.4, 116.1 (d, $^3J_{\text{C-F}} = 16.3$ Hz), 35.4; IR (KBr): 3064, 1665, 1595, 1500, 1298, 1225, 1092, 1019, 813, 688 (cm^{-1}); HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{14}\text{F}_2\text{N}_2\text{O}_3\text{Na}$ [$\text{M}+\text{Na}$] $^+$: 415.0865; found: 415.0851.

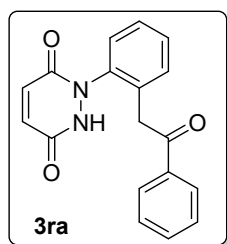
2-(3-(2-oxo-2-phenylethyl)naphthalen-2-yl)-2,3-dihydrophthalazine-1,4-dione (3qa)



White solid (57.2 mg, 70% yield). Eluents for column chromatography: dichloromethane/ethyl acetate (45:1 v/v) to petroleum ether/ethyl acetate (10:1 v/v). ^1H NMR (DMSO- d_6 , 500 MHz) δ 11.82 (s, 1H), 8.19 (d, $J = 5.0$ Hz, 1H), 8.03-7.85 (m, 7H), 7.75 (d, $J = 10.0$ Hz, 2H), 7.60-7.54 (m, 2H), 7.42-7.39 (m, 1H), 7.29-7.26 (m, 2H), 4.46 (s, 2H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ 197.4, 136.9, 133.9, 133.3, 132.9, 132.8, 132.6, 132.3, 130.6, 129.4, 128.8, 128.4, 128.1, 127.7, 127.6,

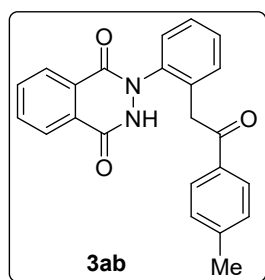
127.4, 127.0, 126.8, 41.7; IR (KBr): 3123, 1665, 1592, 1503, 1298, 1265, 1195, 1092, 898, 688 (cm⁻¹); HRMS (ESI) m/z calcd for C₂₆H₁₈N₂O₃Na [M+Na]⁺: 429.1210; found: 429.1198.

1-(2-(2-oxo-2-phenylethyl)phenyl)-1,2-dihydropyridazine-3,6-dione (3ra)



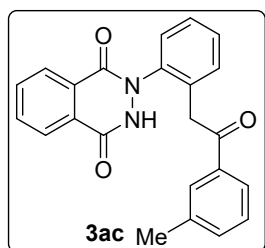
White solid (40.6 mg, 66% yield). Eluents for column chromatography: dichloromethane/ethyl acetate (45:1 v/v) to petroleum ether/ethyl acetate (10:1 v/v). ¹H NMR (DMSO-*d*₆, 500 MHz) δ 11.27 (s, 1H), 7.83 (d, *J* = 10.0 Hz, 2H), 7.58 (s, 1H), 7.47-7.32 (m, 6H), 7.04-7.02 (m, 1H), 6.88-6.86 (m, 1H), 4.25 (s, 2H); ¹³C NMR (DMSO-*d*₆, 125 MHz) δ 197.0, 158.1, 153.2, 141.2, 136.9, 133.9, 133.6, 133.2, 131.9, 129.1, 128.9, 128.5, 128.4, 128.2, 128.0, 41.5; IR (KBr): 3075, 2924, 2598, 1680, 1588, 1515, 1269, 839, 754, 688 (cm⁻¹); HRMS (ESI) m/z calcd for C₁₈H₁₄N₂O₃Na [M+Na]⁺: 329.0897; found: 329.0889.

2-(2-(2-oxo-2-(*p*-tolyl)ethyl)phenyl)-2,3-dihydrophthalazine-1,4-dione (3ab)^[3]



White solid (56.9 mg, 77% yield). Eluents for column chromatography: dichloromethane/ethyl acetate (24:1 v/v) to petroleum ether/ethyl acetate (10:1 v/v). ¹H NMR (DMSO-*d*₆, 500 MHz) δ 11.78 (s, 1H), 8.15 (d, *J* = 10.0 Hz, 1H), 7.89-7.87 (m, 2H), 7.85-7.82 (m, 1H), 7.60 (d, *J* = 10.0 Hz, 2H), 7.44-7.39 (m, 4H), 7.04 (d, *J* = 10.0 Hz, 2H), 4.24 (s, 2H), 2.20 (s, 3H); ¹³C NMR (DMSO-*d*₆, 125 MHz) δ 196.6, 157.5, 150.6, 143.4, 141.0, 134.2, 133.9, 133.4, 132.4, 131.6, 129.1, 129.0, 128.6, 128.5, 128.2, 127.7, 126.8, 126.2, 124.9, 41.0, 21.2.

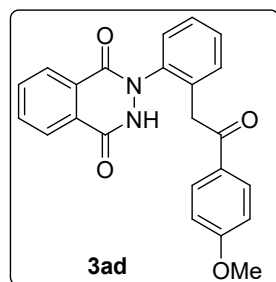
2-(2-(2-oxo-2-(*m*-tolyl)ethyl)phenyl)-2,3-dihydrophthalazine-1,4-dione (3ac)^[3]



White solid (59.0 mg, 80% yield). Eluents for column chromatography: dichloromethane/ethyl acetate (45:1 v/v) to petroleum ether/ethyl acetate (10:1 v/v). ¹H NMR (DMSO-*d*₆, 500 MHz) δ 11.79 (s, 1H), 8.18 (d, *J* = 10.0 Hz, 1H), 7.91-7.85 (m, 3H), 7.54-7.42 (m, 6H), 7.22-7.5 (m, 2H), 4.27 (s, 2H), 2.18 (s, 3H); ¹³C NMR (DMSO-*d*₆, 125 MHz) δ 197.3, 157.5, 141.0, 137.9, 136.7,

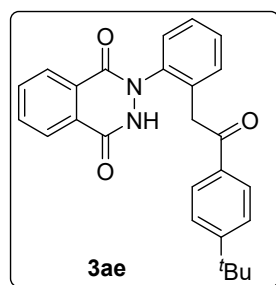
133.9, 133.6, 133.5, 132.4, 131.7, 129.1, 128.7, 128.6, 128.5, 128.5, 128.4, 127.8, 126.8, 126.2, 125.4, 124.3, 41.1, 21.0.

2-(2-(2-(4-methoxyphenyl)-2-oxoethyl)phenyl)-2,3-dihydrophthalazine-1,4-dione (3ad)^[3]



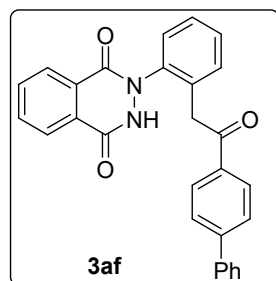
White solid (45.1 mg, 58% yield). Eluents for column chromatography: dichloromethane/ethyl acetate (45:1 v/v) to petroleum ether/ethyl acetate (10:1 v/v). ¹H NMR (DMSO-*d*₆, 500 MHz) δ 11.78 (s, 1H), 8.17 (d, *J* = 10.0 Hz, 1H), 7.89-7.83 (m, 3H), 7.70 (d, *J* = 10.0 Hz, 2H), 7.43-7.39 (m, 4H), 6.76-6.74 (m, 2H), 4.21 (s, 2H), 3.71 (s, 3H); ¹³C NMR (DMSO-*d*₆, 125 MHz) δ 195.4, 163.0, 133.4, 132.4, 131.5, 130.4, 129.5, 129.1, 128.6, 127.7, 126.8, 126.2, 113.6, 55.5, 40.7.

2-(2-(2-(4-(tert-butyl)phenyl)-2-oxoethyl)phenyl)-2,3-dihydrophthalazine-1,4-dione (3ae)



White solid (54.2 mg, 66% yield). Eluents for column chromatography: dichloromethane/ethyl acetate (45:1 v/v) to petroleum ether/ethyl acetate (10:1 v/v). ¹H NMR (DMSO-*d*₆, 500 MHz) δ 11.77 (s, 1H), 8.17 (d, *J* = 5.0 Hz, 1H), 7.90-7.82 (m, 3H), 7.67 (d, *J* = 5.0 Hz, 2H), 7.43-7.40 (m, 4H), 7.27 (d, *J* = 5.0 Hz, 2H), 4.25 (s, 2H), 1.19 (s, 9H); ¹³C NMR (DMSO-*d*₆, 125 MHz) δ 196.8, 156.4, 134.3, 134.2, 133.8, 132.7, 131.8, 129.4, 128.9, 128.8, 128.4, 128.0, 127.1, 125.6, 41.2, 35.1, 31.2; IR (KBr): 3427, 2961, 1658, 1592, 1496, 1294, 1026, 824, 762, 696 (cm⁻¹); HRMS (ESI) *m/z* calcd for C₂₆H₂₄N₂O₃Na [M+Na]⁺: 435.1679; found: 435.1660.

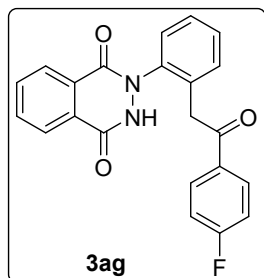
2-(2-(2-([1,1'-biphenyl]-4-yl)-2-oxoethyl)phenyl)-2,3-dihydrophthalazine-1,4-dione (3af)



White solid (45.6 mg, 53% yield). Eluents for column chromatography: dichloromethane/ethyl acetate (45:1 v/v) to petroleum ether/ethyl acetate (10:1 v/v). ¹H NMR (DMSO-*d*₆, 500 MHz) δ 11.82 (s, 1H), 8.18 (d, *J* = 5.0 Hz, 1H), 7.89-7.87 (m, 1H), 7.84-7.80 (m, 4H), 7.60 (d, *J* = 5.0 Hz,

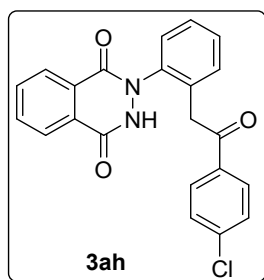
2H), 7.55 (d, $J = 5.0$ Hz, 2H), 7.48-7.45 (m, 3H), 7.42-7.38 (m, 4H), 4.33 (s, 2H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ 196.6, 144.4, 139.0, 135.4, 133.8, 133.4, 132.4, 131.6, 129.2, 129.1, 128.8, 128.6, 128.5, 127.8, 127.1, 126.8, 126.7, 41.1; IR (KBr): 2924, 1636, 1599, 1493, 1349, 1291, 1221, 993, 758, 692 (cm^{-1}); HRMS (ESI) m/z calcd for $\text{C}_{28}\text{H}_{20}\text{N}_2\text{O}_3\text{Na}$ [$\text{M}+\text{Na}$] $^+$: 455.1366; found: 455.1342.

2-(2-(2-(4-fluorophenyl)-2-oxoethyl)phenyl)-2,3-dihydrophthalazine-1,4-dione (3ag)^[3]



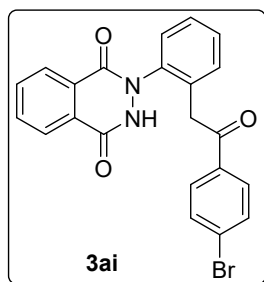
White solid (44.7 mg, 60% yield). Eluents for column chromatography: dichloromethane/ethyl acetate (24:1 v/v) to petroleum ether/ethyl acetate (10:1 v/v). ^1H NMR (DMSO- d_6 , 500 MHz) δ 11.76 (s, 1H), 8.14 (d, $J = 10.0$ Hz, 1H), 7.90-7.89 (m, 2H), 7.86-7.82 (m, 2H), 7.81-7.78 (m, 1H), 7.45-7.40 (m, 4H), 7.09-7.06 (m, 2H), 4.27 (s, 2H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ 195.7, 164.9 (d, $^1J_{\text{C-F}} = 250.0$ Hz), 157.5, 150.7, 141.0, 133.7, 133.5, 133.3 (d, $^4J_{\text{C-F}} = 2.5$ Hz), 132.4, 131.7, 131.1 (d, $^3J_{\text{C-F}} = 8.8$ Hz), 129.1, 128.5 (d, $^3J_{\text{C-F}} = 8.8$ Hz), 127.8, 126.8, 124.9, 124.3, 115.5 (d, $^2J_{\text{C-F}} = 22.5$ Hz), 41.1.

2-(2-(2-(4-chlorophenyl)-2-oxoethyl)phenyl)-2,3-dihydrophthalazine-1,4-dione (3ah)^[3]



White solid (51.8 mg, 66% yield). Eluents for column chromatography: dichloromethane/ethyl acetate (24:1 v/v) to petroleum ether/ethyl acetate (10:1 v/v). ^1H NMR (DMSO- d_6 , 500 MHz) δ 11.76 (s, 1H), 8.13 (d, $J = 5.0$ Hz, 1H), 7.92-7.83 (m, 3H), 7.71 (d, $J = 10.0$ Hz, 2H), 7.45-7.40 (m, 4H), 7.31 (d, $J = 10.0$ Hz, 2H), 4.26 (s, 2H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ 196.2, 141.0, 138.0, 135.3, 133.6, 133.5, 132.4, 131.7, 129.9, 129.0, 128.6, 127.8, 126.7, 124.2, 41.1.

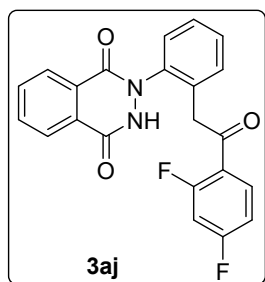
2-(2-(2-(4-bromophenyl)-2-oxoethyl)phenyl)-2,3-dihydrophthalazine-1,4-dione (3ai)



White solid (46.4 mg, 53% yield). Eluents for column chromatography: dichloromethane/ethyl

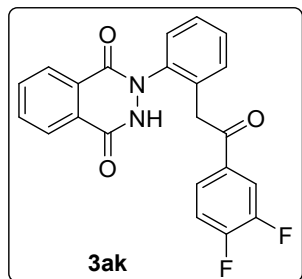
acetate (24:1 v/v) to petroleum ether/ethyl acetate (10:1 v/v). ^1H NMR (DMSO- d_6 , 500 MHz) δ 11.77 (s, 1H), 8.13 (d, $J = 5.0$ Hz, 1H), 7.90-7.84 (m, 3H), 7.63 (d, $J = 5.0$ Hz, 2H), 7.45-7.40 (m, 6H), 4.26 (s, 2H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ 196.4, 157.4, 150.6, 135.6, 133.6, 133.5, 132.4, 131.7, 131.5, 130.0, 129.0, 128.6, 128.6, 128.5, 127.8, 127.2, 126.7, 126.1, 124.2, 41.1; IR (KBr): 3067, 2924, 1639, 1584, 1496, 1397, 1349, 1217, 1066, 692 (cm^{-1}); HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{15}\text{BrN}_2\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 457.0158; found: 457.0144.

2-(2-(2-(2,4-difluorophenyl)-2-oxoethyl)phenyl)-2,3-dihydrophthalazine-1,4-dione (3aj)



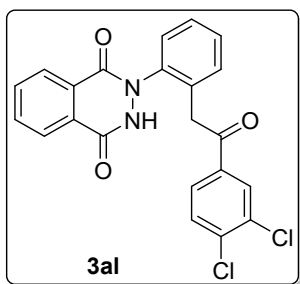
White solid (57.9 mg, 74% yield). Eluents for column chromatography: dichloromethane/ethyl acetate (24:1 v/v) to petroleum ether/ethyl acetate (10:1 v/v). ^1H NMR (DMSO- d_6 , 500 MHz) δ 11.82 (s, 1H), 8.12 (d, $J = 10.0$ Hz, 1H), 7.91-7.90 (m, 2H), 7.86-7.82 (m, 1H), 7.58-7.53 (m, 1H), 7.46-7.40 (m, 4H), 7.13-7.08 (m, 1H), 6.96-6.92 (m, 1H), 4.24 (s, 2H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ 194.0, 157.4, 133.6, 133.1, 132.5, 131.9, 131.0, 129.0, 128.6, 128.4, 127.9, 126.7, 126.2, 124.3, 122.7, 112.1 (d, $^2J_{\text{C-F}} = 21.3$ Hz), 104.9 (t, $^2J_{\text{C-F}} = 25.0$ Hz), 44.8 (d, $^4J_{\text{C-F}} = 6.3$ Hz); IR (KBr): 3067, 2924, 1691, 1636, 1602, 1493, 1257, 1103, 853, 692 (cm^{-1}); HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{14}\text{F}_2\text{N}_2\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 415.0865; found: 415.0848.

2-(2-(2-(3,4-difluorophenyl)-2-oxoethyl)phenyl)-2,3-dihydrophthalazine-1,4-dione (3ak)



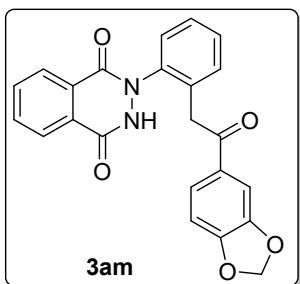
White solid (44.1 mg, 56% yield). Eluents for column chromatography: dichloromethane/ethyl acetate (45:1 v/v) to petroleum ether/ethyl acetate (10:1 v/v). ^1H NMR (DMSO- d_6 , 500 MHz) δ 11.76 (s, 1H), 8.13 (d, $J = 5.0$ Hz, 1H), 7.93-7.84 (m, 3H), 7.71-7.67 (m, 1H), 7.60 (s, 1H), 7.48-7.41 (m, 4H), 7.35-7.30 (m, 1H), 4.27 (s, 2H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ 195.2, 134.2, 133.6 (d, $^3J_{\text{C-F}} = 10.0$ Hz), 132.4, 131.8, 129.1, 128.6 (d, $^4J_{\text{C-F}} = 2.5$ Hz), 127.9, 126.7, 125.9 (q, $^4J_{\text{C-F}} = 3.8$ Hz), 124.2, 117.7 (d, $^3J_{\text{C-F}} = 17.5$ Hz), 117.3 (d, $^3J_{\text{C-F}} = 17.5$ Hz), 41.0; IR (KBr): 3072, 1632, 1602, 1515, 1426, 1349, 1279, 1155, 890, 692 (cm^{-1}); HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{14}\text{F}_2\text{N}_2\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 415.0865; found: 415.0849.

2-(2-(2-(3,4-dichlorophenyl)-2-oxoethyl)phenyl)-2,3-dihydrophthalazine-1,4-dione (3al)



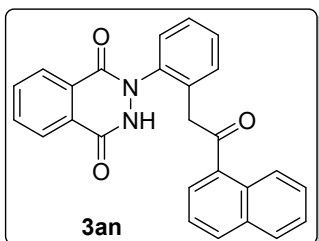
White solid (47.4 mg, 56% yield). Eluents for column chromatography: dichloromethane/ethyl acetate (45:1 v/v) to petroleum ether/ethyl acetate (10:1 v/v). ^1H NMR (DMSO- d_6 , 500 MHz) δ 11.76 (s, 1H), 8.09 (d, $J = 10.0$ Hz, 1H), 7.92-7.81 (m, 4H), 7.64 (d, $J = 10.0$ Hz, 1H), 7.50-7.40 (m, 5H), 4.27 (s, 2H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ 195.6, 136.8, 135.8, 133.5, 132.4, 131.8, 131.6, 130.8, 129.8, 128.9, 128.5, 128.0, 127.9, 126.6, 124.1, 41.0; IR (KBr): 2924, 1636, 1602, 1496, 1393, 1206, 1026, 821, 754, 692 (cm^{-1}); HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{14}\text{Cl}_2\text{N}_2\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 447.0274; found: 447.0262.

2-(2-(2-(benzo[d][1,3]dioxol-5-yl)-2-oxoethyl)phenyl)-2,3-dihydrophthalazine-1,4-dione (3am)



White solid (49.9 mg, 62% yield). Eluents for column chromatography: dichloromethane/ethyl acetate (45:1 v/v) to petroleum ether/ethyl acetate (10:1 v/v). ^1H NMR (DMSO- d_6 , 500 MHz) δ 11.78 (s, 1H), 8.15 (d, $J = 5.0$ Hz, 1H), 7.90-7.89 (m, 2H), 7.85-7.82 (m, 1H), 7.41-7.39 (m, 4H), 7.35-7.33 (m, 1H), 7.13 (s, 1H), 6.71-6.70 (m, 1H), 6.00 (s, 2H), 4.18 (s, 2H); ^{13}C NMR (125 MHz, DMSO) δ 195.3, 157.5, 151.3, 147.6, 141.0, 134.3, 133.5, 132.4, 131.6, 131.3, 129.1, 128.6, 128.5, 127.7, 126.8, 124.6, 124.3, 107.8, 107.5, 102.1, 99.8, 40.9; IR (KBr): 3075, 2917, 1669, 1592, 1496, 1441, 1353, 1254, 1037, 692 (cm^{-1}); HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{16}\text{N}_2\text{O}_5\text{Na}$ $[\text{M}+\text{Na}]^+$: 423.0951; found: 423.0938.

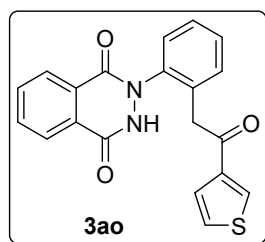
2-(2-(2-(naphthalen-1-yl)-2-oxoethyl)phenyl)-2,3-dihydrophthalazine-1,4-dione (3an)^[3]



White solid (53.5 mg, 66% yield). Eluents for column chromatography: dichloromethane/ethyl acetate (45:1 v/v) to petroleum ether/ethyl acetate (10:1 v/v). ^1H NMR (DMSO- d_6 , 500 MHz) δ 11.82 (s, 1H), 8.13-8.09 (m, 2H), 7.94-7.78 (m, 7H), 7.54-7.52 (m, 1H), 7.46-7.42 (m, 4H), 7.39-7.34 (m, 2H), 4.47 (s, 2H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ 200.6, 157.4, 135.4, 133.5, 133.4,

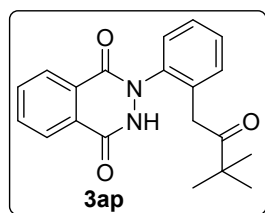
133.3, 132.4, 132.4, 131.9, 129.4, 129.1, 128.6, 128.5, 128.4, 127.9, 127.5, 126.7, 126.4, 125.5, 124.6, 124.3, 45.1.

2-(2-(2-oxo-2-(thiophen-3-yl)ethyl)phenyl)-2,3-dihydrophthalazine-1,4-dione (**3ao**)



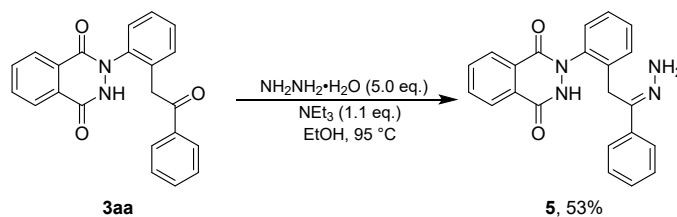
White solid (39.9 mg, 55% yield). Eluents for column chromatography: dichloromethane/ethyl acetate (45:1 v/v) to petroleum ether/ethyl acetate (10:1 v/v). ¹H NMR (DMSO-*d*₆, 500 MHz) δ 11.78 (s, 1H), 8.25 (s, 1H), 8.19 (d, *J* = 10.0 Hz, 1H), 7.92 (s, 2H), 7.87 (s, 1H), 7.41 (s, 5H), 7.28 (s, 1H), 4.17 (s, 2H); ¹³C NMR (DMSO-*d*₆, 125 MHz) δ 191.2, 157.6, 141.7, 133.9, 133.6, 132.5, 131.5, 129.2, 128.6, 128.6, 128.5, 127.8, 127.3, 126.8, 126.7, 126.2, 124.4, 42.2; IR (KBr): 3097, 2924, 1658, 1636, 1496, 1397, 1287, 1243, 1199, 692 (cm⁻¹); HRMS (ESI) *m/z* calcd for C₂₀H₁₄N₂O₃SNa [M+Na]⁺: 385.0617; found: 385.0605.

2-(2-(3,3-dimethyl-2-oxobutyl)phenyl)-2,3-dihydrophthalazine-1,4-dione (**3ap**)^[3]



White solid (17.3 mg, 26% yield). Eluents for column chromatography: dichloromethane/ethyl acetate (45:1 v/v) to petroleum ether/ethyl acetate (10:1 v/v). ¹H NMR (DMSO-*d*₆, 500 MHz) δ 11.89 (s, 1H), 8.28 (d, *J* = 5.0 Hz, 1H), 8.01-8.00 (m, 1H), 7.96-7.89 (m, 2H), 7.38-7.38 (m, 3H), 7.32-7.30 (m, 1H), 3.86 (s, 2H), 0.85 (s, 9H); ¹³C NMR (DMSO-*d*₆, 125 MHz) δ 210.9, 157.3, 150.6, 141.0, 133.8, 133.2, 132.7, 132.3, 129.2, 128.3, 128.1, 127.5, 126.9, 125.0, 124.4, 43.8, 39.4, 26.2.

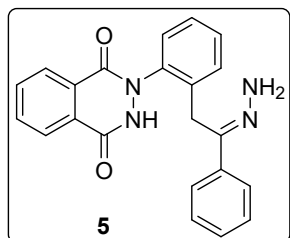
4. Synthesis of (*E*)-2-(2-(2-hydrazono-2-phenylethyl)phenyl)-2,3-dihydrophthalazine-1,4-dione (**5**)^[4]



3aa (0.2 mmol, 71.3 mg) was added slowly a mixture of hydrazine monohydrate (1 mmol, 50.1 mg) and triethylamine (0.22 mmol, 22.3 mg) at room temperature. The

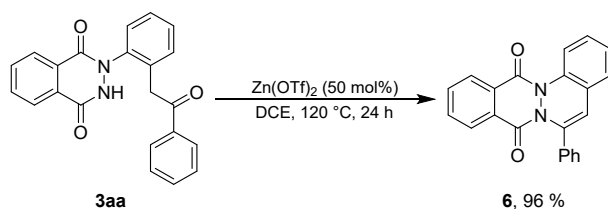
mixture was heated at 95°C for 1 h and sealed with a Teflon lined cap. Then, the solvent was removed under reduced pressure, and the residue was purified via silica gel chromatography (eluent: petroleum ether/ethyl acetate = 1:2) to give product **5** in 53% yield.

(E)-2-(2-(2-hydrazono-2-phenylethyl)phenyl)-2,3-dihydrophthalazine-1,4-dione (5**)**



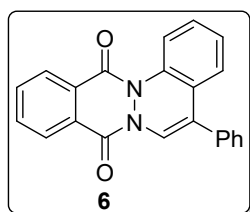
White solid (39.6 mg, 53% yield). ¹H NMR (DMSO-*d*₆, 500 MHz) δ 11.92 (s, 1H), 8.32 (d, *J* = 10.0 Hz, 1H), 8.05 (d, *J* = 5.0 Hz, 1H), 7.99-7.92 (m, 2H), 7.57 (d, *J* = 10.0 Hz, 2H), 7.46 (d, *J* = 10.0 Hz, 1H), 7.39-7.32 (m, 2H), 7.25-7.22 (m, 2H), 7.15-7.12 (m, 1H), 7.08 (d, *J* = 10.0 Hz, 1H), 6.53 (s, 2H) 3.81 (s, 2H); ¹³C NMR (126 MHz, DMSO) δ 157.71, 151.16, 142.06, 141.23, 139.36, 133.90, 133.76, 132.68, 129.21, 129.00, 128.79, 128.32, 128.09, 127.54, 127.16, 127.02, 125.28, 124.91, 124.60, 26.61. IR (KBr): 2924, 2851, 1650, 1584, 1496, 1327, 1291, 1199, 762, 692 (cm⁻¹); HRMS (ESI) *m/z* calcd for C₂₂H₁₈N₄O₂Na [M+Na]⁺: 393.1322; found: 393.1310.

5. Synthesis of 6-phenylphthalazino[2,3-*a*]cinnoline-8,13-dione (6**)^[5]**



The mixture of **3aa** (0.2 mmol, 71.3 mmg), Zn(OTf)₂ (50m%, 36.4 mg) and DCE (1 mL) was sealed with a Teflon lined cap. The reaction mixture was stirred at 120 °C for 24 h. Then, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) gave the product **6** in 96% yield.

5-phenylphthalazino[2,3-*a*]cinnoline-8,13-dione (6**)^[3]**

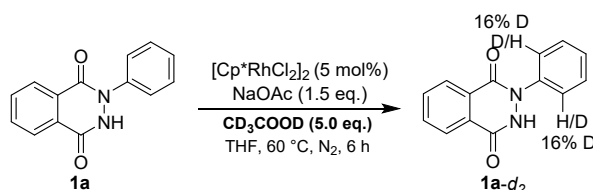


Yellow solid (64.8 mg, 96% yield). ¹H NMR (DMSO-*d*₆, 500 MHz) δ 8.36 (d, *J* = 10.0 Hz, 1H),

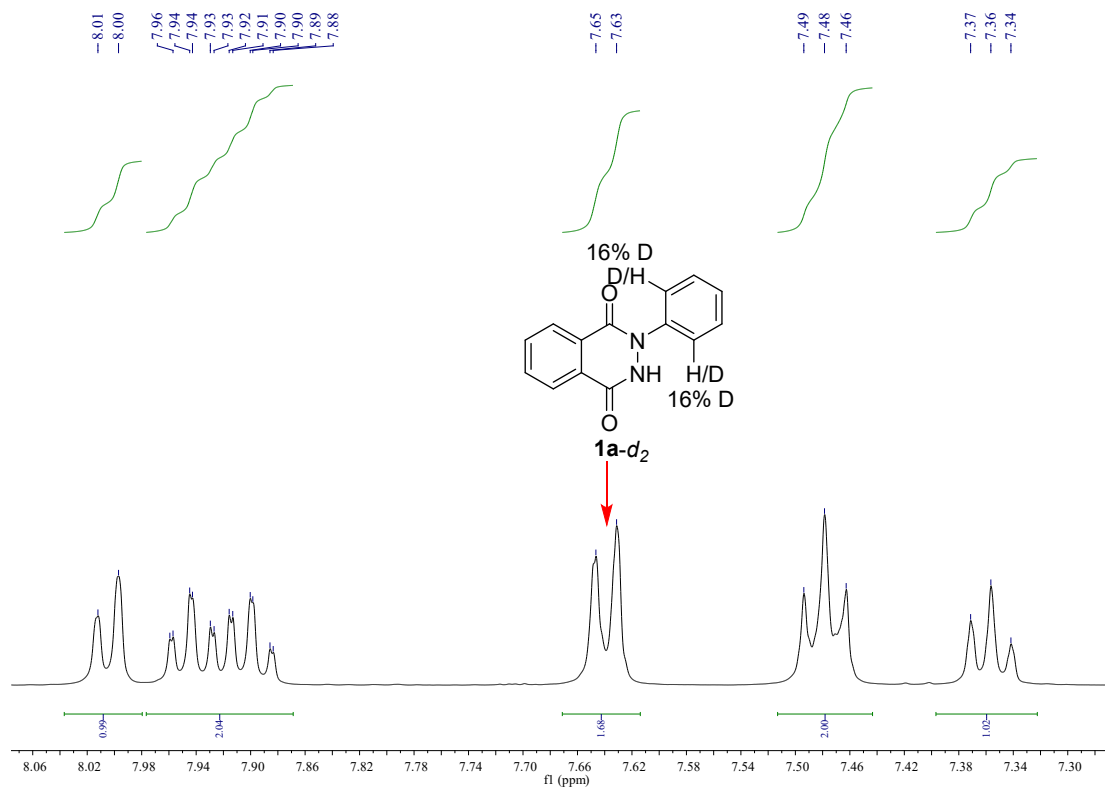
8.07-7.96 (m, 3H), 7.89 (d, $J = 10.0$ Hz, 1H), 7.42 (d, $J = 5.0$ Hz, 1H) 7.34-7.25 (m, 7H), 6.77 (s, 1H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ 157.9, 156.1, 139.0, 136.1, 134.6, 134.4, 133.9, 129.7, 129.1, 128.5, 128.4, 128.4, 128.3, 127.3, 126.7, 126.3, 126.2, 126.2, 124.8, 118.8, 116.1.

6. Control Experiments

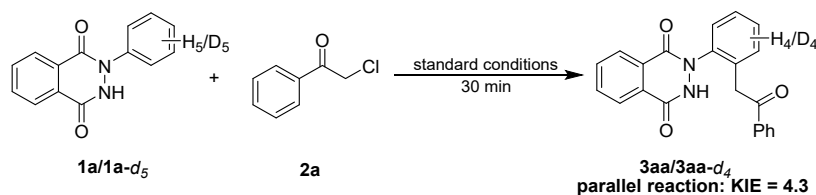
(1) H/D exchange experiment



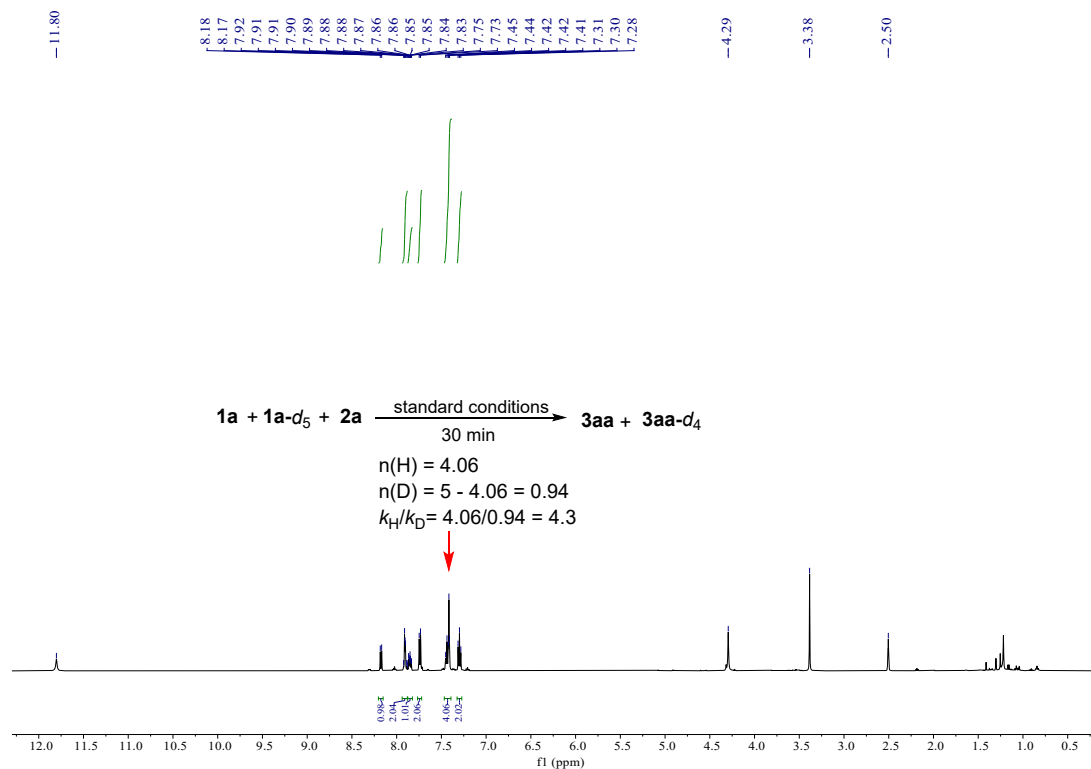
A reaction flask was charged with a mixture of $[\text{Cp}^*\text{RhCl}_2]_2$ (6.2 mg, 0.01 mmol, 5 mol %), NaOAc (24.6 mg, 0.3 mmol, 1.5 equiv.), **1a** (0.20 mmol), **2a** (0.4 mmol, 2.0 equiv.), CD_3COOD (64.1 mg, 1.0 mmol, 5.0 equiv.) and THF (1.0 mL). The reaction was stirred at 60 °C under N_2 for 6 h, then immediately quenched with EtOAc. The volatiles were removed under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether /ethyl acetate = 3:1) to afford **1a- d_2** . The result was observed by ^1H NMR determination.



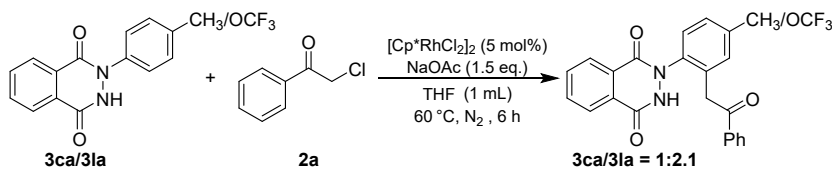
(2) Experiment of deuterium kinetic isotope effect



A reaction flask was charged with a mixture of [Cp**RhCl*₂]₂ (6.2 mg, 0.01 mmol, 5 mol %), NaOAc (24.6 mg, 0.3 mmol, 1.5 equiv.), **1a** (0.10 mmol), **1a-d₅** (0.10 mmol), **2a** (0.2 mmol, 2.0 equiv.) and THF (1.0 mL). The reaction was stirred at 60 °C under N₂ for 30 min, then immediately quenched with EtOAc. The volatiles were removed under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: dichloromethane = 24:1/ethyl acetate to petroleum ether/ethyl acetate = 10:1) to afford **3aa** and **3aa-d₄**. A 4.3 of KIE was observed by ¹H NMR determination.

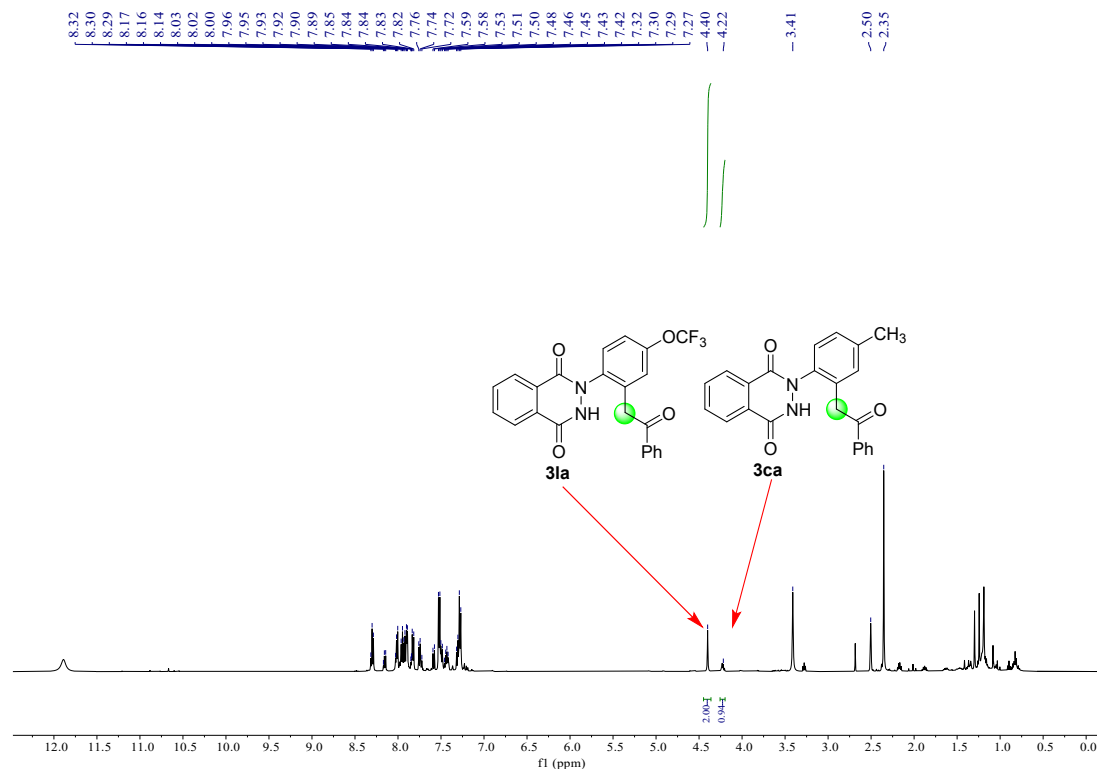


(3) Experiment of competition experiment between **1c** and **1k**.



A reaction flask was charged with a mixture of [Cp**RhCl*₂]₂ (6.2 mg, 0.01 mmol, 5 mol %), NaOAc (24.6 mg, 0.3 mmol, 1.5 equiv.), **1c** (0.20 mmol), **1k** (0.20 mmol), **2a** (0.4 mmol, 2.0 equiv.) and THF (1.0 mL). The reaction was stirred at 60 °C under N₂ for 6

h, then immediately quenched with EtOAc. The volatiles were removed under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: dichloromethane = 45:1/ethyl acetate to petroleum ether/ethyl acetate = 10:1). The ratio 2.1 of **3ca** and **3la** was observed by ¹H NMR determination.

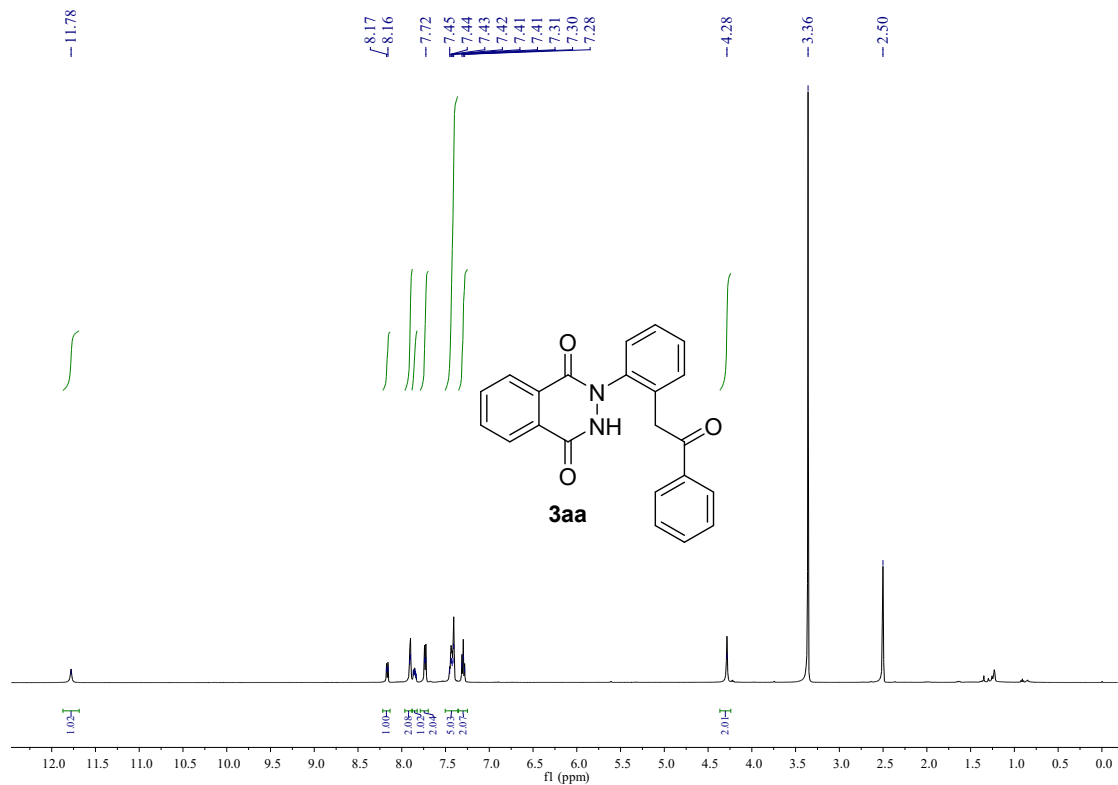


7. References:

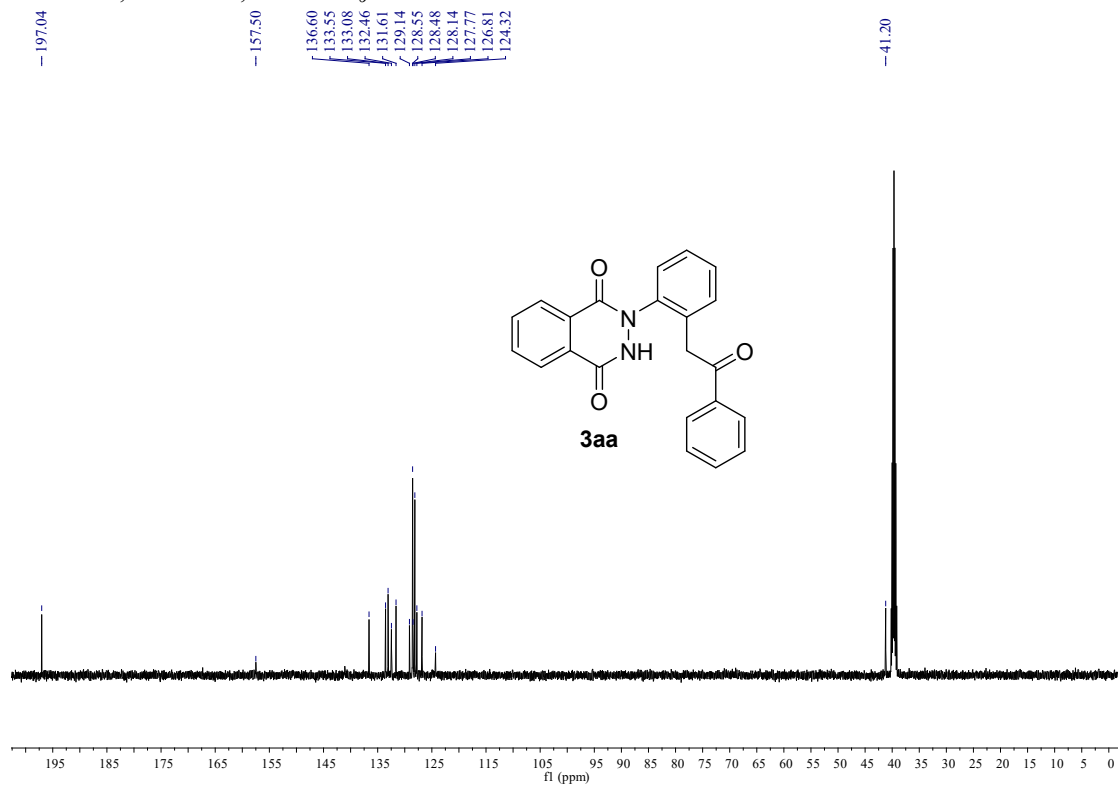
1. Prakash, R.; Bora, B. R.; Boruah, R. C.; Gogoi, S. *Org. Lett.* **2018**, *20*, 2297.
2. a) Zhou, J.; Li, J.; Li, Y.; Wu, C.; He, G.; Yang, Q.; Zhou, Y.; Liu, H. *Org. Lett.* **2018**, *20*, 7645.
b) Yin, C.; Wu, W.; Hu, Y.; Tan, X.; You, C.; Liu, Y.; Chen, Z.; Dong, X.; Zhang X. *Adv. Synth. Catal.* **2018**, *11*, 2119.
3. Karishma, P.; Agarwal, D. S.; Laha, B.; Mandal, S. K.; Sakhuja, R. *Chem. Asian J.* **2019**, *14*, 4274.
4. Pan, C.; Yuan, C.; Chen, D.; Chen, Y.; Yu, J. *Asian J. Org. Chem.* **2022**, *11*, e202100809.
5. Pan, C.; Yuan, C.; Yu, J. *Asian J. Org. Chem.* **2022**, *11*, e202200346.

8. Copies of ^1H and ^{13}C NMR Spectra of Products

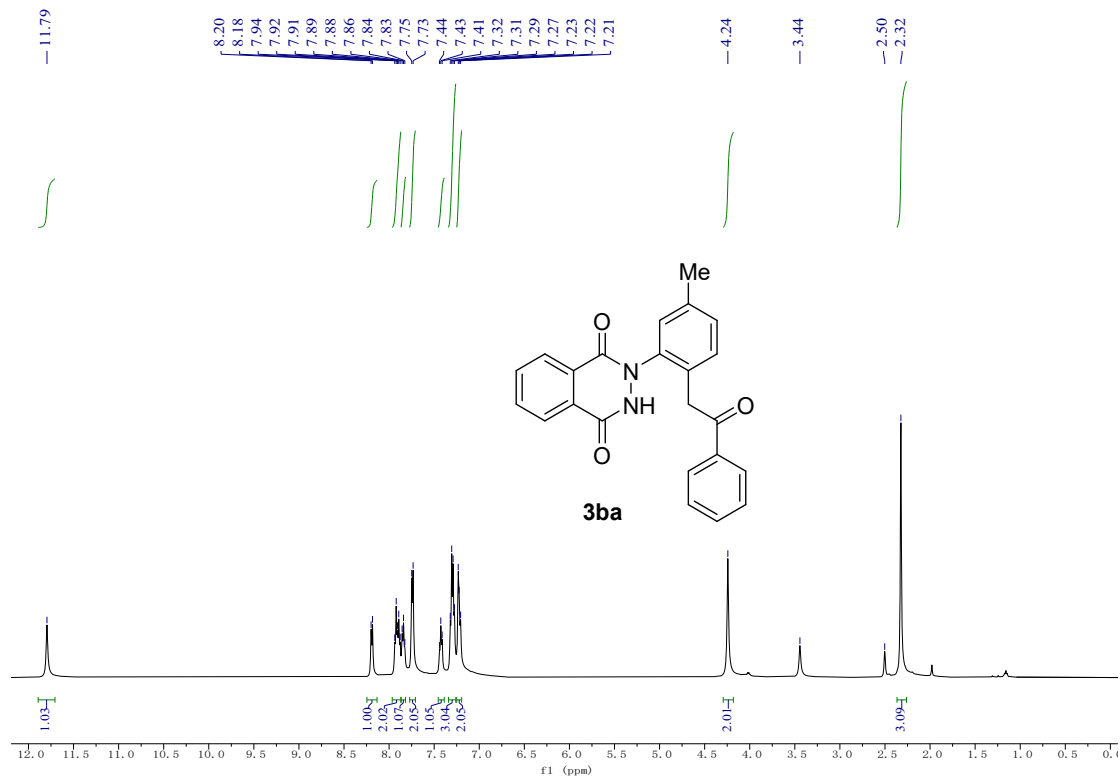
^1H NMR, 500 MHz, $\text{DMSO-}d_6$



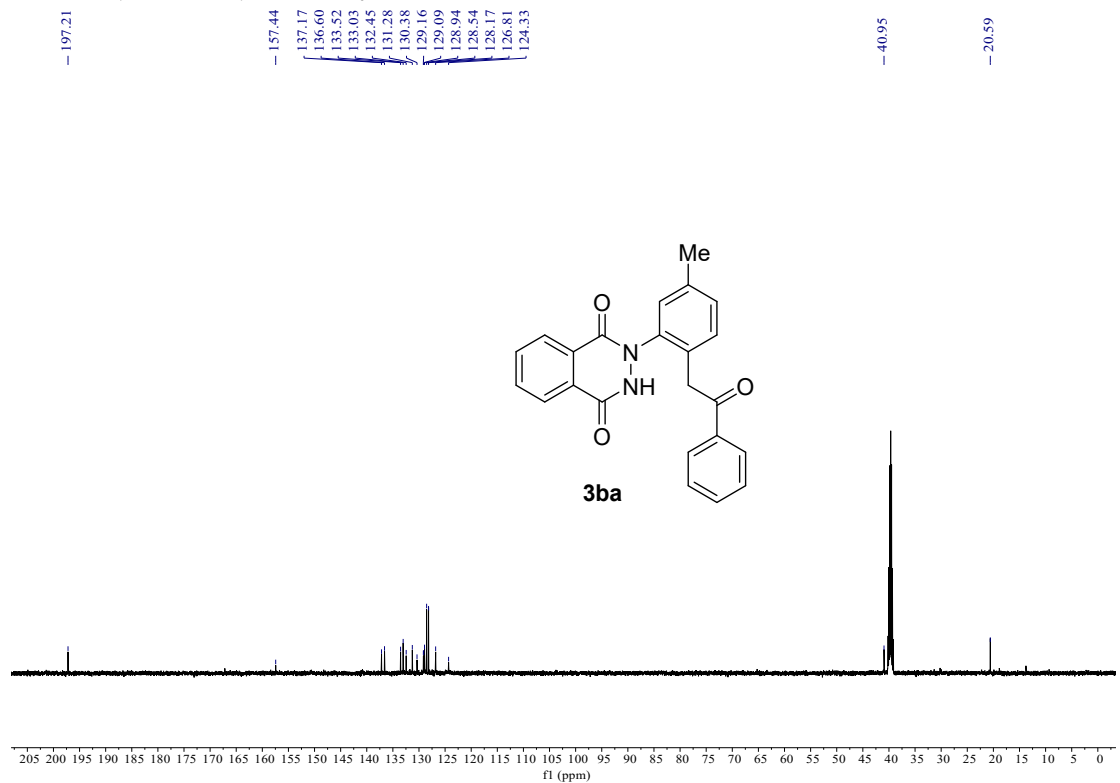
^{13}C NMR, 125 MHz, $\text{DMSO-}d_6$



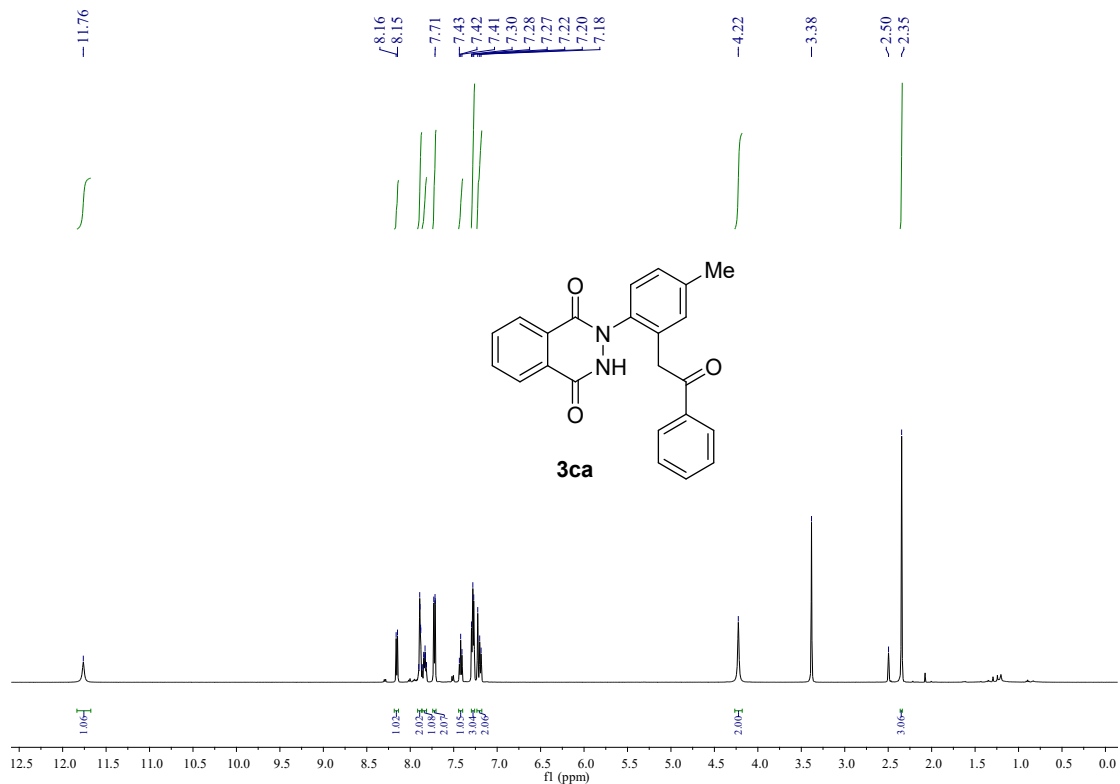
¹H NMR, 500 MHz, DMSO-d₆



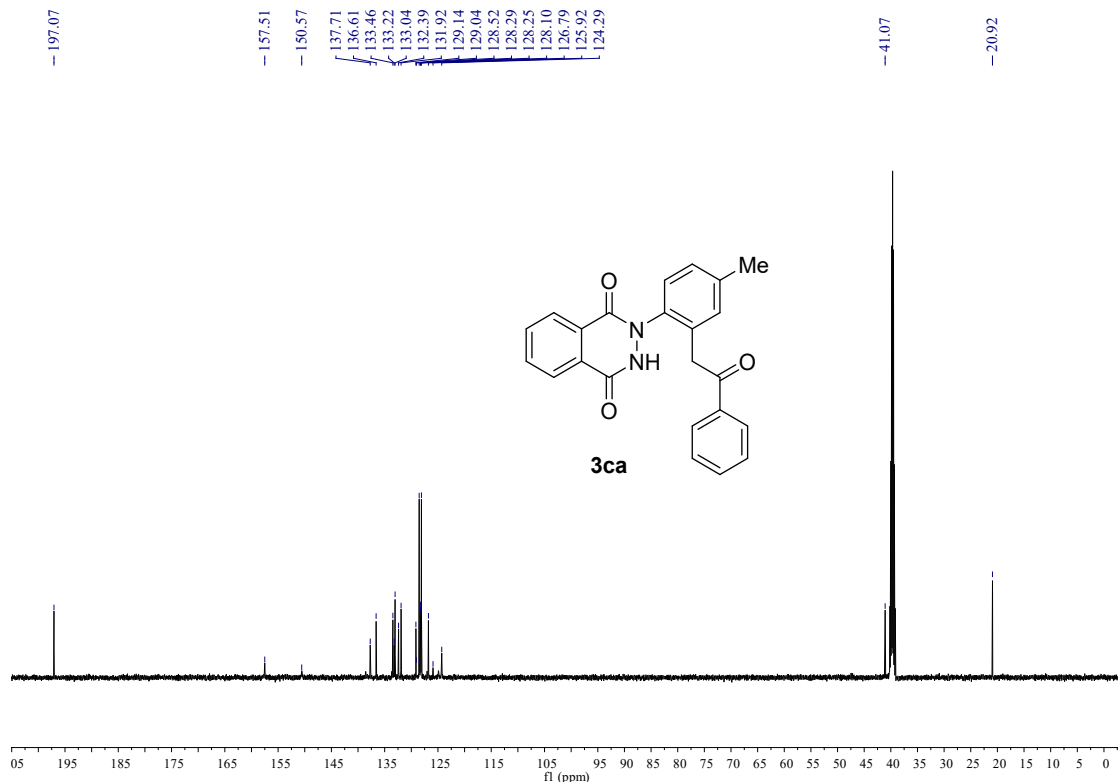
¹³C NMR, 125 MHz, DMSO-d₆



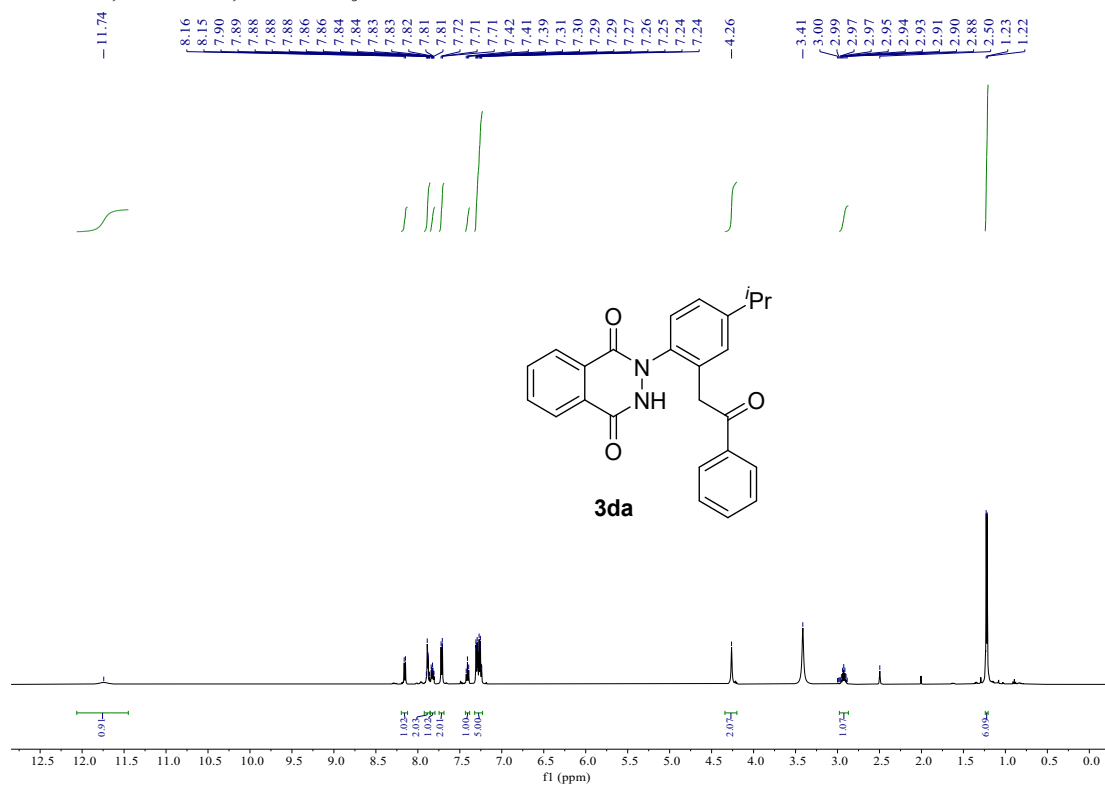
¹H NMR, 500 MHz, DMSO-*d*₆



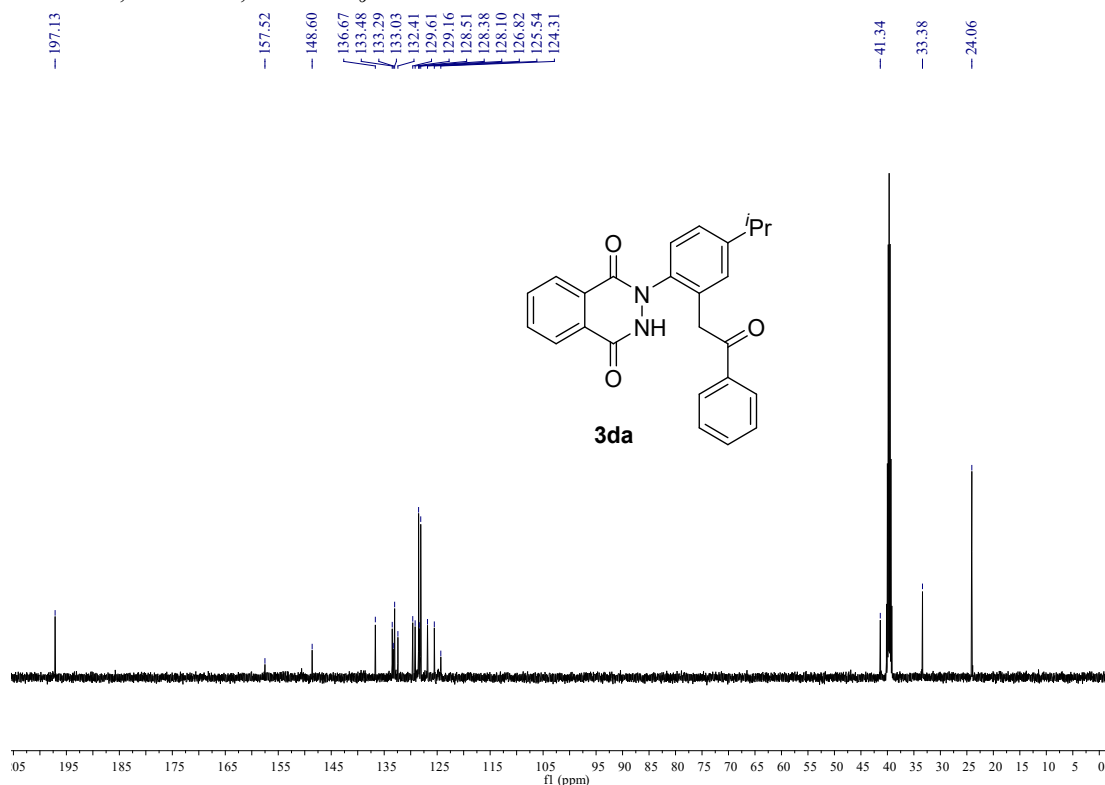
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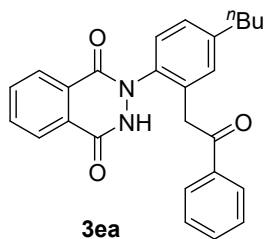
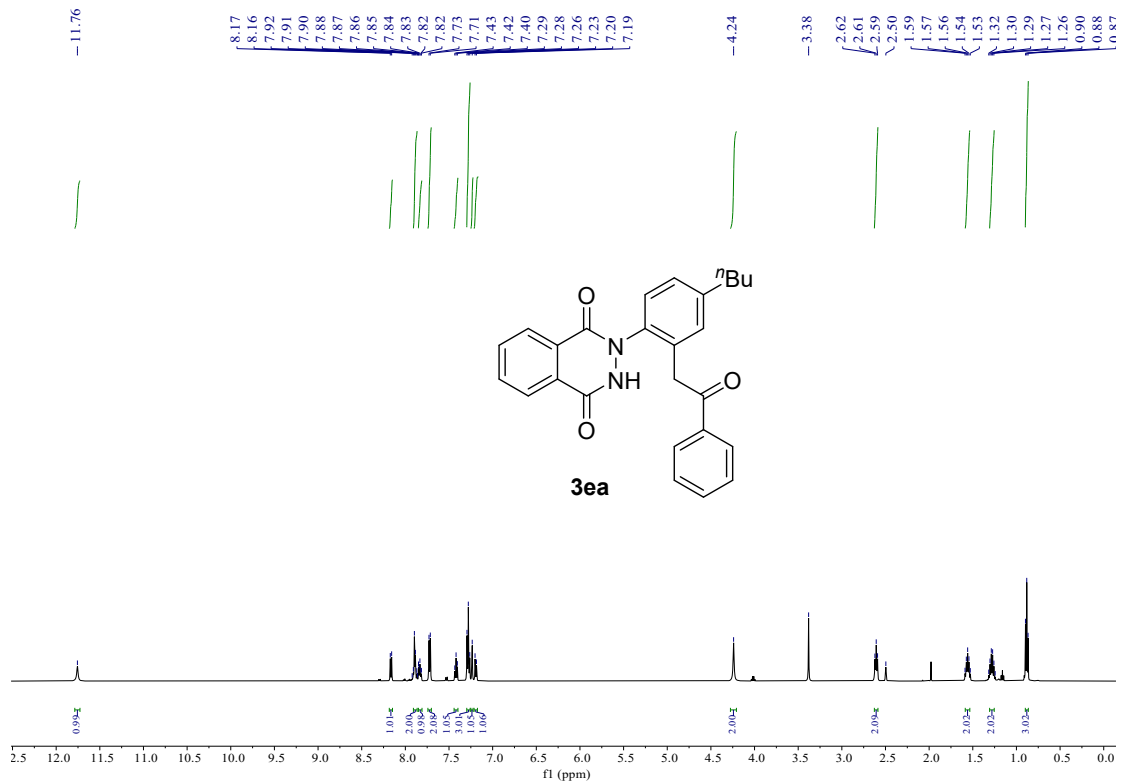
^1H NMR, 500 MHz, $\text{DMSO}-d_6$



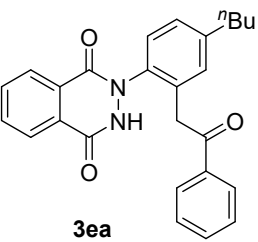
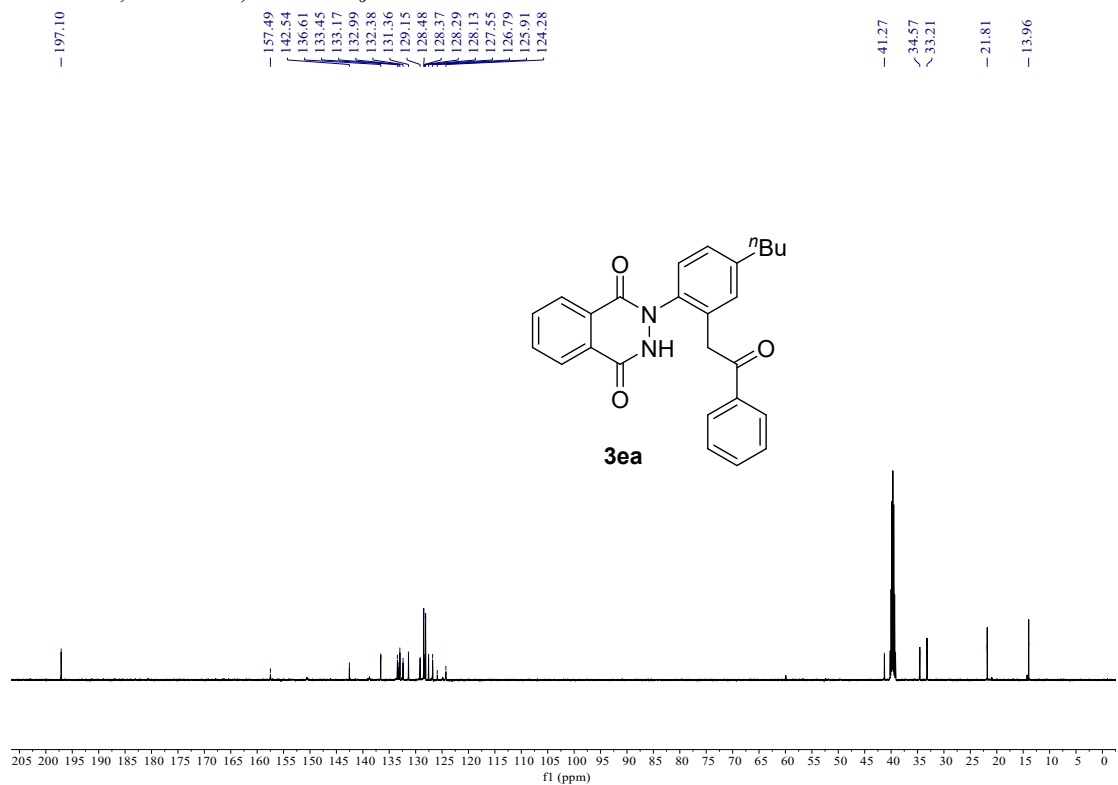
^{13}C NMR, 125 MHz, $\text{DMSO}-d_6$



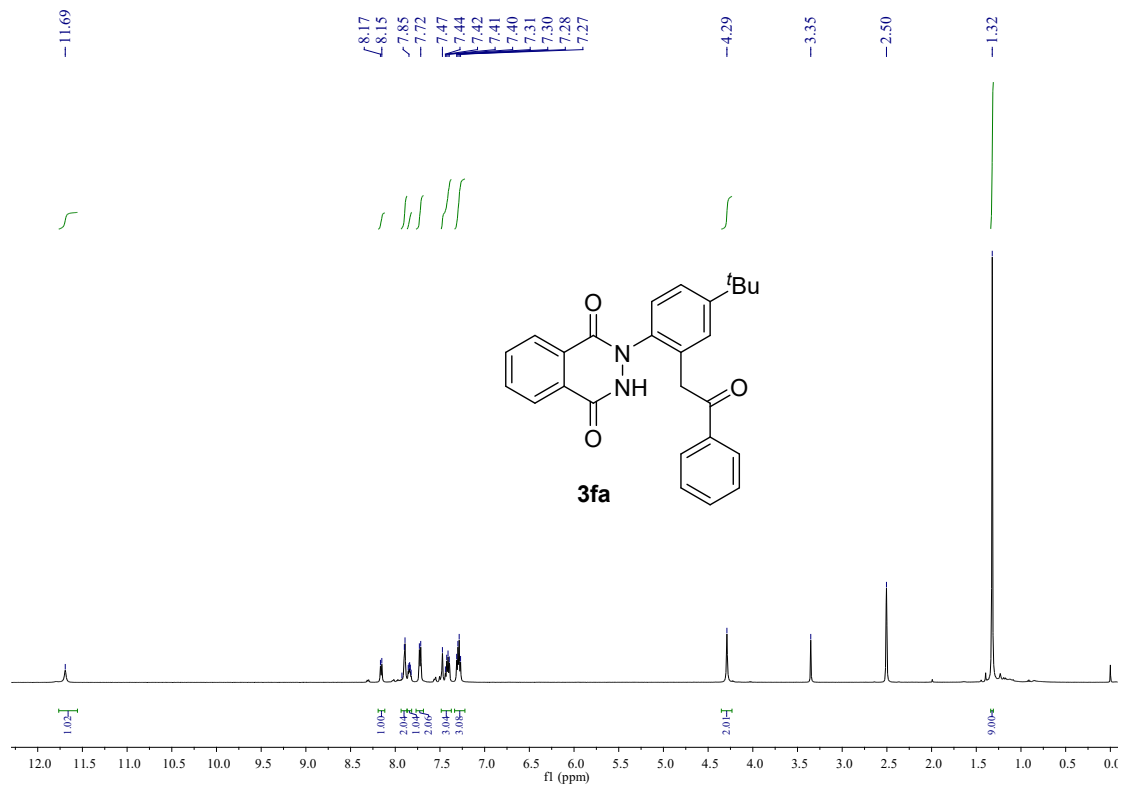
¹H NMR, 500 MHz, DMSO-d₆



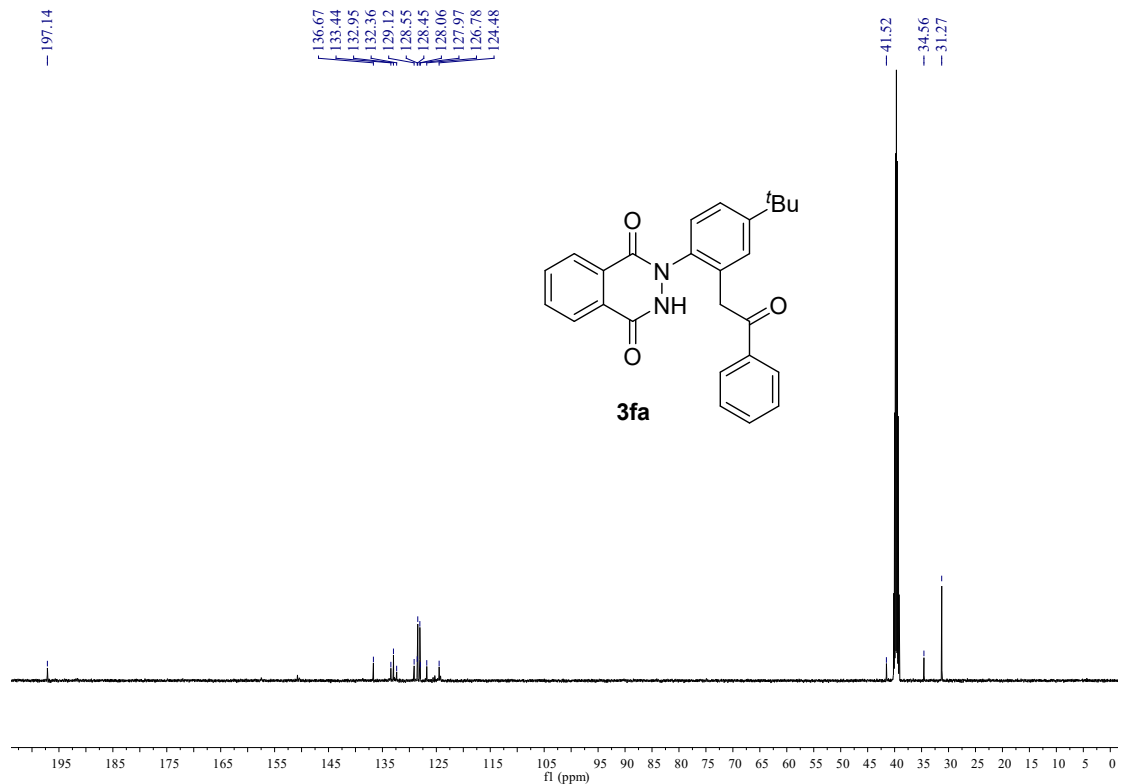
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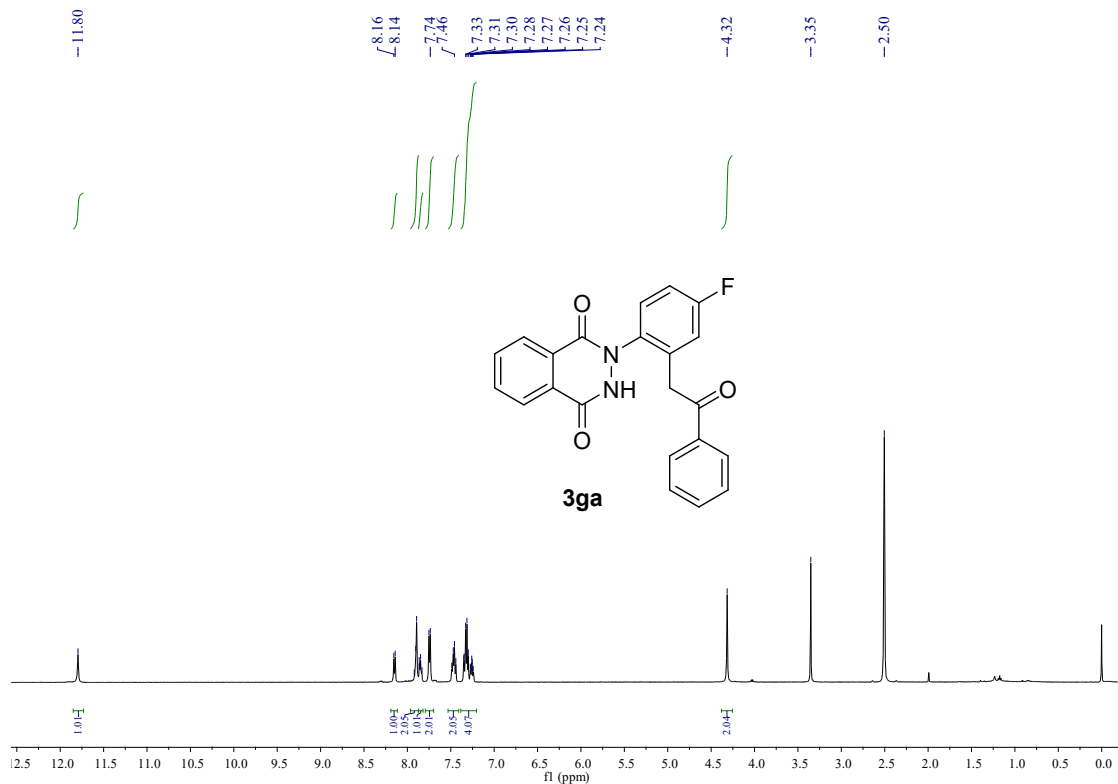
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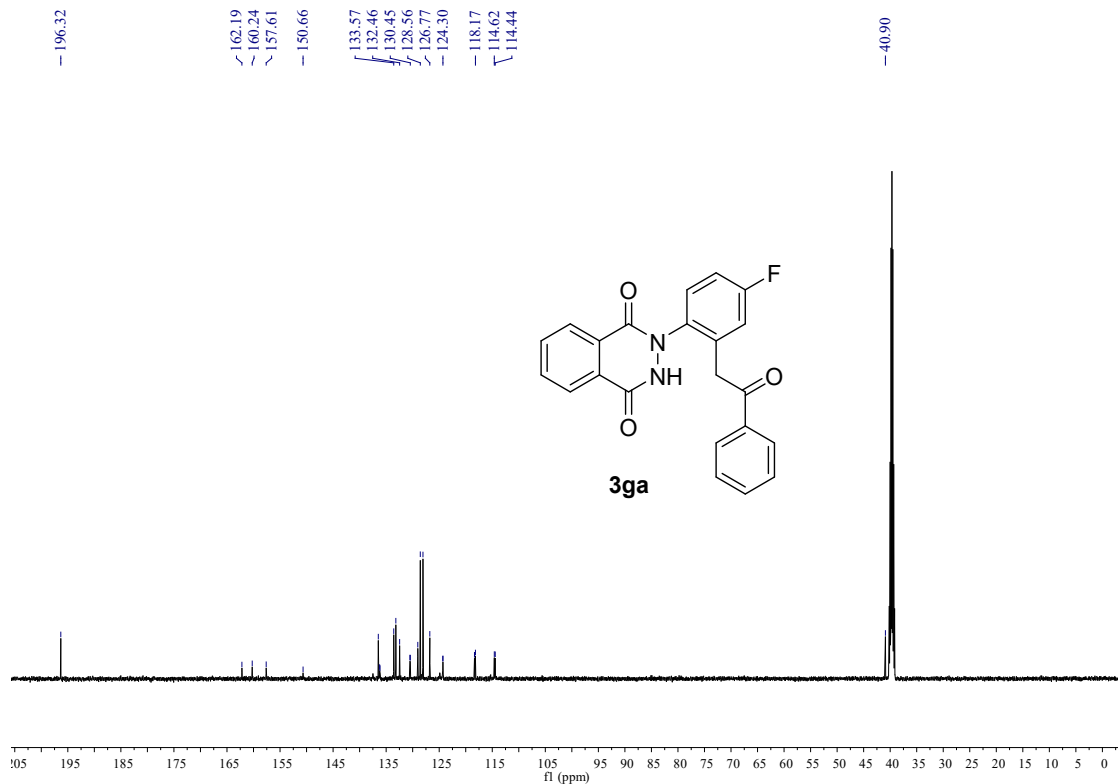
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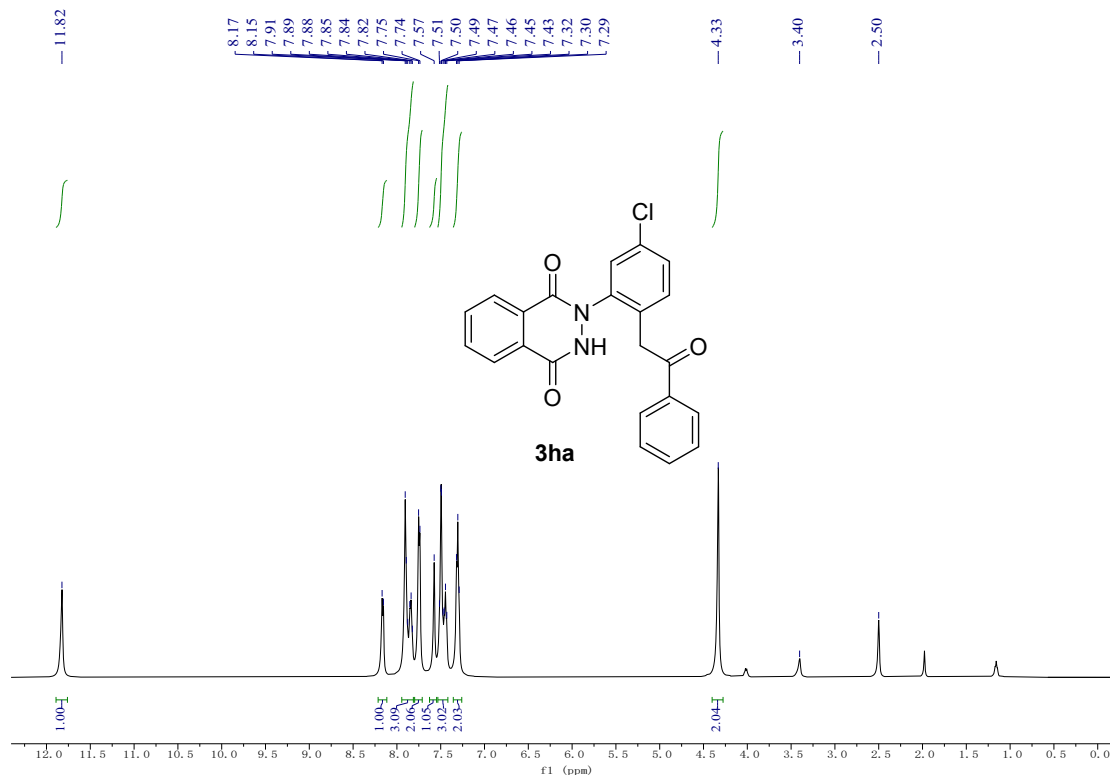
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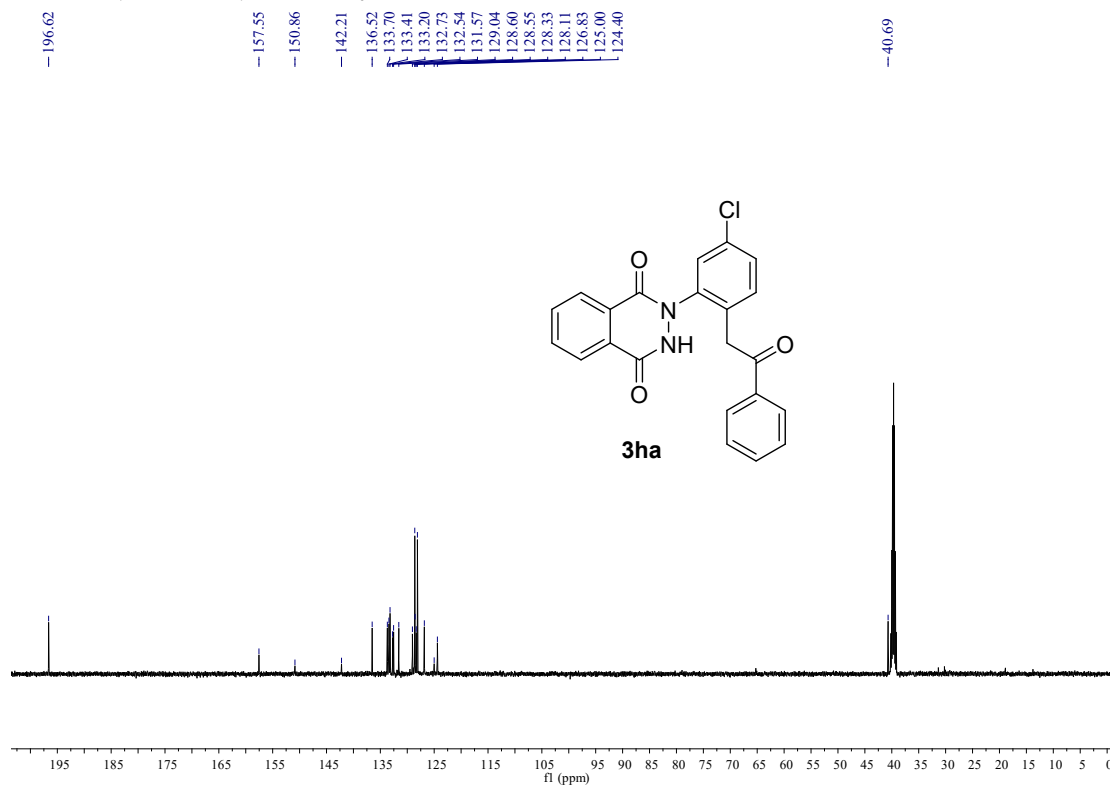
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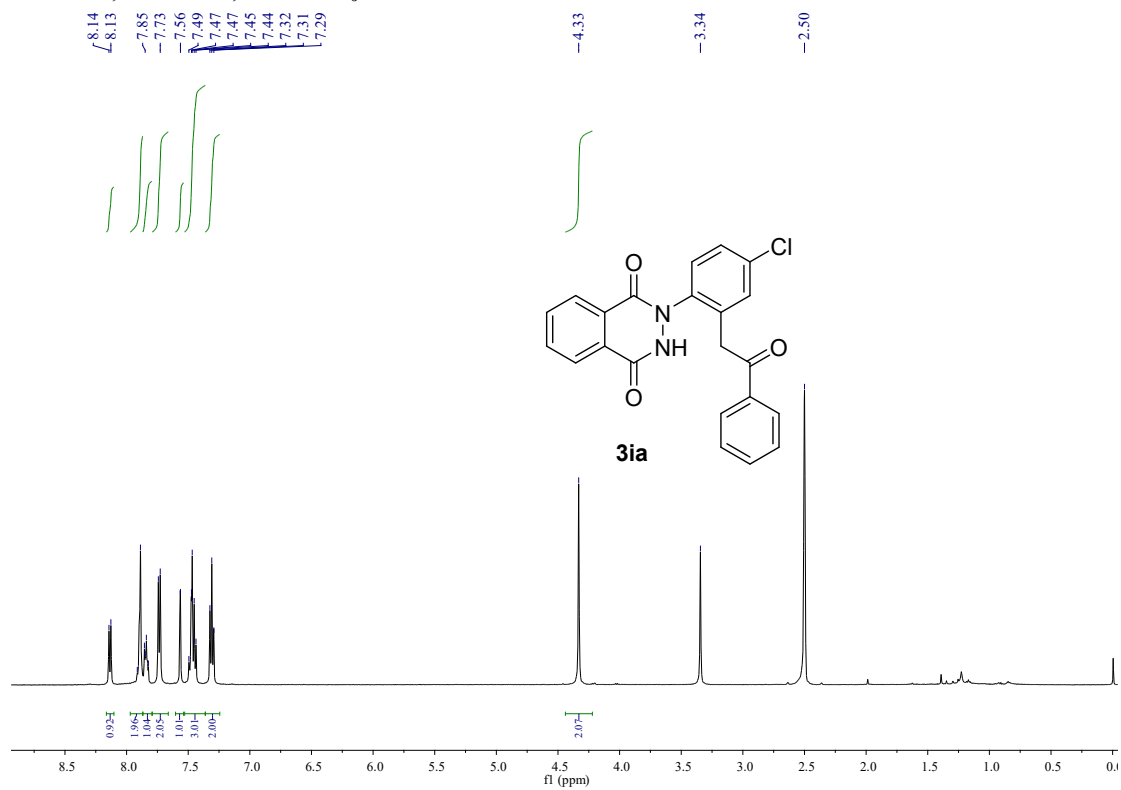
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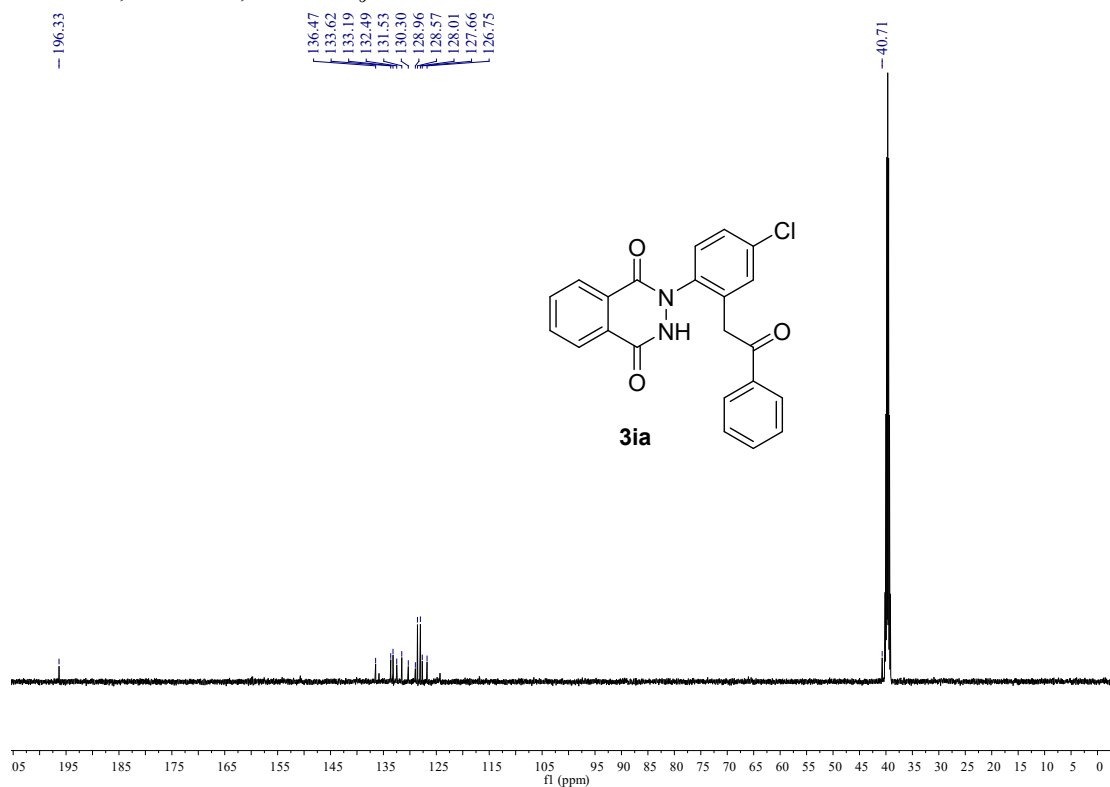
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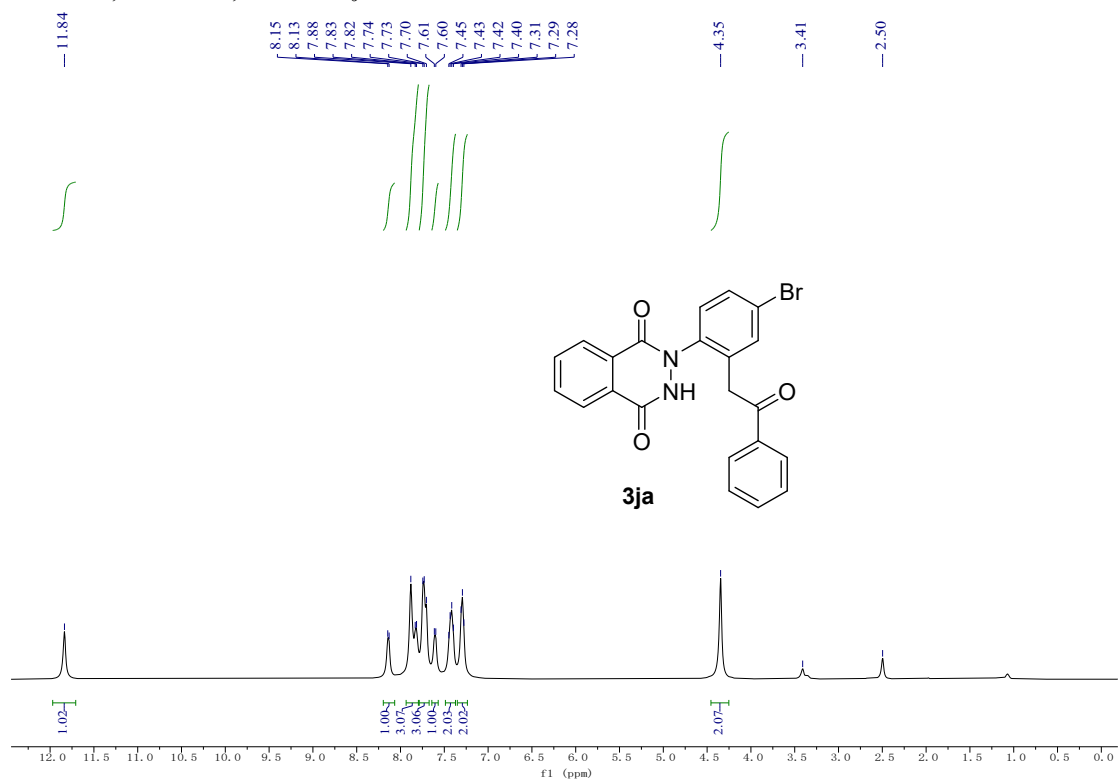
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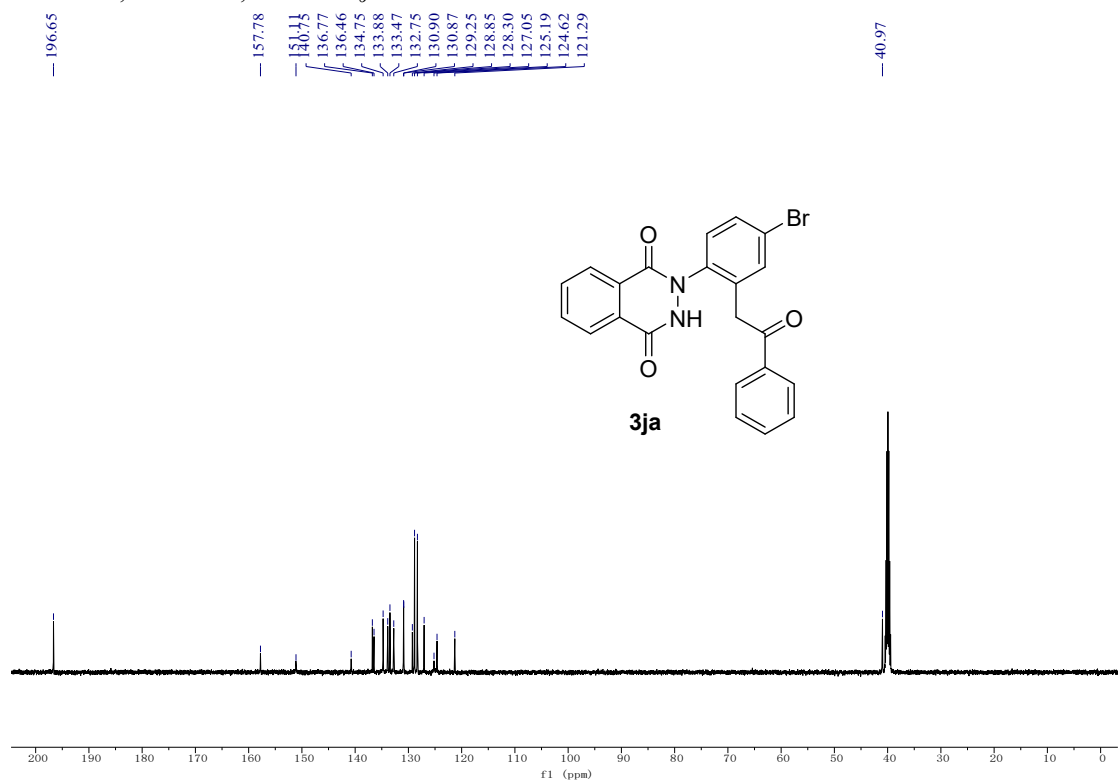
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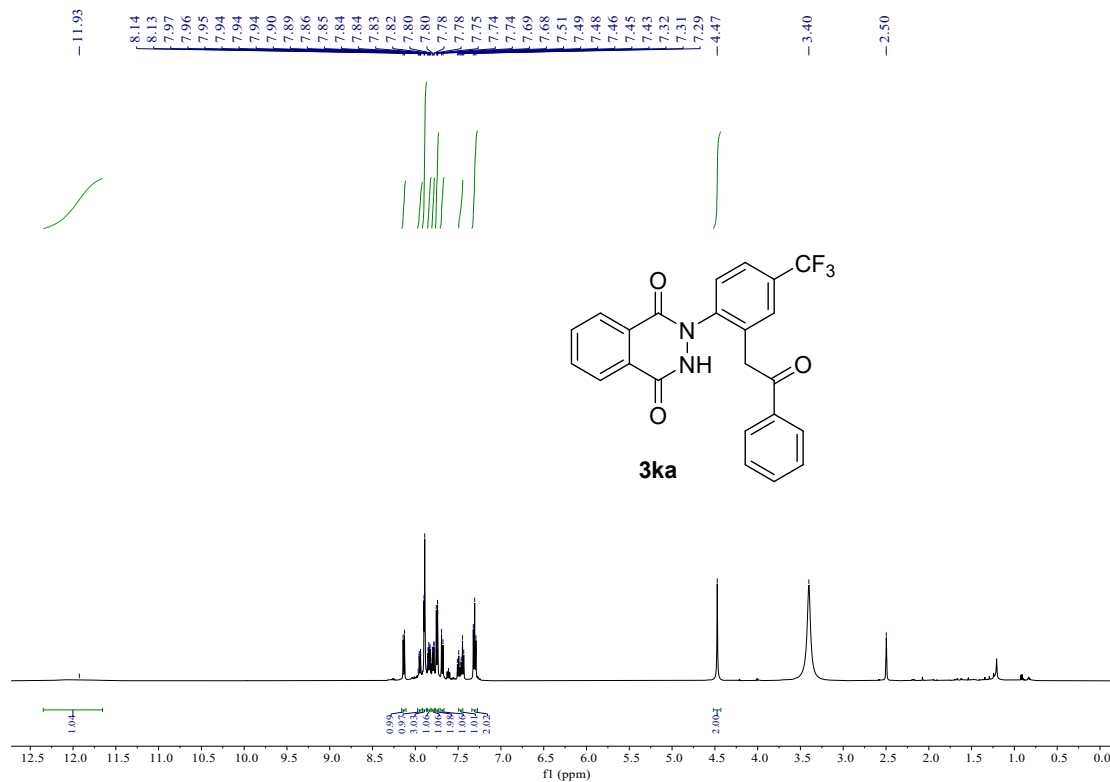
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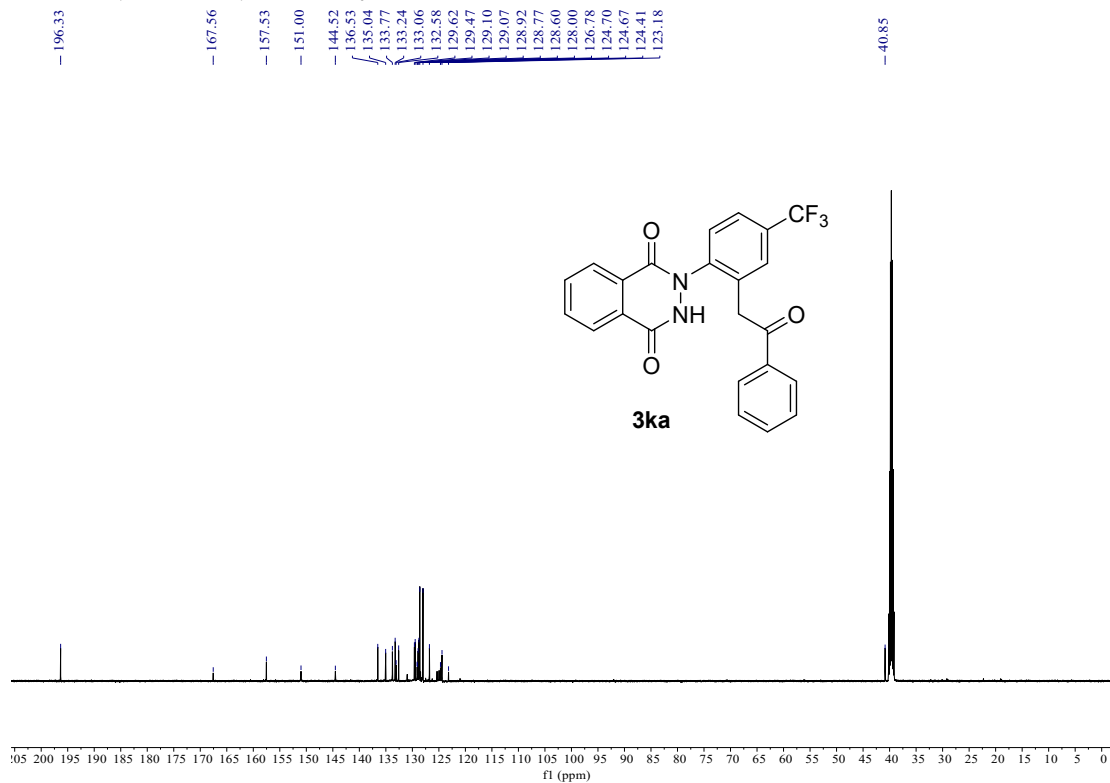
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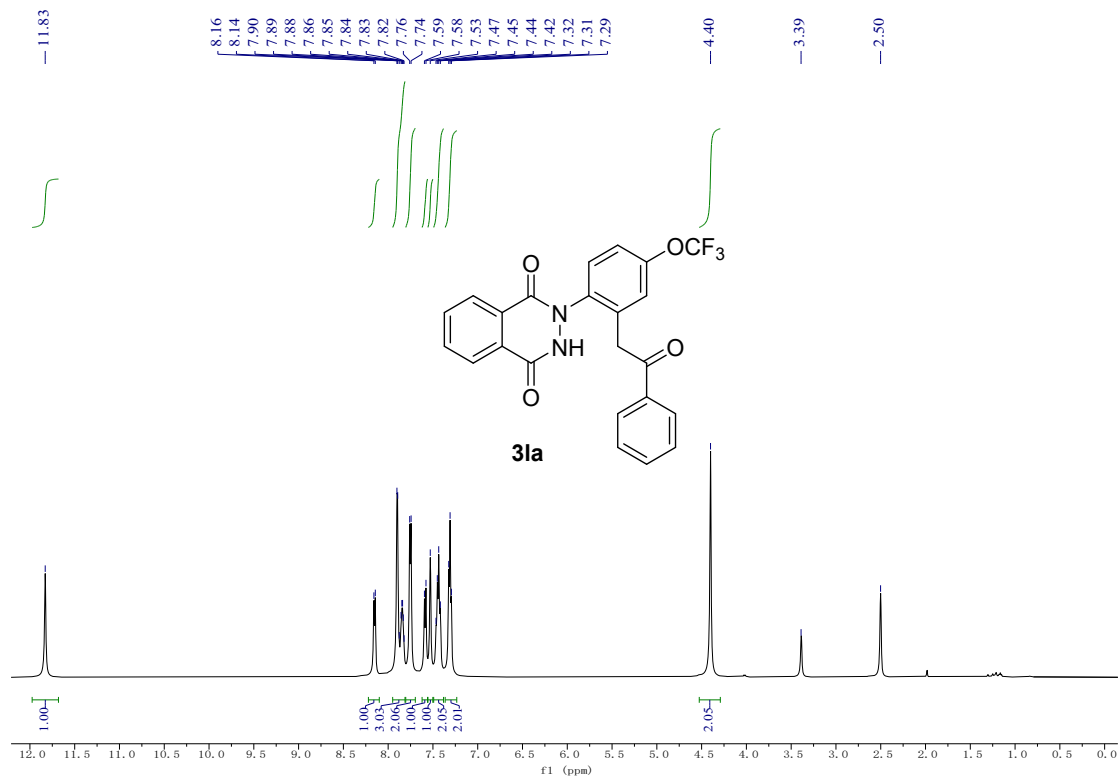
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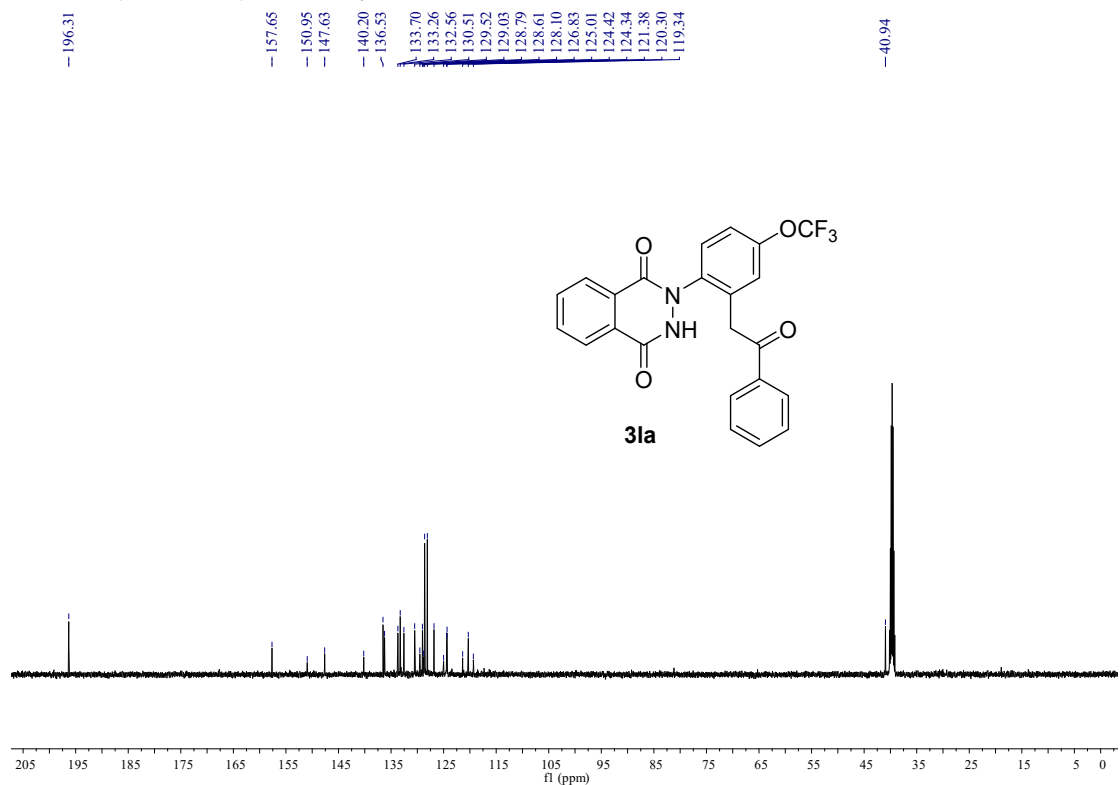
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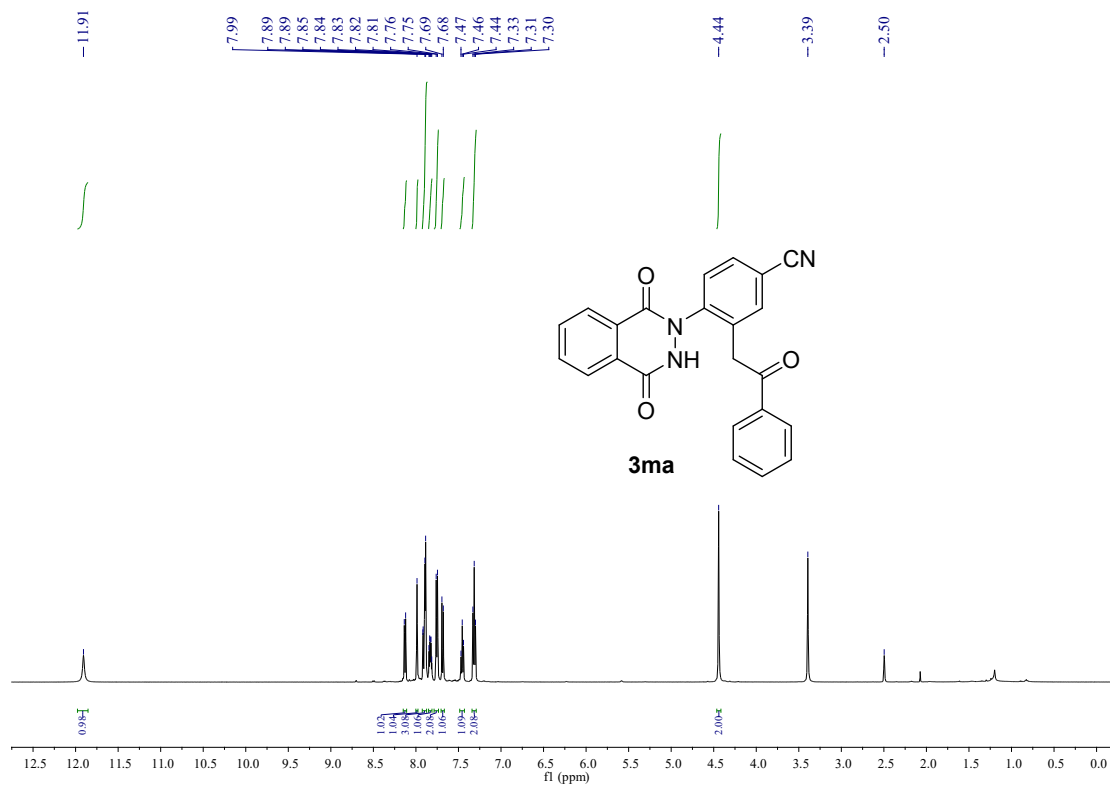
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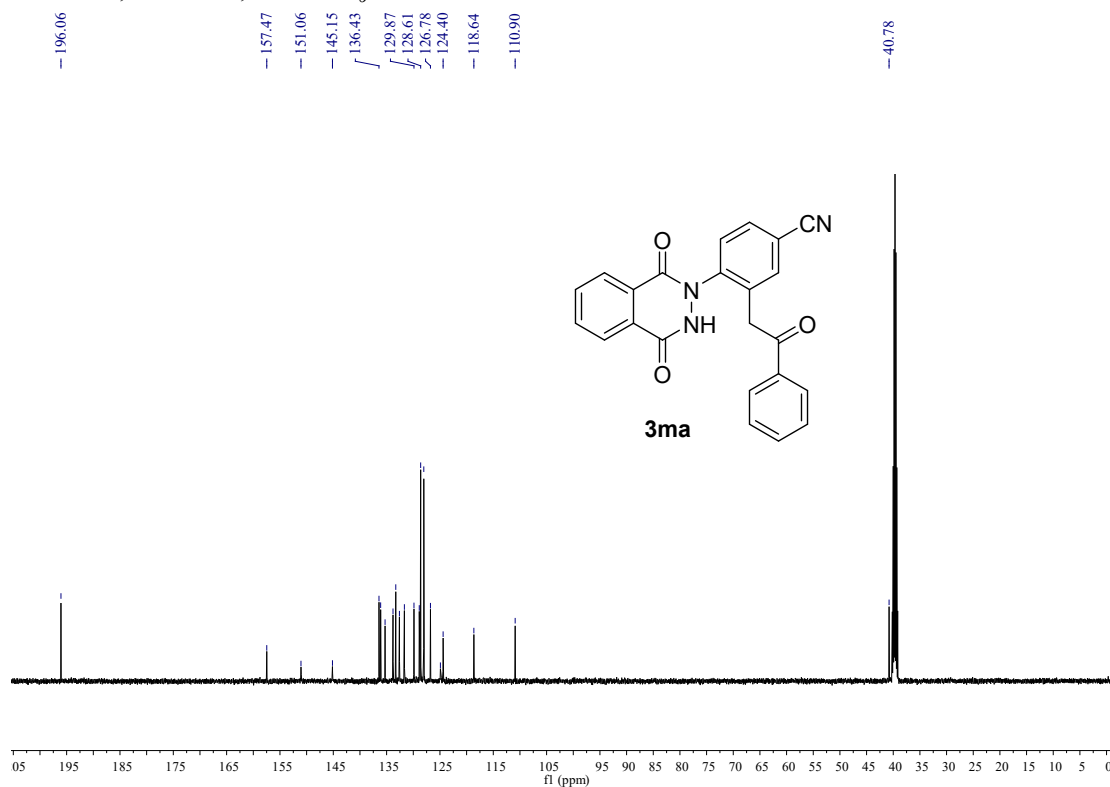
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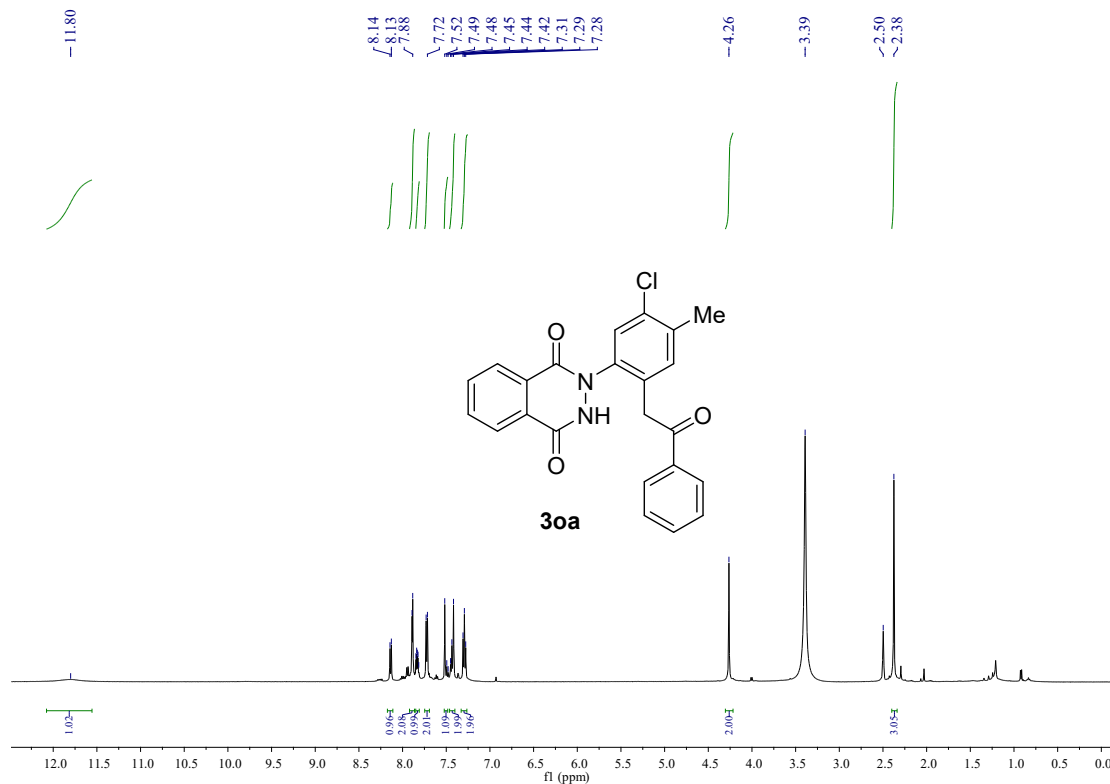
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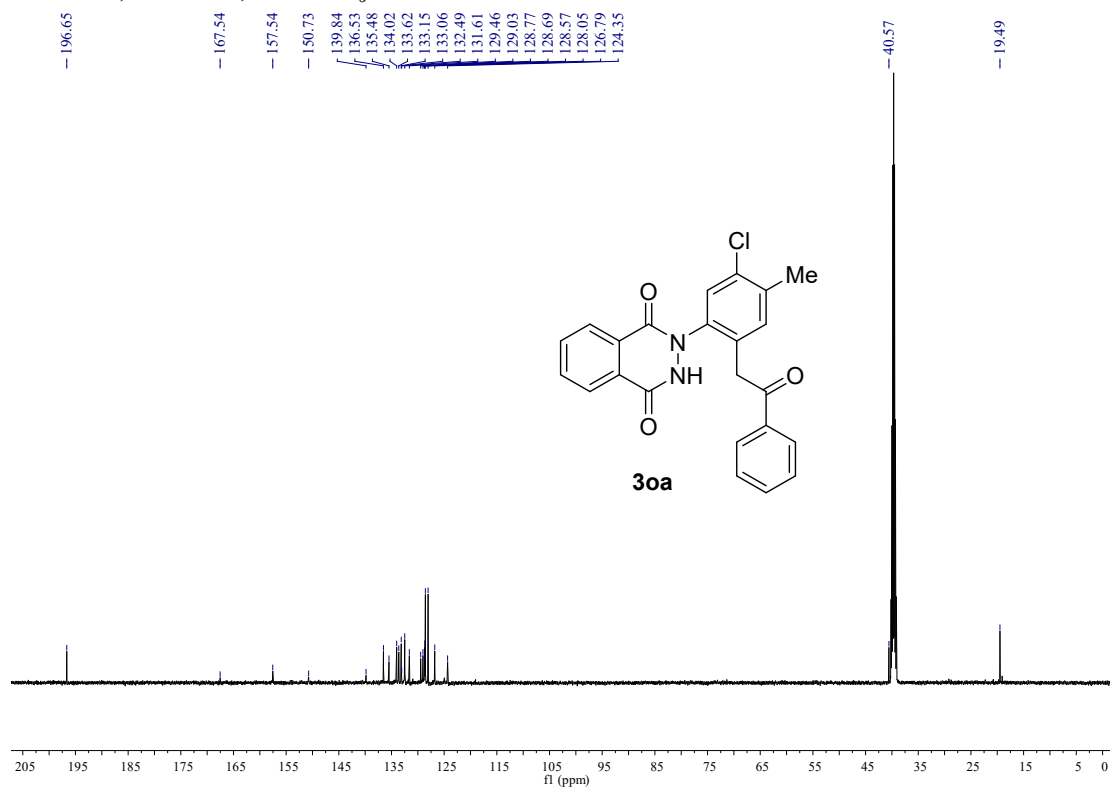
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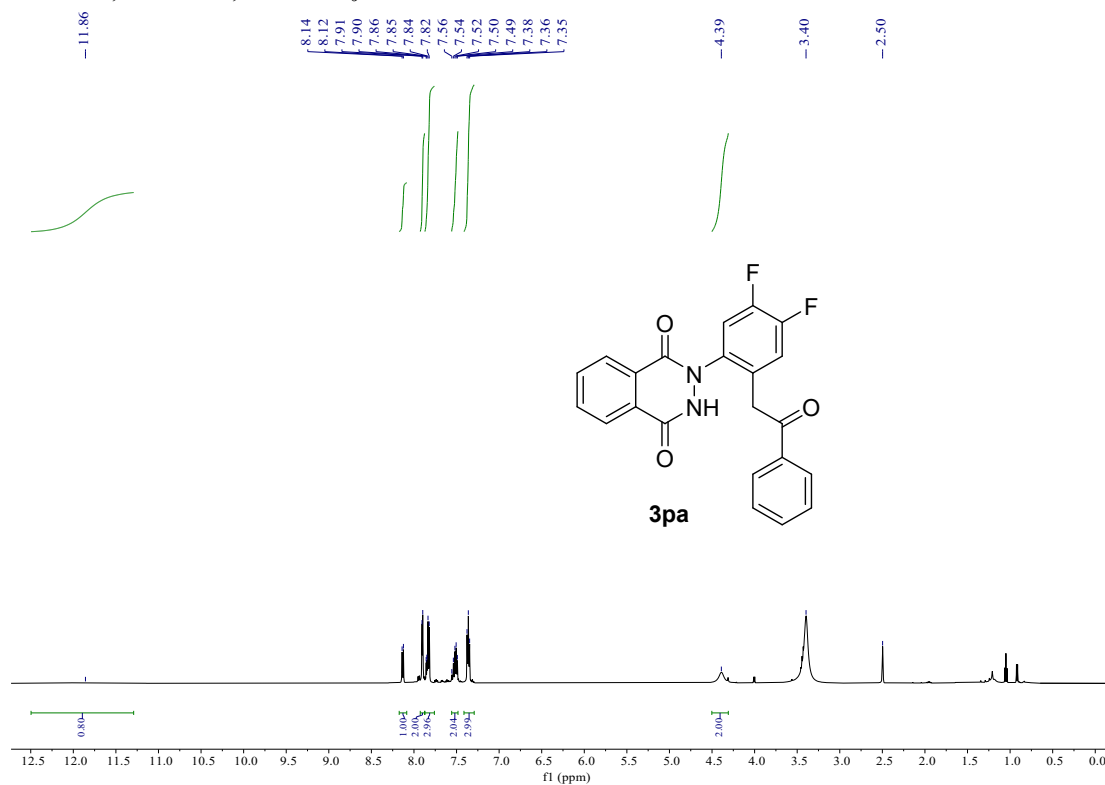
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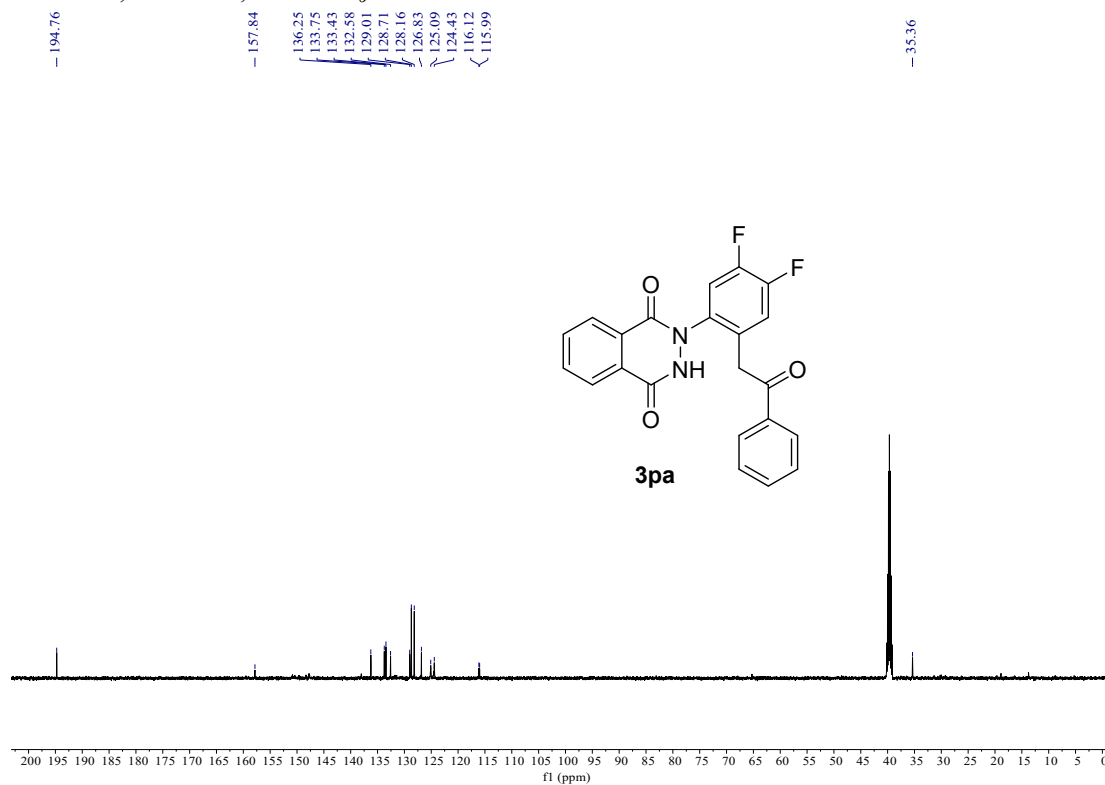
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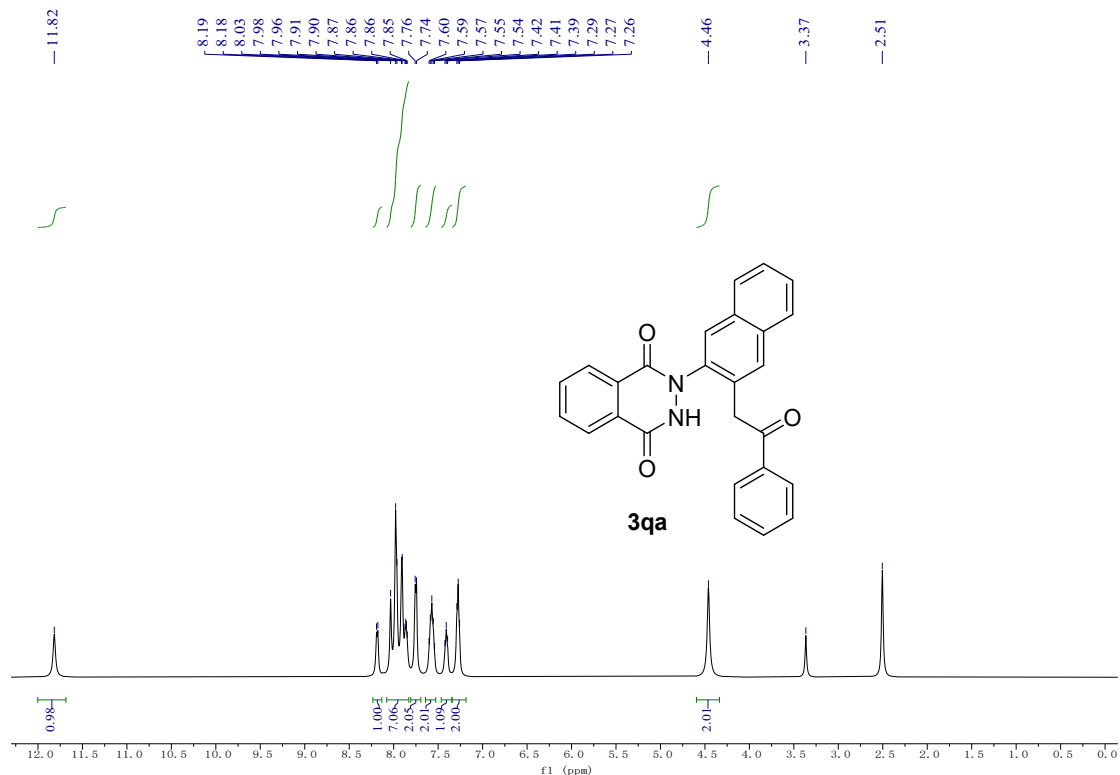
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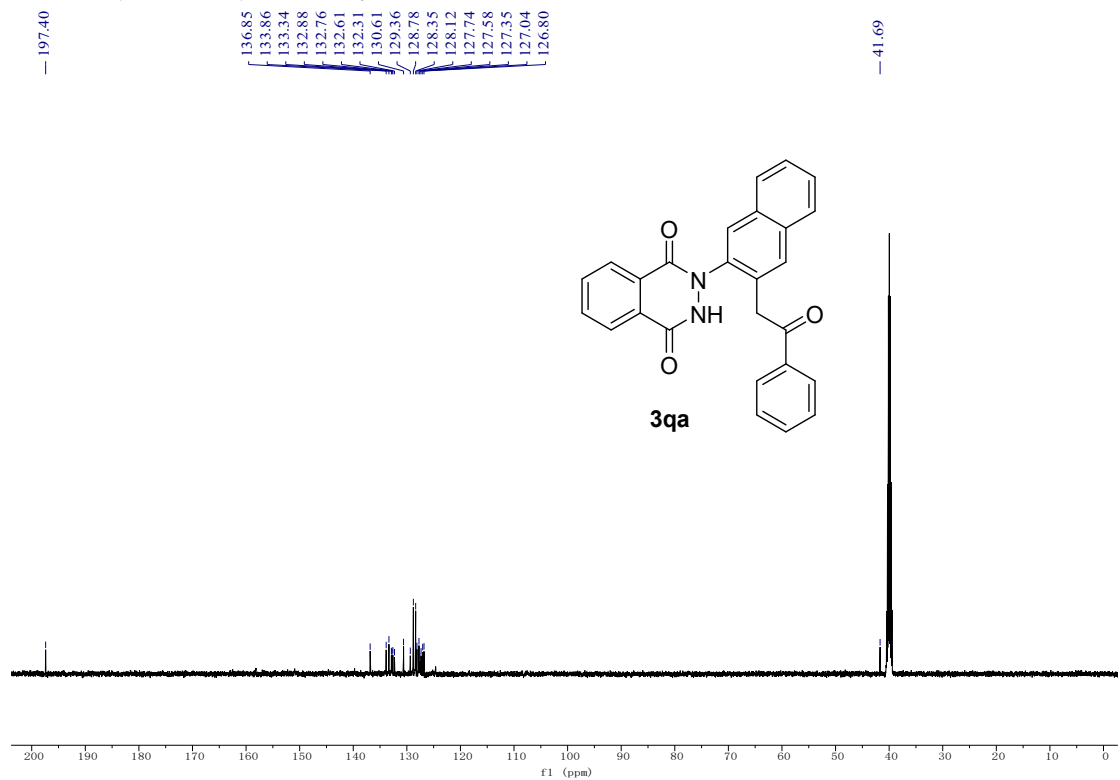
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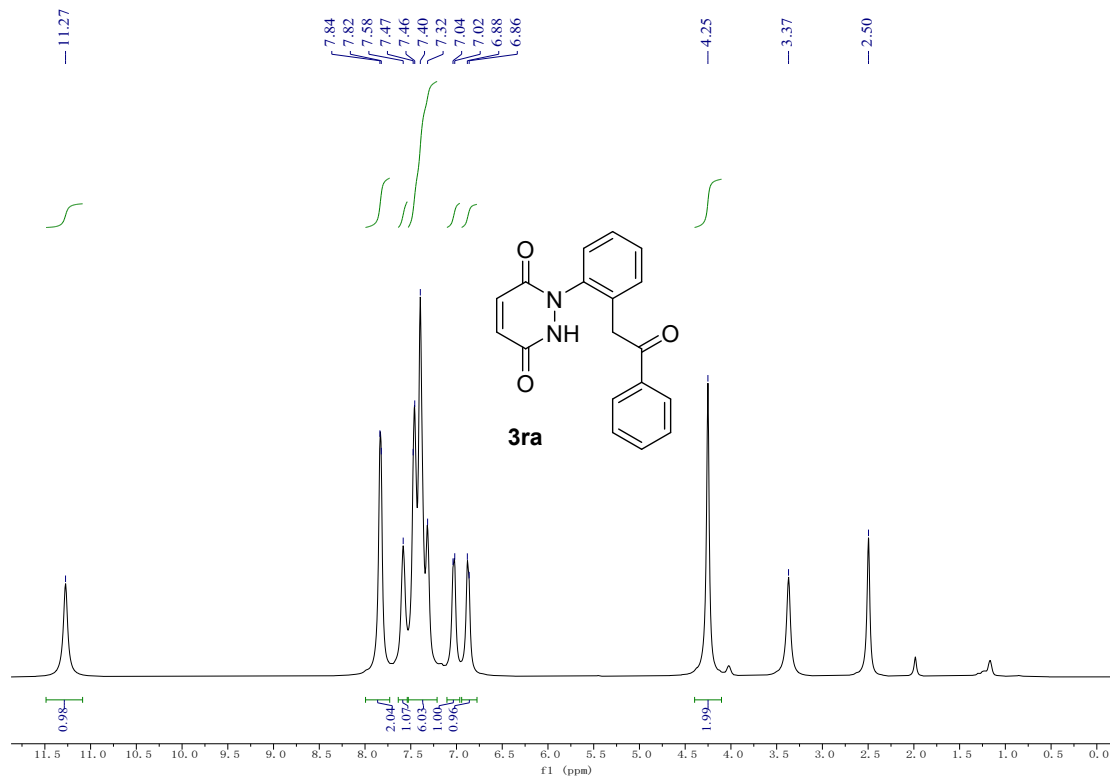
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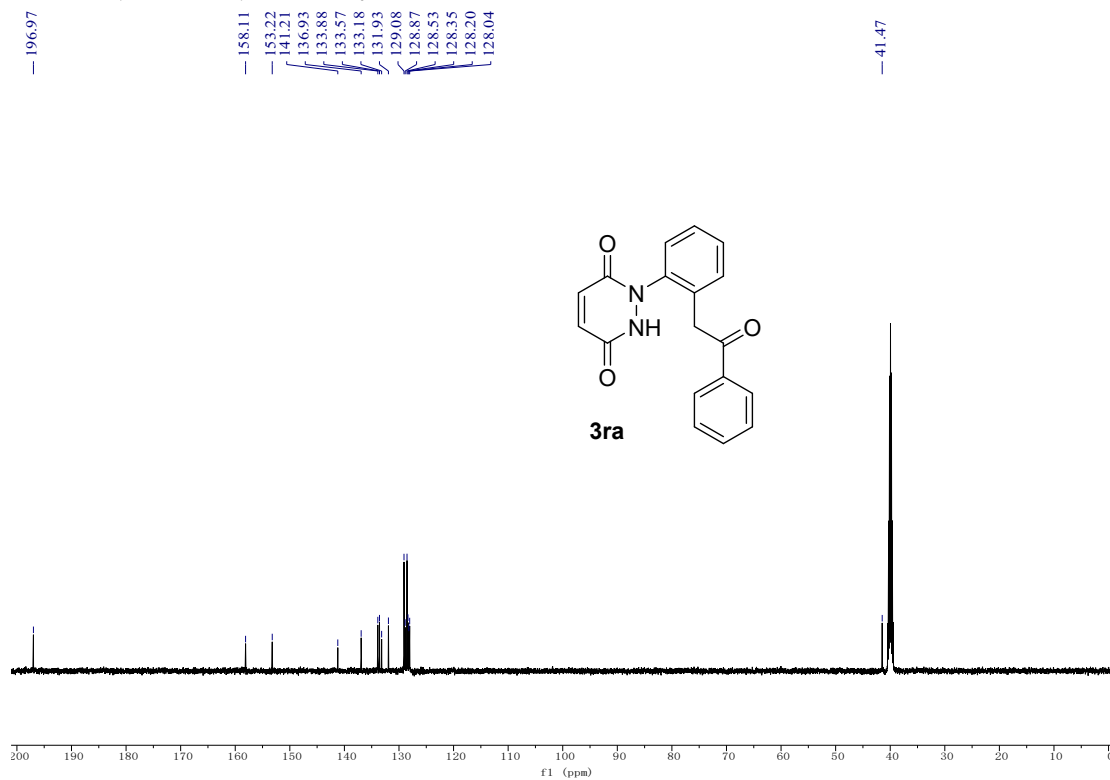
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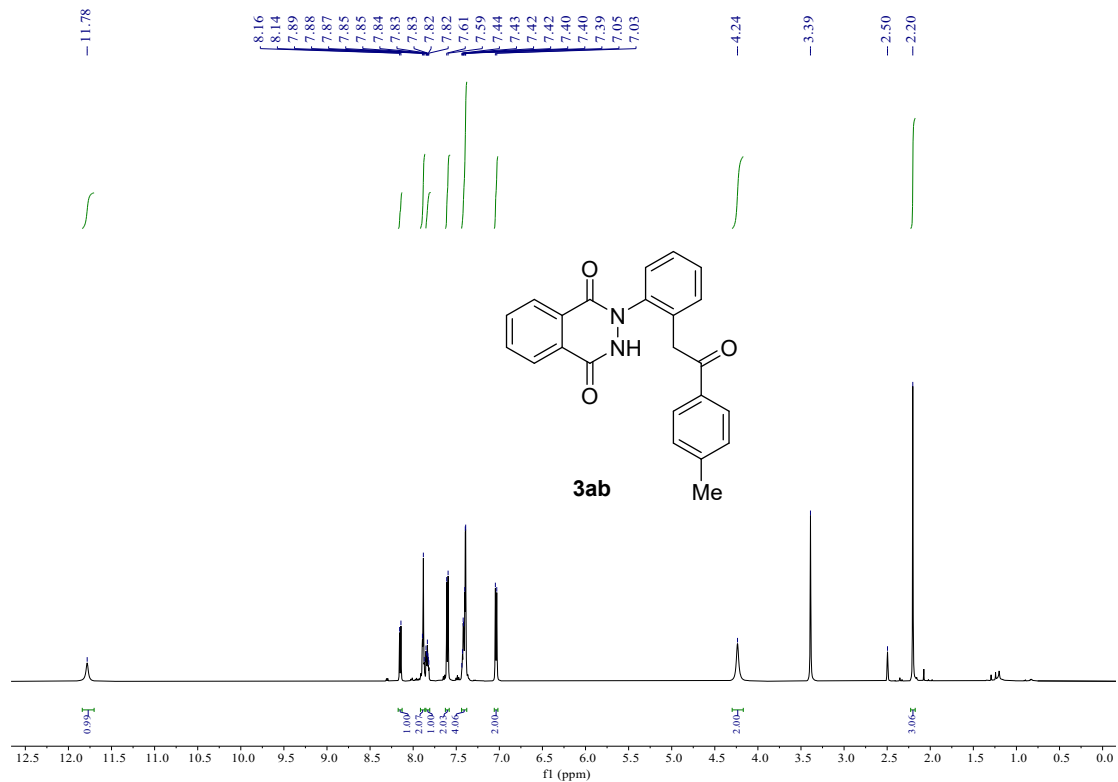
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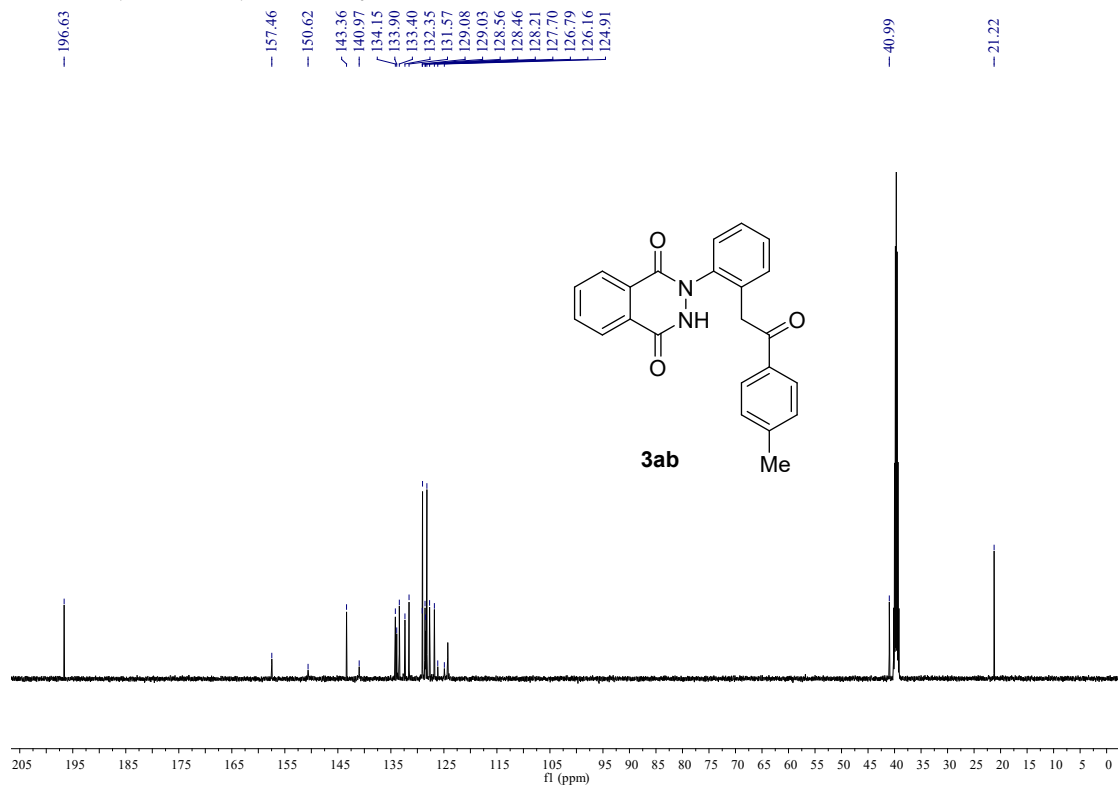
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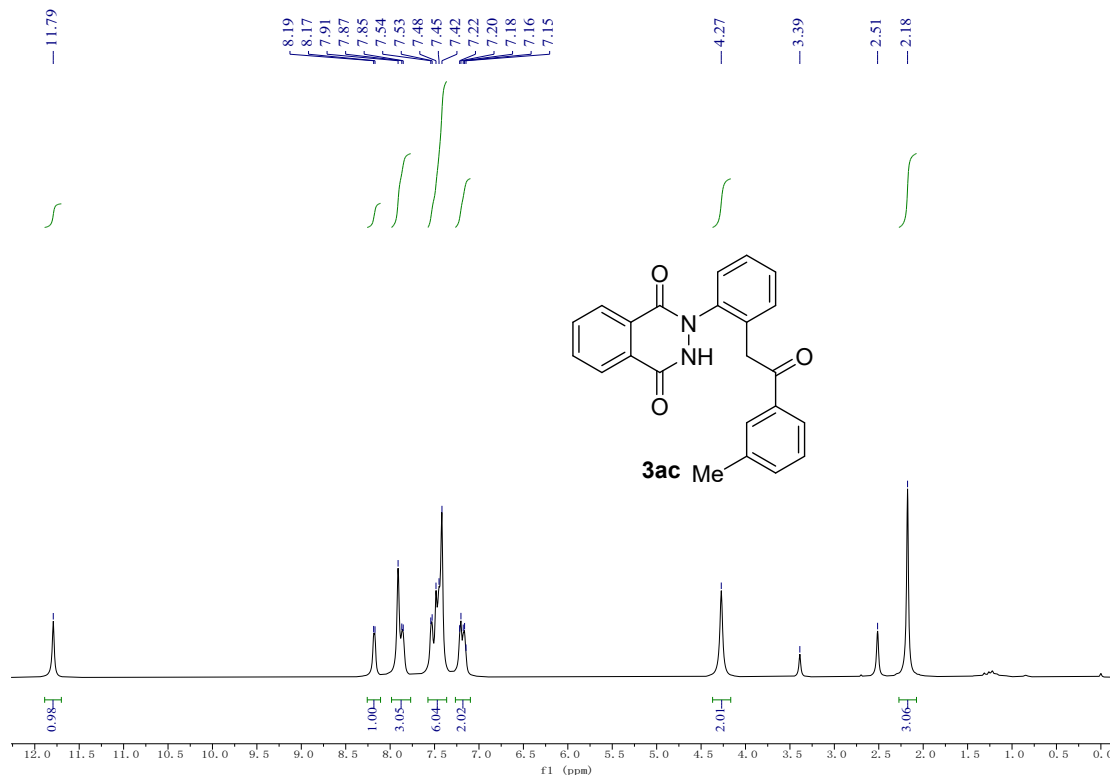
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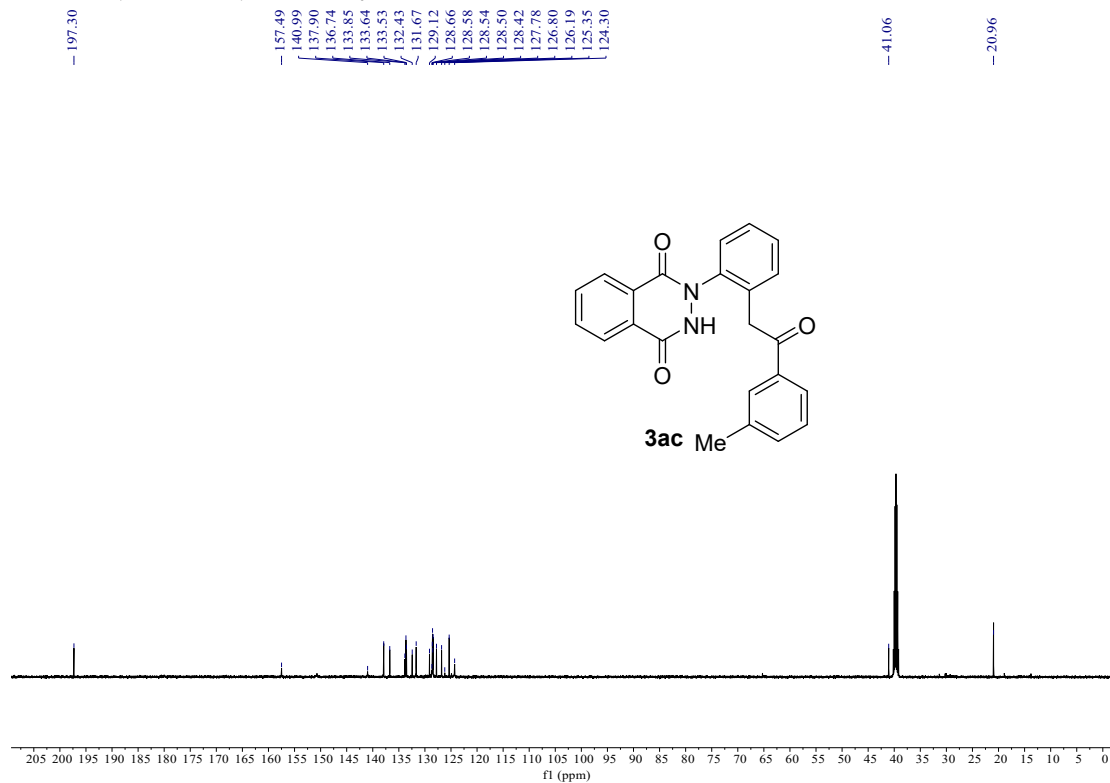
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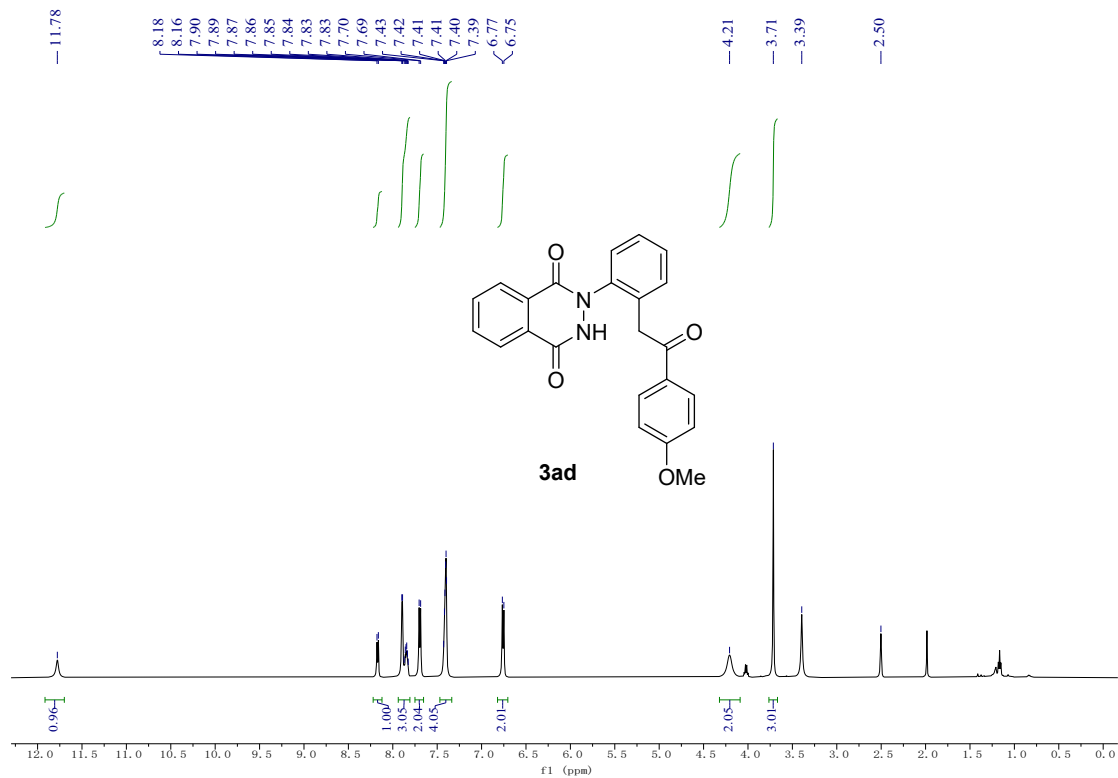
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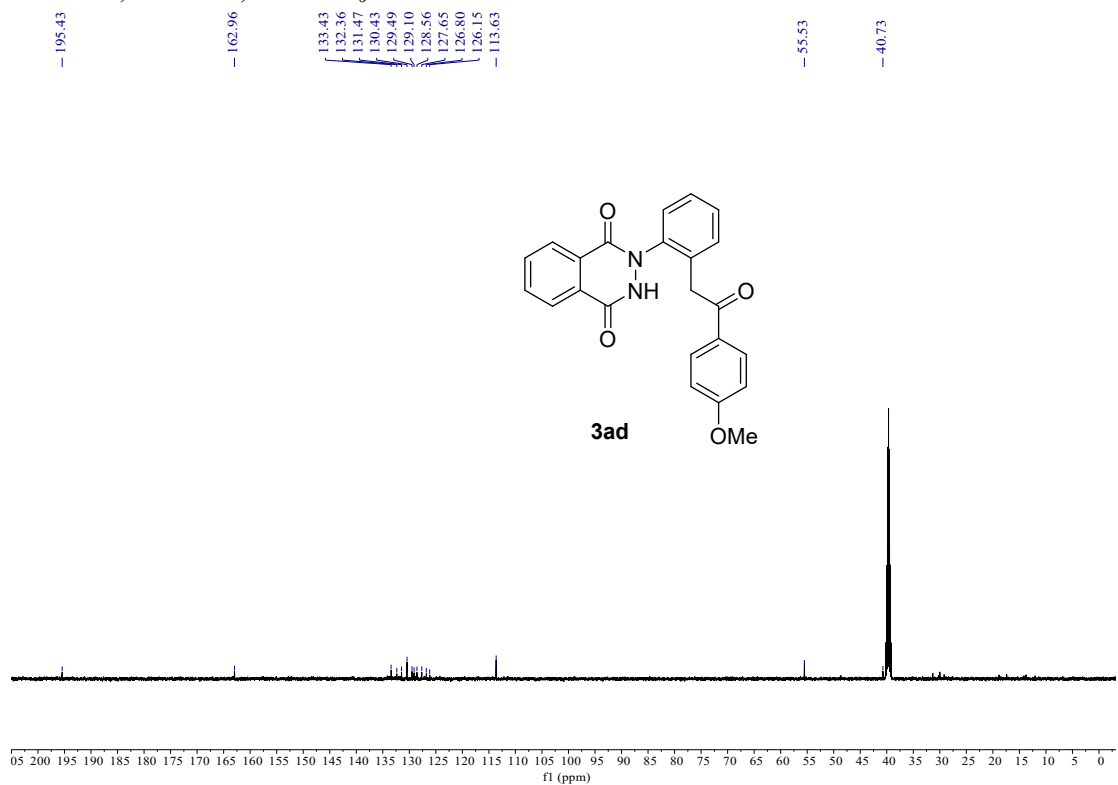
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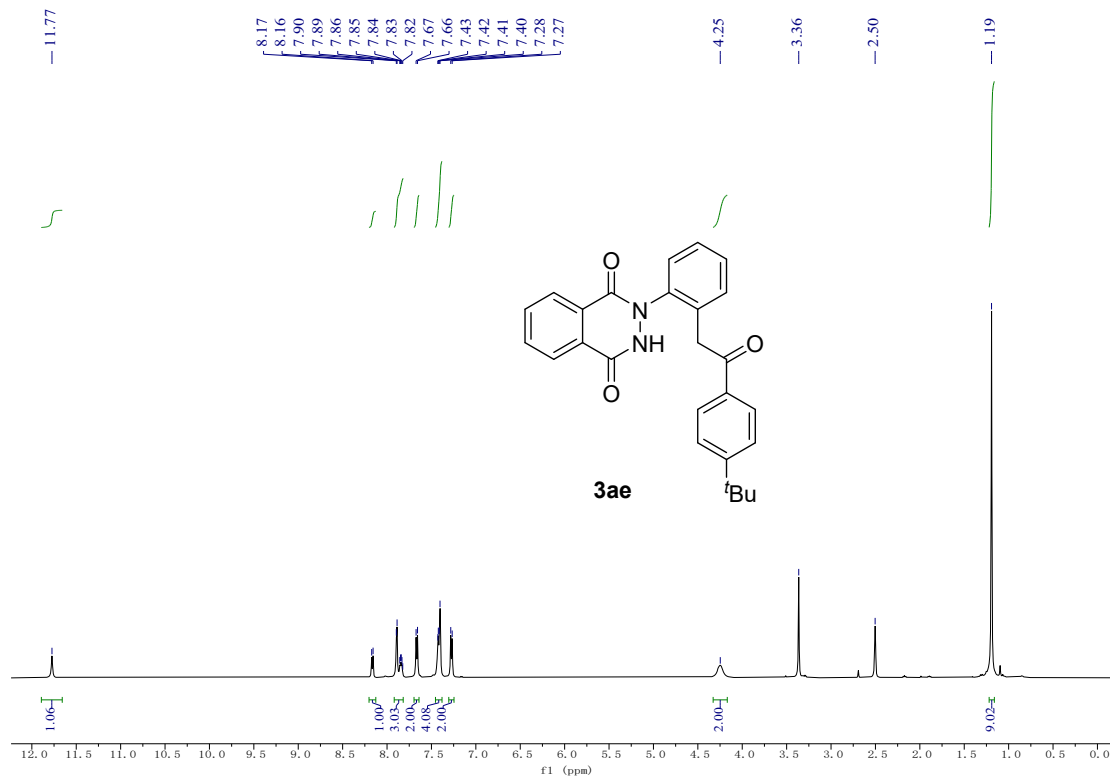
¹H NMR, 500 MHz, DMSO-d₆



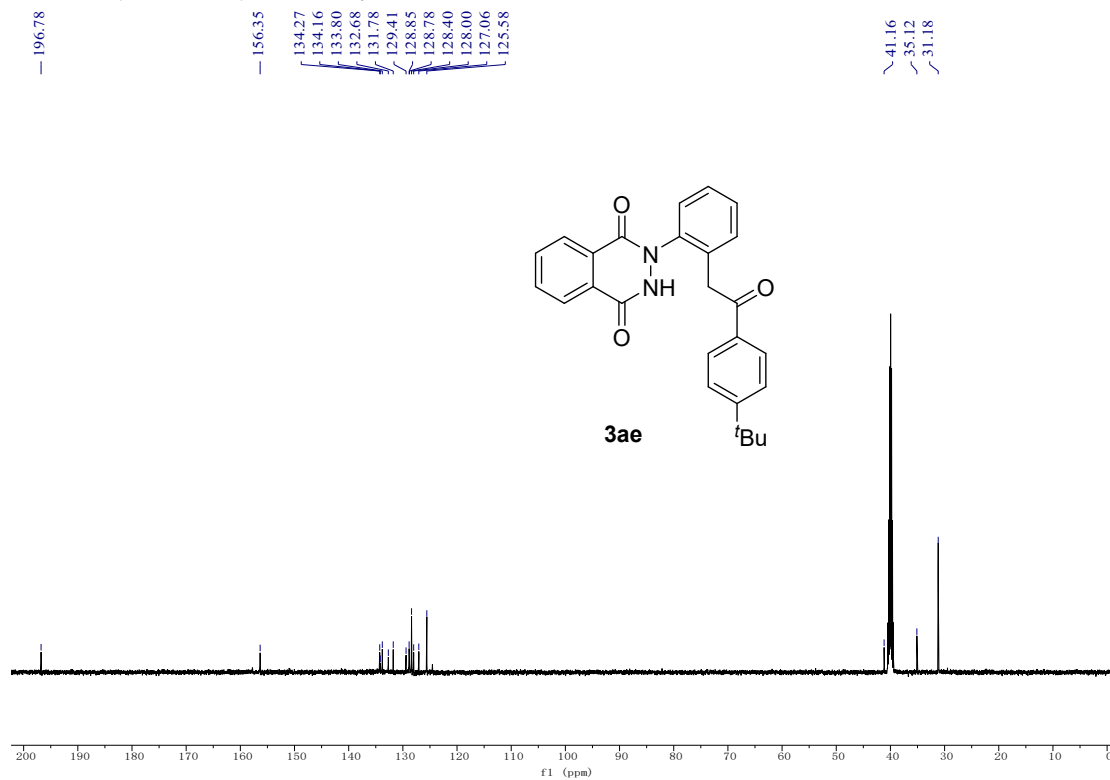
¹³C NMR, 125 MHz, DMSO-d₆



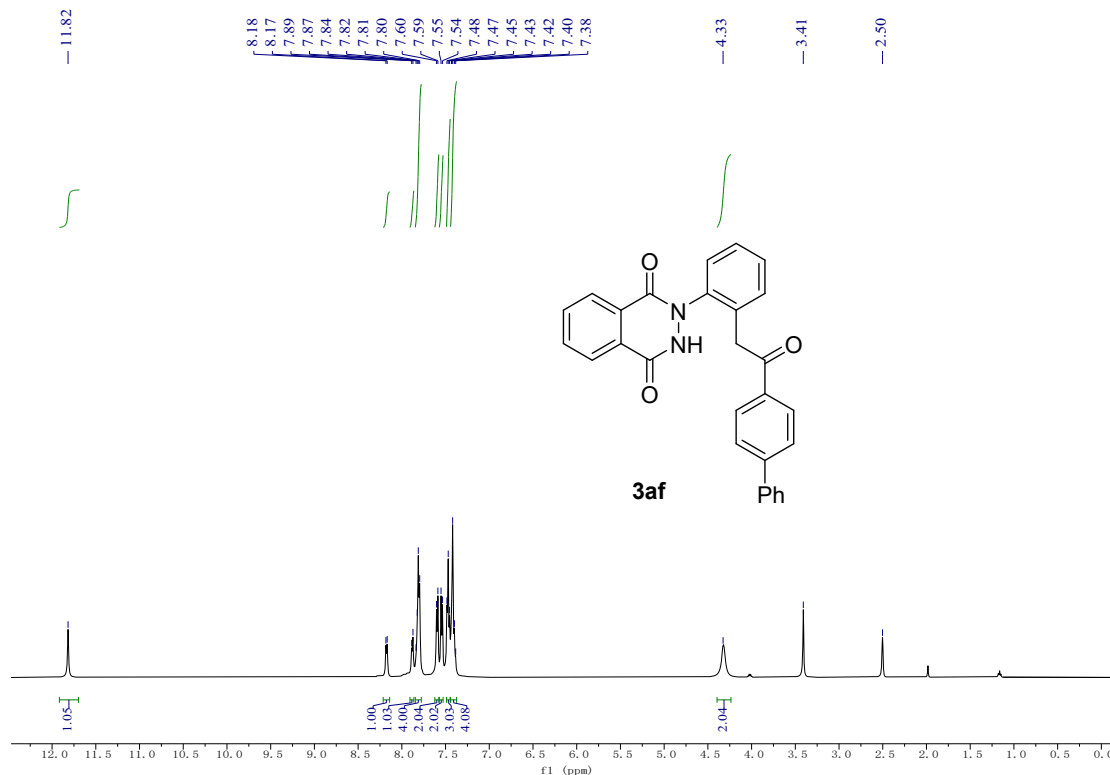
^1H NMR, 500 MHz, $\text{DMSO-}d_6$



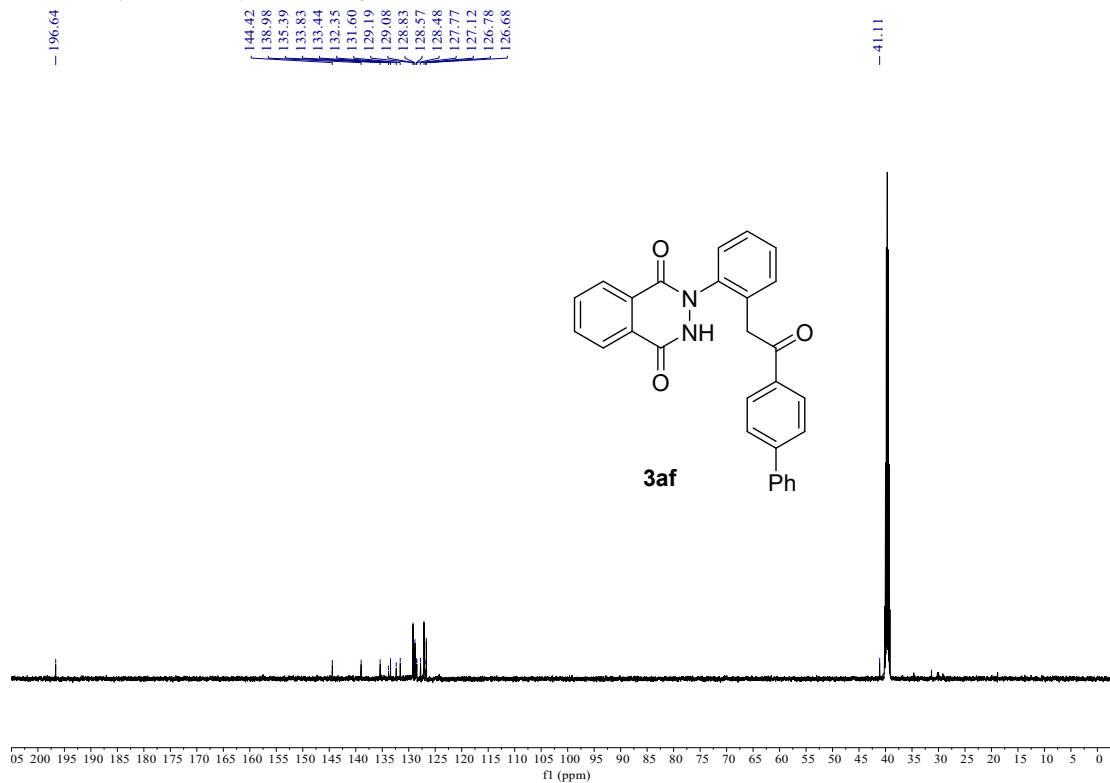
^{13}C NMR, 125 MHz, $\text{DMSO-}d_6$



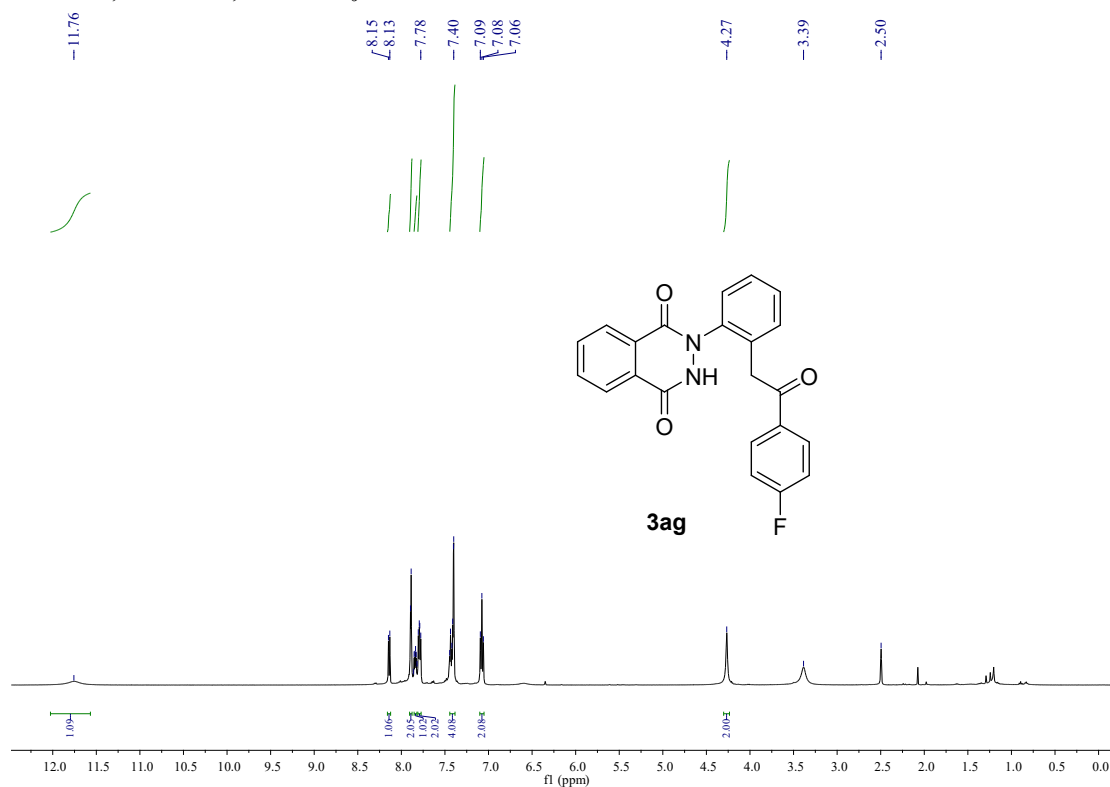
¹H NMR, 500 MHz, DMSO-d₆



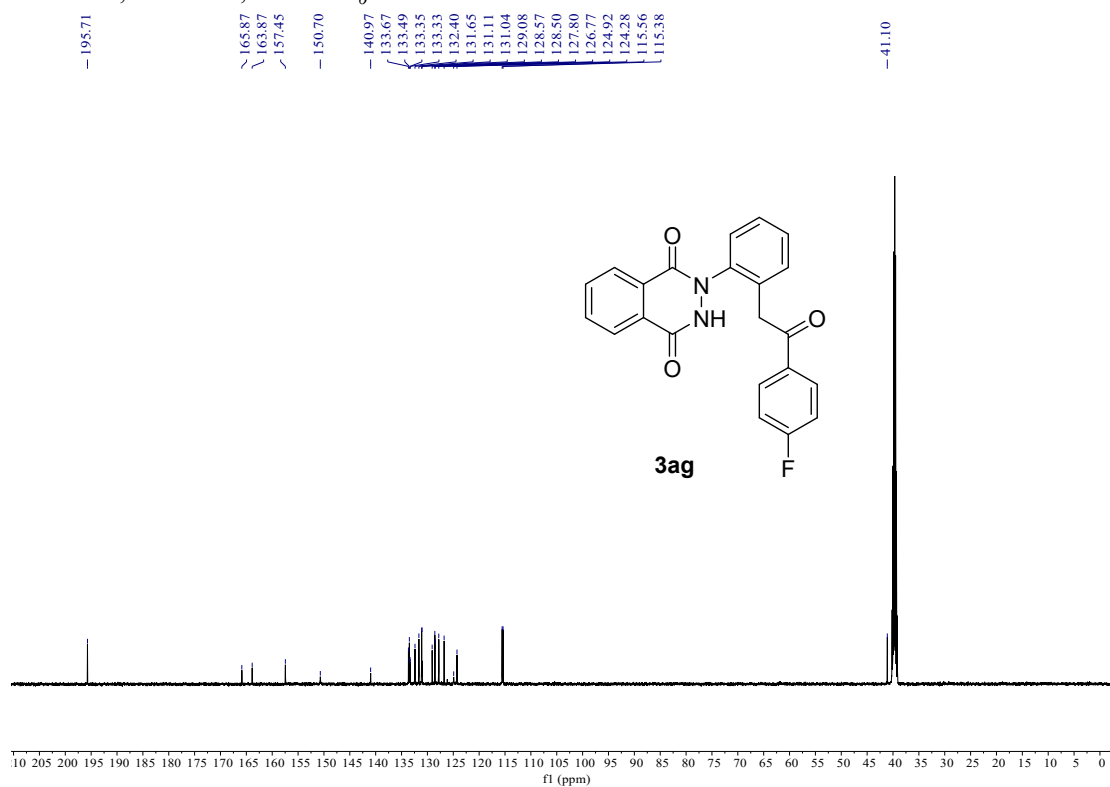
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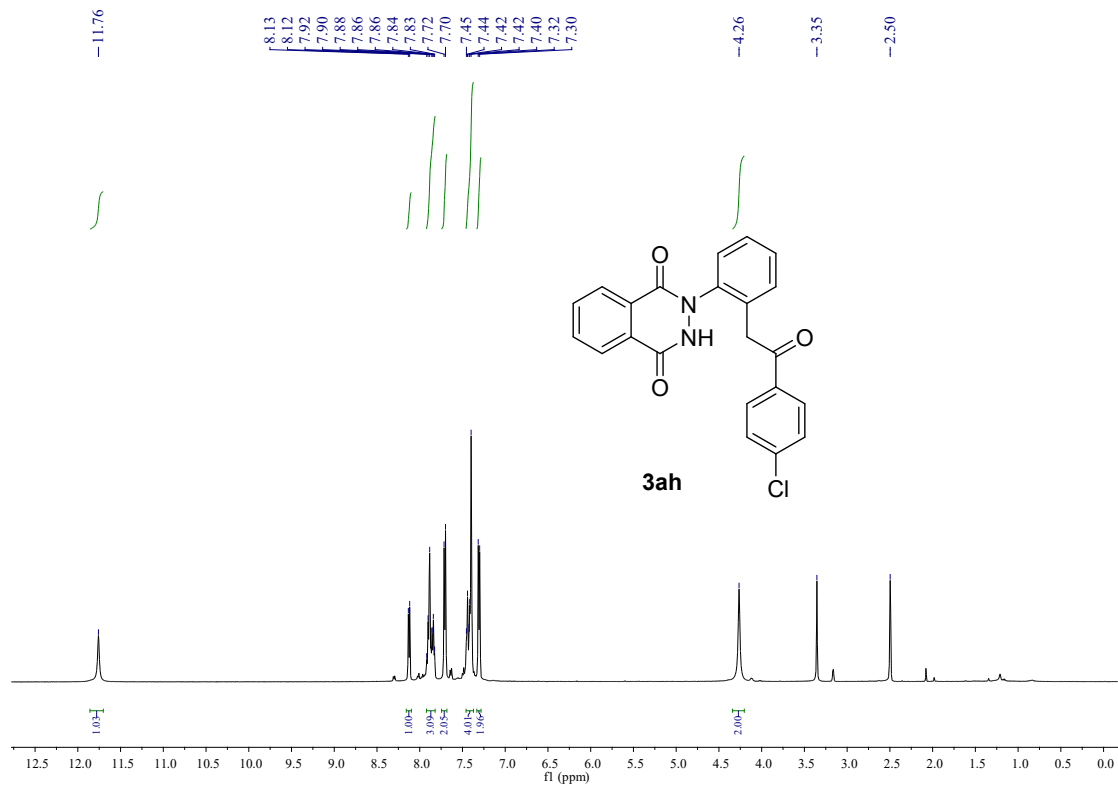
¹H NMR, 500 MHz, DMSO-d₆



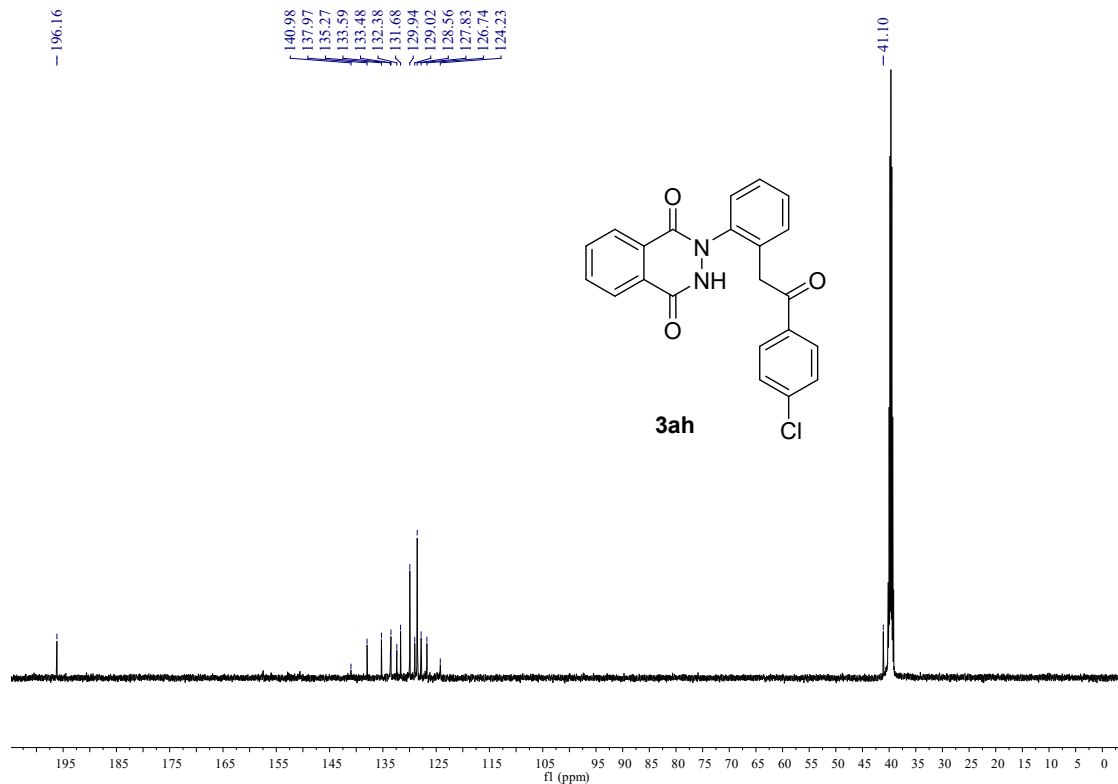
¹³C NMR, 125 MHz, DMSO-d₆



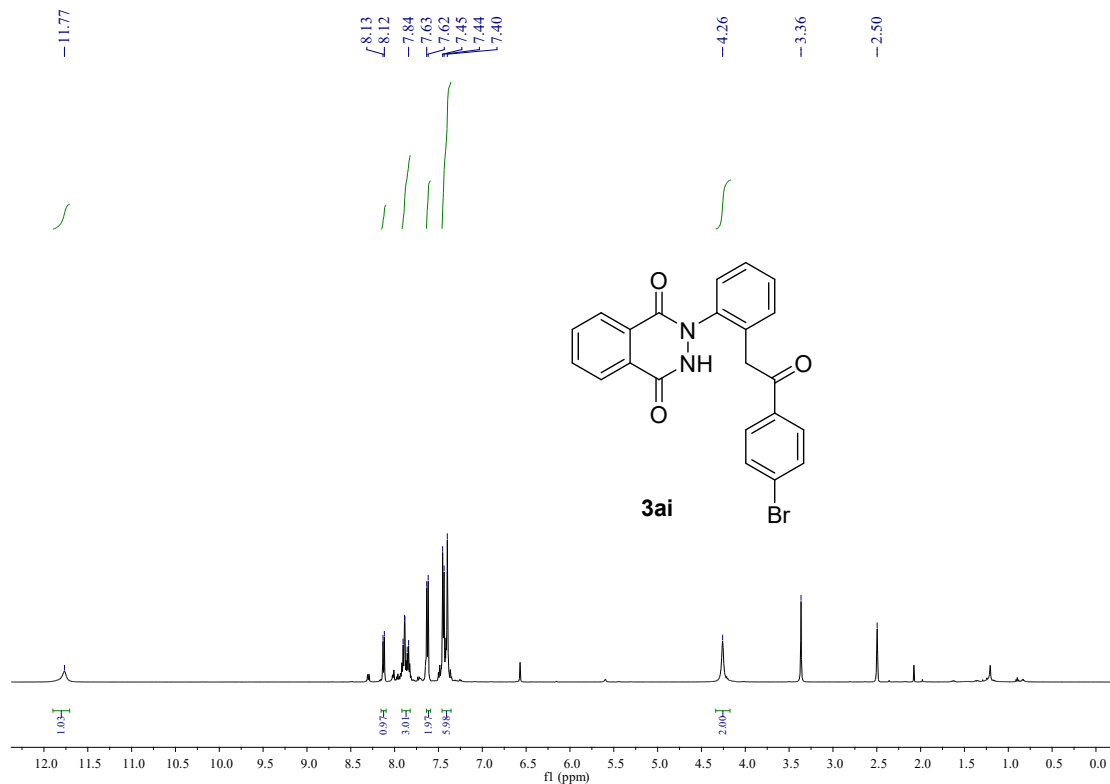
¹H NMR, 500 MHz, DMSO-d₆



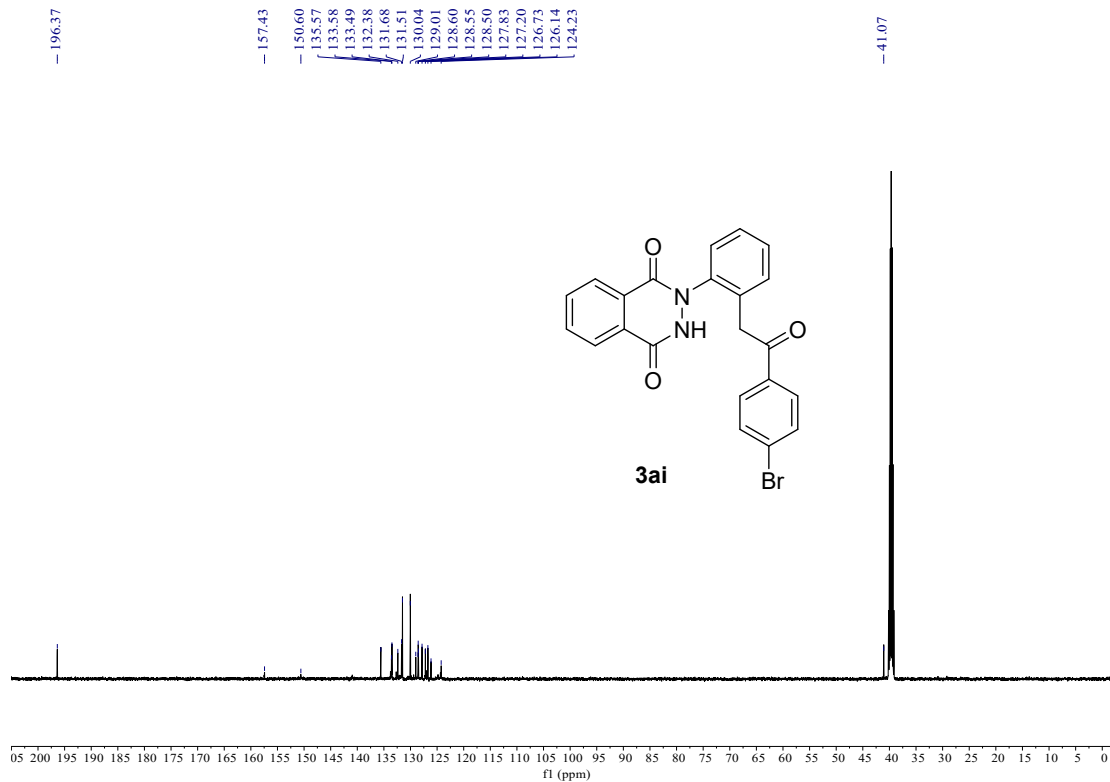
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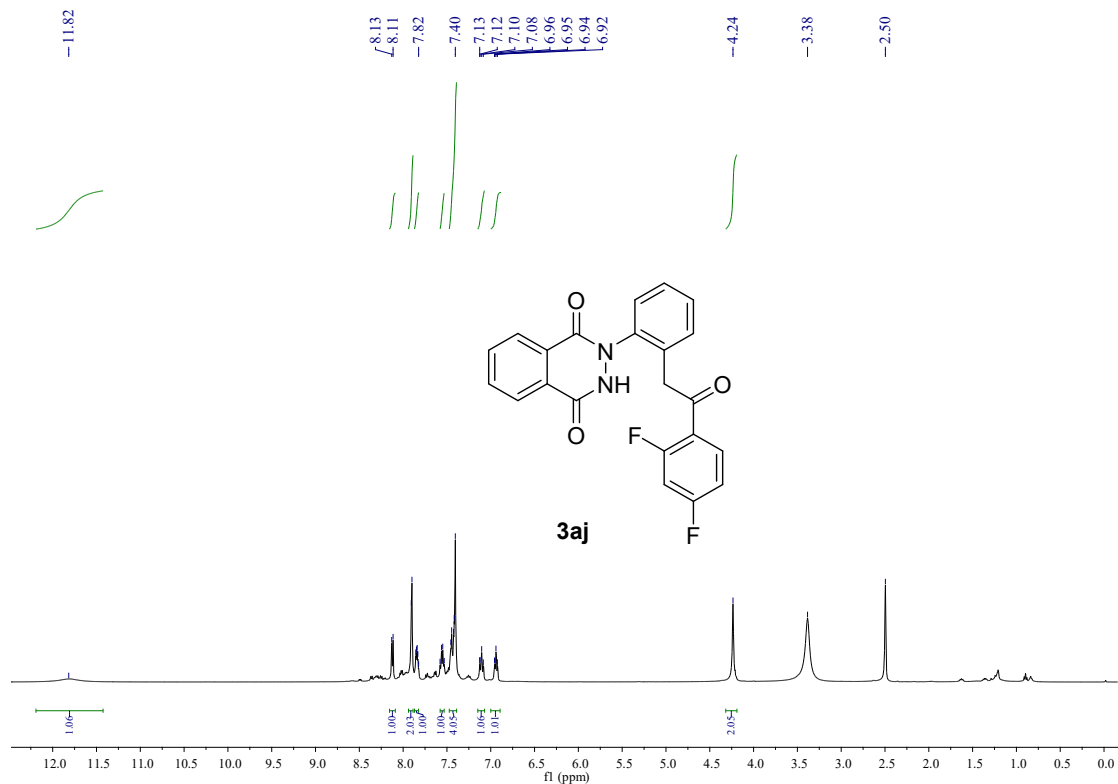
¹H NMR, 500 MHz, DMSO-d₆



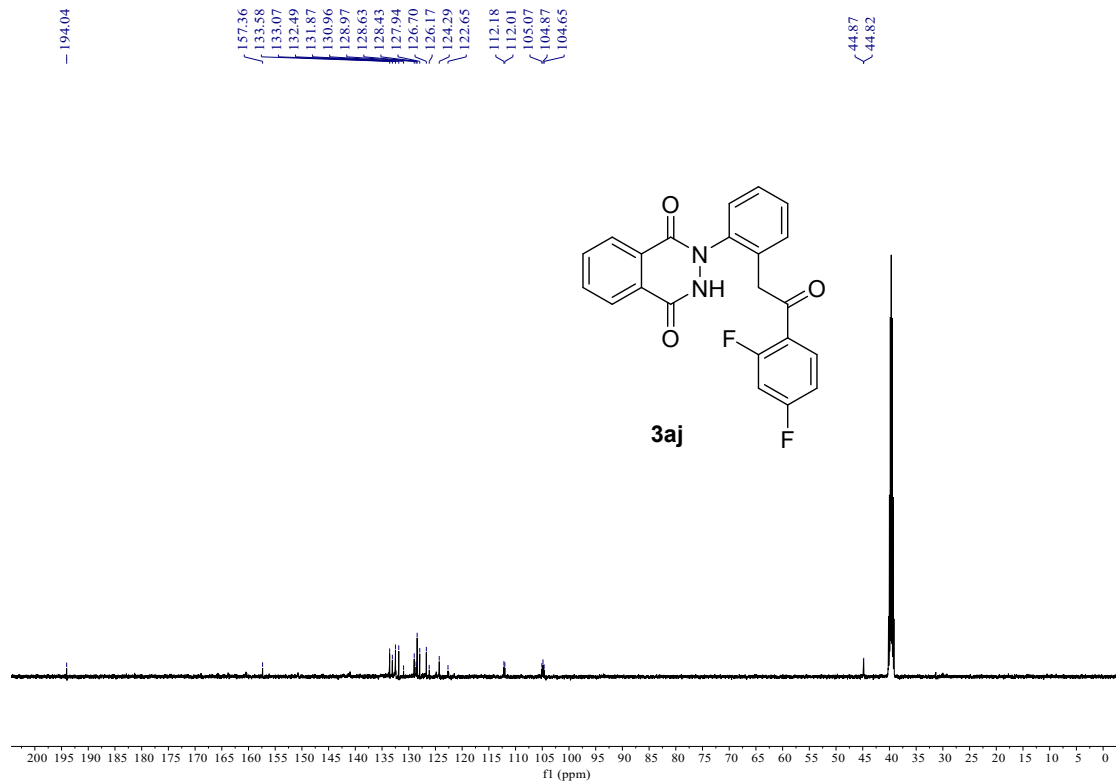
¹³C NMR, 125 MHz, DMSO-d₆



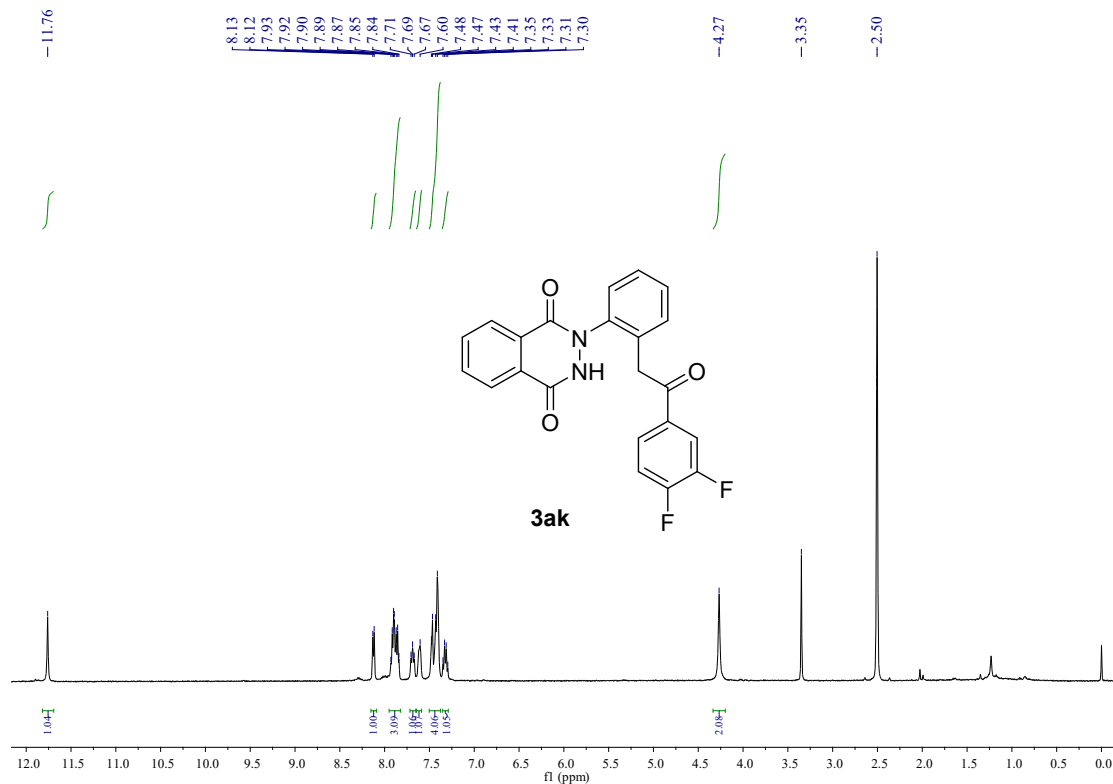
^1H NMR, 500 MHz, $\text{DMSO-}d_6$



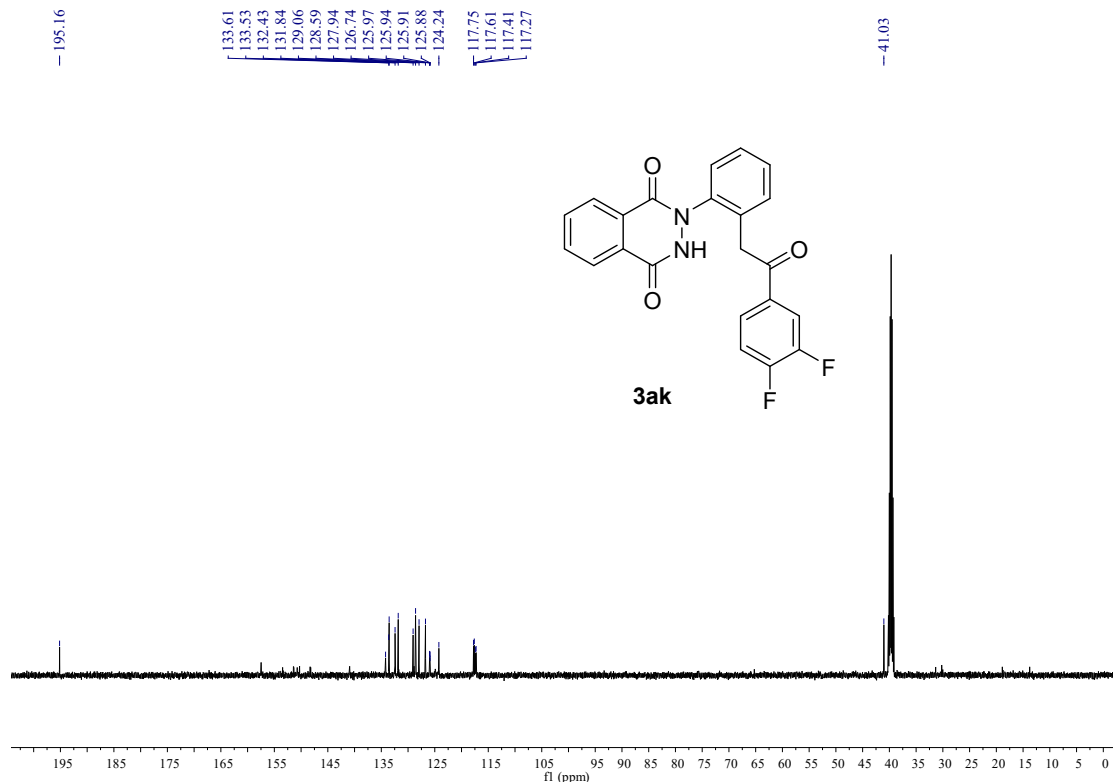
^{13}C NMR, 125 MHz, $\text{DMSO-}d_6$



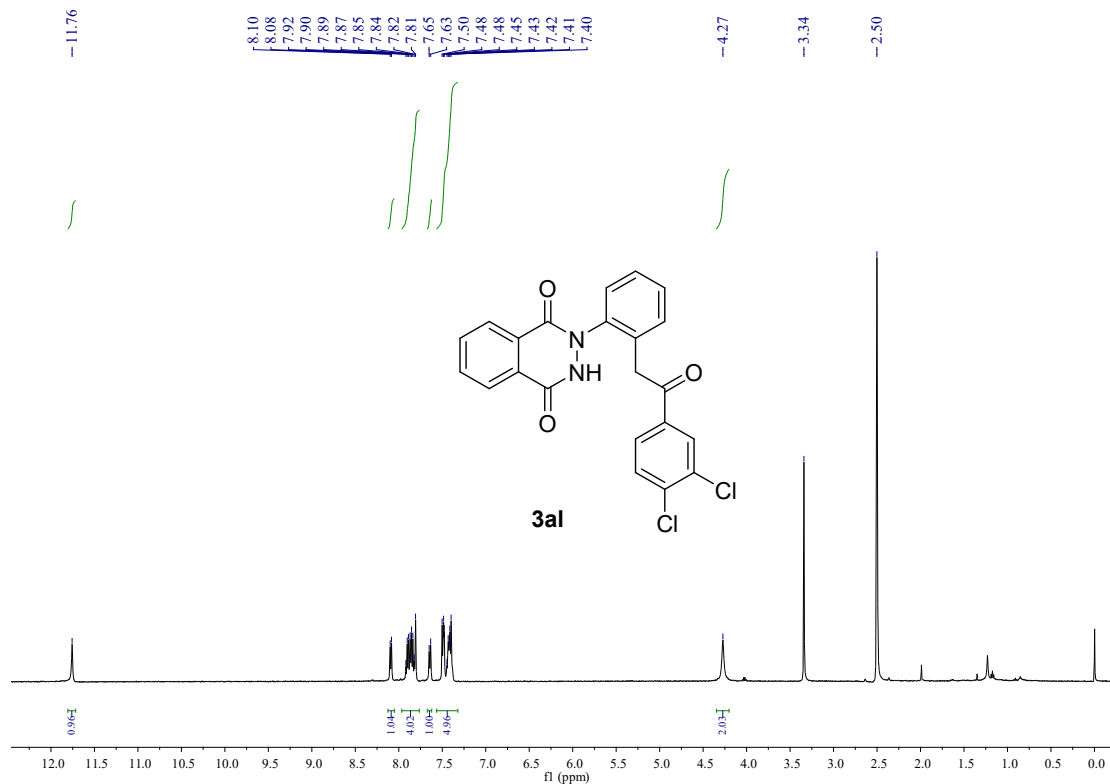
¹H NMR, 500 MHz, DMSO-d₆



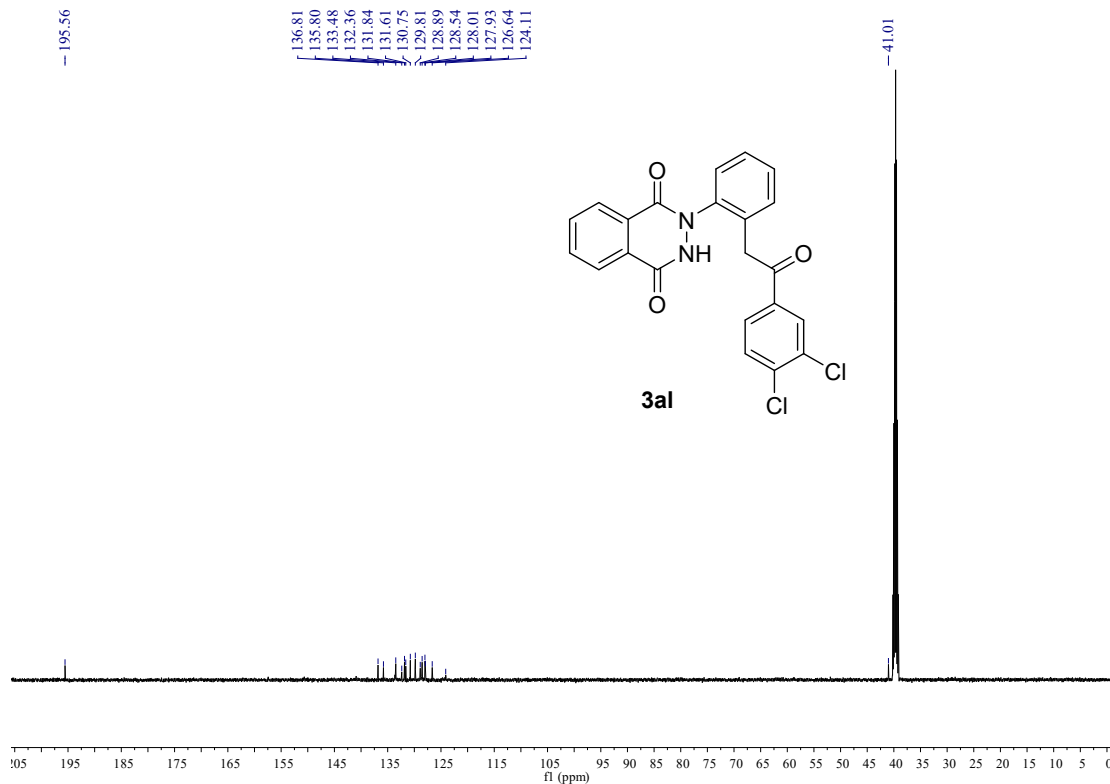
¹³C NMR, 125 MHz, DMSO-d₆



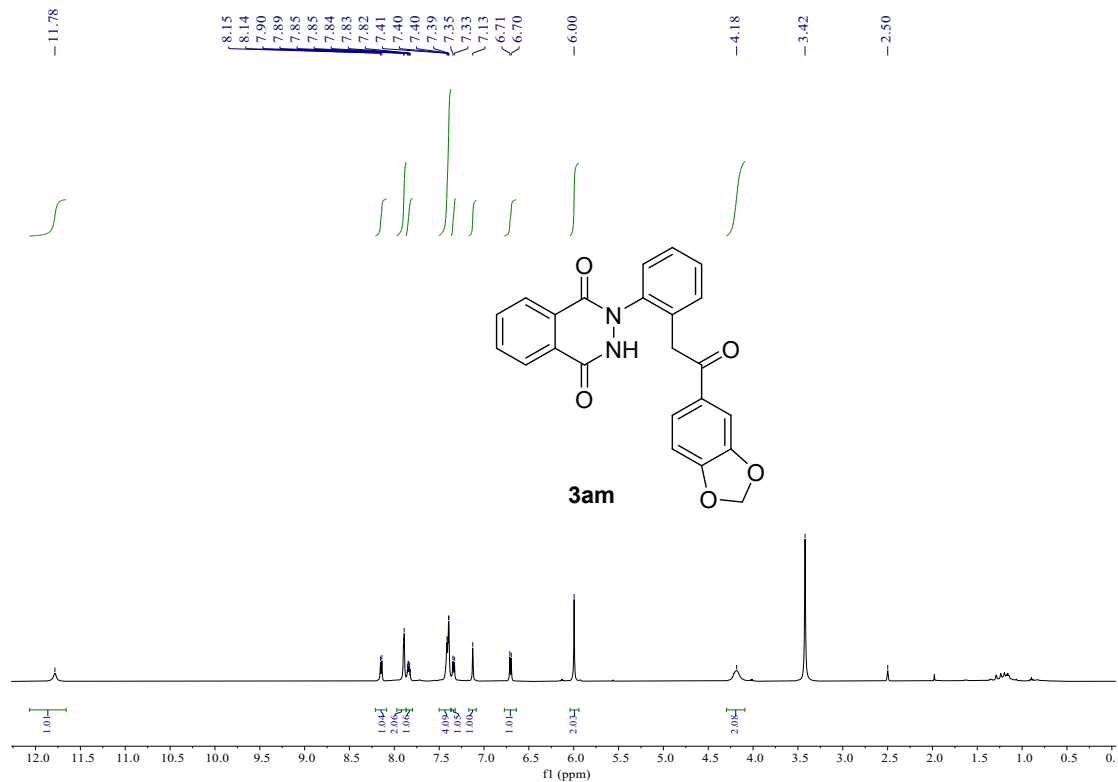
¹H NMR, 500 MHz, DMSO-d₆



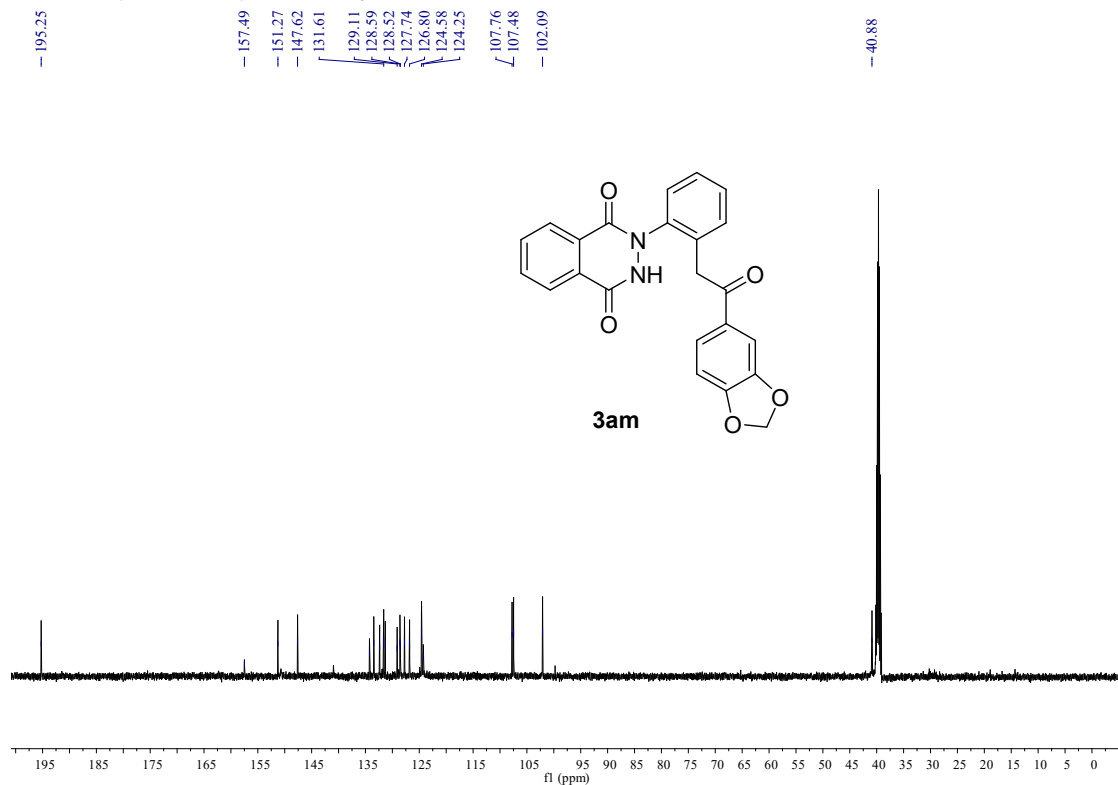
¹³C NMR, 125 MHz, DMSO-d₆



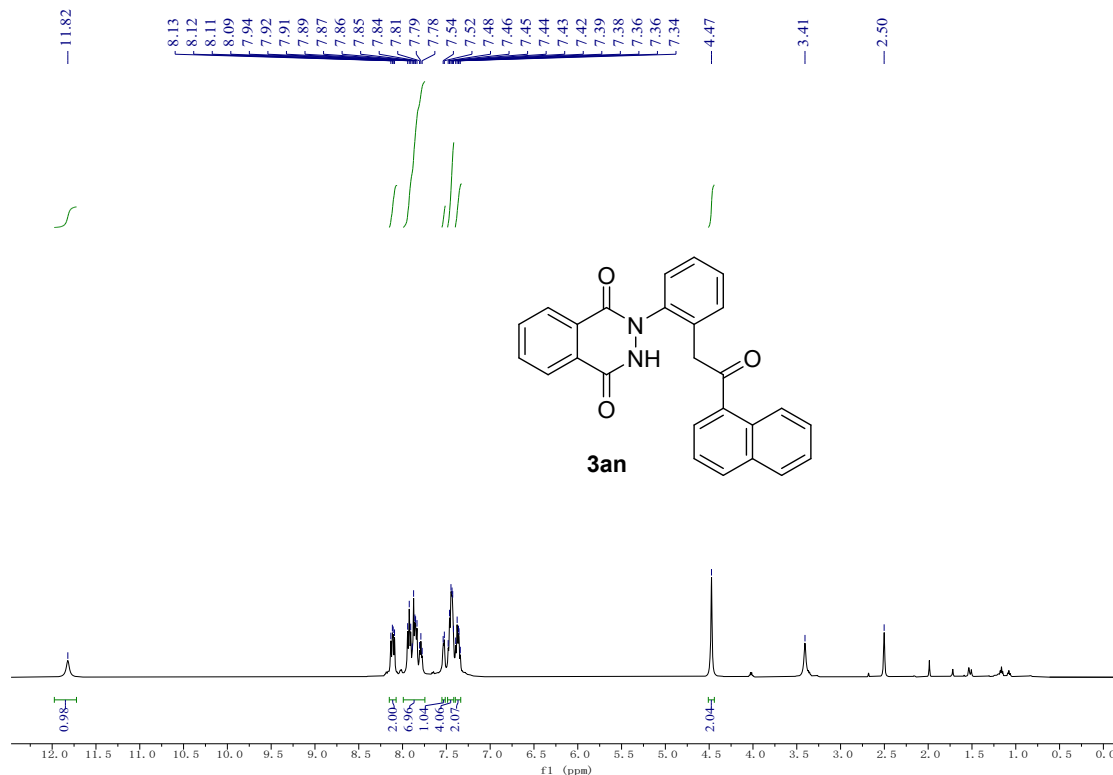
¹H NMR, 500 MHz, DMSO-d₆



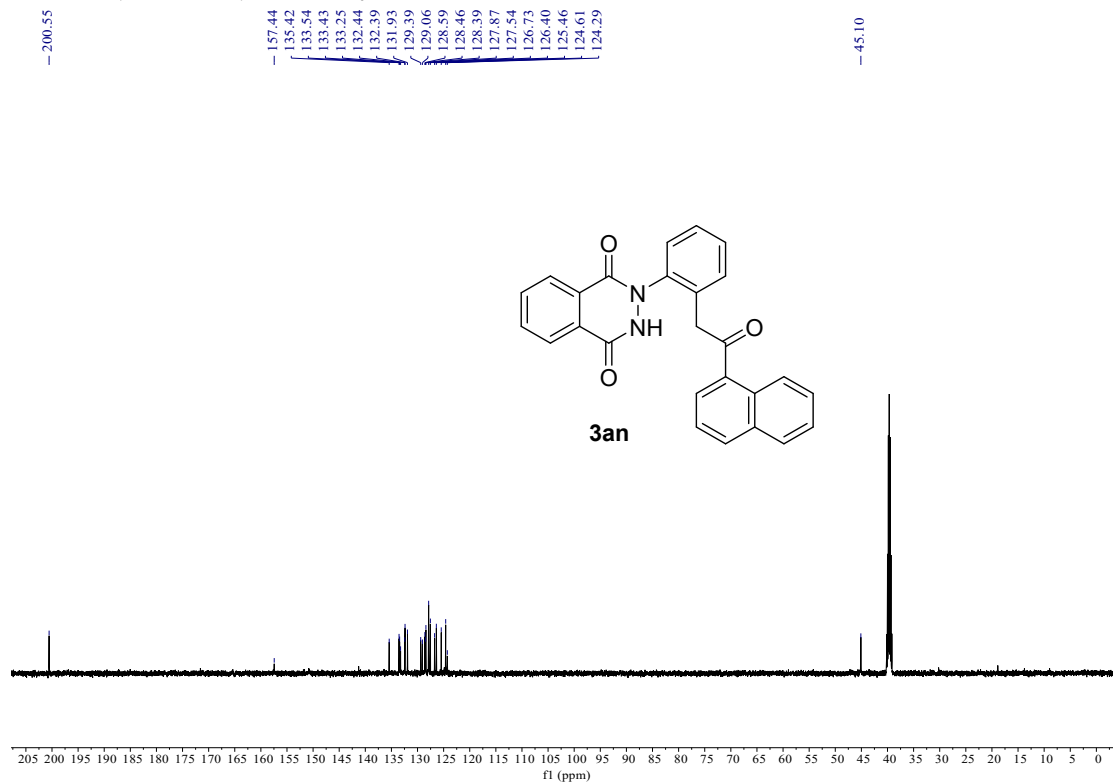
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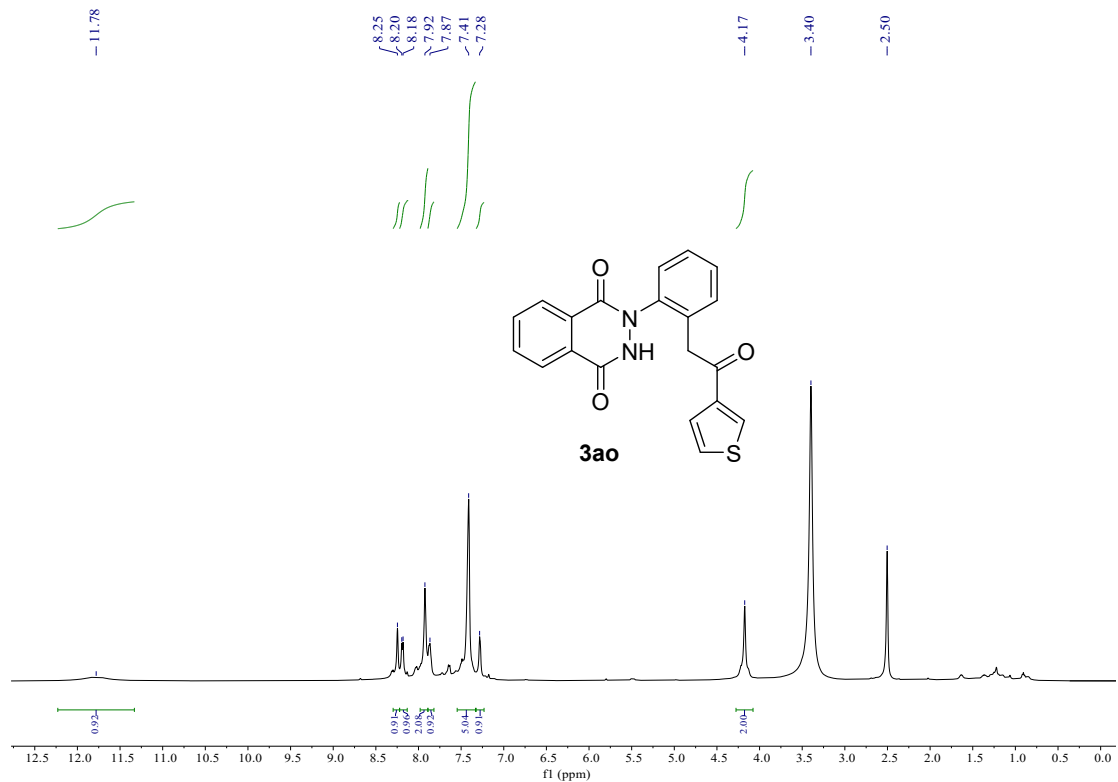
¹H NMR, 500 MHz, DMSO-d₆



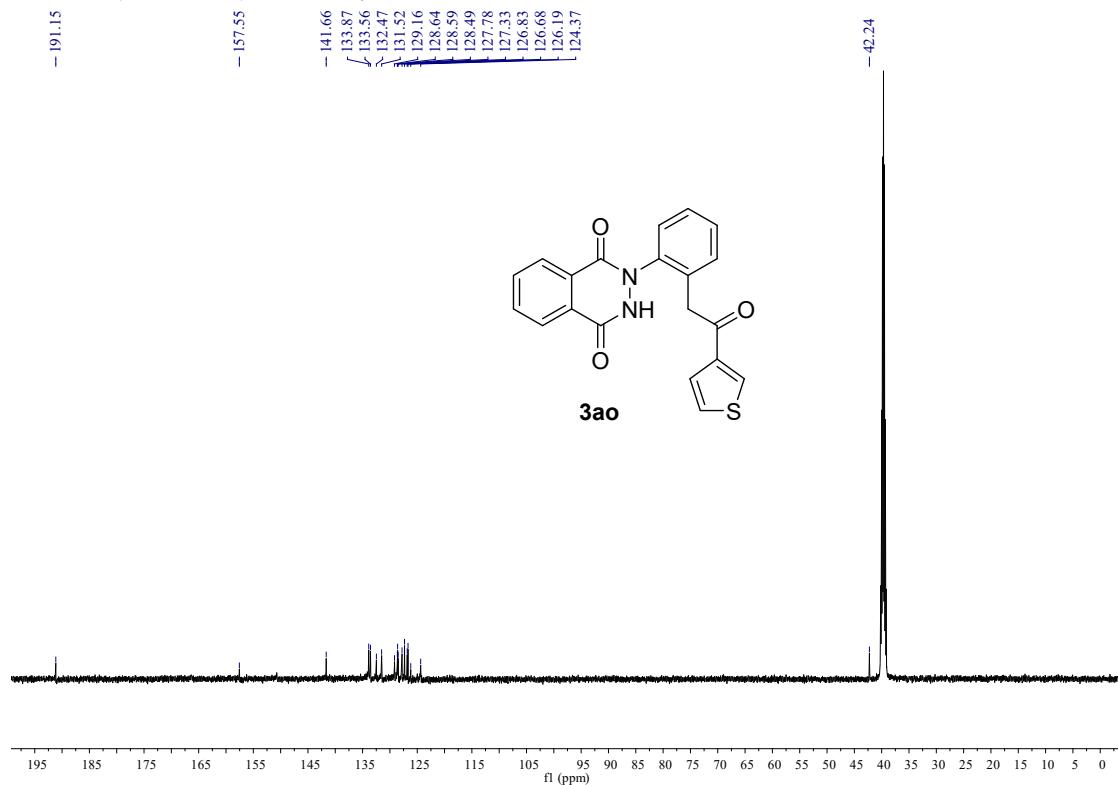
¹³C NMR, 125 MHz, DMSO-d₆



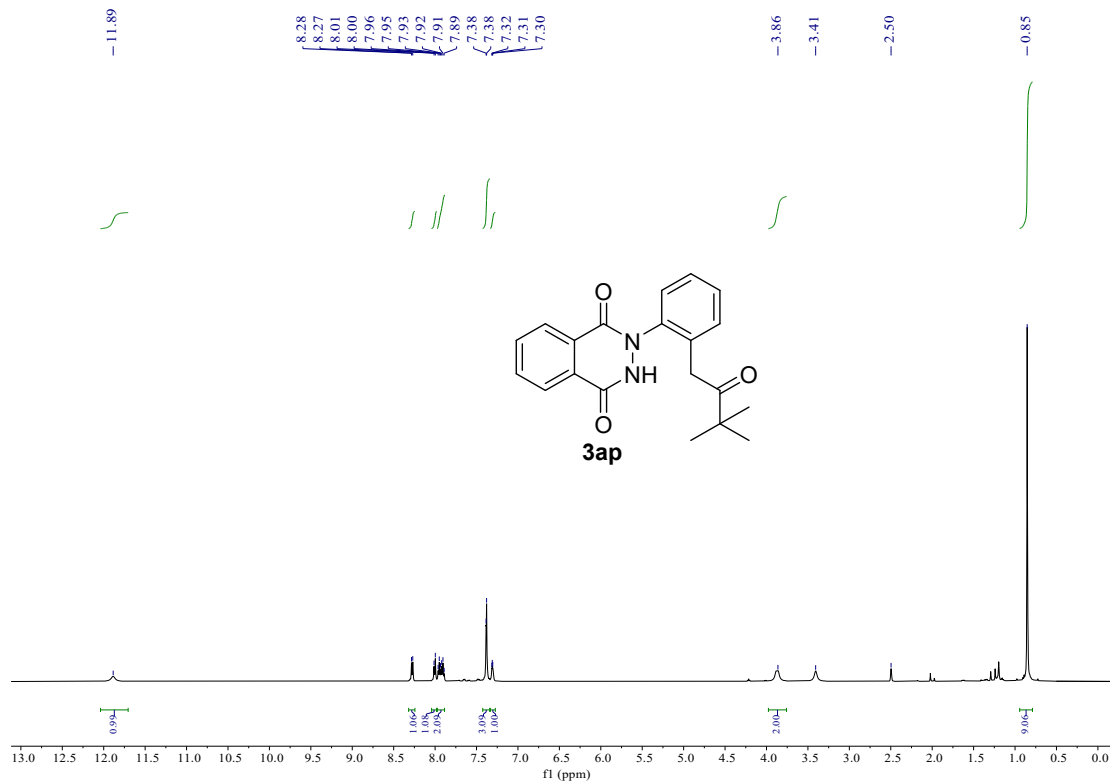
^1H NMR, 500 MHz, $\text{DMSO}-d_6$



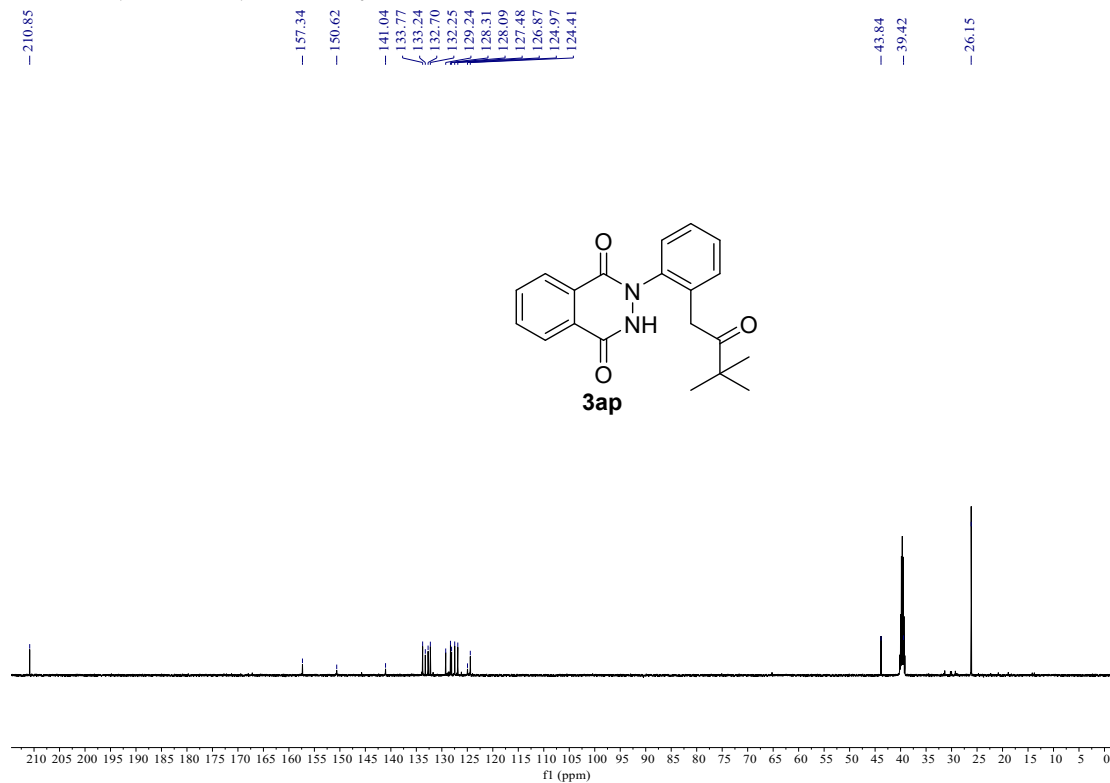
^{13}C NMR, 125 MHz, $\text{DMSO}-d_6$



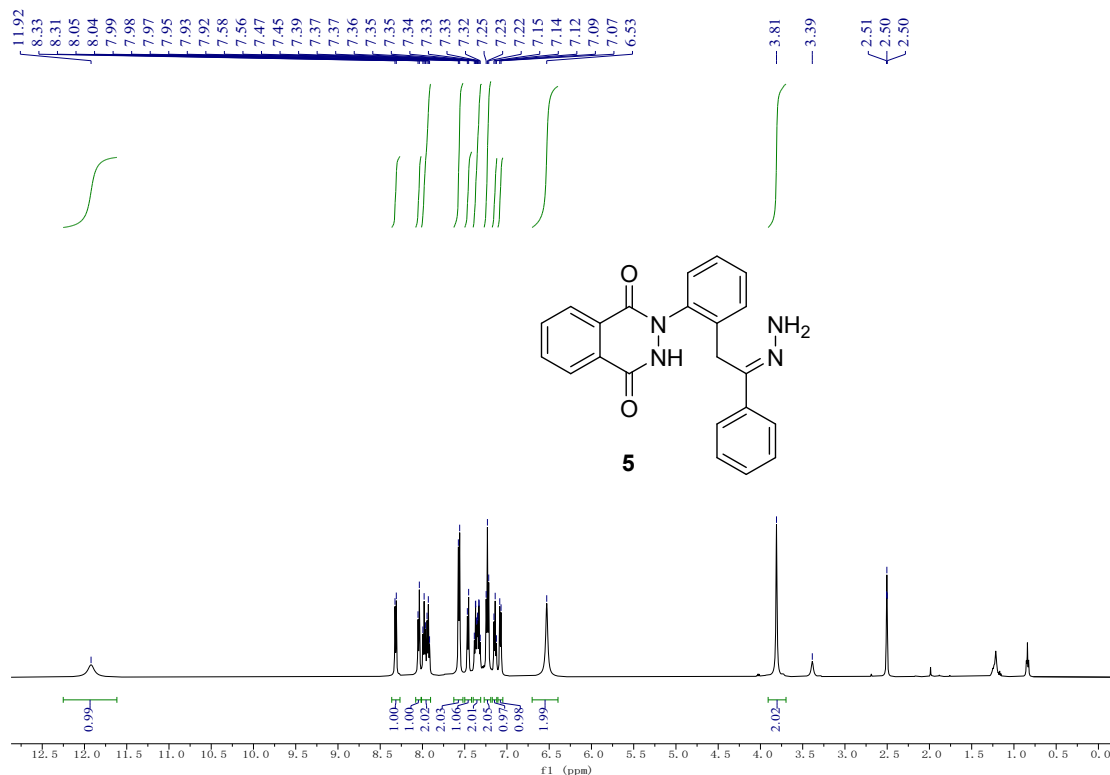
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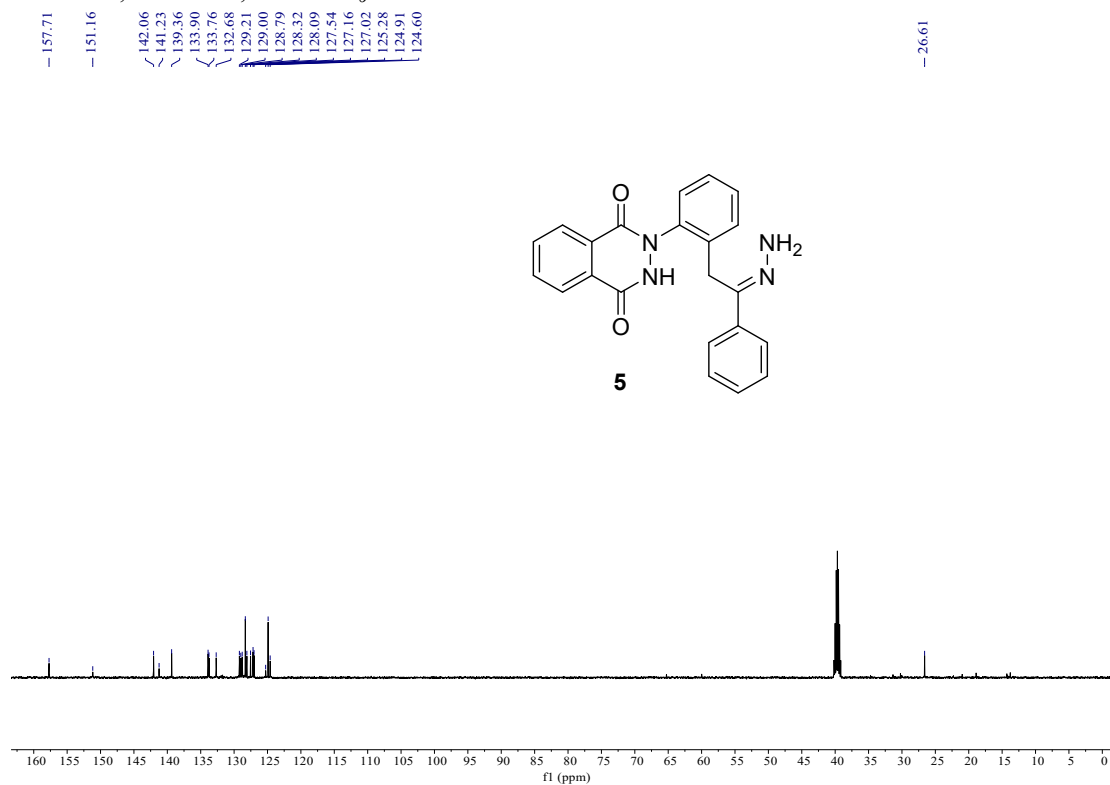
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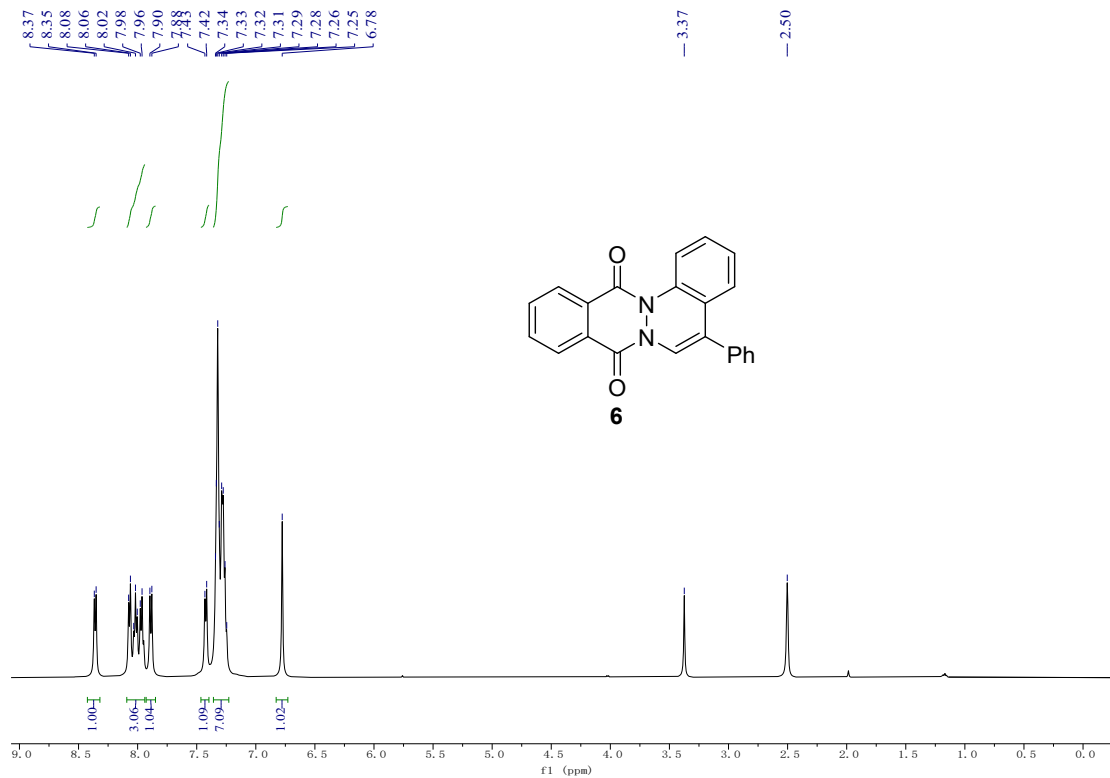
¹H NMR, 500 MHz, DMSO-d₆



¹³C NMR, 125 MHz, DMSO-d₆



¹H NMR, 500 MHz, DMSO-d₆



¹³C NMR, 125 MHz, DMSO-d₆

