Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

A Barton nitrite ester-type remote functionalization and cyclization of *N*-nitrosobenzamides

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1. General information

All commercially available reagents, unless otherwise indicated, were used without further purification. Reactions were monitored by thin layer chromatography (TLC) with 0.2 mm silica gel-coated HSGF 254 plates, visualized by UV light at 254 or 365 nm, and subsequently developed using ceric ammonium molybdate solution as appropriate. Products were isolated and purified by column chromatography on 200-300 mesh silica gel.

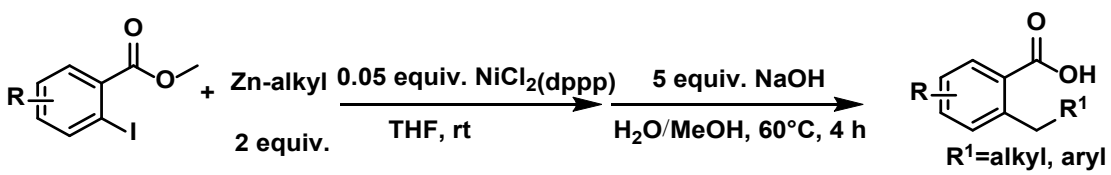
^{1}H NMR and **^{13}C NMR** (400 and 101 MHz, respectively) spectra were recorded on Bruker AM-400 MHz instruments in $CDCl_3$、DMSO- d_6 or DCM-d_4. **^{1}H NMR** chemical shifts (δ) were reported in ppm relative to tetramethylsilane (TMS) with the solvent residual signal as an internal standard ($CDCl_3$: δ 7.26 ppm, DMSO- d_6 :2.50 ppm, DCM-d_4: δ 5.32 ppm). Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q =quartet, br = broad single, m = multiplet), coupling constant (Hz), and integration. **^{13}C NMR** chemical shifts (δ) were reported in ppm relative to tetramethylsilane (TMS) with the solvent residual signal as an internal standard ($CDCl_3$: δ 77.16 ppm, DMSO- d_6: 39.52 ppm, DCM-d_4: δ 53.84 ppm). High resolution mass spectra and were performed on Bruker Daltonics APEXII 47e Specifications. High-resolution mass spectra (HRMS) data were measured by means of the ESI technique on Fourier transform ion cyclotron resonance mass analyzer.

2. Synthesis of the substrates

2.1 Preparation of the Organozinc Reagents[1]

A 25 mL round-bottomed flask was charged with zinc powder (1.5 equiv.) and heated to 70 ℃ under high vacuum for 30 min. After back-filling with argon, I_2 (0.05 equiv.) and DMA (1.5 M) were added, and the resulting heterogenous red mixture was allowed to stir until the red color of the iodine had faded. Then, the alkyl halide (1 equiv.) was added. The colorless reaction mixture was allowed to stir for 12 h at 70 ℃， then the mixture was allowed to cool to room temperature. The gray solution was passed through dry celite and stored under argon.

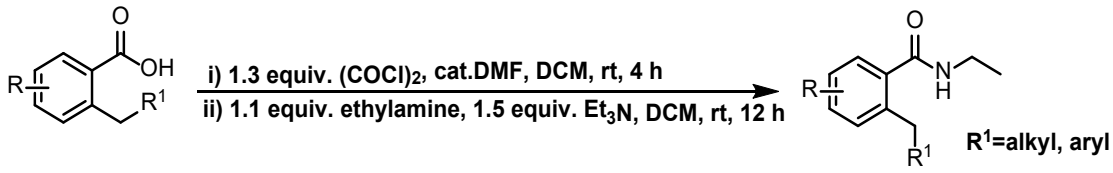
2.2 General Procedure for the Preparation of 2-alkylbenzoic acid Derivatives



Following the general procedure with slightly modification [2]. A 100 mL flask was charged with $NiCl_2$(dppp) (406 mg, 0.75 mmol) and a stir bar in air. The flask was sealed with a septum and backfilled with Ar. A solution of the Methyl 2-iodobenzoate (15 mmol) in dry THF (10 mL) was added via syringe. After stirring for 3-4 min at rt, the corresponding alkylzinc bromide (0.5 M THF solution, 30 mmol) was added, and the reaction mixture was stirred at room temperature for the indicated time and the corresponding Negishi coupling products in 23-90% yield after 18 hours. Side products, besides the unconverted starting materials, included the biaryl coupling adduct and the dehalogenated esters. The reaction mixture was then transferred with EtOAc (40 mL) to a separatory funnel containing water (40 mL), the product was extracted with EtOAc (3×30 mL) and the combined organic extracts were washed with water (60 mL) and brine (80 mL). After drying (anhydrous Na_2SO_4), the solution was filtered and concentrated and the residue was purified by silica gel column chromatography (petroleum ether: EtOAc = 20:1).

To a solution of methyl 2-alkylbenzoate (10 mmol) in MeOH (20 mL) was added 20 mL H_2O and sodium hydroxide (5 equiv.) and the resulting mixture stirred at 60 ℃ for 4 hours before adjusted pH to 2 with 1M HCl. The reaction mixture was extracted with EtOAc (3 × 10 mL). The organic phase was combined and dried over anhydrous Na_2SO_4, filtered and evaporated to dryness in vacuo, afforded compound as a solid. Further crystallization from EtOAc–petroleum ether gave pure 2-alkylbenzoic acid.

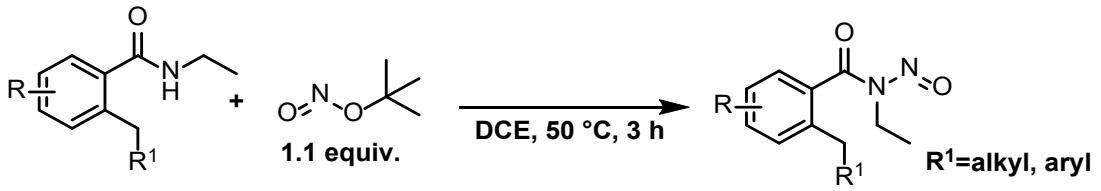
2.3 General Procedure for the Preparation of 2-alkyl-*N*-ethylbenzamide Derivatives



A 101 mL round-bottom flask was charged with 2-alkylbenzoic acid (8 mmol), dry DCM (20 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 ℃and stirred for 5 minutes. Then, $(COCl)_2$ (0.89 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 4 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.[3]

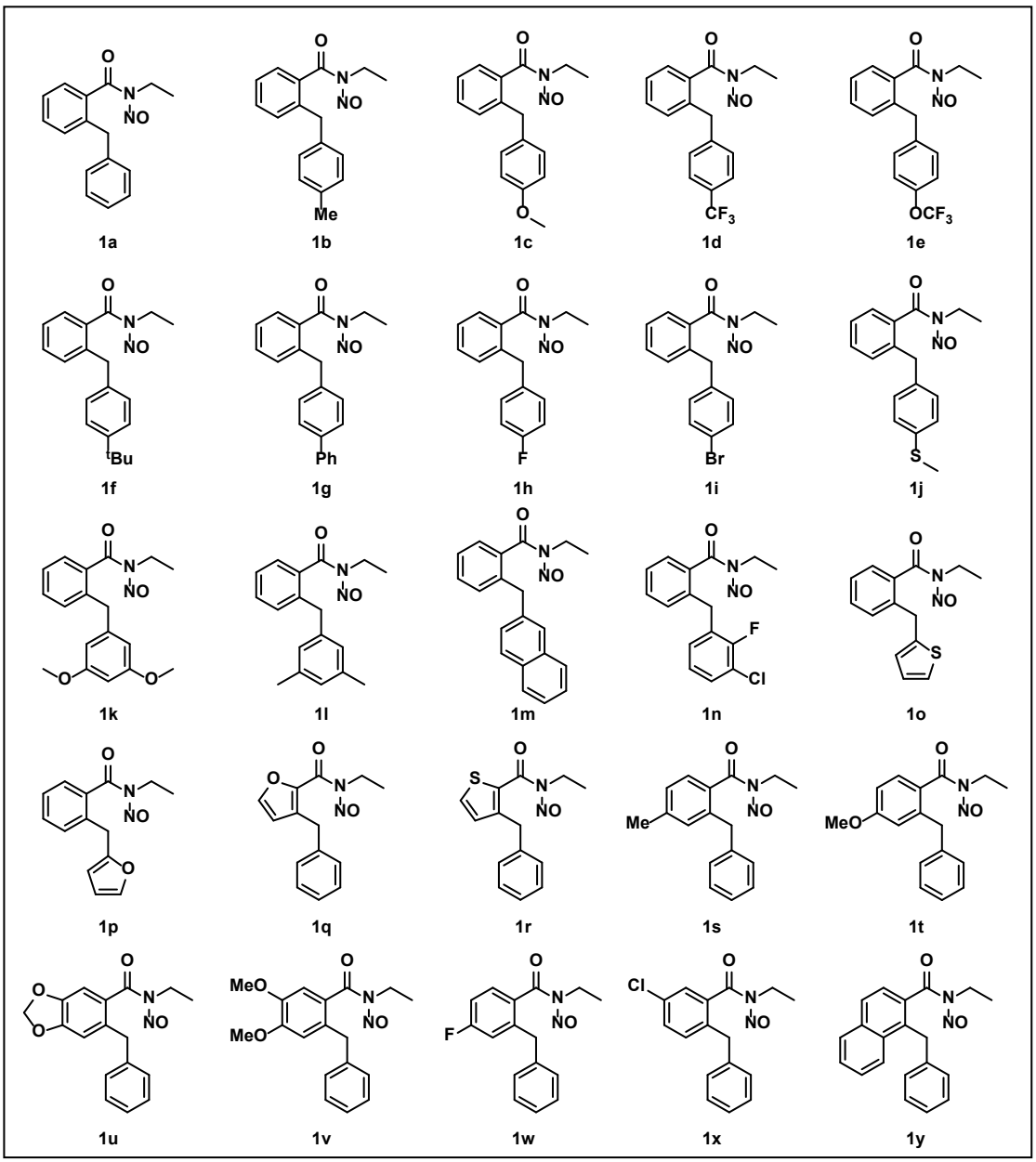
To a solution of ethylamine (4.4 mL,2.0 M in THF, 1.1 equiv.) and Et_3N (1.67 mL, 1.5 equiv.) in dry DCM (20 mL), acid chloride (1.0 equiv.) was added dropwise at 0 °C and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added, the organic layer was separated and the aqueous layer was extracted with DCM (3 x 30 mL). The combined organic layer was washed with saturated aqueous $NaHCO_3$ (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (35% ethyl acetate in petroleum ether as eluent) to afford corresponding amide as white solid.[4]

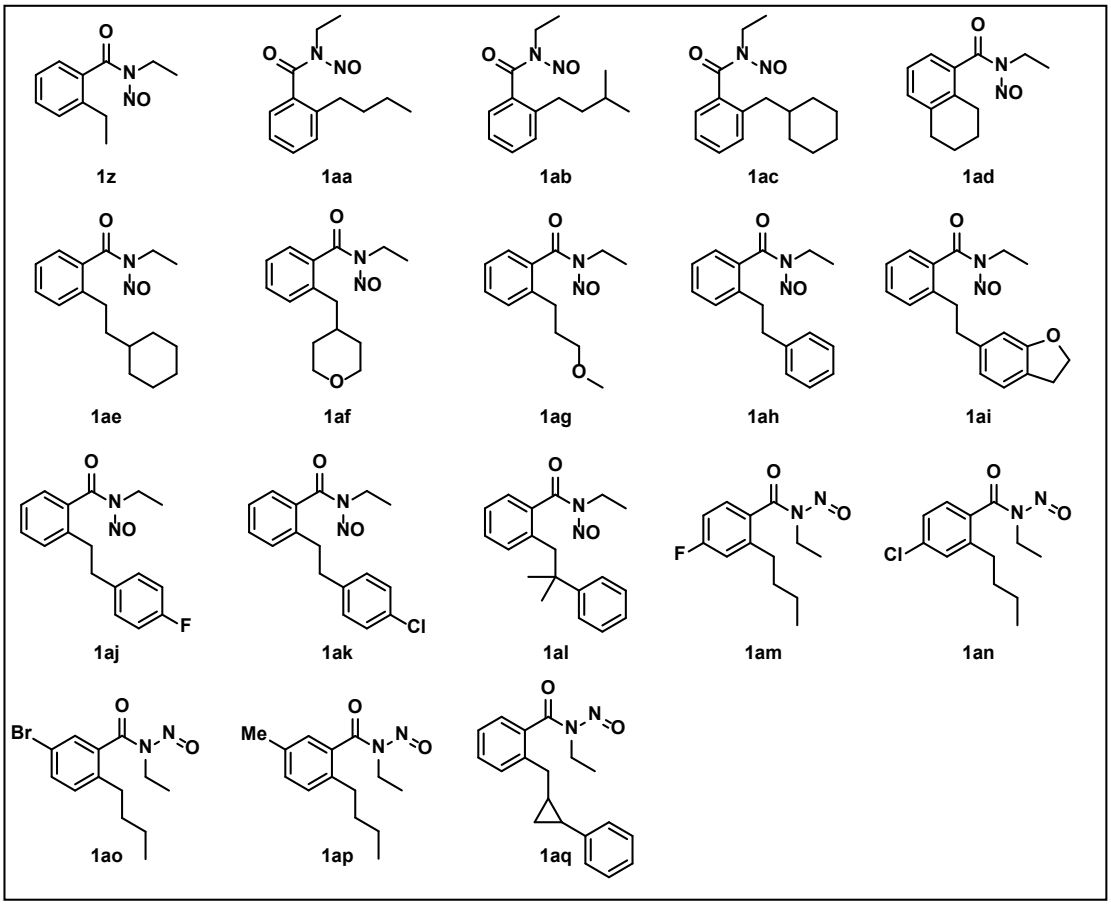
2.4 General Procedure for the Preparation of *N*-ethyl-*N*-nitrosobenzamides[5]



A 50 mL round-bottom flask was charged with *N*-ethyl-*N*-nitrosobenzamides, dry DCE (0.2 M) and tert-Butyl nitrite (1.1 equiv.) under inert gas atmosphere. The reaction mixture was stirred at 50 ℃ for 3 h.The organic solvent was removed in vacuo and the resulting crude was purified by chromatography on silica gel (10% ethyl acetate in petroleum ether as eluent) to afford pure product as a yellow liquid.

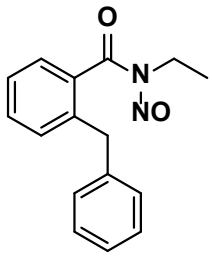
2.5 List of *N*-ethyl-*N*-nitrosobenzamides





2.6 Characterization of 1a-1ap

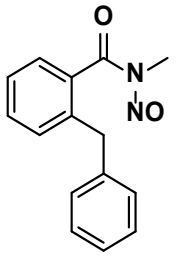
2-benzyl-*N*-ethyl-*N*-nitrosobenzamide (1a)



1a

Yellow solid. Melting point: 40-41°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48-7.41 (td, *J* = 7.4, 1.8 Hz, 1H), 7.39 – 7.28 (m, 3H), 7.21 (dd, *J* = 8.1, 6.4 Hz, 2H), 7.17 – 7.10 (m, 1H), 7.10 – 7.03 (m, 1H), 4.11 (s, 2H), 3.79 (q, *J* = 7.2 Hz, 2H), 0.91 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.3, 139.5, 139.2, 134.3, 130.8, 130.5, 129.1, 128.7, 128.3, 126.3, 125.9, 39.3, 34.1, 11.7.

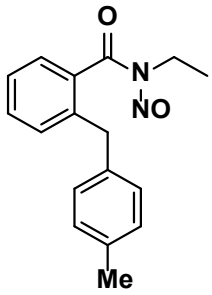
2-benzyl-*N*-methyl-*N*-nitrosobenzamide (1a')



1a′

Yellow solid. Melting point: 40-41°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 (ddd, *J* = 7.7, 7.0, 1.7 Hz, 1H), 7.39 – 7.28 (m, 3H), 7.22 – 7.16 (m, 2H), 7.16 – 7.10 (m, 1H), 7.07 – 7.00 (m, 2H), 4.08 (s, 2H), 3.06 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.35, 139.43, 139.29, 134.15, 130.74, 130.61, 129.15, 128.68, 128.25, 126.30, 125.96, 39.46, 25.61.

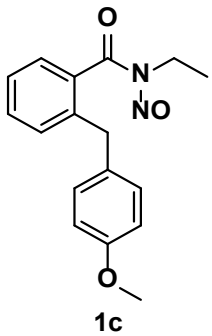
N-ethyl-2-(4-methylbenzyl)-*N*-nitrosobenzamide (1b)



1b

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.39 (m, 1H), 7.38 –7.28 (m, 3H), 7.06 – 7.00 (m, 2H), 6.96 (d, *J* = 8.1 Hz, 2H), 4.06 (s, 2H), 3.81 (q, *J* = 7.1 Hz, 2H), 2.29 (s, 3H), 0.94 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.3, 139.5, 136.4, 135.8, 134.2, 130.7, 130.5, 128.9, 128.6, 125.8, 38.8, 34.1, 20.9, 11.7.

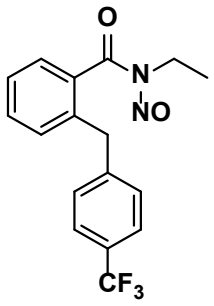
N-ethyl-2-(4-methoxybenzyl)-*N*-nitrosobenzamide (1c)



1c

Yellow solid. Melting point: 49-51 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (td, *J* = 7.42-7.38, 1.7 Hz, 1H), 7.35 – 7.23 (m, 3H), 6.99 – 6.90 (m, 2H), 6.76 – 6.68 (m, 2H), 4.00 (s, 2H), 3.78 (q, *J* = 7.2 Hz, 2H), 3.72 (s, 3H), 0.91 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.3, 158.0, 139.6, 134.2, 131.6, 130.6, 130.5, 130.0, 128.6, 125.8, 113.7, 55.2, 38.4, 34.1, 11.7.

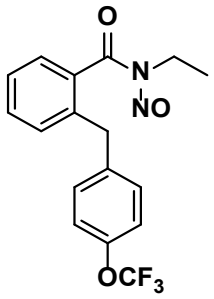
N-ethyl-*N*-nitroso-2-(4-(trifluoromethyl) benzyl) benzamide (1d)



1d

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 7.5, 1.8 Hz, 3H), 7.38 – 7.31 (m, 2H), 7.29 (t, *J* = 6.2 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 4.16 (s, 2H), 3.78 (q, *J* = 7.1 Hz, 2H), 0.86 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.2, 143.93 (q, J = 1.8 Hz), 138.4, 134.3, 131.1, 131.0, 129.5, 129.3, 128.8 (d, *J* = 32.4 Hz), 126.45, 125.4 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 271.9 Hz), 39.2, 34.3, 11.8.

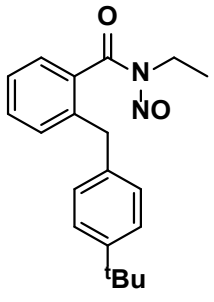
***N*-ethyl-*N*-nitroso-2-(4-(trifluoromethoxy) benzyl) benzamide (1e)**



1e

Yellow solid. Melting point: 45-46 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.40 (m, 1H), 7.39 – 7.27 (m, 3H), 7.07 (t, *J* = 7.5 Hz, 4H), 4.12 (s, 2H), 3.78 (q, *J* = 7.2 Hz, 2H), 0.90 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.2, 147.6 (q, *J* = 2.0 Hz), 138.6, 138.4, 134.2, 130.9, 130.8, 130.4, 129.1, 126.2, 120.9, 120.4 (q, *J* = 256.8 Hz). 38.6, 34.1, 11.6.

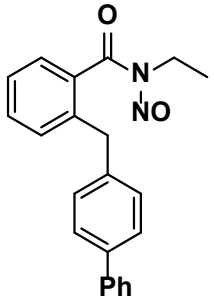
2-(4-(tert-butyl) benzyl)-*N*-ethyl-*N*-nitrosobenzamide (1f)



1f

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 (ddd, *J* = 7.8, 6.7, 1.9 Hz, 1H), 7.36 – 7.28 (m, 3H), 7.24 – 7.18 (m, 2H), 7.02 – 6.94 (m, 2H), 4.08 (s, 2H), 3.77 (q, J = 7.1 Hz, 2H), 1.27 (s, 9H), 0.89 (t, *J* = 7.1 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.3, 149.1, 139.5, 136.5, 134.3, 130.8, 130.5, 128.8, 128.7, 125.8, 125.2, 38.8, 34.3, 34.0, 31.3, 11.7.

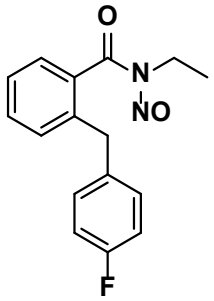
2-([1,1 -biphenyl]-4-ylmethyl)-*N*-ethyl-*N*-nitrosobenzamide (1g)



1g

Yellow solid. Melting point:85-86 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 – 7.51 (m, 2H), 7.51 – 7.40 (m, 5H), 7.39 – 7.31 (m, 4H), 7.17 – 7.09 (m, 2H), 4.16 (s, 2H), 3.79 (q, *J* = 7.1 Hz, 2H), 0.90 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.3, 140.8, 139.23, 139.17, 138.7, 134.2, 130.9, 130.6, 129.5, 128.9, 128.7, 127.1, 127.0, 126.9, 126.0, 39.0, 34.1, 11.7.

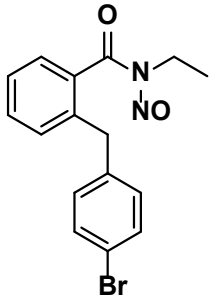
***N*-ethyl-2-(4-fluorobenzyl)-*N*-nitrosobenzamide (1h)**



1h

Yellow solid. Melting point:44-45 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (td, *J* = 7.3, 1.9 Hz, 1H), 7.37 – 7.23 (m, 3H), 7.10 – 6.96 (m, 2H), 6.93 – 6.82 (m, 2H), 4.05 (s, 2H), 3.78 (q, *J* = 7.1 Hz, 2H), 0.91 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.2, 161.4, 130.69 (d, *J* = 7.2 Hz), 139.0, 135.28, 135.25, 134.2, 130.7 (d, *J* = 7.2 Hz), 130.49 (d, *J* = 8.0 Hz), 128.9, 126.1, 115.07 (d, *J* = 21.3 Hz), 38.4, 34.1, 11.7.

2-(4-bromobenzyl)-*N*-ethyl-*N*-nitrosobenzamide (1i)

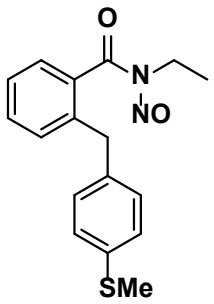


1i

Yellow solid. Melting point: 44-45 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (td, *J* = 7.4, 1.9 Hz, 1H), 7.35 – 7.23 (m, 5H), 6.94 – 6.88 (m, 2H), 4.03 (s, 2H), 3.79 (q, *J* = 7.1 Hz, 2H), 0.90 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.1, 138.6, 138.5, 134.1, 131.3, 130.8, 130.7,

128.9, 128.3, 126.1, 120.1, 38.6, 34.1, 11.7.

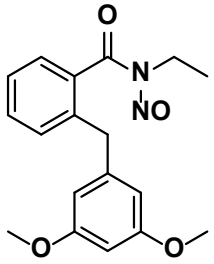
***N*-ethyl-2-(4-(methylthio) benzyl)-*N*-nitrosobenzamide (1j)**



1j

Yellow solid. Melting point: 49-51 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (td, *J* = 7.4, 1.8 Hz, 1H), 7.36 – 7.22 (m, 3H), 7.12 – 7.05 (m, 2H), 7.00 – 6.92 (m, 2H), 4.03 (s, 2H), 3.78 (q, *J* = 7.1 Hz, 2H), 2.41 (s, 3H), 0.90 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.2, 139.1, 136.6, 136.1, 134.2, 130.7, 130.6, 129.6, 128.8, 126.9, 126.0, 38.7, 34.1, 16.1, 11.7.

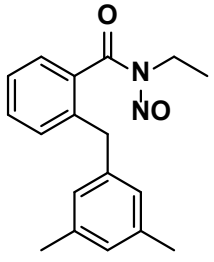
2-(3,5-dimethoxybenzyl)-*N*-ethyl-*N*-nitrosobenzamide (1k)



1k

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 – 7.38 (m, 1H), 7.38 – 7.25 (m, 3H), 6.25 (t, *J* = 2.3 Hz, 1H), 6.21 (d, *J* = 2.3 Hz, 2H), 4.02 (s, 2H), 3.83 (q, *J* = 7.1 Hz, 2H), 3.69 (s, 6H), 0.94 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.2, 160.7, 141.8, 138.8, 134.2, 130.7, 130.5, 128.6, 125.9, 107.2, 98.3, 55.1, 39.4, 34.1, 11.7.

2-(3,5-dimethylbenzyl)-*N*-ethyl-*N*-nitrosobenzamide (1l)

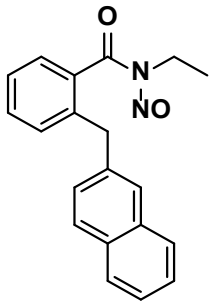


1l

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 (td, *J* = 7.3, 1.9 Hz, 1H), 7.38 – 7.26 (m, 3H), 6.77 (s, 1H), 6.65 (s, 2H), 4.04 (s, 2H), 3.77 (q, *J* = 7.1 Hz, 2H), 2.20 (s, 6H), 0.88 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.3, 139.4, 139.3, 137.8, 134.2, 130.8, 130.5, 128.6, 127.8,

127.0, 125.8, 39.1, 34.0, 21.1, 11.6.

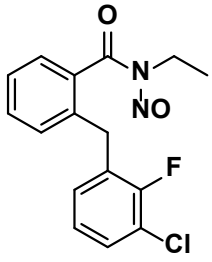
***N*-ethyl-2-(naphthalen-2-ylmethyl)-*N*-nitrosobenzamide (1m)**



1m

Yellow solid. Melting point: 61-63 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 – 7.70 (m, 1H), 7.66 (dd, *J* = 8.9, 3.6 Hz, 2H), 7.49 – 7.37 (m, 4H), 7.36 – 7.27 (m, 3H), 7.17 (dd, *J* = 8.4, 1.8 Hz, 1H), 4.25 (s, 2H), 3.67 (q, *J* = 7.1 Hz, 2H), 0.73 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.3, 139.1, 137.0, 134.3, 133.3, 132.0, 130.9, 130.6, 128.8, 128.0, 127.50, 127.47, 127.45, 127.4, 126.03, 126.02, 125.5, 39.4, 34.0, 11.5.

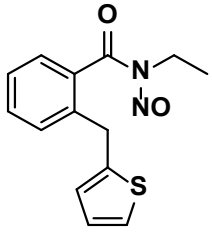
2-(3-chloro-2-fluorobenzyl)-*N*-ethyl-*N*-nitrosobenzamide (1n)



1n

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (td, *J* = 7.4, 1.9 Hz, 1H), 7.39 – 7.28 (m, 3H), 7.21 (td, *J* = 7.1, 2.6 Hz, 1H), 6.93 – 6.83 (m, 2H), 4.12 (s, 2H), 3.95 – 3.76 (m, 2H), 0.98 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.1, 156.1 (d, *J* = 248.3 Hz), 137.3, 134.1, 130.8, 130.7, 129.2 (d, *J* = 3.6 Hz), 129.0, 128.8, 128.5 (d, *J* = 15.5 Hz), 126.3, 124.3 (d, *J* = 4.7 Hz), 121.0 (d, *J* = 18.2 Hz), 34.2, 32.0 (d, *J* = 3.2 Hz), 11.7.

***N*-ethyl-*N*-nitroso-2-(thiophen-2-ylmethyl) benzamide (1o)**

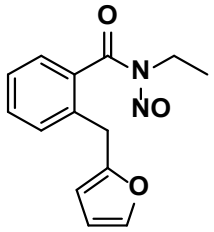


1o

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 (td, *J* = 7.4, 1.8 Hz, 1H), 7.42 – 7.28 (m, 3H), 7.12 – 7.06 (m, 1H), 6.82 (dd, *J* = 5.2, 3.4 Hz, 1H), 6.66 (dt, *J* = 3.5, 1.0 Hz, 1H), 4.28 (s, 2H), 3.86 (q,

J = 7.1 Hz, 2H), 0.98 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.9, 142.3, 138.7, 133.8, 130.7, 130.3, 129.0, 126.5, 126.2, 125.9, 124.3, 34.1, 33.5, 11.8.

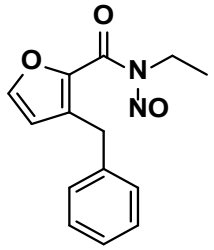
***N*-ethyl-2-(furan-2-ylmethyl)-*N*-nitrosobenzamide (1p)**



1p

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 – 7.39 (m, 1H), 7.37 – 7.28 (m, 3H), 7.20 (dd, J = 1.9, 0.9 Hz, 1H), 6.18 (dd, J = 3.2, 1.9 Hz, 1H), 5.87 (dt, J = 3.2, 0.9 Hz, 1H), 4.08 (s, 2H), 3.88 (q, J = 7.1 Hz, 2H), 1.01 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.0, 153.0, 141.6, 136.5, 134.0, 130.7, 130.4, 128.9, 126.3, 110.1, 107.0, 34.2, 32.1, 11.8.

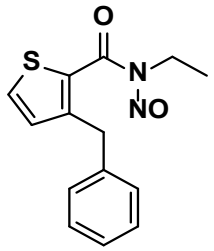
3-benzyl-*N*-ethyl-*N*-nitrosofuran-2-carboxamide (1q)



1q

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 (d, J = 1.7 Hz, 1H), 7.35 – 7.18 (m, 5H), 6.36 (d, J = 1.7 Hz, 1H), 4.16 (s, 2H), 3.91 (q, J = 7.1 Hz, 2H), 1.08 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.5, 146.1, 141.8, 139.0, 137.6, 128.8, 128.6, 126.5, 114.5, 35.1, 32.1, 12.1.

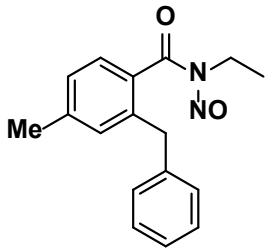
3-benzyl-*N*-ethyl-*N*-nitrosothiophene-2-carboxamide (1r)



1r

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (d, J = 5.1 Hz, 1H), 7.33 – 7.17 (m, 5H), 6.88 (d, J = 5.1 Hz, 1H), 4.42 (s, 2H), 3.94 (q, J = 7.1 Hz, 2H), 1.05 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.1, 152.4, 139.8, 134.1, 130.6, 128.9, 128.5, 126.3, 125.7, 36.8, 34.8, 12.0.

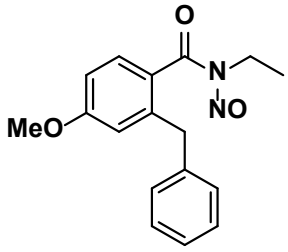
2-benzyl-*N*-ethyl-4-methyl-*N*-nitrosobenzamide (1s)



1s

Yellow solid. Melting point:38-39 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 (dd, *J* = 8.8, 1.7 Hz, 1H), 7.21 – 7.14 (m, 2H), 7.14 – 7.07 (m, 3H), 7.06 – 7.01 (m, 2H), 4.06 (s, 2H), 3.75 (q, *J* = 7.1 Hz, 2H), 2.36 (s, 3H), 0.87 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.3, 141.0, 139.8, 139.4, 131.6, 131.3, 129.1, 129.0, 128.3, 126.6, 126.2, 39.3, 34.1, 21.4, 11.7.

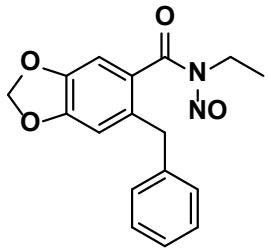
2-benzyl-*N*-ethyl-4-methoxy-*N*-nitrosobenzamide (1t)



1t

Yellow solid. Melting point: 68-68 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.1 Hz, 1H), 7.21 – 7.14 (m, 2H), 7.14 – 7.09 (m, 1H), 7.05 (dd, *J* = 7.2, 1.5 Hz, 2H), 6.83 – 6.75 (m, 2H), 4.10 (s, 2H), 3.81 (s, 3H), 3.76 (q, *J* = 7.2 Hz, 2H), 0.87 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.6, 161.4, 142.3, 139.6, 131.5, 129.0, 128.3, 126.2, 116.9, 110.8, 55.3, 39.5, 34.3, 11.7.

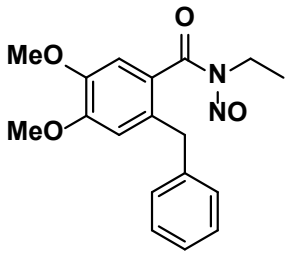
6-benzyl-*N*-ethyl-*N*-nitrosobenzo[*d*][1,3]dioxole-5-carboxamide (1u)



1u

Yellow solid. Melting point: 48-50 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 (dd, *J* = 8.1, 6.5 Hz, 2H), 7.16 – 7.08 (m, 1H), 7.08 – 6.97 (m, 2H), 6.79 (s, 1H), 6.71 (s, 1H), 5.97 (s, 2H), 3.99 (s, 2H), 3.77 (q, *J* = 7.1 Hz, 2H), 0.90 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.4, 149.6, 145.6, 139.7, 134.9, 128.9, 128.31, 128.28, 126.9, 126.3, 110.9, 109.1, 101.7, 38.9, 34.3, 11.7.

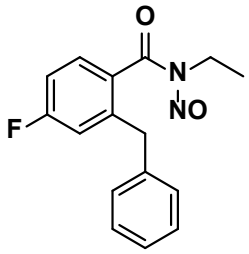
2-benzyl-*N*-ethyl-4,5-dimethoxy-*N*-nitrosobenzamide (1v)



1v

Yellow solid. Melting point: 99-101 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 – 7.16 (m, 2H), 7.17 – 7.10 (m, 1H), 7.08 – 6.98 (m, 2H), 6.87 (s, 1H), 6.76 (s, 1H), 4.03 (s, 2H), 3.86 (d, *J* = 7.2 Hz, 6H), 3.78 (q, *J* = 7.1 Hz, 2H), 0.91 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.7, 150.8, 146.8, 139.9, 133.2, 128.8, 128.3, 126.2, 125.9, 113.6, 112.3, 56.1, 55.9, 39.0, 34.4, 11.7.

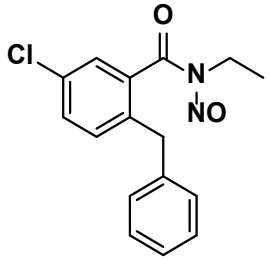
2-benzyl-*N*-ethyl-4-fluoro-*N*-nitrosobenzamide (1w)



1w

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 (ddd, *J* = 8.7, 4.2, 1.8 Hz, 1H), 7.22 (tt, *J* = 6.6, 1.2 Hz, 2H), 7.19 – 7.13 (m, 1H), 7.08 – 7.03 (m, 2H), 7.01 (ddd, *J* = 8.8, 7.1, 2.1 Hz, 2H), 4.09 (s, 2H), 3.79 (q, *J* = 7.1 Hz, 2H), 0.91 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.4, 163.7 (d, *J* = 251.5 Hz), 142.8 (d, *J* = 8.1 Hz), 138.7, 131.1 (d, *J* = 9.1 Hz), 130.2 (d, *J* = 3.4 Hz), 129.1, 128.4, 126.6, 117.8 (d, *J* = 22.0 Hz), 113.1 (d, *J* = 22.0 Hz), 39.19, 39.17, 34.2, 11.7.

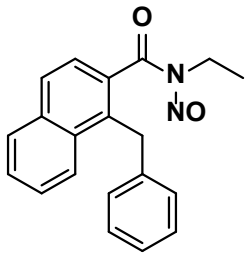
2-benzyl-5-chloro-*N*-ethyl-*N*-nitrosobenzamide (1x)



1x

Yellow solid. Melting point: 50-52 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 8.3, 2.3 Hz, 1H), 7.33 (d, *J* = 2.2 Hz, 1H), 7.25 – 7.17 (m, 3H), 7.17 – 7.10 (m, 1H), 7.06 – 6.98 (m, 2H), 4.04 (s, 2H), 3.76 (q, *J* = 7.1 Hz, 2H), 0.90 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.0, 138.9, 137.6, 135.7, 132.1, 132.0, 130.5, 129.1, 128.5, 128.4, 126.5, 38.7, 34.1, 11.7.

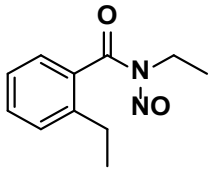
benzyl-*N*-ethyl-*N*-nitroso-2-naphthamide (1y)



1y

Yellow solid. Melting point: 55-58 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 – 7.98 (m, 1H), 7.93 – 7.78 (m, 2H), 7.52 (dddd, *J* = 21.2, 8.3, 6.8, 1.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.19 (dd, *J* = 8.1, 6.5 Hz, 2H), 7.15 – 7.10 (m, 1H), 7.10 – 7.05 (m, 2H), 4.56 (s, 2H), 3.92 (q, *J* = 7.1 Hz, 2H), 1.02 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.9, 139.7, 134.8, 134.3, 132.8, 132.2, 128.7, 128.4, 128.3, 127.10, 127.08, 127.0, 126.1, 125.3, 124.4, 35.3, 34.1, 11.9.

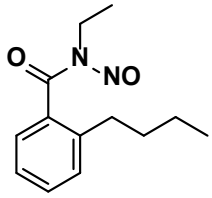
***N*-2-diethyl-*N*-nitrosobenzamide (1z)**



1z

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (td, *J* = 7.5, 1.6 Hz, 1H), 7.36 – 7.29 (m, 2H), 7.29 – 7.22 (m, 1H), 3.98 (q, *J* = 7.1 Hz, 2H), 2.64 (q, *J* = 7.6 Hz, 2H), 1.23 – 1.17 (m, 3H), 1.11 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.6, 141.9, 133.7, 130.6, 128.9, 128.0, 125.4, 34.1, 26.4, 15.2, 11.9.

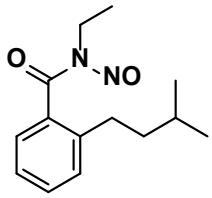
2-butyl-*N*-ethyl-*N*-nitrosobenzamide (1aa)



1aa

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (td, *J* = 7.5, 1.5 Hz, 1H), 7.30 (ddd, *J* = 7.6, 3.1, 1.3 Hz, 2H), 7.25 (td, *J* = 7.4, 1.2 Hz, 1H), 3.98 (q, *J* = 7.1 Hz, 2H), 2.65 – 2.57 (m, 2H), 1.60 – 1.48 (m, 2H), 1.29 (h, *J* = 7.3 Hz, 2H), 1.11 (t, *J* = 7.1 Hz, 3H), 0.86 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.6, 140.8, 133.9, 130.4, 129.6, 128.1, 125.4, 34.1, 33.2, 33.1, 22.5, 13.8, 11.9.

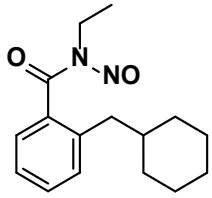
***N*-ethyl-2-isopentyl-*N*-nitrosobenzamide (1ab)**



1ab

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (td, *J* = 7.5, 1.6 Hz, 1H), 7.30 (dt, *J* = 7.6, 1.9 Hz, 2H), 7.28 – 7.24 (m, 1H), 3.98 (q, *J* = 7.1 Hz, 2H), 2.65 – 2.56 (m, 2H), 1.53 (dt, *J* = 13.0, 6.5 Hz, 1H), 1.48 – 1.42 (m, 2H), 1.11 (t, *J* = 7.1 Hz, 3H), 0.86 (d, *J* = 6.5 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.6, 141.0, 133.9, 130.5, 129.6, 128.1, 125.4, 40.3, 34.2, 31.3, 27.9, 22.3, 11.9.

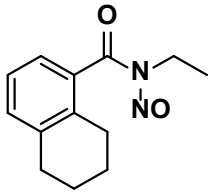
2-(cyclohexylmethyl)-*N*-ethyl-*N*-nitrosobenzamide (1ac)



1ac

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (td, *J* = 7.4, 1.6 Hz, 1H), 7.31 – 7.26 (m, 1H), 7.22 (t, *J* = 7.2 Hz, 2H), 3.96 (q, *J* = 7.1 Hz, 2H), 2.49 (d, *J* = 7.2 Hz, 2H), 1.67 – 1.51 (m, 6H), 1.43 (ddp, *J* = 11.0, 7.1, 3.7 Hz, 1H), 1.08 (t, *J* = 7.1 Hz, 6H), 0.90 – 0.75 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.6, 139.4, 134.2, 130.5, 130.1, 128.2, 125.4, 41.1, 39.4, 34.1, 33.2, 33.1, 26.3, 26.1, 11.8.

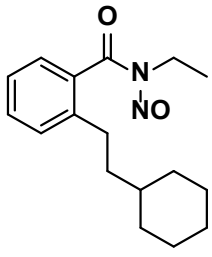
***N*-ethyl-*N*-nitroso-5,6,7,8-tetrahydronaphthalene-1-carboxamide (1ad)**



1ad

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 – 7.12 (m, 3H), 3.98 (q, *J* = 7.1 Hz, 2H), 2.83 (t, *J* = 5.8 Hz, 2H), 2.67 (t, *J* = 5.7 Hz, 2H), 1.87 – 1.73 (m, 4H), 1.12 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.9, 137.9, 134.5, 134.4, 131.4, 125.1, 125.1, 34.1, 29.6, 26.9, 22.6, 22.5, 12.0.

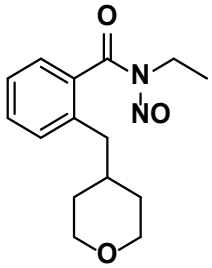
2-(2-cyclohexylethyl)-*N*-ethyl-*N*-nitrosobenzamide (1ae)



1ae

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (td, *J* = 7.5, 1.6 Hz, 1H), 7.30 (dt, *J* = 7.8, 1.8 Hz, 2H), 7.27 – 7.21 (m, 1H), 3.98 (q, *J* = 7.1 Hz, 2H), 2.66 – 2.57 (m, 2H), 1.65 (tdd, *J* = 13.8, 6.7, 2.2 Hz, 5H), 1.48 – 1.39 (m, 2H), 1.25 – 1.05 (m, 7H), 0.92 – 0.78 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.6, 141.2, 133.9, 130.5, 129.6, 128.1, 125.3, 38.9, 37.5, 34.2, 33.1, 30.8, 26.5, 26.2, 11.9.

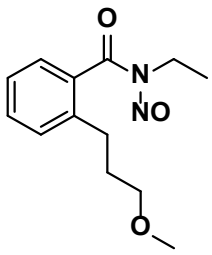
***N*-ethyl-*N*-nitroso-2-((tetrahydro-2*H*-pyran-4-yl) methyl) benzamide (1af)**



1af

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 1H), 7.33 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.27 (dtd, *J* = 7.9, 3.6, 1.2 Hz, 2H), 3.99 (q, *J* = 7.1 Hz, 2H), 3.94 – 3.85 (m, 2H), 3.26 (td, *J* = 11.8, 2.1 Hz, 2H), 2.59 (d, *J* = 7.3 Hz, 2H), 1.73 (ttt, *J* = 11.2, 7.4, 3.8 Hz, 1H), 1.48 (ddq, *J* = 13.0, 4.0, 2.1 Hz, 2H), 1.26 (dtd, *J* = 13.3, 11.8, 4.5 Hz, 2H), 1.11 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.4, 138.7, 134.2, 130.5, 130.3, 128.4, 125.7, 67.8, 40.6, 36.8, 34.1, 32.9, 11.9.

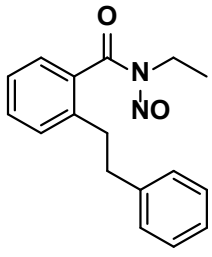
***N*-ethyl-2-(3-methoxypropyl)-*N*-nitrosobenzamide (1ag)**



1ag

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (td, *J* = 7.5, 1.6 Hz, 1H), 7.32 (dd, *J* = 7.7, 1.4 Hz, 2H), 7.26 (td, *J* = 7.4, 1.2 Hz, 1H), 3.98 (q, *J* = 7.1 Hz, 2H), 3.31 (t, *J* = 6.2 Hz, 2H), 3.27 (s, 3H), 2.73 – 2.67 (m, 2H), 1.88 – 1.80 (m, 2H), 1.11 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.4, 140.0, 134.1, 130.6, 129.7, 128.2, 125.5, 71.4, 58.3, 34.1, 30.8, 29.7, 11.8.

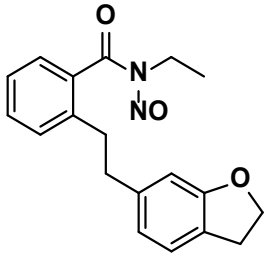
***N*-ethyl-*N*-nitroso-2-phenethylbenzamide (1ah)**



1ah

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 1H), 7.34 – 7.20 (m, 5H), 7.18 – 7.13 (m, 1H), 7.12 – 7.07 (m, 2H), 3.96 (q, *J* = 7.1 Hz, 2H), 2.94 (ddd, *J* = 9.7, 5.8, 2.2 Hz, 2H), 2.87 (ddd, *J* = 10.0, 5.8, 2.2 Hz, 2H), 1.08 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.3, 141.1, 139.9, 133.8, 130.5, 129.9, 128.5, 128.4, 128.3, 126.0, 125.6, 37.5, 35.5, 34.2, 12.0.

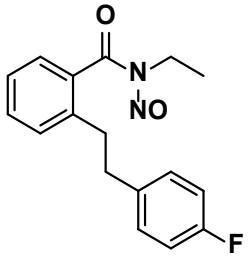
2-(2-(2,3-dihydrobenzofuran-6-yl) ethyl)-*N*-ethyl-*N*-nitrosobenzamide (1ai)



1ai

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 1H), 7.34 – 7.21 (m, 3H), 6.89 (d, *J* = 1.8 Hz, 1H), 6.83 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.64 (d, *J* = 8.1 Hz, 1H), 4.51 (t, *J* = 8.7 Hz, 2H), 3.95 (q, *J* = 7.1 Hz, 2H), 3.12 (t, *J* = 8.7 Hz, 2H), 2.93 – 2.86 (m, 2H), 2.85 – 2.75 (m, 2H), 1.08 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.3, 158.4, 140.0, 133.8, 133.1, 130.5, 129.9, 128.5, 127.7, 127.0, 125.5, 124.9, 108.9, 71.1, 37.0, 36.0, 34.1, 29.7, 12.0.

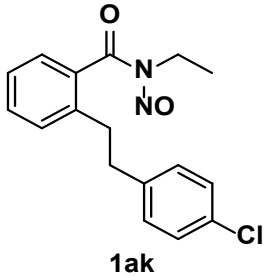
***N*-ethyl-2-(4-fluorophenethyl)-*N*-nitrosobenzamide (1aj)**



1aj

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (td, *J* = 7.4, 1.6 Hz, 1H), 7.32 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.29 – 7.22 (m, 2H), 7.03 (ddd, *J* = 8.5, 5.5, 2.5 Hz, 2H), 6.94 – 6.88 (m, 2H), 3.96 (q, *J* = 7.1 Hz, 2H), 2.92 (ddd, *J* = 9.2, 5.9, 2.1 Hz, 2H), 2.88 – 2.82 (m, 2H), 1.09 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.3, 161.3 (d, *J* = 243.8 Hz), 139.6, 136.7 (d, *J* = 3.2 Hz), 133.8, 130.6, 130.0, 129.7 (d, *J* = 7.8 Hz), 128.6, 125.7, 115.1 (d, *J* = 21.0 Hz), 114.98, 36.6, 35.6, 34.2, 12.0.

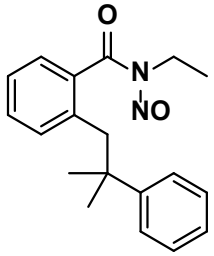
2-(4-chlorophenethyl)-*N*-ethyl-*N*-nitrosobenzamide (1ak)



1ak

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 (td, *J* = 7.5, 1.6 Hz, 1H), 7.31 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.25 (ddd, *J* = 12.7, 7.0, 1.2 Hz, 2H), 7.21 – 7.15 (m, 2H), 7.03 – 6.98 (m, 2H), 3.95 (q, *J* = 7.1 Hz, 2H), 2.92 (ddd, *J* = 9.3, 6.2, 2.0 Hz, 2H), 2.84 (ddd, *J* = 8.6, 6.1, 2.0 Hz, 2H), 1.07 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.2, 139.5, 139.4, 133.7, 131.7, 130.6, 129.9, 129.7, 128.6, 128.4, 125.7, 36.8, 35.3, 34.1, 11.9.

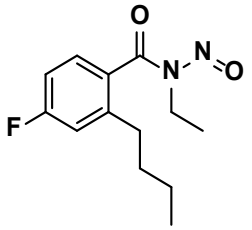
_N_-ethyl-2-(2-methyl-2-phenylpropyl)-_N_-nitrosobenzamide (1al)



1al

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 – 7.17 (m, 7H), 7.13 (ddt, *J* = 5.9, 4.4, 3.3 Hz, 1H), 6.79 – 6.72 (m, 1H), 3.90 (q, *J* = 7.1 Hz, 2H), 3.10 (s, 2H), 1.25 (s, 6H), 1.07 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.3, 148.2, 137.8, 134.5, 132.0, 129.7, 129.1, 128.0, 126.2, 125.8, 125.4, 46.7, 39.4, 34.1, 28.5, 11.8.

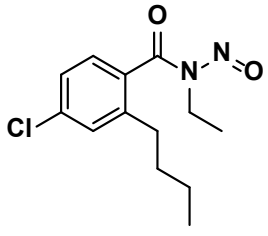
2-butyl-_N_-ethyl-4-fluoro-_N_-nitrosobenzamide (1am)



1am

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 8.5, 5.7 Hz, 1H), 7.00 (dd, *J* = 9.9, 2.6 Hz, 1H), 6.94 (td, *J* = 8.3, 2.5 Hz, 1H), 3.96 (q, *J* = 7.1 Hz, 2H), 2.65 – 2.57 (m, 2H), 1.54 (tt, *J* = 7.9, 6.5 Hz, 2H), 1.29 (h, *J* = 7.3 Hz, 2H), 1.09 (t, *J* = 7.2 Hz, 3H), 0.86 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101MHz, $CDCl_3$) δ 173.7, 163.7 (d, *J* = 250.6 Hz), 144.4 (d, *J* = 8.1 Hz), 130.5 (d, *J* = 8.9 Hz), 129.9 (d, *J* = 3.3 Hz), 116.5 (d, *J* = 21.6 Hz), 112.6 (d, *J* = 22.0 Hz), 34.2, 33.03, 33.02, 32.8, 22.4, 13.7, 11.9.

2-butyl-4-chloro-_N_-ethyl-_N_-nitrosobenzamide (1an)

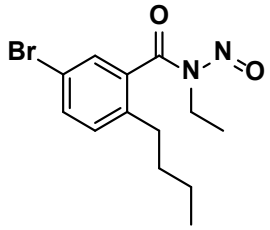


1an

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 1.6 Hz, 1H), 7.24 (d, *J* = 0.9 Hz, 2H), 3.96

(q, *J* = 7.1 Hz, 2H), 2.62 – 2.54 (m, 2H), 1.59 – 1.48 (m, 2H), 1.29 (h, *J* = 7.4 Hz, 2H), 1.10 (t, *J* = 7.1 Hz, 3H), 0.86 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.7, 143.0, 136.5, 132.3, 129.7, 129.5, 125.7, 34.2, 32.92, 32.88, 22.4, 13.7, 11.9.

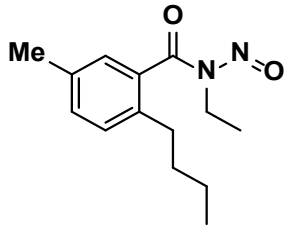
5-bromo-2-butyl-*N*-ethyl-*N*-nitrosobenzamide (1ao)



1ao

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 8.3, 2.2 Hz, 1H), 7.43 (d, *J* = 2.1 Hz, 1H), 7.17 (d, *J* = 8.3 Hz, 1H), 3.96 (q, *J* = 7.1 Hz, 2H), 2.57 – 2.48 (m, 2H), 1.55 – 1.45 (m, 2H), 1.27 (h, *J* = 7.3 Hz, 2H), 1.10 (t, *J* = 7.1 Hz, 3H), 0.85 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.1, 139.6, 135.7, 133.3, 131.3, 130.6, 119.0, 34.2, 32.9, 32.6, 22.4, 13.7, 11.9.

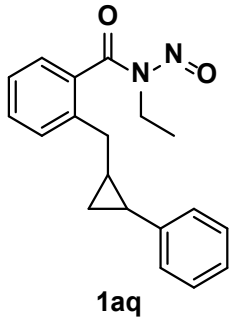
2-butyl-*N*-ethyl-5-methyl-*N*-nitrosobenzamide (1ap)



1ap

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 – 7.16 (m, 2H), 7.12 (d, *J* = 1.7 Hz, 1H), 3.98 (q, *J* = 7.1 Hz, 2H), 2.63 – 2.49 (m, 2H), 2.33 (s, 3H), 1.56 – 1.47 (m, 2H), 1.28 (h, *J* = 7.3 Hz, 2H), 1.11 (t, *J* = 7.1 Hz, 3H), 0.85 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.8, 137.7, 135.1, 133.8, 131.3, 129.6, 128. 5, 34.1, 33.2, 32.7, 22.5, 20.8, 13.8, 11.9.

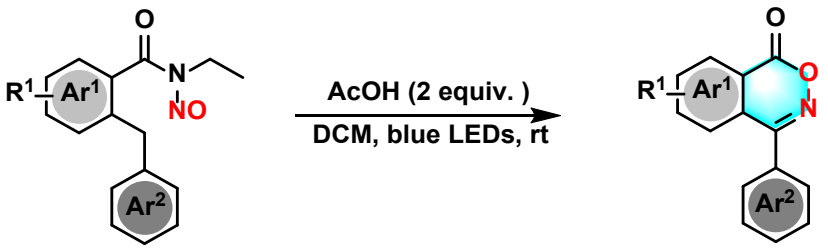
***N*-ethyl-*N*-nitroso-2-((2-phenylcyclopropyl) methyl) benzamide**



1aq

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 – 7.37 (m, 2H), 7.35 – 7.18 (m, 4H), 7.16 – 7.07 (m, 1H), 7.05 – 6.96 (m, 2H), 3.96 (q, *J* = 7.1 Hz, 2H), 2.84 – 2.68 (m, 2H), 1.76 (dt, *J* = 9.2, 4.9 Hz, 1H), 1.40 – 1.23 (m, 1H), 1.09 (t, *J* = 7.1 Hz, 3H), 0.91 (ddt, *J* = 30.5, 8.6, 5.2 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.5, 142.8, 139.5, 133.8, 130.6, 129.4, 128.28, 128.25, 125.7, 125.6, 125.4, 37.2, 34.2, 23.5, 23.3, 16.2, 12.0.

3. General procedures for the Barton-type reaction

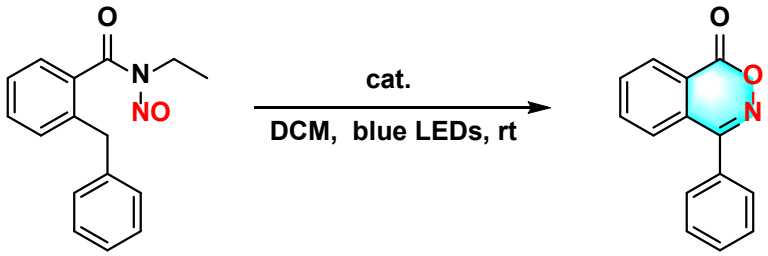


1 2

A 10 mL of Schlenk tube equipped with a rubber septum and magnetic stirring bar, *N*-ethyl-*N*-nitrosobenzamides (0.1mmol, 1.0 equiv.) and AcOH (11.5 μL, 2 equiv.) were charged, DCM (0.025 M) was added, then the vessel was bubbled with a stream of argon for 20 min via a syringe needle and the tightly sealed tube was irradiated with a 3 W blue LED at about 20 ℃ (the distance between the tube and the light source was about 0.5 cm), unless otherwise stated. Upon completion (as judged by TLC analysis), silica was added to the reaction and then concentrated in vacuo. The crude residue was then purified by flash chromatography on silica gel (EtOAc: petroleum ether as an eluent) to give the products. (The yields were based on the ^{1}NMR analysis using 4-nitroacetophenone as the internal standard) Note, isolated yields following purification by flash-column chromatography in parenthesis.

3.1 Optimization of the reaction conditions

Table 1. The background reaction



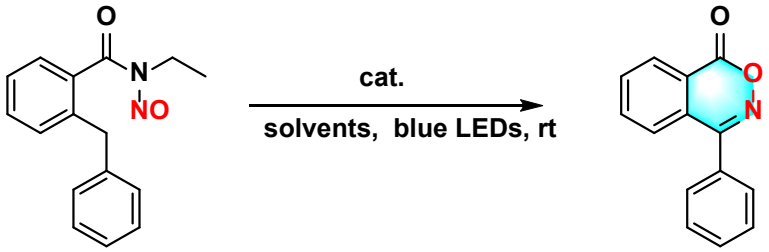
1a 2a

Entry[a]	Cat.	Additive[b]	Light source	Yield[c]

1	$Ru(bpy)_3Cl_2$			52%
2	$Ir(ppy)_3$			N.D.
3	$Ru(bpy)_3Cl_2$	DABCO		13%
4	$Ru(bpy)_3Cl_2$	K_2CO_3		57%
5[d]	$Ru(bpy)_3Cl_2$	AcOH		57%
6	$Ru(bpy)_3Cl_2$	HCl		56%
7				69%
8			purple LEDs	60%
9			green LEDs	N.D.
10[e]			no *hv*	N.D.
11[f]			no *hv* + 50℃	N.D.
12[g]				58%
13		AcOH (1.equiv.)		90%
14		AcOH (2.equiv.)		92%
15		AcOH (3.equiv.)		92%
16[h]		AcOH (2.equiv.)		84%
17		Et_3N (2.equiv.)		15%

[a]Unless otherwise noted, the reactions were carried out with **1a** (0.1 mmol), additive (1.equiv.) in CH_2Cl_2(0.025M) under Ar protection and irradiation (λmax = 450 nm) at room temperature for a certain time. [b]DABCO (triethylenediamine), AcOH (acetic acid). [c]The yields were determined by ^1H NMR spectroscopic analysis. N.D. = not detected. [d]The molar absorption coefficient (ε) of $Ru(bpy)_3Cl_2$ around 450 nm is much larger than that of *N*-nitrosobenzamide **1a**, indicating that $Ru(bpy)_3Cl_2$ is preferentially excited in the mixture of $Ru(bpy)_3Cl_2$ and **1a**. Due to the less efficient energy transfer process between the excited $Ru(bpy)_3Cl_2$ and **1a**, the photoreaction is slower than that in the absence of $Ru(bpy)_3Cl_2$.[5,6] [e]no light. [f]the reaction runs in DCE. [g]2-benzyl-*N*-methyl-*N*-nitrosobenzamide was used. [h]Under air.

Table 2. Screening of solvents



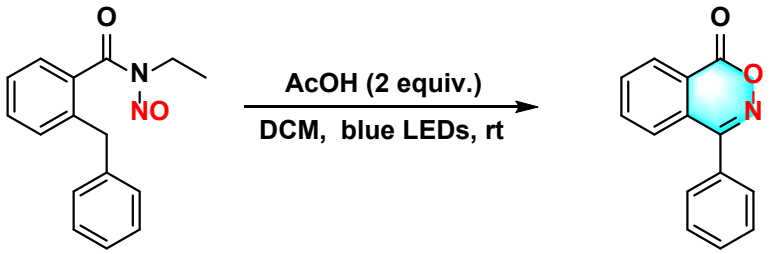
1a **2a**

Entry[a]	Solvent	Yield[b]
1	DCE	61%
2	THF	19%
3	$CHCl_3$	56%
4	DMF	34%
5	dioxane	40%
6	MeOH	30%
7	PhMe	60%

8	CH_3CN	60%
9	EA	59%
10	DCM	69%

[a]Unless otherwise noted, the reactions were carried out with **1a** (0.1 mmol) in solvents (0.025M) under Ar protection and irradiation (λ_{max} = 450 nm) at room temperature for a certain time. [b]The yields were determined by ^{1}H NMR spectroscopic analysis.

Table 3. Screening of reaction concentration



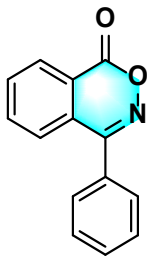
1a **2a**

Entry[a]	Concentration (mol/L)	Yield[b]
1	0.2	89%
2	0.1	89%
3	0.05	92%
4	0.025	93%
5	0.01	92%

[a]Unless otherwise noted, the reactions were carried out with **1a** (0.1 mmol) and AcOH (2 equiv.) in DCM under Ar protection and irradiation (λmax = 450 nm) at room temperature for a certain time. [b]The yields were determined by ^{1}H NMR spectroscopic analysis.

3.2 Characterization of products 2a-2ap

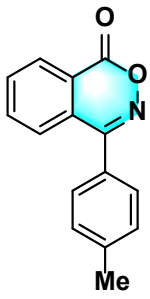
4-phenyl-1*H*-benzo[*d*][1,2]oxazin-1-one (2a)



2a

White solid (24.1 mg, 90%). Melting point: 164-165 °C .**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.49 – 8.39 (m, 1H), 7.93 – 7.82 (m, 2H), 7.64 – 7.50 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.5, 157.2, 135.3, 133.8, 131.0, 130.4, 129.3, 128.9, 128.7, 127.5, 127.2, 122.8.
HRMS (ESI, m/z): $[M+H]^+$ Calcd for $C_{14}H_{10}NO_2$ 224.0706; Found 224.0709.

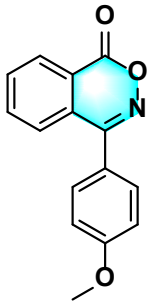
4-(p-tolyl)-1*H*-benzo[*d*][1,2]oxazin-1-one (2b)



2b

White solid (21.1 mg, 89%). Melting point: 163-164 ºC .**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.47 – 8.40 (m, 1H), 7.92 – 7.81 (m, 2H), 7.63 – 7.53 (m, 1H), 7.50 – 7.44 (m, 2H), 7.36 (d, *J* = 7.9 Hz, 2H), 2.46 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.6, 157.2, 140.6, 135.2, 133.7, 129.6, 129.2, 128.7, 128.1, 127.5, 127.4, 122.8, 21.4.
HRMS (ESI, m/z): $[M+H]^+$ Calcd for $C_{15}H_{12}NO_2$ 238.0863; Found 238.0863.

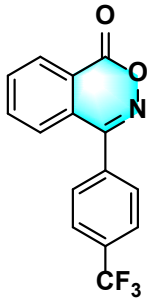
4-(4-methoxyphenyl)-1*H*-benzo[*d*][1,2]oxazin-1-one (2c)



2c

White solid (24.0 mg, 88%). Melting point: 125-127 ºC .**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.43 (dd, *J* = 5.9, 3.3 Hz, 1H), 7.86 (dt, *J* = 7.4, 3.7 Hz, 2H), 7.64 – 7.57 (m, 1H), 7.56 – 7.48 (m, 2H), 7.10 – 7.02 (m, 2H), 3.89 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.6, 161.2, 156.9, 135.2, 133.6, 130.8, 128.7, 127.5, 127.4, 123.1, 122.8, 114.3, 55.4.
HRMS (ESI, m/z): $[M+H]^+$ Calcd for $C_{15}H_{12}NO_3$ 254.0812; Found 254.0812.

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

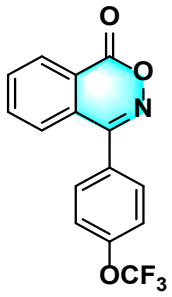


2d

White solid (26.2 mg, 90%). Melting point: 203-205 ºC .**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.51 – 8.40 (m, 1H), 7.97 – 7.86 (m, 2H), 7.83 (d, *J* = 8.1 Hz, 2H), 7.77 – 7.71 (m, 2H), 7.56 – 7.45 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.0, 156.2, 135.6, 134.7 (q, *J* = 1.5 Hz), 134.2, 132.4 (q, *J*

= 32.9 Hz), 131.9, 129.9, 129.0, 127.0, 126.7, 125.9 (q, J = 3.7 Hz), 123.6 (d, J = 272.4 Hz), 122.7. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.86.
HRMS (ESI, m/z): $[M+H]^+$ Calcd for $C_{15}H_9F_3NO_2$ 292.0580; Found 292.0580.

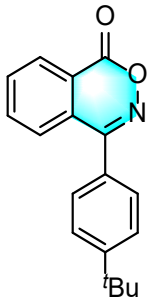
4-(4-(trifluoromethoxy) phenyl)-1*H*-benzo[*d*][1,2]oxazin-1-one (2e)



2e

White solid (26.8 mg, 88%). Melting point: 113-114 °C .**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.51 – 8.41 (m, 1H), 7.96 – 7.85 (m, 2H), 7.71 – 7.61 (m, 2H), 7.59 – 7.49 (m, 1H), 7.42 (d, J = 8.2 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.2, 156.2, 150.7 (q, J = 1.9 Hz), 135.5, 134.1, 131.1, 129.6, 129.0, 127.1, 126.9, 122.7, 121.3, 120.3 (d, J = 258.5 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -57.70.
HRMS (ESI, m/z): $[M+H]^+$ Calcd for $C_{15}H_9F_3NO_3$ 308.0529; Found 308.0529.

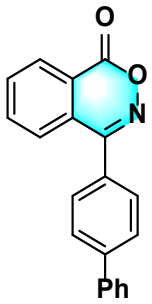
4-(4-(tert-butyl) phenyl)-1*H*-benzo[*d*][1,2]oxazin-1-one (2f)



2f

White solid (25.9 mg, 93%). Melting point: 159-161 °C .**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.49 – 8.40 (m, 1H), 7.92 – 7.82 (m, 2H), 7.65 – 7.60 (m, 1H), 7.59 – 7.55 (m, 2H), 7.54 – 7.49 (m, 2H), 1.38 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.6, 157.2, 153.7, 135.2, 133.7, 129.1, 128.7, 128.0, 127.6, 127.4, 125.9, 122.8, 34.9, 31.2.
HRMS (ESI, m/z): $[M+H]^+$ Calcd for $C_{18}H_{18}NO_2$ 280.1332; Found 280.1332.

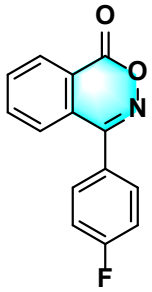
4-([1,1 -biphenyl]-4-yl)-1*H*-benzo[*d*][1,2]oxazin-1-one (2g)



2g

White solid (26.3 mg, 88%). Melting point: 185-187 °C .**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.47 (dd, *J* = 5.9, 3.3 Hz, 1H), 7.90 (dd, *J* = 5.9, 3.3 Hz, 2H), 7.81 – 7.75 (m, 2H), 7.70 – 7.61 (m, 5H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.45 – 7.37 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.5, 157.0, 143.3, 139.9, 135.3, 133.8, 129.8, 129.0, 128.8, 128.0, 127.6, 127.4, 127.22, 127.17, 122.8.
HRMS (ESI, m/z): $[M+H]^+$ Calcd for $C_{20}H_{14}NO_2$ 300.1019; Found 300.1019.

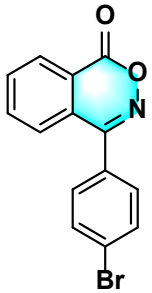
4-(4-fluorophenyl)-1*H*-benzo[*d*][1,2]oxazin-1-one (2h)



2h

White solid (27.2 mg, 95%). Melting point: 199-200 °C .**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.51 – 8.41 (m, 1H), 7.96 – 7.85 (m, 2H), 7.65 – 7.49 (m, 3H), 7.27 (t, *J* = 8.6 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.0 (d, *J* = 251.5 Hz), 163.3, 156.4, 135.4, 133.9, 131.4 (d, *J* = 8.5 Hz), 128.9, 127.2, 127.1, 127.1 (d, *J* = 3.6 Hz), 122.8, 116.18 (d, *J* = 22.0 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -109.55.
HRMS (ESI, m/z): $[M+H]^+$ Calcd for $C_{14}H_9FNO_2$ 242.0612; Found 242.0612.

4-(4-bromophenyl)-1*H*-benzo[*d*][1,2]oxazin-1-one (2i)



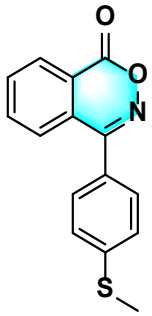
2i

White solid (27.2 mg, 90%). Melting point: 203-205 °C .**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.50 –

8.40 (m, 1H), 7.89 (td, *J* = 6.2, 3.4 Hz, 2H), 7.74 – 7.66 (m, 2H), 7.59 – 7.40 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.2, 156.4, 135.4, 134.0, 132.2, 130.9, 130.0, 129.0, 127.1, 126.9, 125.0, 122.8.

HRMS (ESI, m/z): $[M+H]^+$ Calcd for $C_{14}H_9BrNO_2$ 301.9811; Found 301.9811.

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

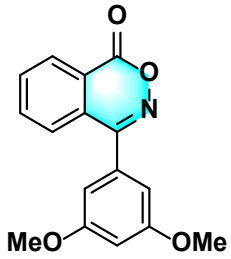


2j

White solid (19.8 mg, 74%). Melting point: 162-163 °C .**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.48 – 8.38 (m, 1H), 7.92 – 7.82 (m, 2H), 7.61 – 7.54 (m, 1H), 7.53 – 7.45 (m, 2H), 7.42 – 7.35 (m, 2H), 2.55 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.4, 156.7, 142.1, 135.3, 133.7, 129.6, 128.8, 127.3, 127.19, 127.16, 126.0, 15.2.

HRMS (ESI, m/z): $[M+H]^+$ Calcd for $C_{15}H_{12}NO_2S$ 270.0583; Found 270.0583.

4-(3,5-dimethoxyphenyl)-1*H*-benzo[*d*][1,2]oxazin-1-one (2k)

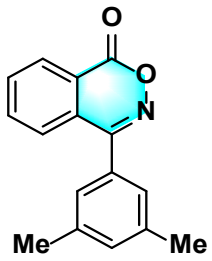


2k

White solid (23.6 mg, 83%). Melting point: 161-162 °C .**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.48 – 8.38 (m, 1H), 7.92 – 7.81 (m, 2H), 7.67 – 7.57 (m, 1H), 6.69 (d, *J* = 2.3 Hz, 2H), 6.64 (t, *J* = 2.3 Hz, 1H), 3.84 (s, 7H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.4, 161.1, 157.1, 135.3, 133.8, 132.7, 128.7, 127.5, 127.2, 122.7, 107.5, 102.3, 55.6.

HRMS (ESI, m/z): $[M+H]^+$ Calcd for $C_{16}H_{14}NO_4$ 284.0917; Found 284.0917.

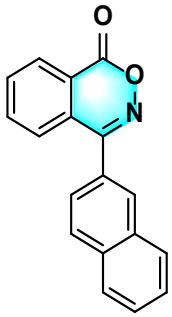
4-(3,5-dimethylphenyl)-1*H*-benzo[*d*][1,2]oxazin-1-one (2l)



2l

White solid (22.8 mg, 91%). Melting point: 161-162 ºC .**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.47 – 8.38 (m, 1H), 7.87 (dd, *J* = 5.9, 3.3 Hz, 2H), 7.62 – 7.53 (m, 1H), 7.22 – 7.14 (m, 3H), 2.40 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.56, 157.38, 138.60, 135.25, 133.64, 131.91, 130.69, 128.58, 127.62, 127.32, 126.93, 122.68, 21.23.
HRMS (ESI, m/z): $[M+H]^+$ Calcd for $C_{16}H_{14}NO_2$ 252.1019; Found 252.1019.

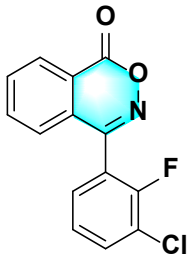
4-(naphthalen-2-yl)-1*H*-benzo[*d*][1,2]oxazin-1-one (2m)



2m

White solid (15.0 mg, 55%). Melting point: 203-204 ºC .**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.54 – 8.44 (m, 1H), 8.12 (d, *J* = 1.7 Hz, 1H), 8.03 (d, *J* = 8.5 Hz, 1H), 7.98 – 7.80 (m, 4H), 7.68 – 7.55 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.5, 157.3, 135.3, 133.9, 133.8, 133.0, 129.5, 128.9, 128.7, 128.5, 128.4, 127.9, 127.6, 127.4, 127.0, 125.9, 122.9.
HRMS (ESI, m/z): $[M+H]^+$ Calcd for $C_{18}H_{12}NO_2$ 274.0863; Found 274.0863.

4-(3-chloro-2-fluorophenyl)-1*H*-benzo[*d*][1,2]oxazin-1-one (2n)

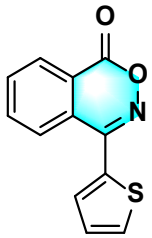


2n

White solid (25.0 mg, 91%). Melting point: 185-187 ºC .**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.50 – 8.39 (m, 1H), 7.95 – 7.83 (m, 2H), 7.65 (ddd, *J* = 8.5, 7.1, 1.7 Hz, 1H), 7.44 (ddd, *J* = 7.7, 6.0, 1.7 Hz, 1H), 7.37 – 7.27 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.0, 155.8 (d, *J* = 252.7 Hz), 152.9, 135.7, 134.3, 133.1, 129.7 (d, *J* = 2.1 Hz), 128.8, 126.79, 126.76 (d, *J* = 2.0 Hz), 125.4 (d, *J*

= 4.7 Hz), 122.2 (d, *J* = 17.2 Hz), 122.1, 120.7 (d, *J* = 15.3 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.88.
HRMS (ESI, m/z): $[M+H]^+$ Calcd for $C_{14}H_8ClFNO_2$ 276.0222; Found 276.0222.

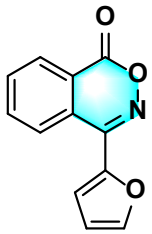
4-(thiophen-2-yl)-1*H*-benzo[*d*][1,2]oxazin-1-one (2o)



2o

White solid (7.9 mg, 34%). Melting point: 137-138 °C .**^{1}H NMR** (400 MHz, $CDCl_3$) δ 1H NMR (400 MHz, CDCl3) δ 8.47 – 8.44 (m, 1H), 8.01 – 7.87 (m, 3H), 7.61 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.52 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.29 – 7.23 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.1, 151.9, 135.5, 133.9, 131.4, 130.3, 129.1, 129.0, 127.8, 127.0, 126.9, 122.6.
HRMS (ESI, m/z): $[M+H]^+$ Calcd for $C_{12}H_8NO_2S$ 230.0270; Found 230.0276.

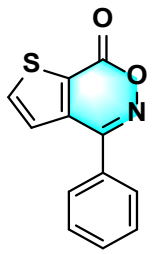
4-(furan-2-yl)-1*H*-benzo[*d*][1,2]oxazin-1-one (2p)



2p

White solid (4.4 mg, 20%). Melting point: 137-138 °C .**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.48 – 8.41 (m, 1H), 8.25 – 8.14 (m, 1H), 7.93 (dtd, *J* = 22.9, 7.5, 1.4 Hz, 2H), 7.74 (dd, *J* = 1.9, 0.8 Hz, 1H), 7.09 (dd, *J* = 3.4, 0.8 Hz, 1H), 6.64 (dd, *J* = 3.4, 1.8 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.1, 148.0, 145.8, 145.3, 135.6, 133.9, 128.9, 127.0, 126.3, 122.5, 113.8, 111.9.
HRMS (ESI, m/z): $[M+H]^+$ Calcd for $C_{12}H_8NO_3$ 214.0499; Found 214.0502.

4-phenyl-7*H*-thieno[3,2-*d*][1,2]oxazin-7-one (2r)

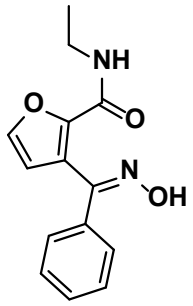


2r

White solid (16.5 mg, 72%). Melting point: 146-148 °C .**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J*

= 5.1 Hz, 1H), 7.73 – 7.64 (m, 2H), 7.63 – 7.51 (m, 3H), 7.35 (d, *J* = 5.2 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.9, 153.6, 137.3, 137.2, 131.6, 131.0, 130.8, 129.1, 128.5, 125.6.
HRMS (ESI, m/z): $[M+H]^+$ Calcd for $C_{12}H_8NO_2S$ 230.0270; Found 230.0277.

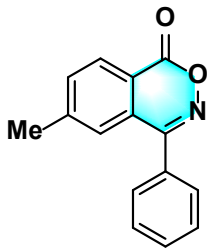
(*E*)-*N*-ethyl-3-((hydroxyimino)(phenyl)methyl) furan-2-carboxamide (2q)



2q

White solid (18.1 mg, 70%). Melting point: 146-148 °C .**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.93 (s, 1H), 7.61 – 7.50 (m, 3H), 7.40 – 7.28 (m, 3H), 6.52 – 6.44 (m, 2H), 3.36 (qd, *J* = 7.2, 5.6 Hz, 2H), 1.12 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.0, 151.5, 144.2, 143.6, 134.8, 129.6, 128.9, 128.4, 128.2, 126.9, 119.8, 113.4, 34.2, 14.6.
HRMS (ESI, m/z): $[M+H]^+$ Calcd for $C_{14}H_{15}N_2O_3$ 259.1077; Found 259.1077.

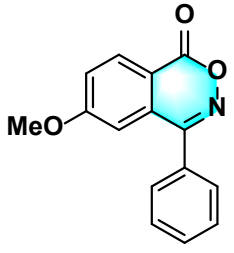
6-methyl-4-phenyl-1*H*-benzo[*d*][1,2]oxazin-1-one (2s)



2s

White solid (21.9 mg, 92%). Melting point: 162-164 °C .**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.0 Hz, 1H), 7.68 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.57 (d, *J* = 2.3 Hz, 5H), 7.30 (dd, *J* = 1.7, 0.9 Hz, 1H), 2.49 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.6, 157.2, 146.8, 134.9, 131.2, 130.3, 129.3, 128.9, 128.8, 127.4, 127.3, 120.3, 22.2.
HRMS (ESI, m/z): $[M+H]^+$ Calcd for $C_{15}H_{12}NO_2$ 238.0863; Found 238.0862.

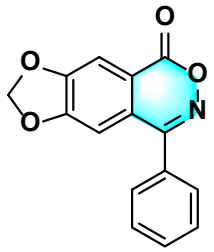
6-methoxy-4-phenyl-1*H*-benzo[*d*][1,2]oxazin-1-one (2t)



2t

White solid (25.4 mg, 99%). Melting point: 127-128 °C .**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.7 Hz, 1H), 7.62 – 7.50 (m, 5H), 7.35 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.90 (d, *J* = 2.5 Hz, 1H), 3.85 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.9, 163.3, 157.0, 131.20, 131.16, 130.3, 129.4, 129.2, 128.9, 120.4, 115.6, 110.9, 55.9.
HRMS (ESI, m/z): $[M+H]^+$ Calcd for $C_{15}H_{12}NO_3$ 254.0812; Found 254.0811.

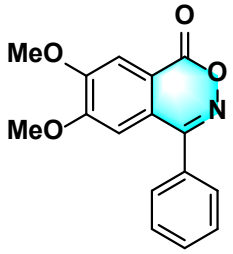
8-phenyl-5*H*-[1,3]dioxolo[4,5:4,5]benzo[1,2 -*d*][1,2]oxazin-5-one (2u)



2u

White solid (24.2 mg, 91%). Melting point: 215-216 °C .**^{1}H NMR** (400 MHz, CD_2Cl_2) δ 7.74 (s, 1H), 7.67 – 7.54 (m, 5H), 6.89 (s, 1H), 6.23 (d, *J* = 0.9 Hz, 2H). **^{13}C NMR** (101 MHz, CD_2Cl_2) δ 163.7, 157.0, 154.2, 152.7, 131.9, 130.6, 129.6, 129.3, 124.6, 119.4, 107.1, 106.5, 103.8.
HRMS (ESI, m/z): $[M+H]^+$ Calcd for $C_{15}H_{10}NO_4$ 268.0604; Found 268.0604.

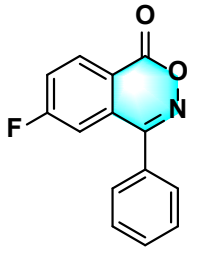
6,7-dimethoxy-4-phenyl-1*H*-benzo[*d*][1,2]oxazin-1-one (2v)



2v

White solid (28.7 mg, 99%). Melting point: 180-181 °C .**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.56 (q, *J* = 3.4 Hz, 5H), 6.85 (s, 1H), 4.04 (s, 3H), 3.84 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.9, 156.5, 154.9, 153.6, 131.4, 130.3, 129.1, 128.9, 122.1, 117.0, 108.7, 107.8, 56.7, 56.3.
HRMS (ESI, m/z): $[M+H]^+$ Calcd for $C_{16}H_{14}NO_4$ 284.0917; Found 284.0916.

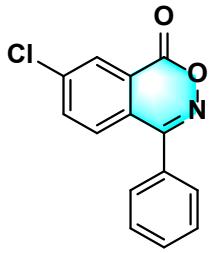
6-fluoro-4-phenyl-1*H*-benzo[*d*][1,2]oxazin-1-one (2w)



2w

White solid (24.0 mg, 99%). Melting point: 178-179 °C .**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.49 (dd, *J* = 8.7, 5.4 Hz, 1H), 7.65 – 7.51 (m, 6H), 7.21 (dd, *J* = 8.7, 2.5 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.6 (d, *J* = 259.1 Hz), 162.5, 156.5 (d, *J* = 2.5 Hz), 132.4 (d, *J* = 9.8 Hz), 130.7, 130.5, 130.0 (d, *J* = 9.6 Hz), 129.2, 129.1, 121.9 (d, *J* = 22.8 Hz), 119.3 (d, *J* = 2.8 Hz), 113.8 (d, *J* = 24.1 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -98.21.
HRMS (ESI, m/z): $[M+H]^+$ Calcd for $C_{14}H_9FNO_2$ 242.0612; Found 242.0613.

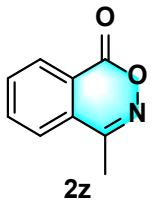
7-chloro-4-phenyl-1*H*-benzo[*d*][1,2]oxazin-1-one (2x)



2x

White solid (19.9 mg, 87%). Melting point: 194-195 °C .**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 2.2 Hz, 1H), 7.80 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.64 – 7.54 (m, 5H), 7.52 (d, J = 8.5 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.4, 156.5, 140.4, 135.6, 130.6, 129.2, 129.13, 129.05, 128.6, 125.6, 124.1.
HRMS (ESI, m/z): $[M+H]^+$ Calcd for $C_{14}H_9ClNO_2$ 258.0316; Found 258.0316.

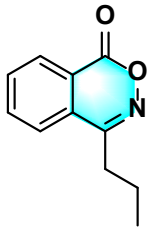
4-methyl-1*H*-benzo[*d*][1,2]oxazin-1-one (2z)



2z

White solid (12.7 mg, 54%). Melting point: 161-162 °C .**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.38 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.94 (td, *J* = 7.7, 1.4 Hz, 1H), 7.86 (td, *J* = 7.6, 1.3 Hz, 1H), 7.70 (d, *J* = 7.7 Hz, 1H), 2.58 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.7, 153.2, 135.5, 133.7, 128.7, 127.5, 125.2, 122.3, 16.7.
HRMS (ESI, m/z): $[M+H]^+$ Calcd for $C_9H_8NO_2$ 162.0550; Found 162.0551.

4-propyl-1*H*-benzo[*d*][1,2]oxazin-1-one (2aa)

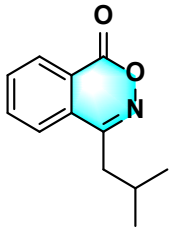


2aa

White solid (12.7 mg, 54%). Melting point: 161-162 °C .**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.39 (dd, *J*

= 7.9, 1.5 Hz, 1H), 7.93 (td, *J* = 7.7, 1.4 Hz, 1H), 7.84 (td, *J* = 7.6, 1.2 Hz, 1H), 7.73 (dt, *J* = 8.1, 0.9 Hz, 1H), 2.97 – 2.88 (m, 2H), 1.83 (h, *J* = 7.4 Hz, 2H), 1.07 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.79, 155.7, 135.3, 133.5, 128.8, 126.9, 124.9, 122.7, 32.4, 20.8, 13.8.
HRMS (ESI, m/z): $[M+H]^+$ Calcd for $C_{11}H_{12}NO_2$ 190.0863; Found 190.0864.

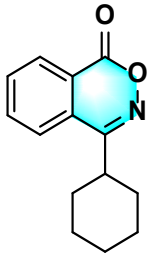
4-isobutyl-1*H*-benzo[*d*][1,2]oxazin-1-one (2ab)



2ab

Yellow oil. (16.2 mg, 80%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.40 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.93 (td, *J* = 7.7, 1.5 Hz, 1H), 7.85 (td, *J* = 7.6, 1.2 Hz, 1H), 7.75 – 7.68 (m, 1H), 2.81 (d, *J* = 7.2 Hz, 2H), 2.16 (dh, *J* = 13.6, 6.8 Hz, 1H), 1.05 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.8, 155.2, 135.3, 133.5, 128.9, 127.1, 125.1, 122.7, 39.1, 27.3, 22.5.
HRMS (ESI, m/z): $[M+H]^+$ Calcd for $C_{12}H_{14}NO_2$ 204.1019; Found 204.1019.

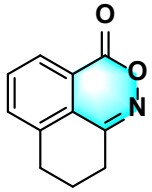
4-cyclohexyl-1*H*-benzo[*d*][1,2]oxazin-1-one (2ac)



2ac

White solid (20.6 mg, 90%). Melting point: 115-116 °C .**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.36 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.92 (td, *J* = 7.7, 1.4 Hz, 1H), 7.85 – 7.73 (m, 2H), 3.06 (tt, *J* = 11.7, 3.1 Hz, 1H), 2.08 – 1.96 (m, 2H), 1.89 (dp, *J* = 10.1, 3.4 Hz, 2H), 1.78 (dddt, *J* = 11.5, 5.0, 3.3, 1.5 Hz, 1H), 1.72 – 1.58 (m, 2H), 1.43 (qt, *J* = 12.9, 3.3 Hz, 2H), 1.36 – 1.19 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.7, 158.7, 135.3, 133.2, 128.8, 126.4, 124.4, 122.7, 39.5, 31.2, 26.3, 25.8.
HRMS (ESI, m/z): $[M+H]^+$ Calcd for $C_{14}H_{16}NO_2$ 230.1176; Found 230.1181.

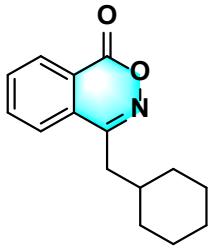
8,9-dihydro-3*H*,7*H*-naphtho[1,8-*cd*][1,2]oxazin-3-one (2ad)



2ad

White solid (10.5 mg, 55%). Melting point: 140-141 °C .**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.79 – 7.67 (m, 2H), 3.03 – 2.90 (m, 4H), 2.13 (p, *J* = 6.2 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.2, 153.6, 139.0, 134.9, 133.4, 126.2, 123.8, 122.3, 28.6, 28.1, 22.3.
HRMS (ESI, m/z): $[M+H]^+$ Calcd for $C_{11}H_{10}NO_2$ 188.0706; Found 188.0707.

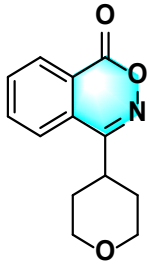
4-(cyclohexylmethyl)-1*H*-benzo[*d*][1,2]oxazin-1-one (2ae)



2ae

Yellow oil. (17.0 mg, 69%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.39 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.93 (td, *J* = 7.7, 1.5 Hz, 1H), 7.85 (td, *J* = 7.6, 1.2 Hz, 1H), 7.71 (dd, *J* = 7.9, 1.2 Hz, 1H), 2.81 (d, *J* = 6.7 Hz, 2H), 1.85 – 1.61 (m, 6H), 1.38 – 1.01 (m, 5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.8, 154.9, 135.3, 133.4, 128.8, 127.1, 125.2, 122.7, 37.8, 36.5, 33.2, 26.1, 26.0.
HRMS (ESI, m/z): $[M+H]^+$ Calcd for $C_{15}H_{18}NO_2$ 244.1332; Found 244.1332.

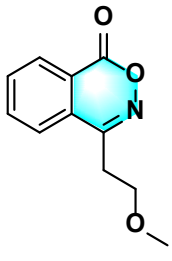
4-(tetrahydro-2*H*-pyran-4-yl)-1*H*-benzo[*d*][1,2]oxazin-1-one (2af)



2af

White solid (19.2 mg, 83%). Melting point: 174-175 °C .**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.44 – 8.38 (m, 1H), 7.94 (td, *J* = 7.7, 1.5 Hz, 1H), 7.85 (td, *J* = 7.6, 1.2 Hz, 1H), 7.77 (dd, *J* = 8.0, 1.2 Hz, 1H), 4.12 (ddd, *J* = 11.7, 4.5, 2.1 Hz, 2H), 3.61 (td, *J* = 11.8, 2.2 Hz, 2H), 3.35 (tt, *J* = 11.4, 3.6 Hz, 1H), 2.08 (dtd, *J* = 13.7, 11.6, 4.3 Hz, 2H), 1.98 – 1.88 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.4, 157.1, 135.4, 133.5, 129.2, 126.2, 124.1, 122.8, 67.7, 36.9, 30.8.
HRMS (ESI, m/z): $[M+H]^+$ Calcd for $C_{13}H_{14}NO_3$ 232.0968; Found 232.0969.

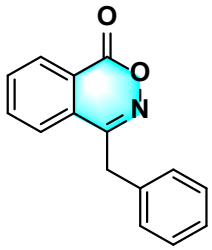
4-(2-methoxyethyl)-1*H*-benzo[*d*][1,2]oxazin-1-one (2ag)



2ag

White solid (11.6 mg, 57%). Melting point: 81-82 °C .**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.42 – 8.35 (m, 1H), 7.93 (td, *J* = 7.7, 1.5 Hz, 1H), 7.85 (td, *J* = 7.6, 1.3 Hz, 1H), 7.79 (dt, *J* = 7.9, 0.9 Hz, 1H), 3.83 (t, *J* = 6.6 Hz, 2H), 3.37 (s, 3H), 3.22 (t, *J* = 6.7 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.6, 154.0, 135.4, 133.6, 128.7, 127.2, 125.3, 122.5, 69.7, 58.9, 30.9.
HRMS (ESI, m/z): $[M+H]^+$ Calcd for $C_{11}H_{12}NO_3$ 206.0812; Found 206.0814.

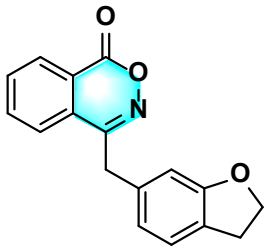
4-benzyl-1*H*-benzo[*d*][1,2]oxazin-1-one (1ah)



2ah

White solid (18.1 mg, 76%). Melting point: 112-113 °C .**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.42 – 8.33 (m, 1H), 7.84 – 7.73 (m, 2H), 7.68 – 7.59 (m, 1H), 7.39 – 7.21 (m, 5H), 4.30 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.6, 154.7, 135.6, 135.3, 133.5, 129.0, 128.8, 128.4, 127.3, 126.8 125.8, 122.9, 37.0.
HRMS (ESI, m/z): $[M+H]^+$ Calcd for $C_{15}H_{12}NO_2$ 238.0863; Found 238.0863.

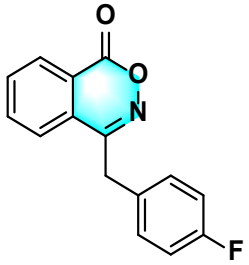
4-((2,3-dihydrobenzofuran-6-yl) methyl)-1*H*-benzo[*d*][1,2]oxazin-1-one (2ai)



2ai

White solid (17.0 mg, 61%). Melting point: 167-168 °C .**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.40 – 8.31 (m, 1H), 7.85 – 7.73 (m, 2H), 7.72 – 7.64 (m, 1H), 7.15 (d, *J* = 2.0 Hz, 1H), 7.08 (dd, *J* = 8.1, 2.0 Hz, 1H), 6.71 (d, *J* = 8.1 Hz, 1H), 4.53 (t, *J* = 8.7 Hz, 2H), 4.20 (s, 2H), 3.15 (t, *J* = 8.7 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.7, 159.4, 155.0, 135.3, 133.4, 128.8, 128.1, 128.0, 127.3, 126.8, 125.9, 124.8, 123.0, 109.5, 71.3, 36.4, 29.6.
HRMS (ESI, m/z): $[M+H]^+$ Calcd for $C_{17}H_{14}NO_3$ 280.0968; Found 280.0968.

4-(4-fluorobenzyl)-1*H*-benzo[*d*][1,2]oxazin-1-one (2aj)

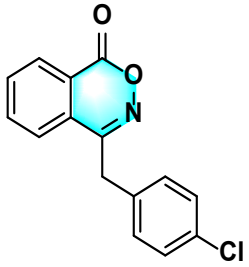


2aj

White solid (23.1 mg, 91%). Melting point: 125-126 ºC .**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.42 – 8.32 (m, 1H), 7.86 – 7.75 (m, 2H), 7.65 – 7.56 (m, 1H), 7.36 – 7.26 (m, 2H), 7.06 – 6.96 (m, 2H), 4.26 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.5, 162.0 (d, *J* = 246.3 Hz), 154.6, 135.4, 133.6, 131.2 (d, *J* = 3.3 Hz), 129.9 (d, *J* = 8.1 Hz), 128.9, 126.6, 125.6, 122.9, 115.93 (d, *J* = 21.6 Hz), 36.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.96.

HRMS (ESI, m/z): $[M+H]^+$ Calcd for $C_{15}H_{11}FNO_2$ 256.0768; Found 256.0768.

4-(4-chlorobenzyl)-1*H*-benzo[*d*][1,2]oxazin-1-one (2ak)

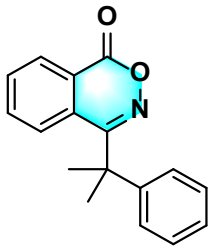


2ak

White solid (14.6 mg, 54%). Melting point: 177-178 ºC .**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.43 – 8.34 (m, 1H), 7.86 – 7.77 (m, 2H), 7.63 – 7.54 (m, 1H), 7.29 (d, *J* = 1.3 Hz, 4H), 4.27 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.4, 154.4, 135.4, 134.0, 133.7, 133.3, 129.7, 129.2, 129.0, 126.6, 125.6, 122.9, 36.3.

HRMS (ESI, m/z): $[M+H]^+$ Calcd for $C_{15}H_{11}ClNO_2$ 272.0473; Found 272.0473.

4-(2-phenylpropan-2-yl)-1*H*-benzo[*d*][1,2] oxazin-1-one (2al)

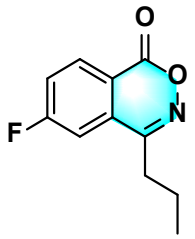


2al

White solid (24.9 mg, 94%). Melting point: 148-150 ºC .**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.36 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.66 (td, *J* = 7.6, 1.1 Hz, 1H), 7.52 (ddd, *J* = 8.8, 7.3, 1.5 Hz, 1H), 7.33 (d, *J* = 5.4 Hz, 4H), 7.28 – 7.21 (m, 1H), 7.15 (d, *J* = 8.2 Hz, 1H), 1.80 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.7, 159.9, 146.5, 134.3, 132.5, 129.1, 128.9, 127.7, 126.9, 126.0, 125.4, 123.3, 45.84, 29.6.

HRMS (ESI, m/z): $[M+H]^+$ Calcd for $C_{17}H_{16}NO_2$ 266.1176; Found 266.1176.

6-fluoro-4-propyl-1*H*-benzo[*d*][1,2]oxazin-1-one (2am)

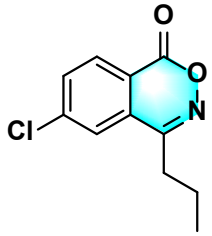


2am

White solid (15.0 mg, 72%). Melting point: 76-78 °C .**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.45 – 8.36 (m, 1H), 7.52 (td, *J* = 8.4, 2.3 Hz, 1H), 7.35 (dd, *J* = 8.7, 2.5 Hz, 1H), 2.92 – 2.83 (m, 2H), 1.88 – 1.73 (m, 2H), 1.06 (td, *J* = 7.4, 1.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.7 (d, *J* = 258.9 Hz), 162.7, 155.0 (d, *J* = 2.6 Hz), 132.3 (d, *J* = 9.9 Hz), 129.5 (d, *J* = 9.5 Hz), 121.5 (d, *J* = 22.8 Hz), 119.1 (d, *J* = 2.7 Hz), 111.4 (d, *J* = 23.4 Hz), 32.4, 20.5, 13.7. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -98.72.

HRMS (ESI, m/z): $[M+H]^+$ Calcd for $C_{11}H_{11}FNO_2$ 208.0768; Found 208.0770.

6-chloro-4-propyl-1*H*-benzo[*d*][1,2]oxazin-1-one (2an)

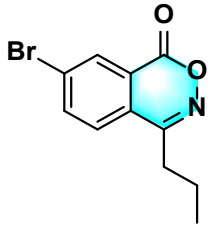


2an

White solid (15.1 mg, 68%). Melting point: 107-108 °C .**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.4 Hz, 1H), 7.78 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.66 (d, *J* = 1.9 Hz, 1H), 2.93 – 2.84 (m, 2H), 1.82 (h, *J* = 7.4 Hz, 2H), 1.07 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.9, 154.8, 142.3, 133.8, 130.6, 128.3, 124.8, 120.9, 32.4, 20.5, 13.7.

HRMS (ESI, m/z): $[M+H]^+$ Calcd for $C_{11}H_{11}ClNO_2$ 224.0473; Found 224.0478.

7-bromo-4-propyl-1*H*-benzo[*d*][1,2]oxazin-1-one (2ao)

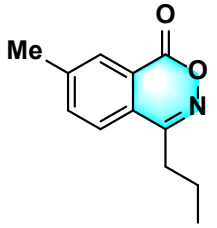


2ao

White solid (17.8 mg, 67%). Melting point: 123-124 °C .**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 2.1 Hz, 1H), 8.02 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.59 (d, *J* = 8.5 Hz, 1H), 2.94 – 2.84 (m, 2H), 1.81

(h, J = 7.4 Hz, 2H), 1.06 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.5, 155.2, 138.6, 131.7, 128.1, 126.6, 125.6, 124.0, 32.4, 20.7, 13.8.
HRMS (ESI, m/z): $[M+H]^+$ Calcd for $C_{11}H_{11}BrNO_2$ 267.9968; Found 267.9968.

7-methyl-4-propyl-1*H*-benzo[d][1,2]oxazin-1-one (2ap)

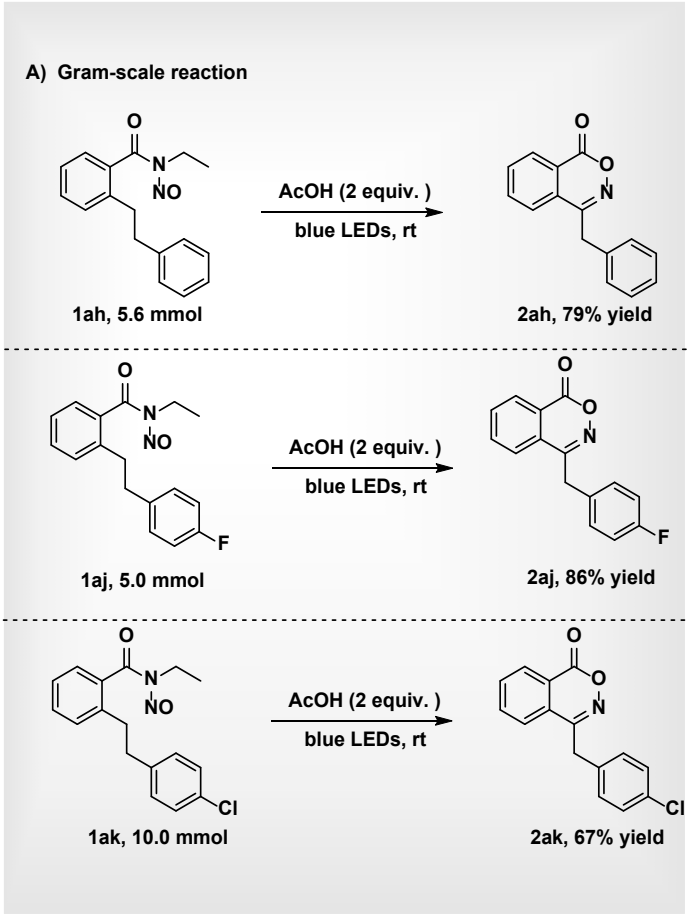


2ap

White solid (18.0 mg, 88%). Melting point: 65-67 ºC .**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 (dt, J = 1.6, 0.8 Hz, 1H), 7.71 (ddd, J = 8.1, 1.9, 0.7 Hz, 1H), 7.60 (d, J = 8.1 Hz, 1H), 2.92 – 2.83 (m, 2H), 2.53 (s, 3H), 1.80 (h, J = 7.4 Hz, 2H), 1.05 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.1, 155.6, 144.6, 136.4, 128.6, 124.9, 124.5, 122.5, 32.4, 21.7, 20.8, 13.8.
HRMS (ESI, m/z): $[M+H]^+$ Calcd for $C_{12}H_{14}NO_2$ 204.1019; Found 204.1021.

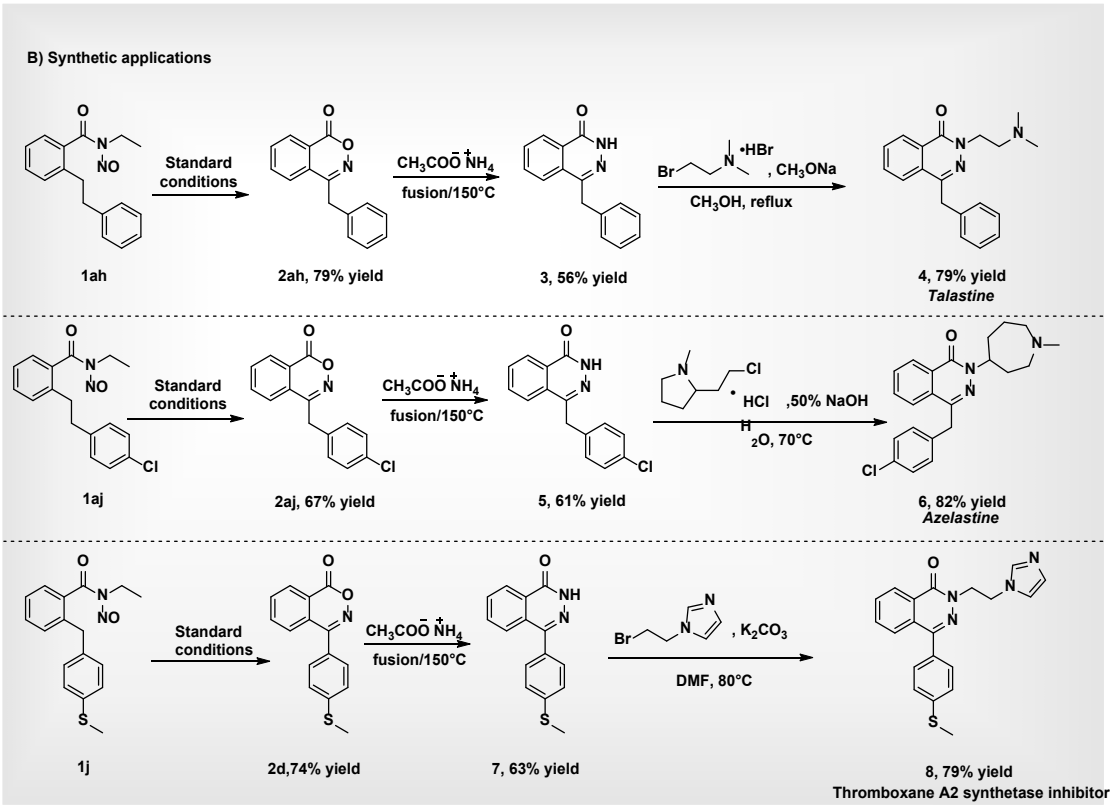
4. Gram-scale reaction and synthetic applications

4.1. Gram-scale reactions



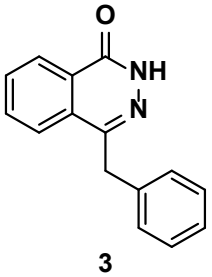
General Procedure：A 250 mL of Schlenk tube equipped with a rubber septum and magnetic stirring bar, *N*-ethyl-*N*-nitrosobenzamides (1.0 equiv.) and AcOH (2 equiv.) were charged, DCM (0.025 M) was added, then the vessel was bubbled with a stream of argon for 20 min via a syringe needle and the tightly sealed tube was irradiated with two 20 W blue LEDs at about 20 ℃ (the distance between the tube and the light source was about 5 cm). Upon completion (as judged by TLC analysis), silica was added to the reaction and then concentrated in vacuo. The crude residue was then purified by flash chromatography on silica gel (EtOAc: petroleum ether as an eluent) to give the products.The isolated yields following purification by flash-column chromatography in parenthesis to give the product **2ah** (white solid ,1.05 g, 79% yield)、**2aj** (white solid ,1.10 g, 86% yield) and **2ak** (white solid ,1.82 g, 67% yield).

4.2. Synthetic applications



The synthesis of phthaloazinones following the general procedure[7] (**3**,**5** and **7**): A mixture of benzoxazine **3** (1.0g, 1equiv.) and ammonium acetate (0.29g, 1 equiv.) was fused for 2h in an oil bath at 150°C. After cooling, the obtained solid was washed with water, filtered off, and recrystallized from ethanol to give the pure products as colorless crystals.

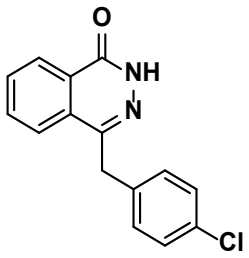
4-benzylphthalazin-1(2*H*)-one (3)



3

White solid (0.56g, 56%). Melting point: 201-202 °C .**^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.61 (s, 1H), 8.25 (dd, J = 7.7, 1.6 Hz, 1H), 7.92 (d, J = 7.9 Hz, 1H), 7.81 (dtd, J = 20.5, 7.3, 1.4 Hz, 2H), 7.34 – 7.23 (m, 4H), 7.22 – 7.13 (m, 1H), 4.29 (s, 2H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 159.4, 145.2, 138.2, 133.4, 131.4, 129.2, 128.6, 128.5, 127.9, 126.4, 126.0, 125.7, 37.7.
HRMS (ESI, m/z): $[M+H]^+$ Calcd for $C_{15}H_{13}N_2O$ 237.1022; Found 237.1022.

4-(4-chlorobenzyl) phthalazin-1(2*H*)-one (5)

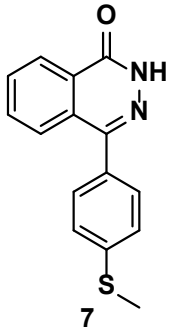


5

White solid (0.61g, 61%). Melting point: 220-222 ºC .**^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.61 (s, 1H), 8.25 (dd, J = 7.8, 1.5 Hz, 1H), 7.95 – 7.76 (m, 3H), 7.33 (s, 4H), 4.29 (s, 2H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 159.4, 144.9, 137.2, 133.5, 131.5, 131.1, 130.5, 129.1, 128.4, 127.9, 126.1, 125.5, 36.8.

HRMS (ESI, m/z): $[M+H]^+$ Calcd for $C_{15}H_{12}ClN_2O$ 271.0633; Found 271.0632.

4-(4-(methylthio) phenyl) phthalazin-1(2*H*)-one (7)

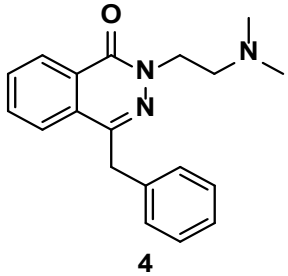


7

White solid (0.25g, 63%). Melting point: 248-250 ºC .**^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.84 (s, 1H), 8.38 – 8.29 (m, 1H), 7.89 (td, J = 6.6, 3.8 Hz, 2H), 7.75 – 7.66 (m, 1H), 7.57 – 7.49 (m, 2H), 7.46 – 7.38 (m, 2H), 2.55 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 159.2, 146.0, 139.5, 133.6, 131.7, 131.4, 129.8, 129.0, 127.9, 126.5, 126.1, 125.6, 14.4.

HRMS (ESI, m/z): $[M+H]^+$ Calcd for $C_{15}H_{14}N_2OS$ 269.0743; Found 269.0743.

4-benzyl-2-(2-(dimethylamino) ethyl) phthalazin-1(2*H*)-one (4)

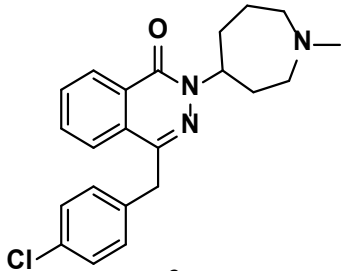


4

Following the general procedure with slightly modification[8]. To the solution of sodium methoxide (7.12 mmol ,3 equiv.) in dry methanol (50 mL) was added 4-benzylphthalazin-1(2*H*)-one **3** (0.56g, 2.37 mmol) and (2-bromoethyl) dimethylammonium bromide (3.56mmol ,1.5 equiv.). The mixture was heated at reflux for 6 hours. Afterwards, the inorganic material was collected by filtration, washed with dry methanol and, the filtrate was evaporated to dryness. Purification by column chromatography using pre-basified silica with AcOEt / MeOH (2:1, v/v) as

eluent afforded **4** as white solid (575 mg, 79% yield). Melting point: 109-111 °C.**^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.31 – 8.24 (m, 1H), 7.97 – 7.90 (m, 1H), 7.82 (dtd, J = 17.1, 7.2, 1.5 Hz, 2H), 7.39 – 7.32 (m, 2H), 7.28 (t, J = 7.6 Hz, 2H), 7.22 – 7.14 (m, 1H), 4.31 (s, 2H), 4.26 (t, J = 6.5 Hz, 2H), 2.70 (t, J = 6.4 Hz, 2H), 2.21 (s, 6H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 159.2, 146.0, 139.5, 133.6, 131.7, 131.4, 129.8, 129.0, 127.9, 126.5, 126.1, 125.6, 14.4.
HRMS (ESI, m/z): $[M+H]^+$ Calcd for $C_{19}H_{22}N_3O$ 308.1757; Found 308.1757.

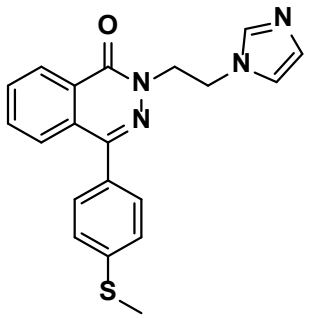
4-(4-chlorobenzyl)-2-(1-methylazepan-4-yl) phthalazin-1(2*H*)-one (6)



6

Following the general procedure with slightly modification[9].To the solution of NaOH (8.15 mmol, 0.33g) in water (3 ml) was added 2-(2-chloroethyl)-*N*-methylpyrrolidine hydrochloride (8.00 mmol, 1.47g) and heated to 70 °C. The mixture was added slowly to the solution of 4-(4-chlorobenzyl)-2-(1-methylazepan-4-yl) phthalazin-1(2H)-one **(6)** (7.41 mmol, 2g) in 50% NaOH a.q. (10 ml) at 70°C and stirred for 1 h. After cooling, the insoluble material was collected by filtration, and dissolved in DCM and extracted with 3N HCl. The aqueous phase was basified with KOH, extracted again with DCM and the organic phase was evaporated to dryness. The resulting crude product was recrystallized from DCM/ hexane to give the pure product as a white solid (2.31g, 82% yield). Melting point: 109-110 °C.**^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.46 (dq, J = 6.8, 3.6 Hz, 1H), 7.69 (dtt, J = 9.5, 6.1, 3.4 Hz, 3H), 7.29 – 7.23 (m, 2H), 7.20 (d, J = 8.4 Hz, 2H), 5.36 (tt, J = 8.9, 5.6 Hz, 1H), 4.27 (s, 2H), 2.79 (ddd, J = 13.4, 7.6, 2.4 Hz, 1H), 2.73 – 2.63 (m, 2H), 2.59 (ddd, J = 13.3, 9.5, 2.1 Hz, 1H), 2.41 (s, 3H), 2.23 (dtd, J = 14.7, 9.2, 2.4 Hz, 1H), 2.15 – 2.01 (m, 3H), 2.00 – 1.91 (m, 1H), 1.78 (tdd, J = 14.5, 8.0, 4.2 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.4, 144.4, 136.3, 132.7, 132.5, 131.1, 130.0, 128.8, 128.6, 128.1, 127.5, 124.4, 59.0, 56.0, 54.4, 47.0, 38.3, 33.2, 32.2, 24.7.
HRMS (ESI, m/z): $[M+H]^+$ Calcd for $C_{22}H_{25}ClN_3O$ 382.1681; Found 382.1681.

2-(2-(1*H*-imidazol-1-yl) ethyl)-4-(4-(methylthio) phenyl) phthalazin-1(2*H*)-one (8)



8

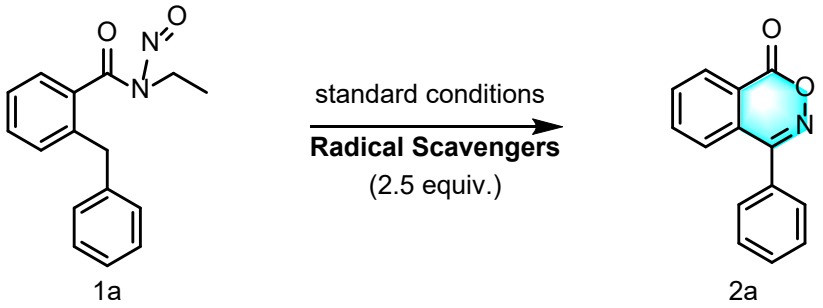
Following the general procedure[10].A mixture of 4-(4-(methylthio)phenyl)phthalazin-1(2*H*)-one (7) (500mg, 1.87 mmol), 1-(2-bromoethyl)imidazole hydrogen bromide (0.56 g, 2.24 mmol), and K_2CO_3 (1.03 g, 5.61 mmol) in DMF (30 mL) was stirred for 5 h at 80 °C. The mixture was cooled, and 2 N HC1 and AcOEt were added to the mixture. The acidic aqueous layer was separated, made alkaline with 5% K_2CO_3 solution, and extracted with AcOEt. The extract was washed with brine, dried, and concentrated under reduced pressure. The residual solid was purified by chromatography on silica gel with $CHCl_3$-MeOH (20:1) and recrystallized from AcOEt-hexane to give of 8 as a white crystal (0.53g, 79 %yield). Melting point: 179-181 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.52 – 8.44 (m, 1H), 7.84 – 7.67 (m, 3H), 7.42 – 7.32 (m, 5H), 7.04 (t, *J* = 1.1 Hz, 1H), 6.95 (t, *J* = 1.3 Hz, 1H), 4.63 (t, *J* = 6.3 Hz, 2H), 4.47 (t, *J* = 6.3 Hz, 2H), 2.54 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.1, 147.2, 140.5, 137.4, 133.2, 131.7, 131.0, 129.7, 129.0, 127.8, 127.1, 126.8, 126.0, 119.1, 51.5, 44.5, 15.4.

HRMS (ESI, m/z): $[M+H]^+$ Calcd for $C_{20}H_{19}N_4OS$ 363.1274; Found 363.1274.

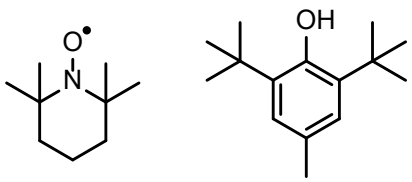
5. Mechanistic investigations

5.1 radical trapping experiment

Influense of Radical Scavengers



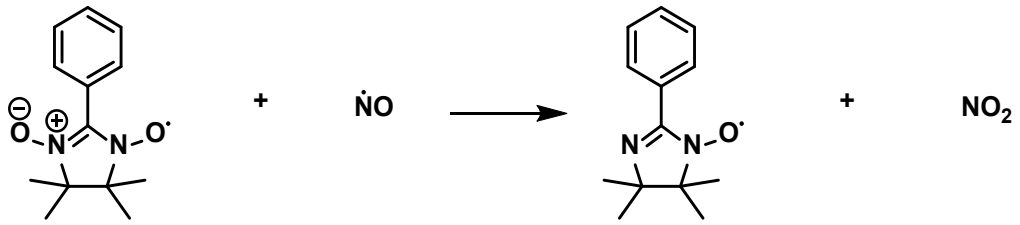
Radical Scavengers	none	**TEMPO**	**BHT**
yield of 2a (%)	90	89	92



A 10 mL of Schlenk tube equipped with a rubber septum and magnetic stirring bar, 1a (0.1 mmol, 1.0 equiv.) and AcOH (0.2 mmol, 2 equiv.), radical scavengers (0.25 mmol, 2.5 equiv.) were added in DCM (0.025 M), then the vessel was bubbled with a stream of argon for 20 min via a syringe needle and the tightly sealed tube was irradiated with 3 W blue LEDs at about 20 ℃ (the distance

between the tube and the light source was about 5 cm). Upon completion (as judged by TLC analysis), silica was added to the reaction and then concentrated in vacuo. The crude residue was then purified by flash chromatography on silica gel (EtOAc: petroleum ether as an eluent) to give the pure product.

5.2 EPR analysis using PTIO



PTIO **PTI**

Detection of radicals resulting from NO· species[11]: To detect the nitric oxide radical (NO·) intermediate, we used visible light (450 nm) to irradiate a solution of 1a containing 2- phenyl-4,4,5,5-tetramethylimidazolin-1-oxyl 3-oxide (PTIO). The reagent PTIO can oxidize the NO· radical to form 2- phenyl-4,4,5,5-tetramethylimidazolin-1-oxyl (PTI) and NO_2· radicals. About 1min of irradiation, the colour of the solution gradually changed from dark blue to clear. We detected a set of EPR signals as shown. Data analysis suggests that an in situ generated NO radical is promptly trapped by PTIO to produce the metastable radical PTI (a_{N1} = 9.38 G, a_{N3} = 4.21 G and g = 2.0060), which is consistent with the previous report. In addition, the formation of PTI was also confirmed by HRMS was shown in Figure S2. The simulated EPR spectrum of PTI is shown in Figure S1-d, which is well-matched with the experimental one.

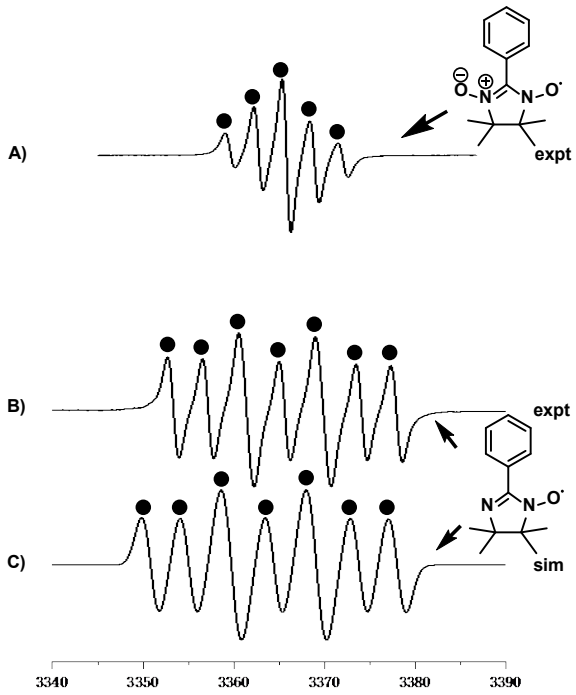
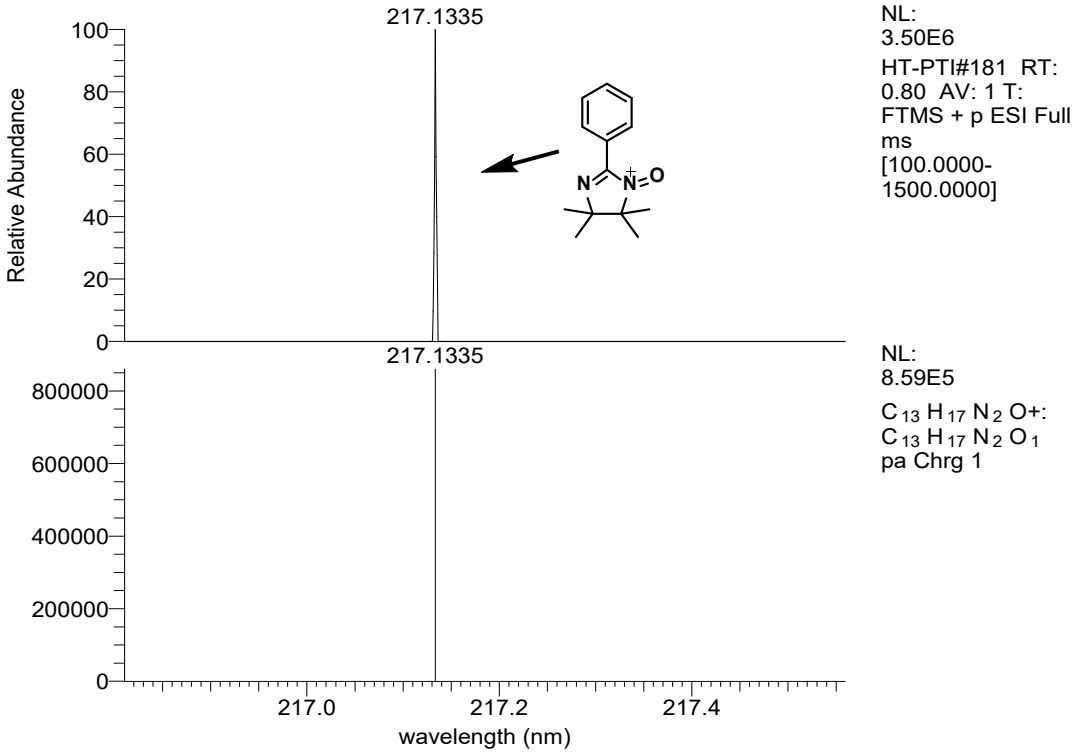
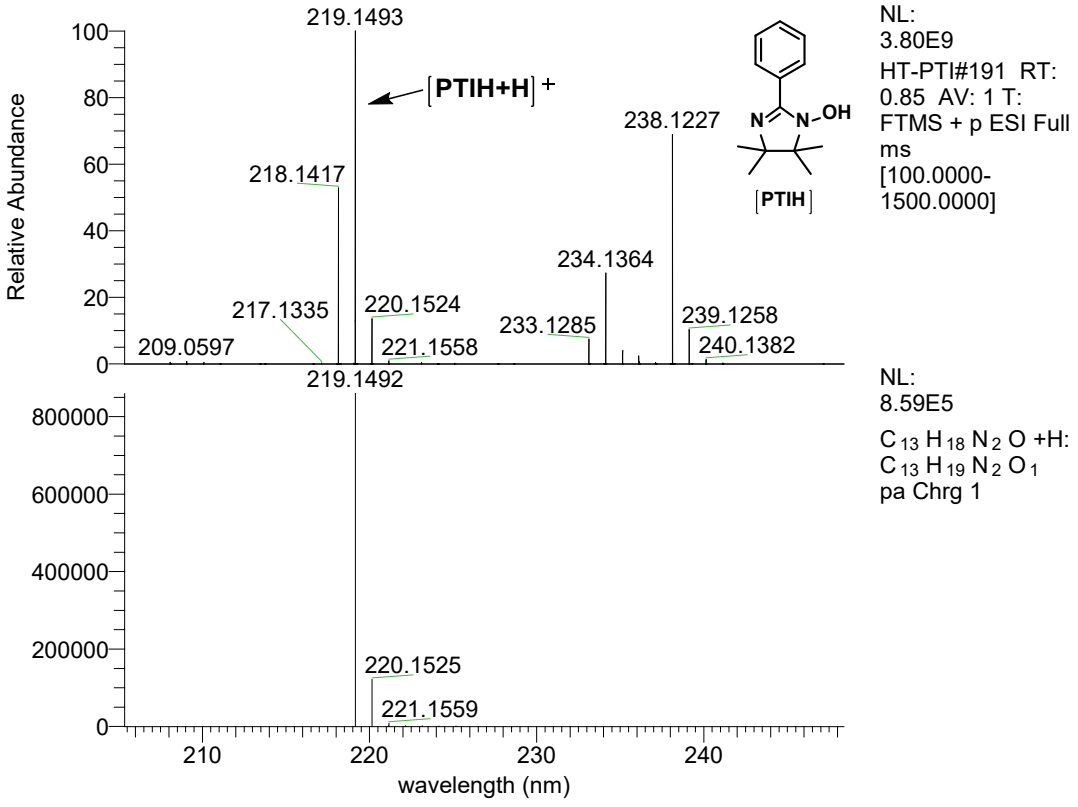


Figure S1. (A) EPR spectrum of a solution containing PTIO (50 μM) and *N*-ethyl-*N*-nitrosobenzamide (**1a**) (50 μM) in DCM. (B) EPR spectrum of this solution upon irradiation with 450 nm light for 1min, and (C) simulated spectrum of trapping the in situ formed NO radical.





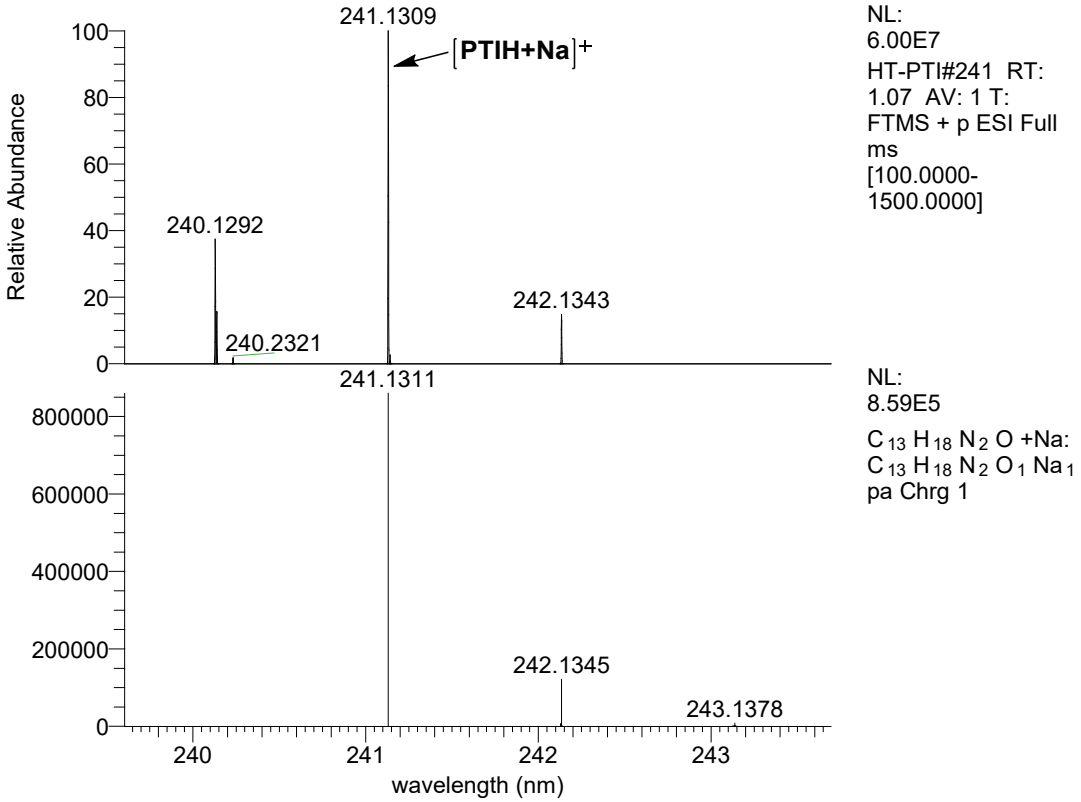
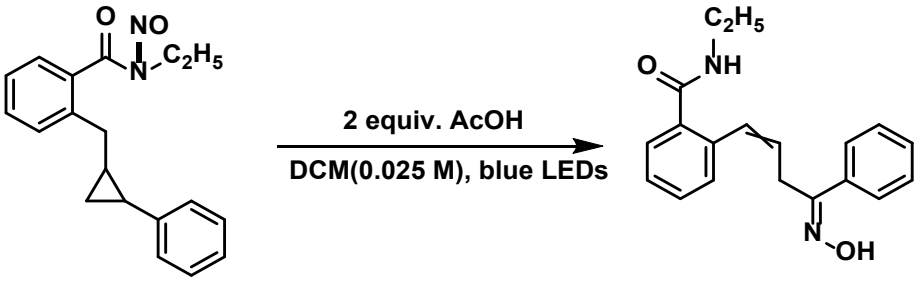


Figure S2. The HRMS spectrum of radical trapping experiments.

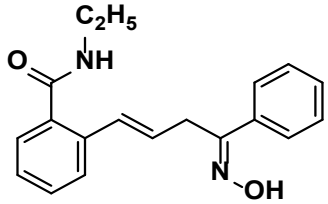
5.3 Radical clock experiments



1aq

2aq, yield 64%
Z/E mixtures

***N*-ethyl-2-((1*E*,4*Z*)-4-(hydroxyimino)-4-phenylbut-1-en-1-yl) benzamide (2aq)**



2aq

General Procedure：A 250 mL of Schlenk tube equipped with a rubber septum and magnetic stirring bar, *N*-ethyl-*N*-nitroso-2-((2-phenylcyclopropyl)methyl)benzamide (0.2 mmol) and AcOH (2 equiv.)

were charged, DCM (0.025 M) was added, then the vessel was bubbled with a stream of argon for 20 min via a syringe needle and the tightly sealed tube was irradiated with a 3W blue LEDs at about 20 °C. Upon completion (as judged by TLC analysis), silica was added to the reaction and then concentrated in vacuo. The crude residue was then purified by flash chromatography on silica gel (EtOAc: petroleum ether as an eluent) to give the products.

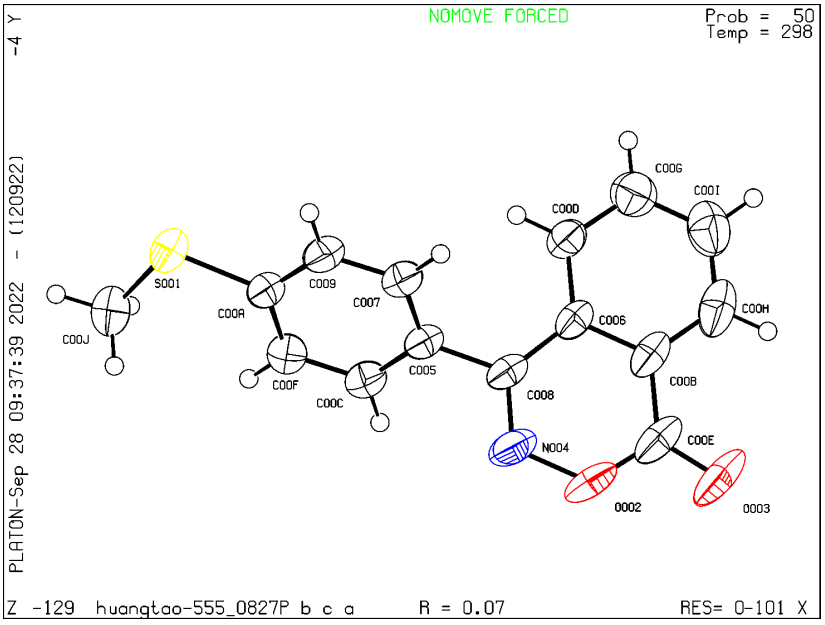
White solid (39.3 mg, 64%). Melting point: 107-108 °C .**^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.02 (s, 1H), 7.70 – 7.64 (m, 2H), 7.44 (ddd, *J* = 8.1, 6.5, 1.4 Hz, 2H), 7.38 (dt, *J* = 4.5, 2.8 Hz, 3H), 7.32 (td, *J* = 7.5, 1.5 Hz, 1H), 7.23 (td, *J* = 7.4, 1.3 Hz, 1H), 6.84 (dt, *J* = 15.8, 1.7 Hz, 1H), 6.26 (dt, *J* = 15.8, 6.5 Hz, 1H), 5.77 (t, *J* = 6.4 Hz, 1H), 3.74 (dd, *J* = 6.6, 1.7 Hz, 2H), 3.35 (qd, *J* = 7.3, 5.7 Hz, 2H), 1.10 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.2, 156.5, 135.5, 135.2, 135.0, 130.0, 129.8, 129.3, 128.6, 127.7, 127.3, 127.1, 126.6, 126.3, 34.9, 30.4, 14.8.

HRMS (ESI, m/z): $[M+H]^+$ Calcd for $C_{19}H_{21}N_2O_2$ 309.1598; Found 309.1599.

6. X-ray crystal structure analysis of 2j and 2aj

6.1 Crystal of 2j (CCDC 2205351)

Single crystal of 2j were obtained by recrystallization from a mixed solvent of CH_2Cl_2/ petroleum ether at room temperature (evaporation in air). The X-ray single-crystal determination was performed on a Bruker APEX II X-ray single crystal diffractometer.



Bond precision:	C-C = 0.0032 A		Wavelength=1.54184
	a=15.8096(3)	b=6.82717(16)	c=23.9478(5)
	alpha=90	beta=90	gamma=90

Temperature:	298 K	
	Calculated	Reported
Volume	2584.80(9)	2584.81(9)
Spacegroup	P b c a	P b c a
Hall group	-P 2ac 2ab	-P 2ac 2ab
Moiety formula	C15 H11 N O2 S	C15 H11 N O2 S
Sum formula	C15 H11 N O2 S	C15 H11 N O2 S
Mr	269.31	269.31
Dx,g cm-3	1.384	1.384
Z	8	8
Mu (mm-1)	2.200	2.200
F000	1120.0	1120.0
F000’	1125.74	
h,k,lmax	20,8,30	19,8,29
Nref	2753	2571
Tmin,Tmax	0.691,0.768	0.398,1.000
Tmin’	0.627	

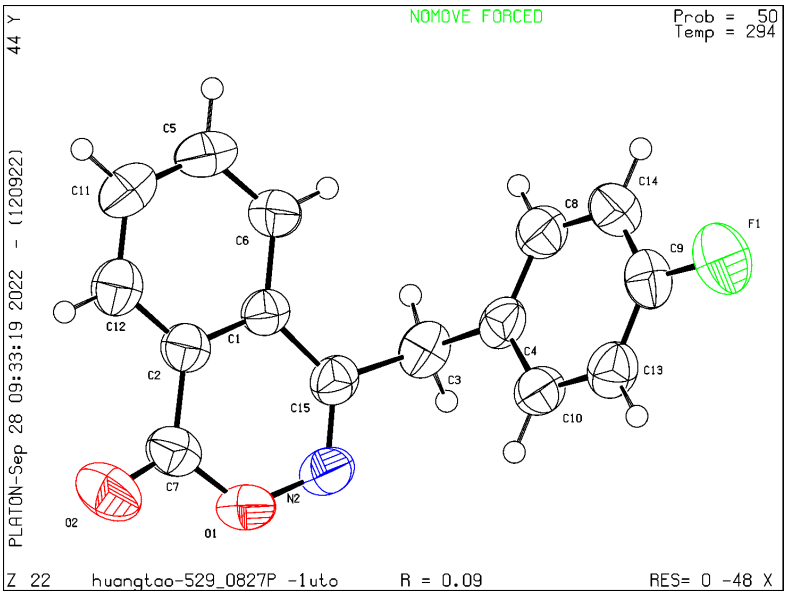
Correction method= # Reported T Limits: Tmin=0.398 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.934 Theta(max)= 77.493
R(reflections)= 0.0652(2204) wR2(reflections)= 0.1892(2571)

S = 1.055 Npar= 173

6.2 Crystal of 2aj (CCDC 2204175)

Single crystal of 2aj were obtained by recrystallization from a mixed solvent of CH_2Cl_2/ petroleum ether at room temperature (evaporation in air). The X-ray single-crystal determination was performed on a Bruker APEX II X-ray single crystal diffractometer.



Bond precision: C-C = 0.0047 A Wavelength=1.54184

Cell:	a=7.6882(10)	b=8.4126(11)	c=10.4035(8)
	alpha=91.427(8)	beta=99.305(9)	gamma=114.923(13)
Temperature:	294 K		

	Calculated	Reported
Volume	598.92(14)	598.92(13)
Spacegroup	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C15 H10 F N O2	C15 H10 F N O2
Sum formula	C15 H10 F N O2	C15 H10 F N O2
Mr	255.24	255.24
Dx,g cm-3	1.415	1.415
Z	2	2
Mu (mm-1)	0.880	0.880
F000	264.0	264.0
F000’	264.91	
h,k,lmax	9,10,13	9,10,13
Nref	2549	2290
Tmin,Tmax	0.846,0.900	0.537,1.000
Tmin’	0.846	

Correction method= # Reported T Limits: Tmin=0.537 Tmax=1.000

AbsCorr = MULTI-SCAN

Data completeness= 0.898 Theta(max)= 77.877

R(reflections)= 0.0886(1594) wR2(reflections)=

0.2674(2290)

S = 1.043 Npar= 173

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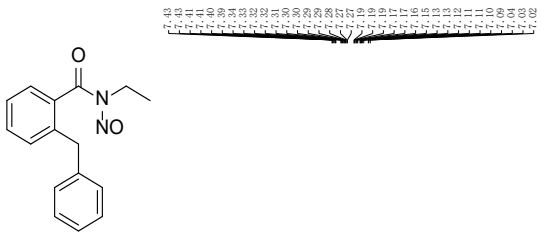
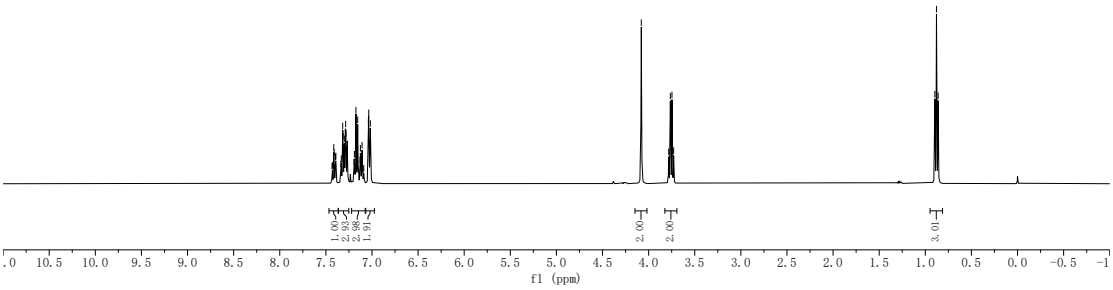
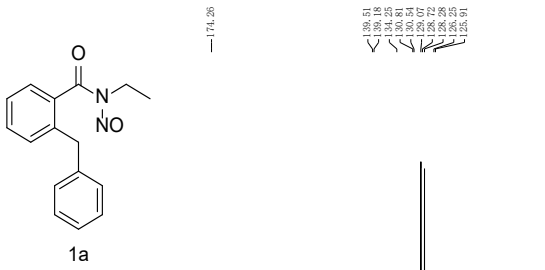
8. NMR spectra for all compounds



1a

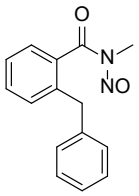
^{1}H NMR (400 MHz, $CDCl_3$)





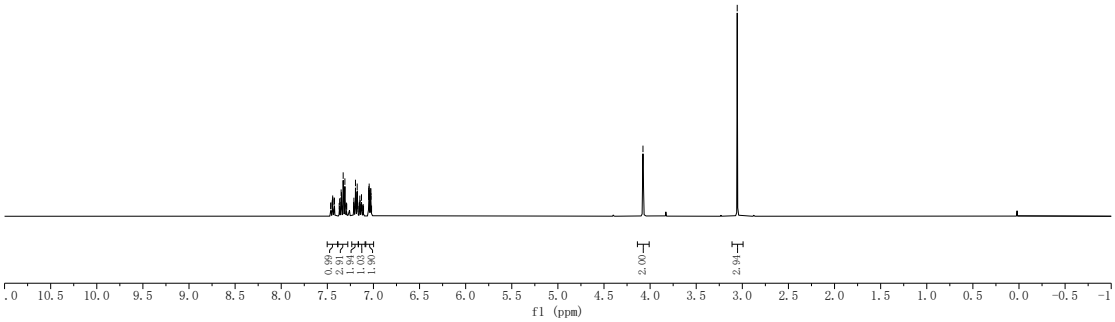
1a

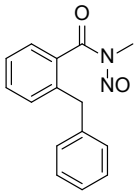
^{13}C NMR (101 MHz, $CDCl_3$)



1a′

^{1}H NMR (400 MHz, $CDCl_3$)





1a′

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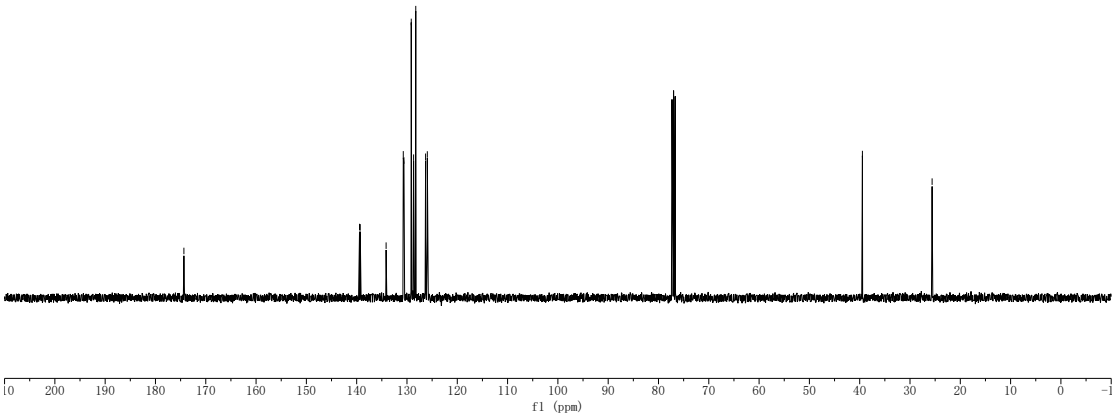

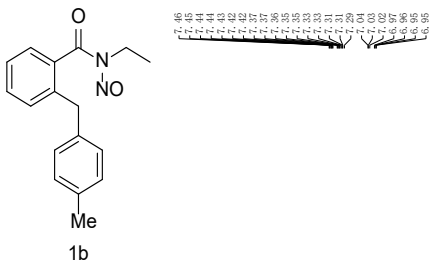

1b

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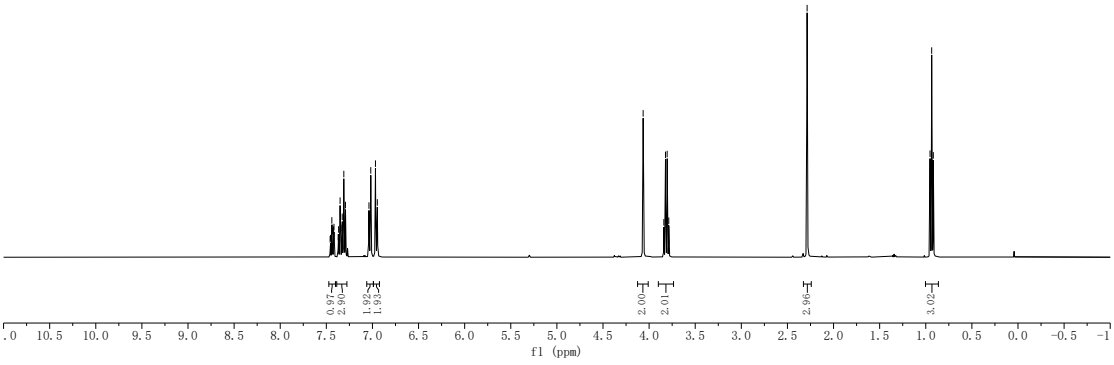

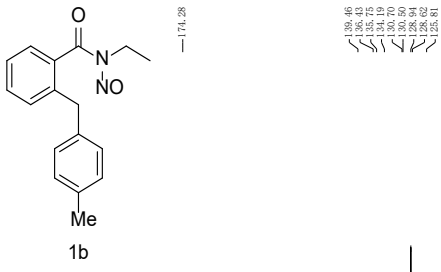

1b

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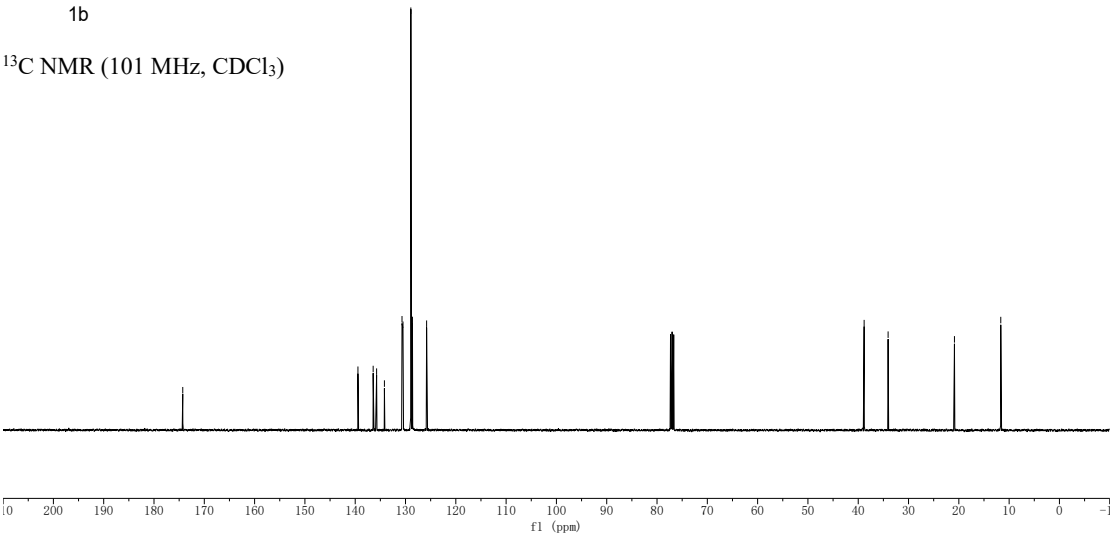

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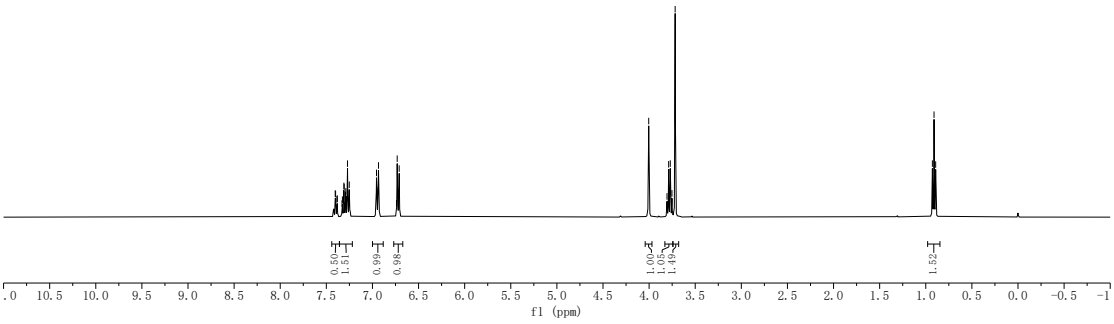

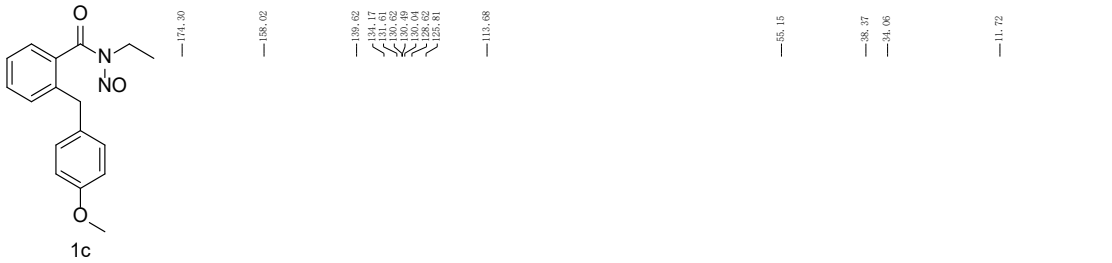

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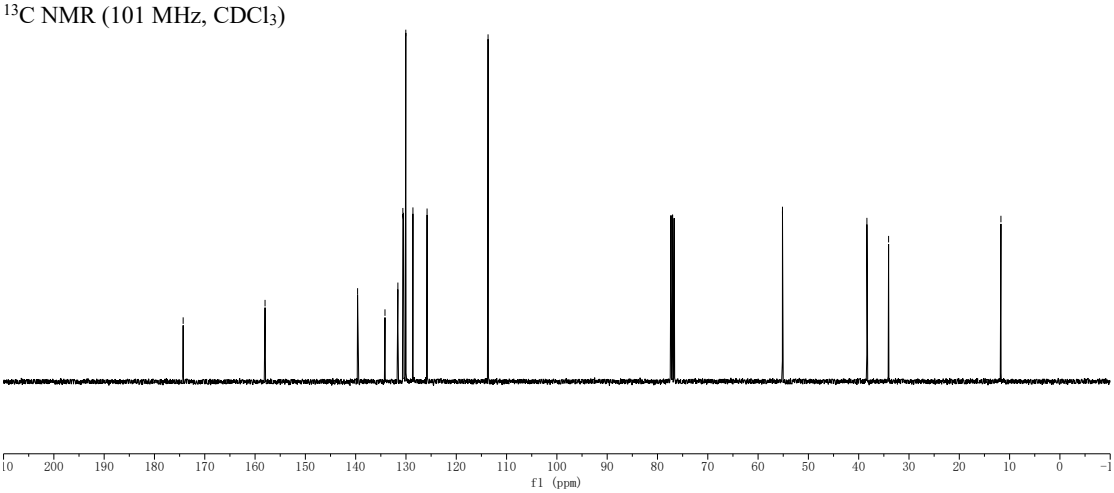

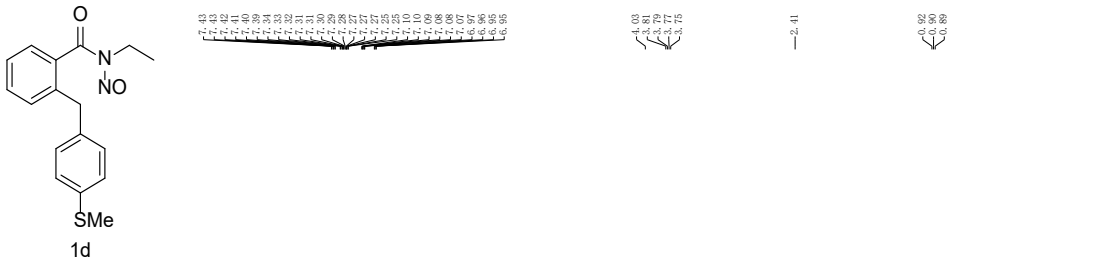

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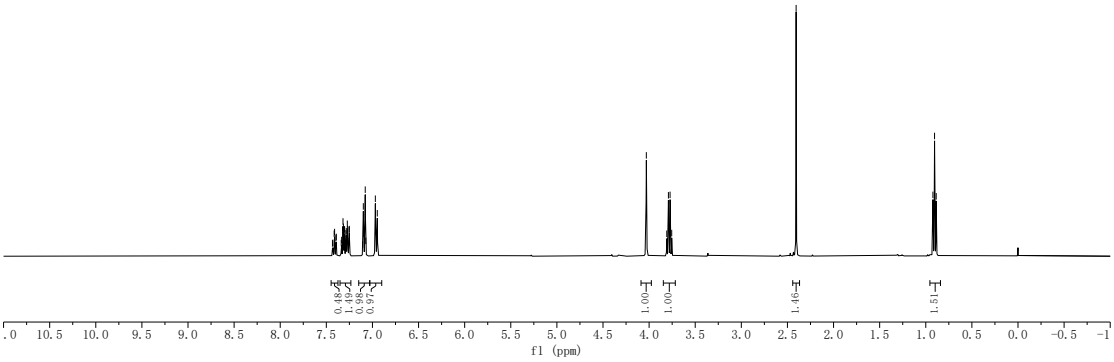

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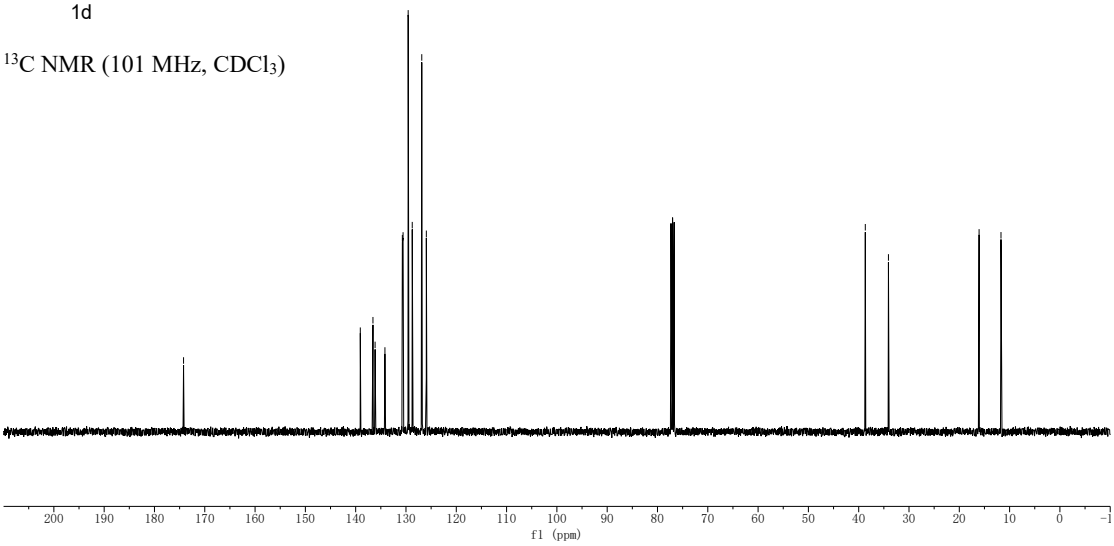

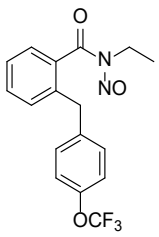

1e

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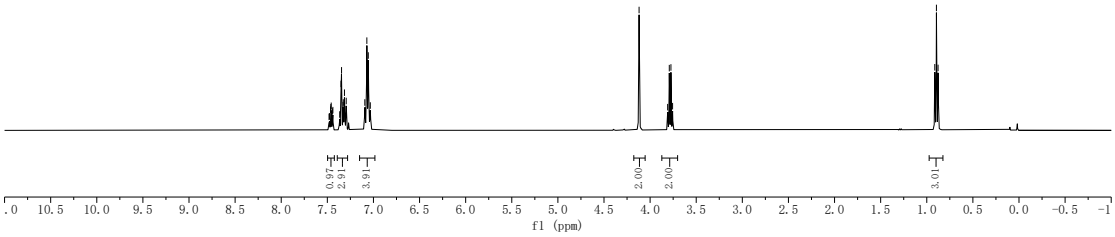

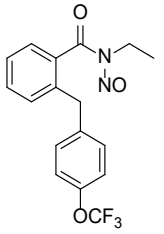

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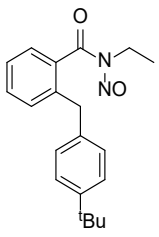

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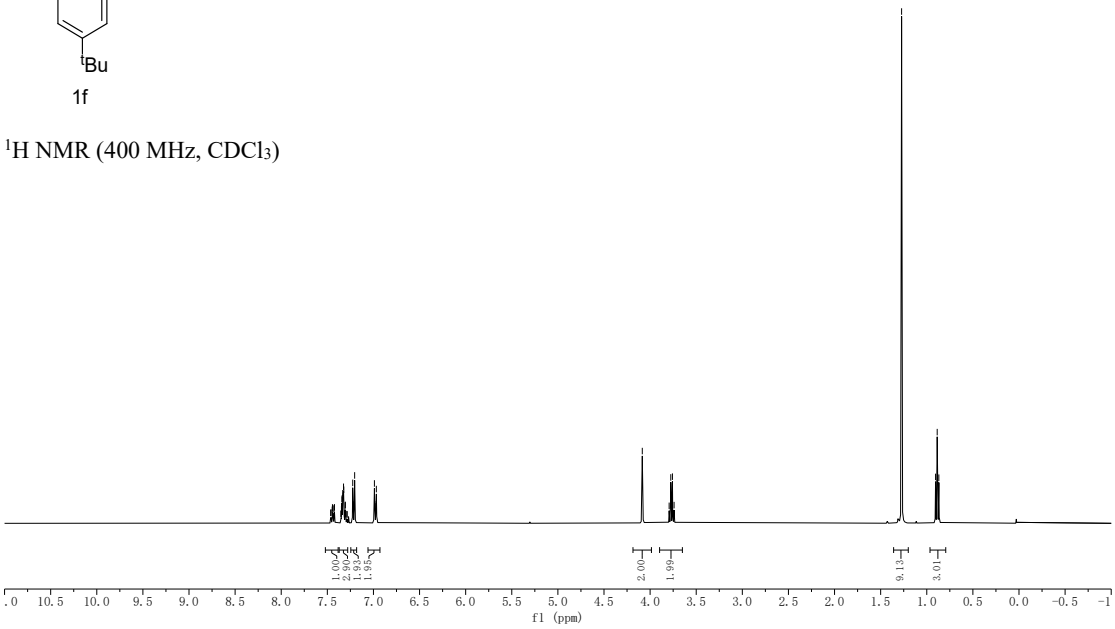

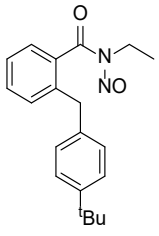

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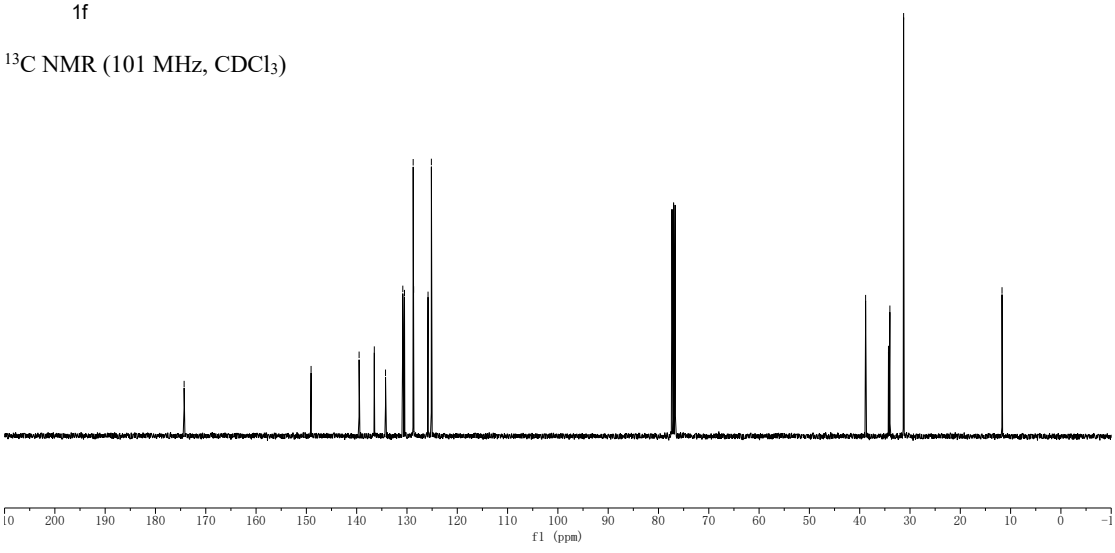

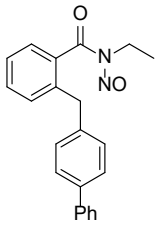

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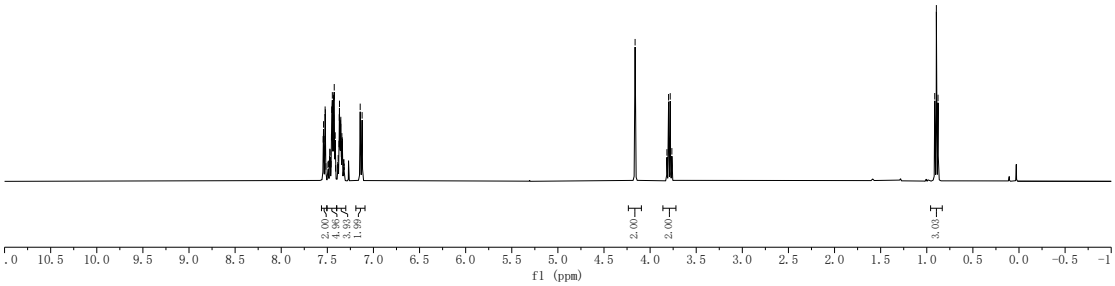

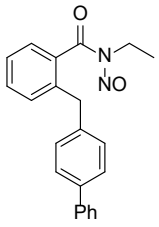

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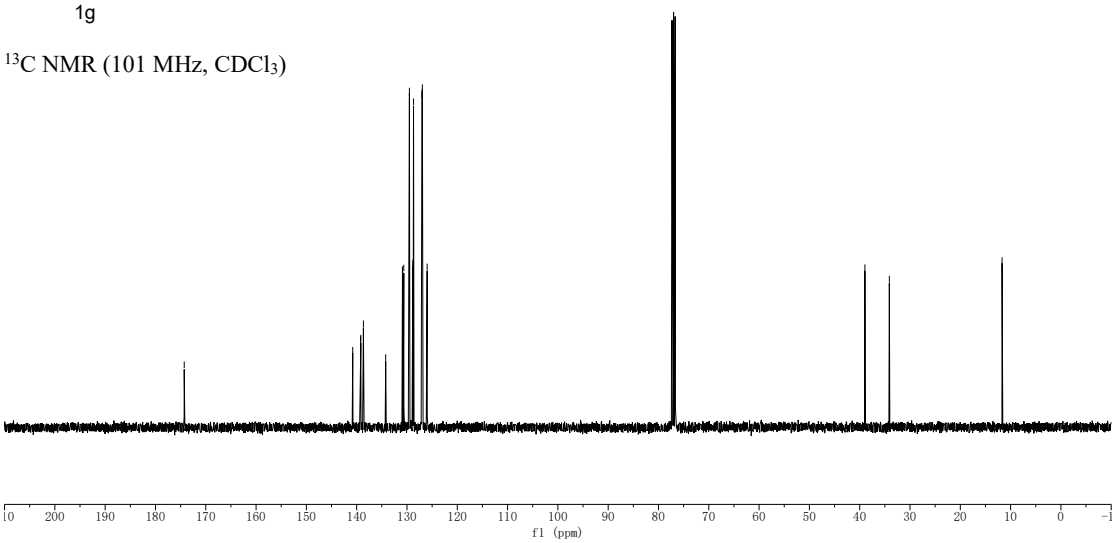

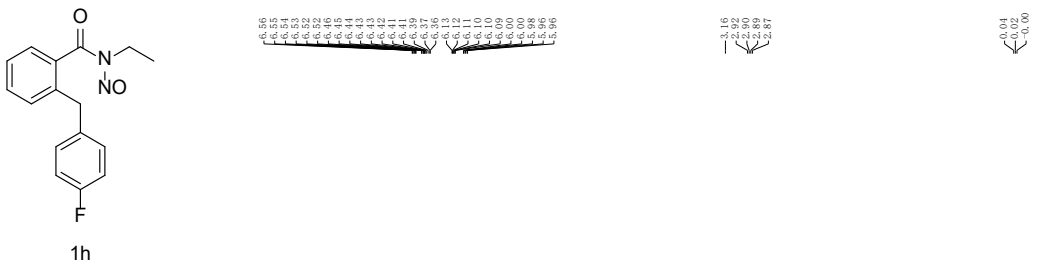

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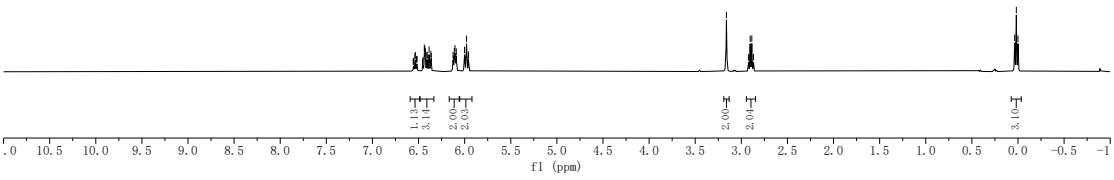

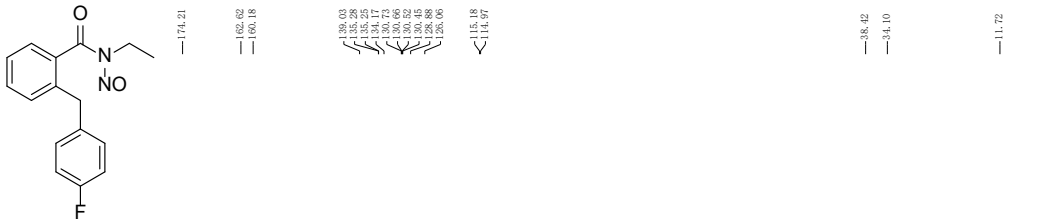

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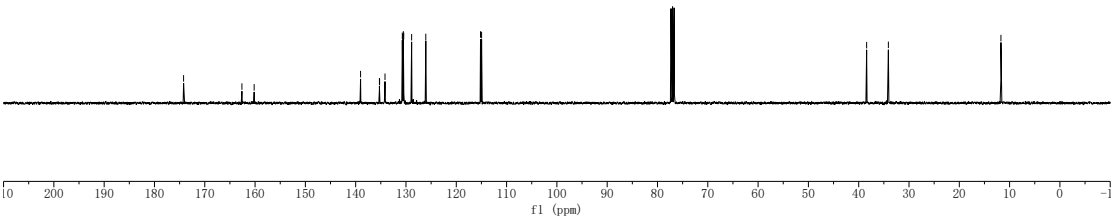

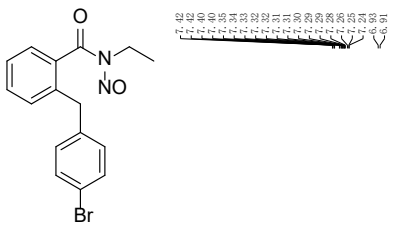

1i

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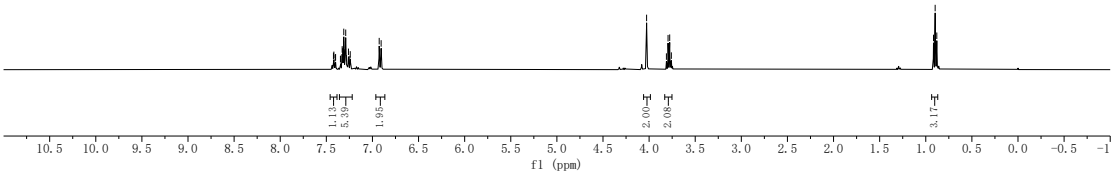

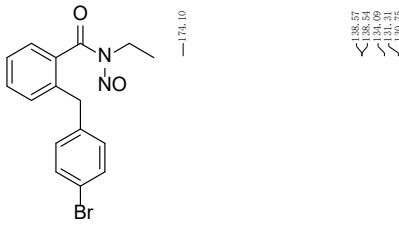

1i

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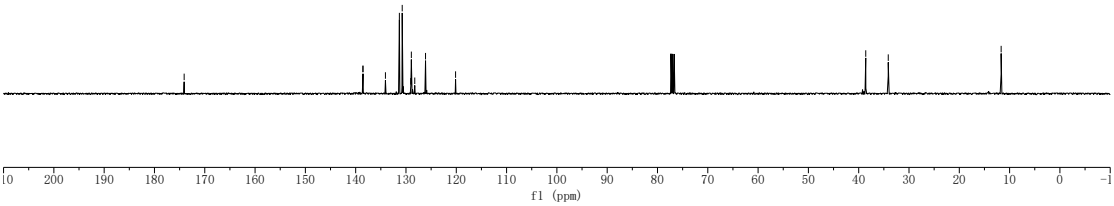

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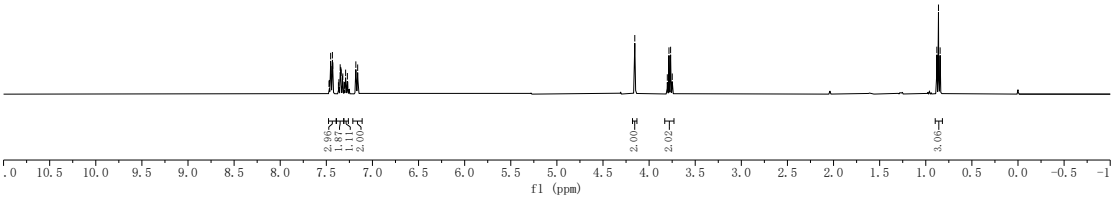

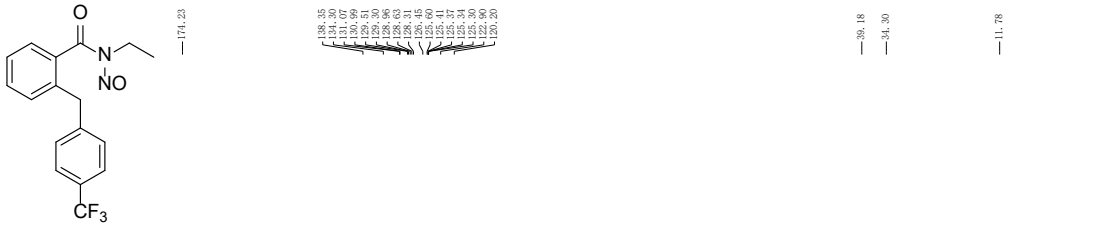

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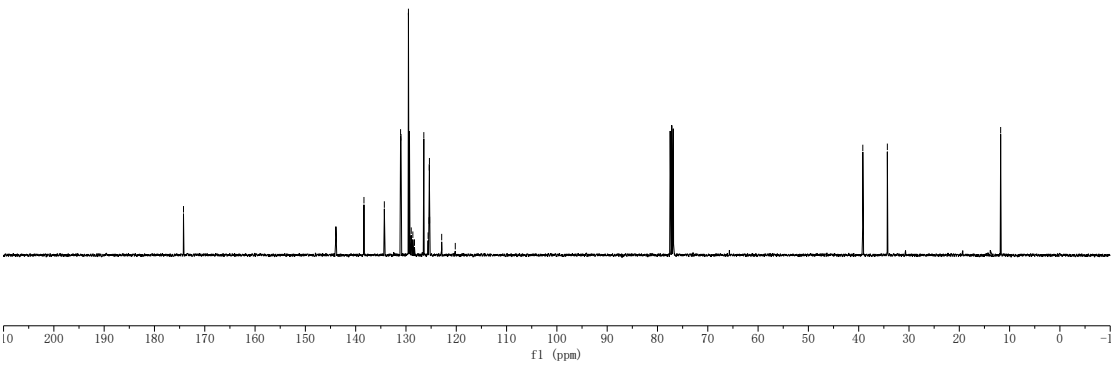

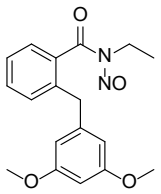

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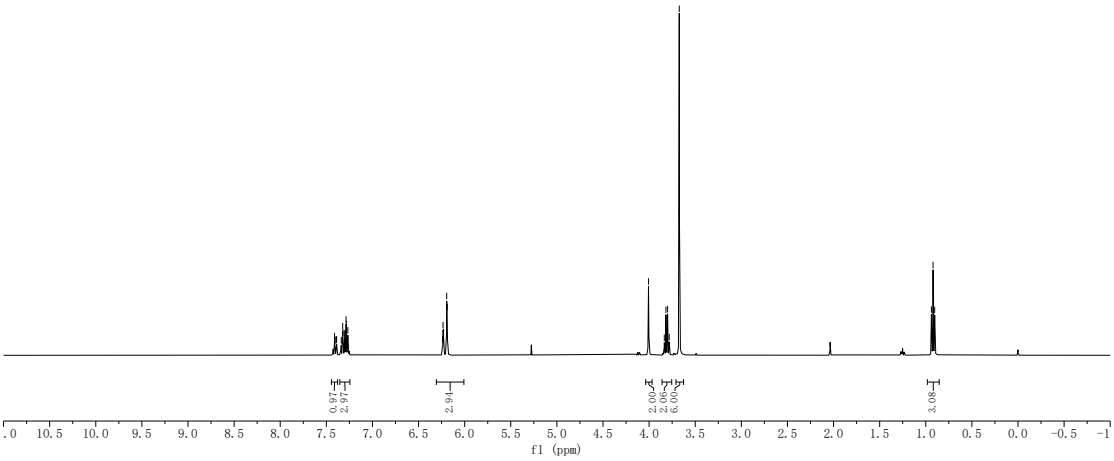

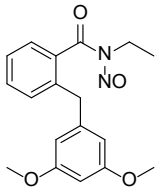

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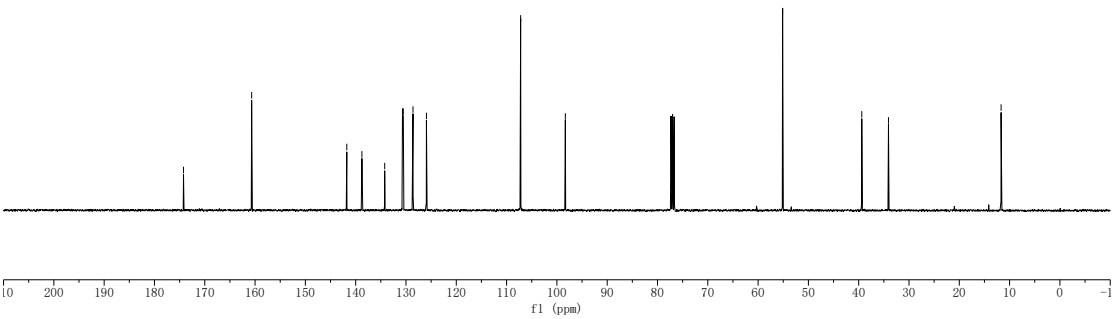

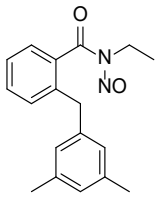

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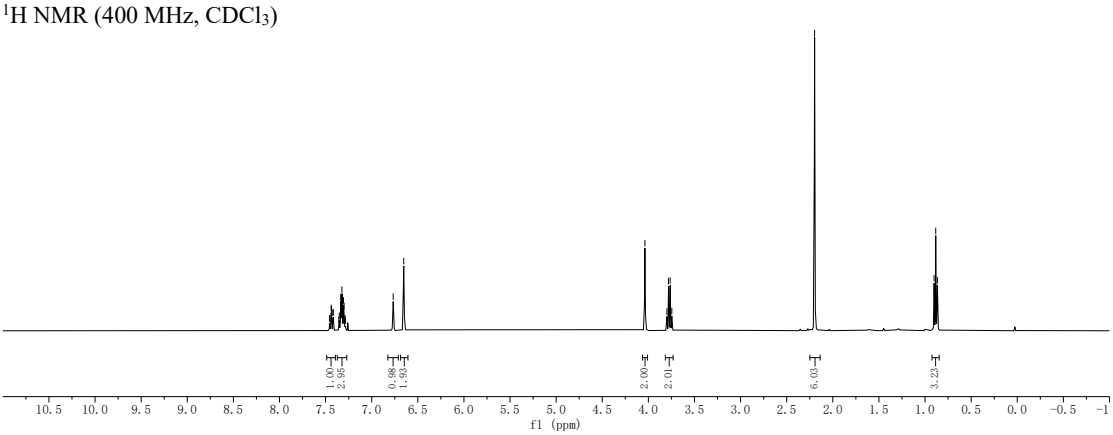

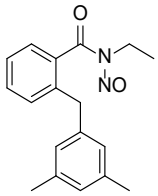

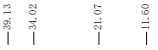

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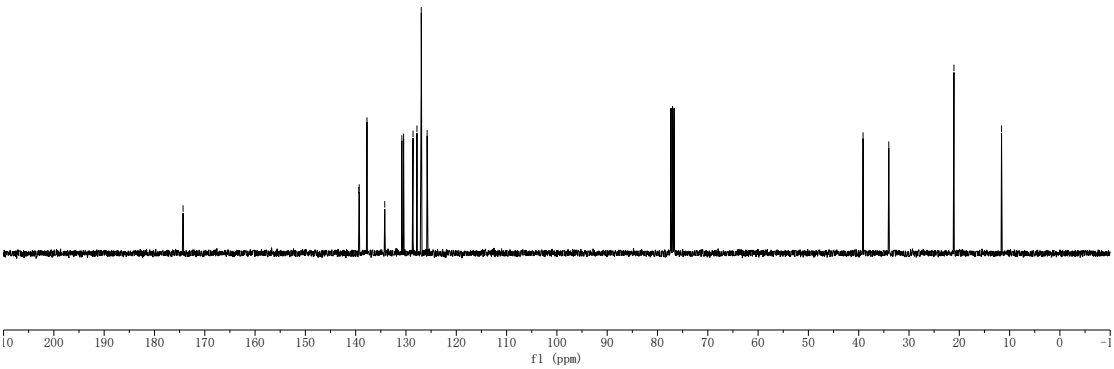

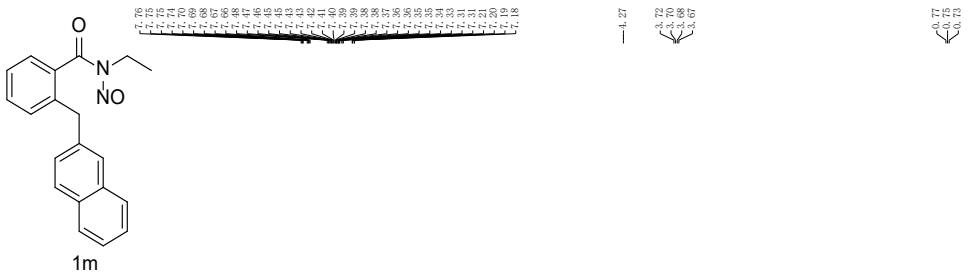

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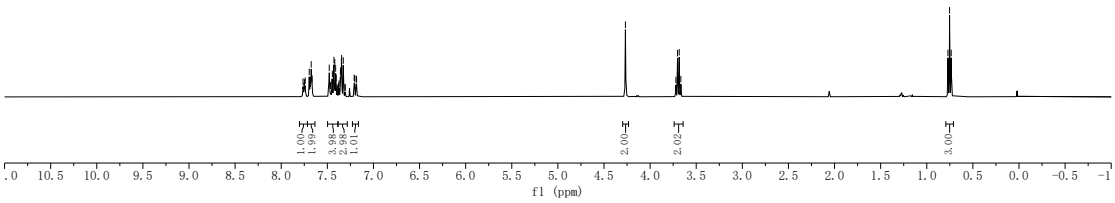

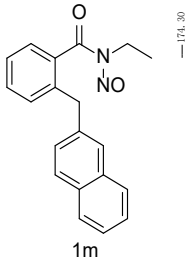

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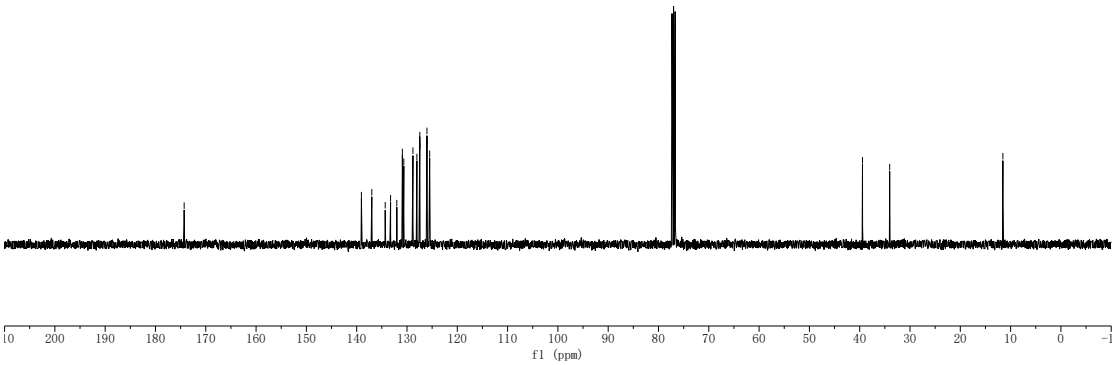
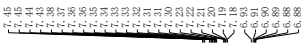
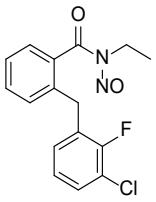
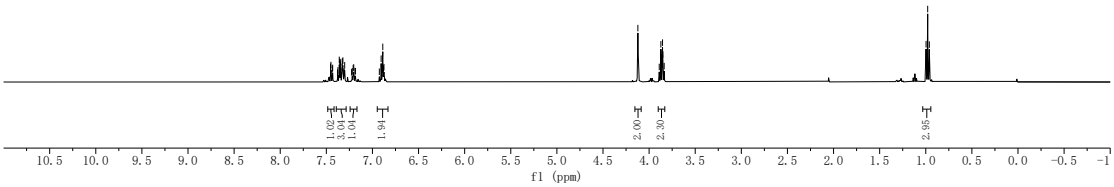


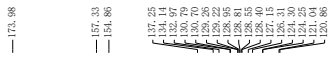


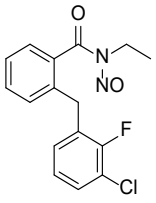


1n

^{1}H NMR (400 MHz, $CDCl_3$)

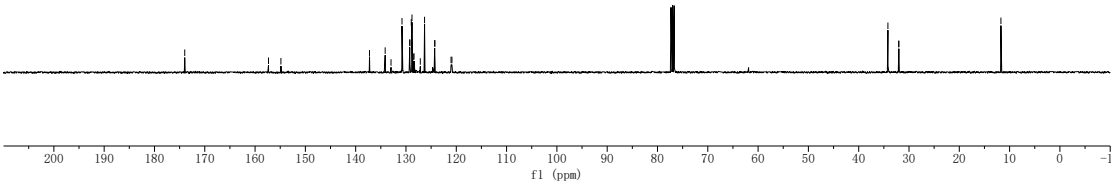


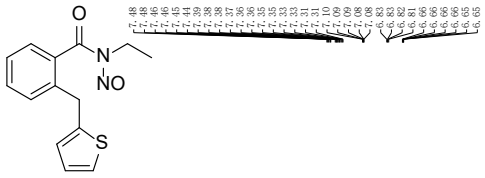




1n

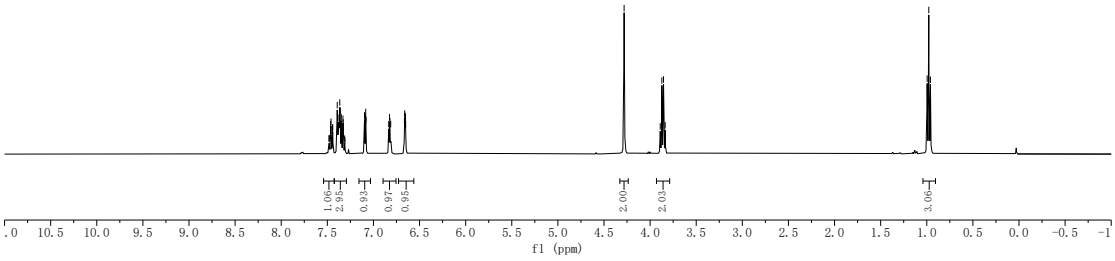
^{13}C NMR (101 MHz, $CDCl_3$)





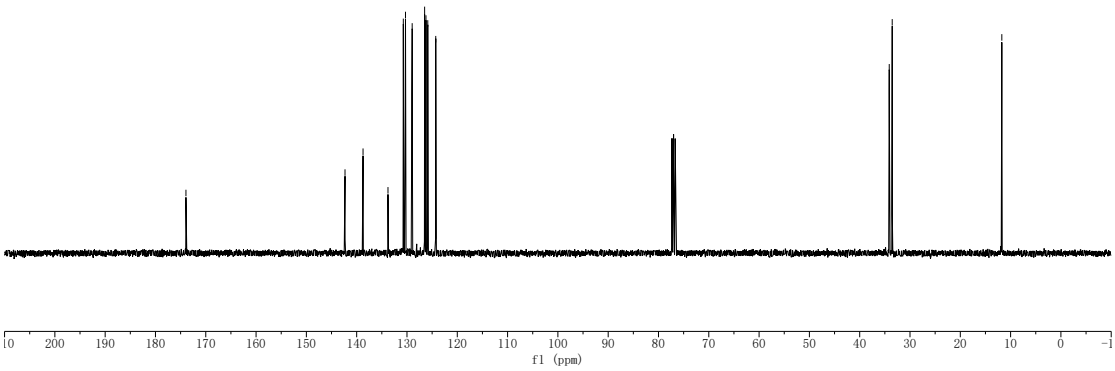
1o

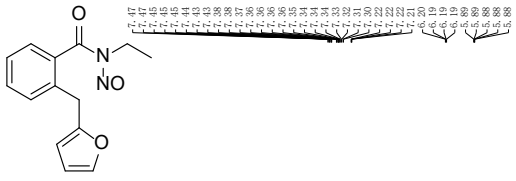
^{1}H NMR (400 MHz, $CDCl_3$)



1o

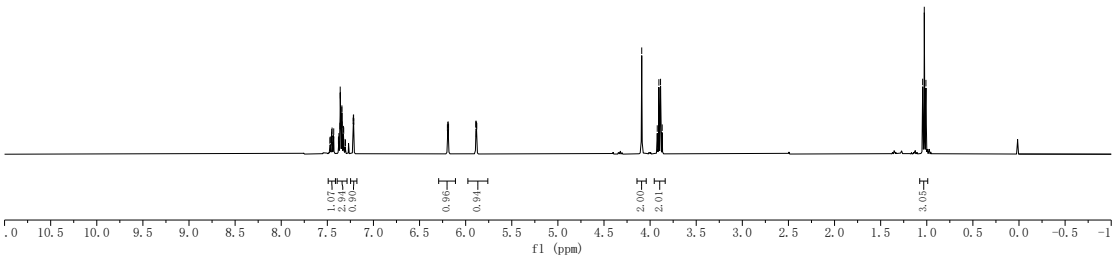
^{13}C NMR (101 MHz, $CDCl_3$)

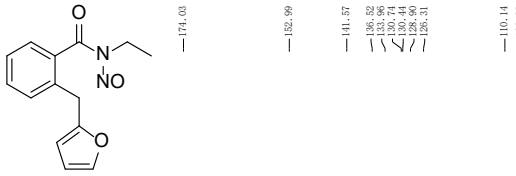




1p

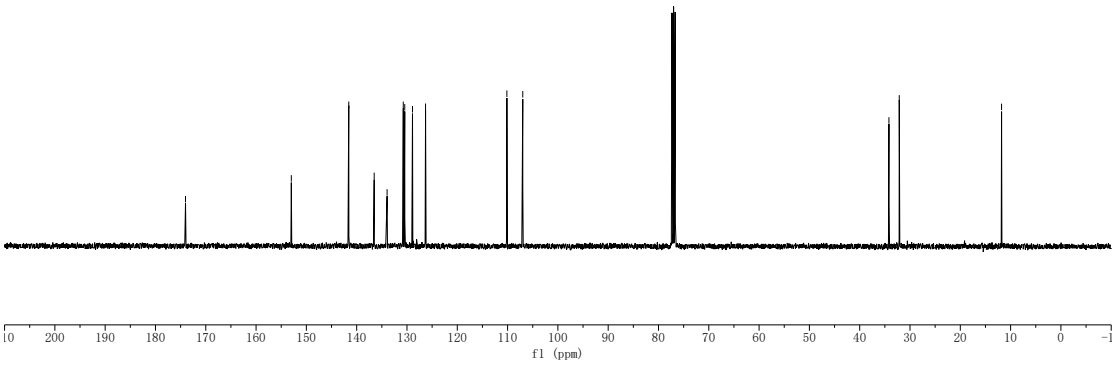
^{1}H NMR (400 MHz, $CDCl_3$)

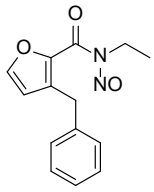




1p

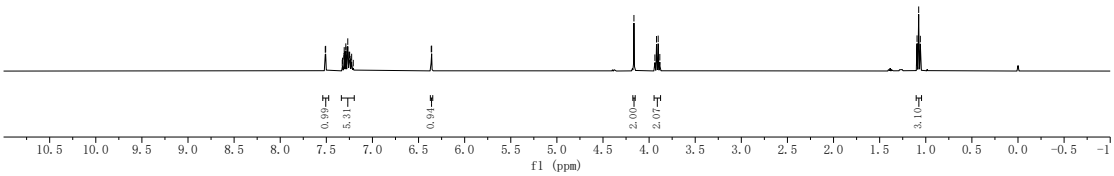
^{13}C NMR (101 MHz, $CDCl_3$)

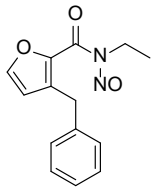




1q

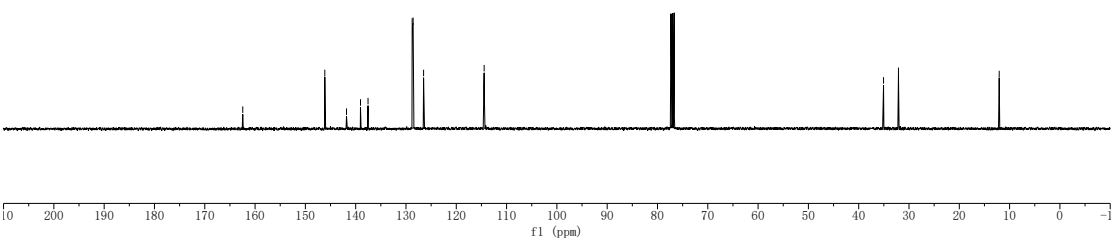
^{1}H NMR (400 MHz, $CDCl_3$)

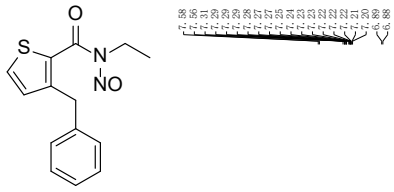




1q

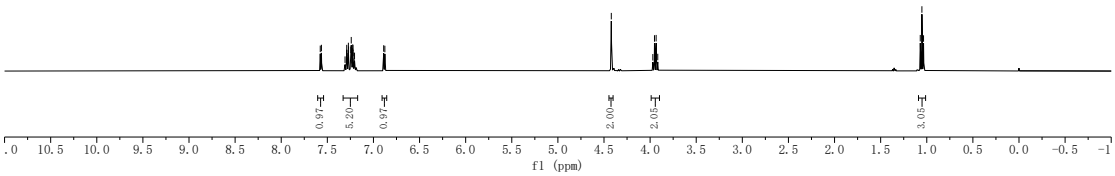
^{13}C NMR (101 MHz, $CDCl_3$)

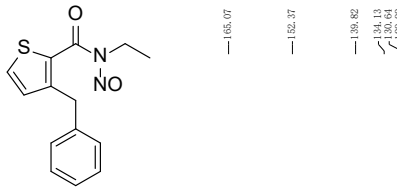




1r

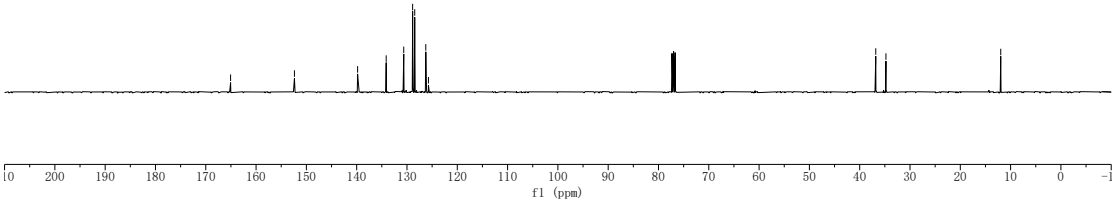
^{1}H NMR (400 MHz, $CDCl_3$)

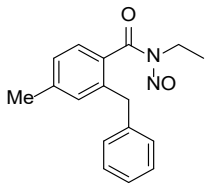




1r

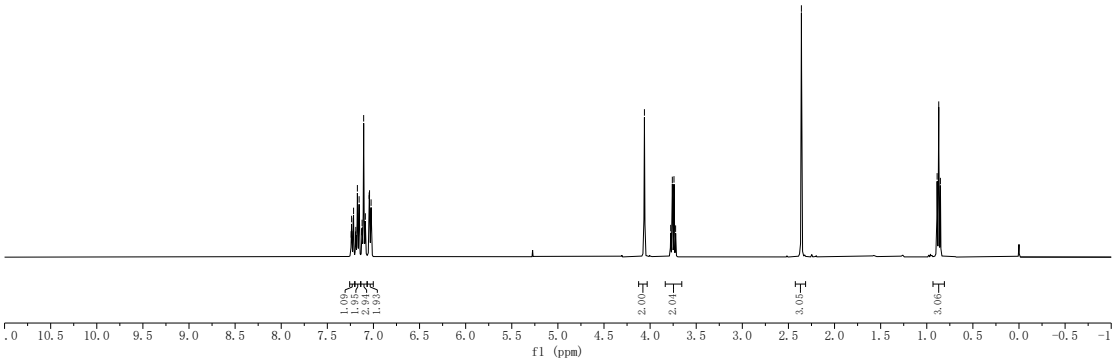
^{13}C NMR (101 MHz, $CDCl_3$)

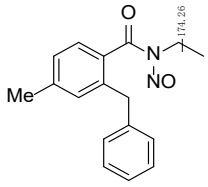




1s

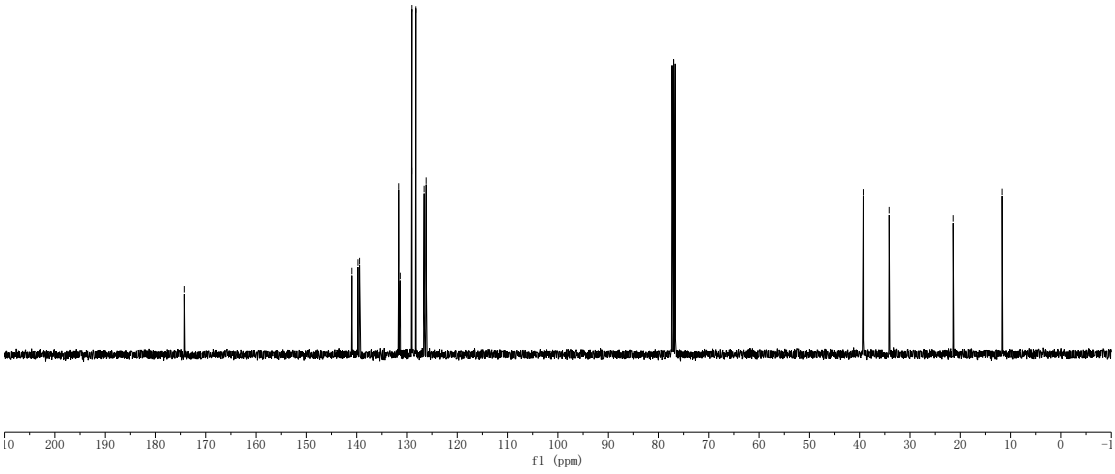
^{1}H NMR (400 MHz, $CDCl_3$)

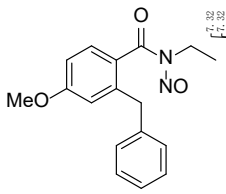




1s

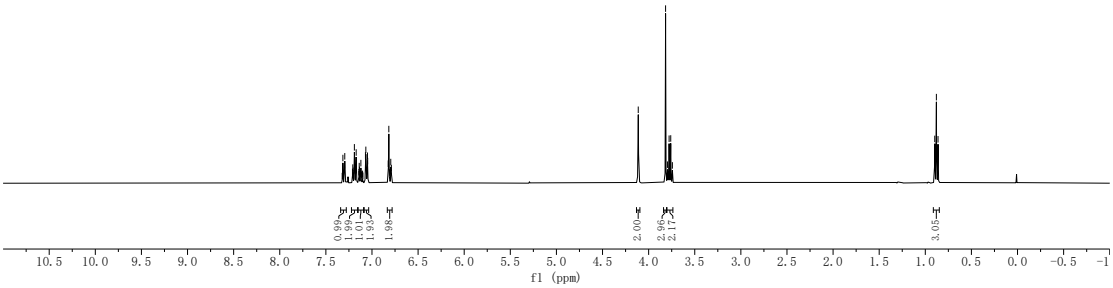
^{13}C NMR (101 MHz, $CDCl_3$)

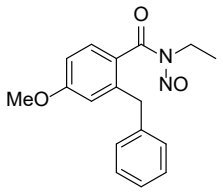




1t

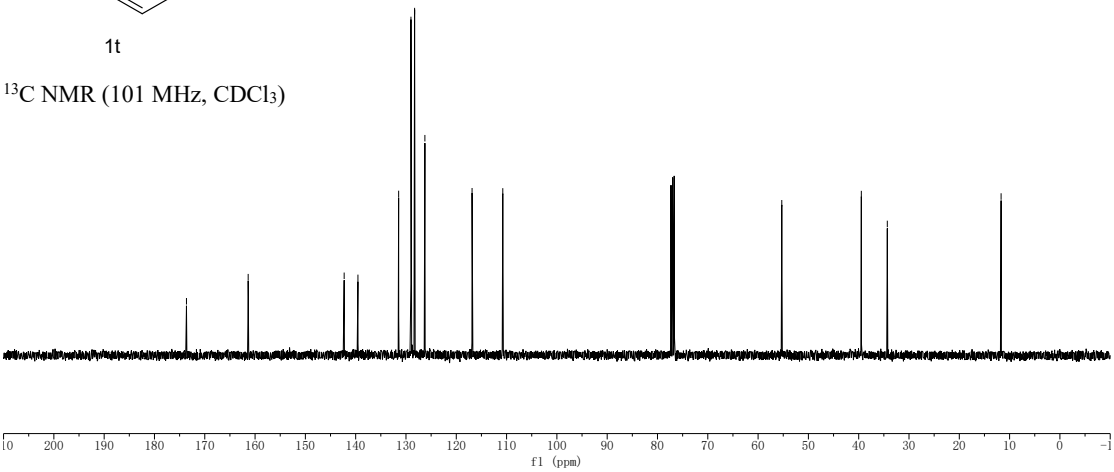
^{1}H NMR (400 MHz, $CDCl_3$)

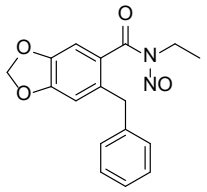




1t

^{13}C NMR (101 MHz, $CDCl_3$)





1u

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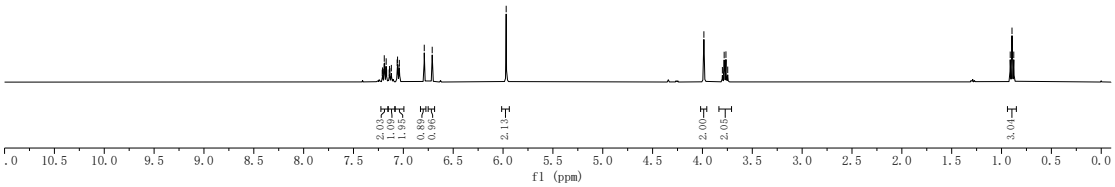
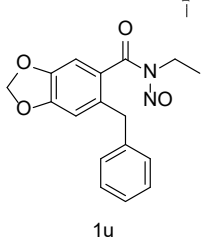
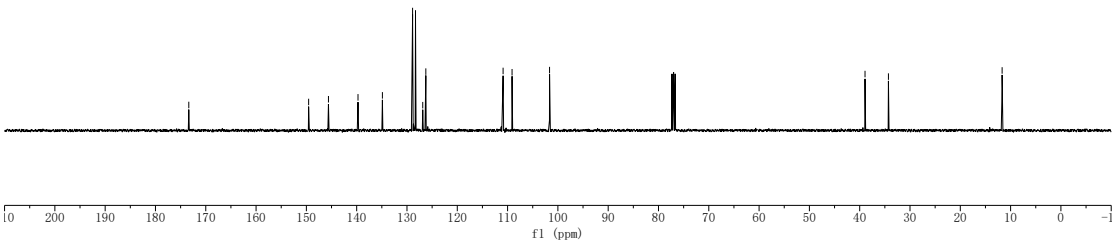
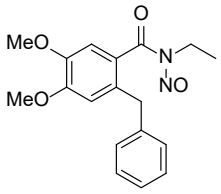




1u

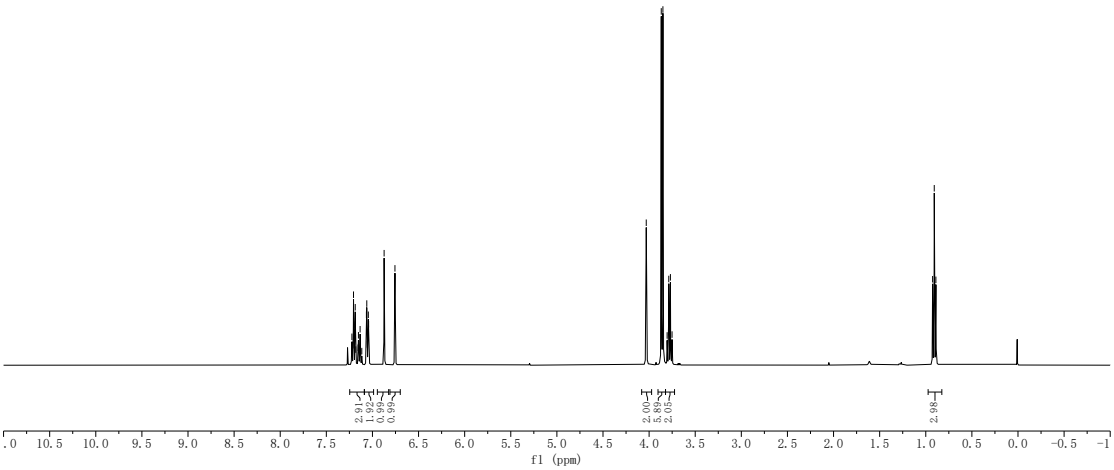
^{13}C NMR (101 MHz, $CDCl_3$)

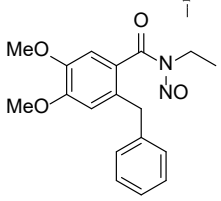




1v

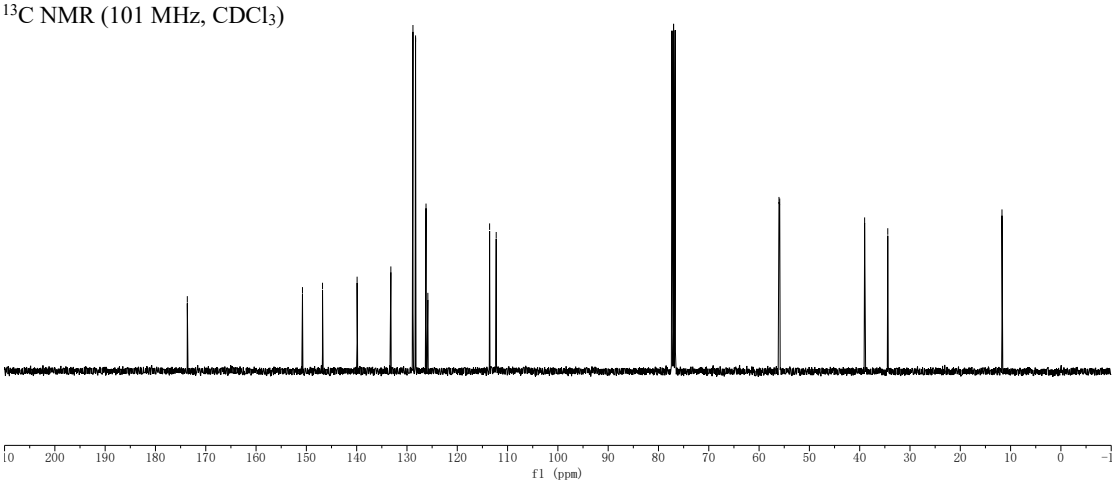
^{1}H NMR (400 MHz, $CDCl_3$)

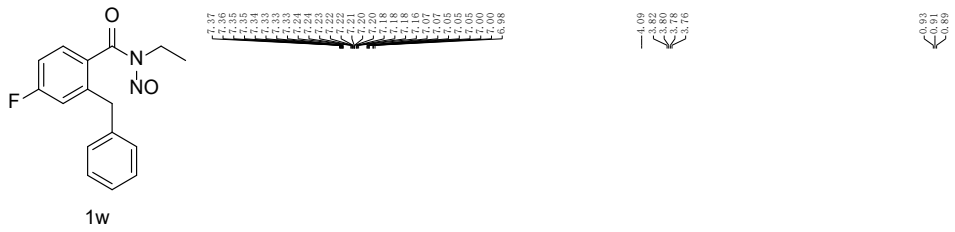




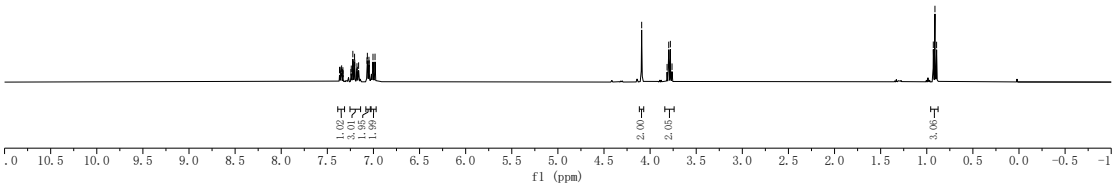
1v

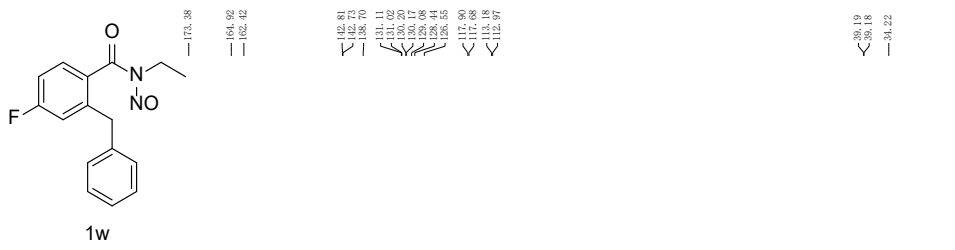
^{13}C NMR (101 MHz, $CDCl_3$)



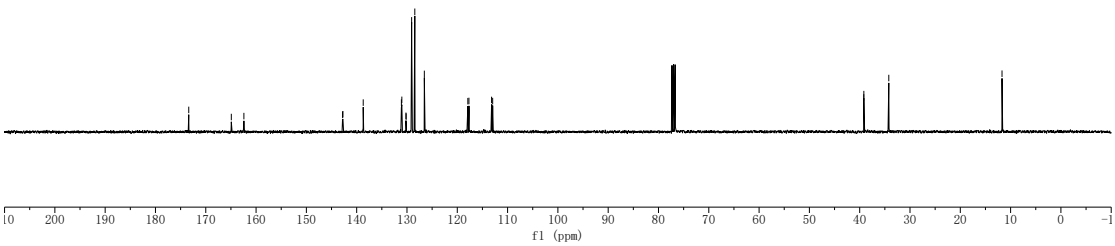


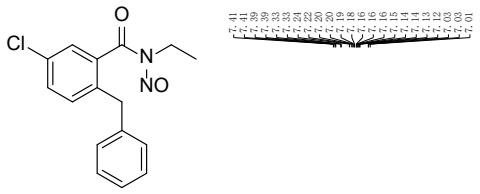
^{1}H NMR (400 MHz, $CDCl_3$)





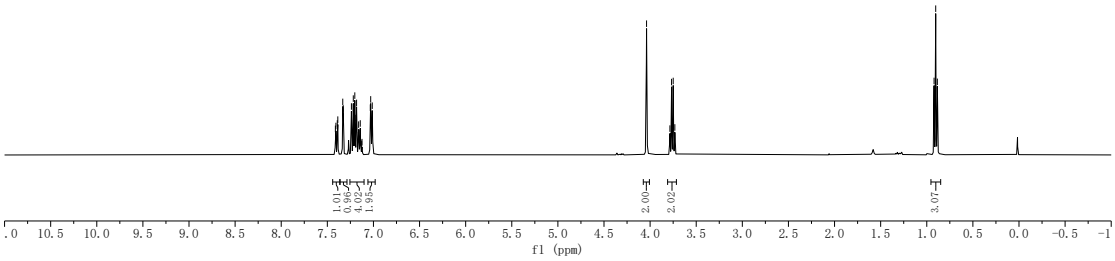
^{13}C NMR (101 MHz, $CDCl_3$)

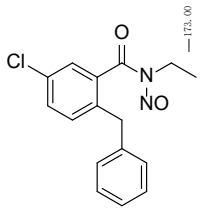




1x

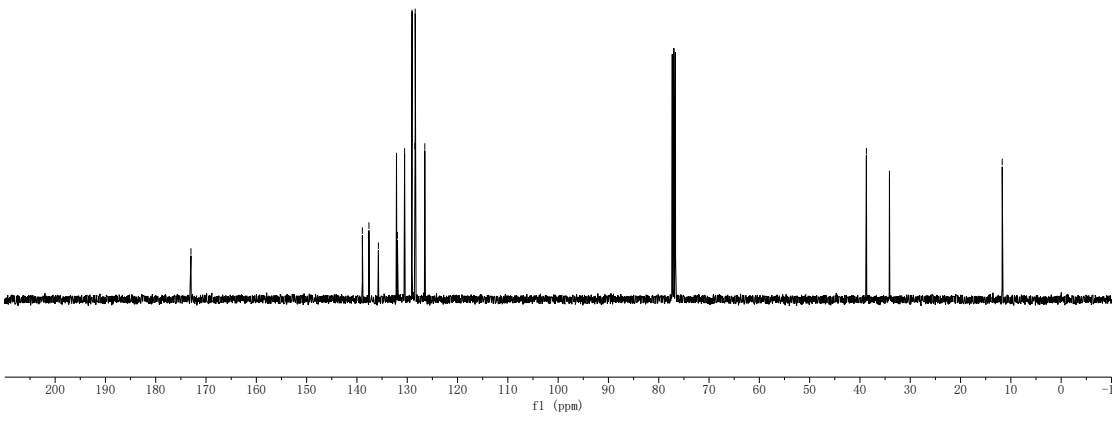
^{1}H NMR (400 MHz, $CDCl_3$)

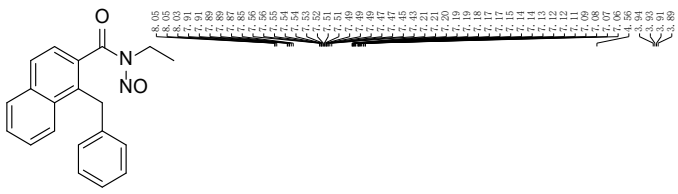




1x

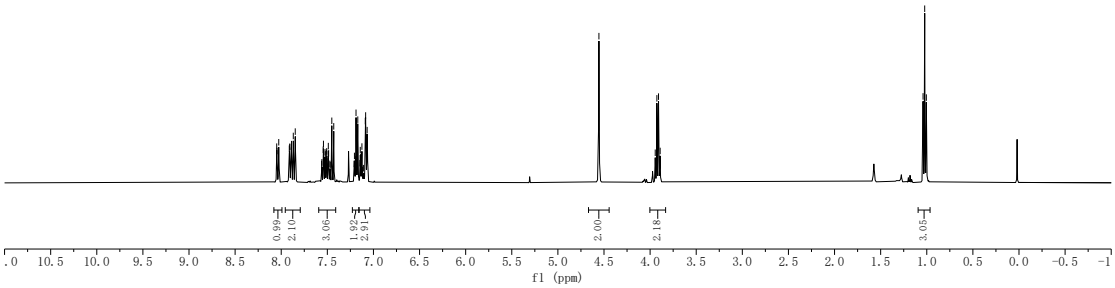
^{13}C NMR (101 MHz, $CDCl_3$)

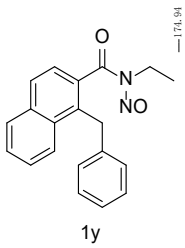




1y

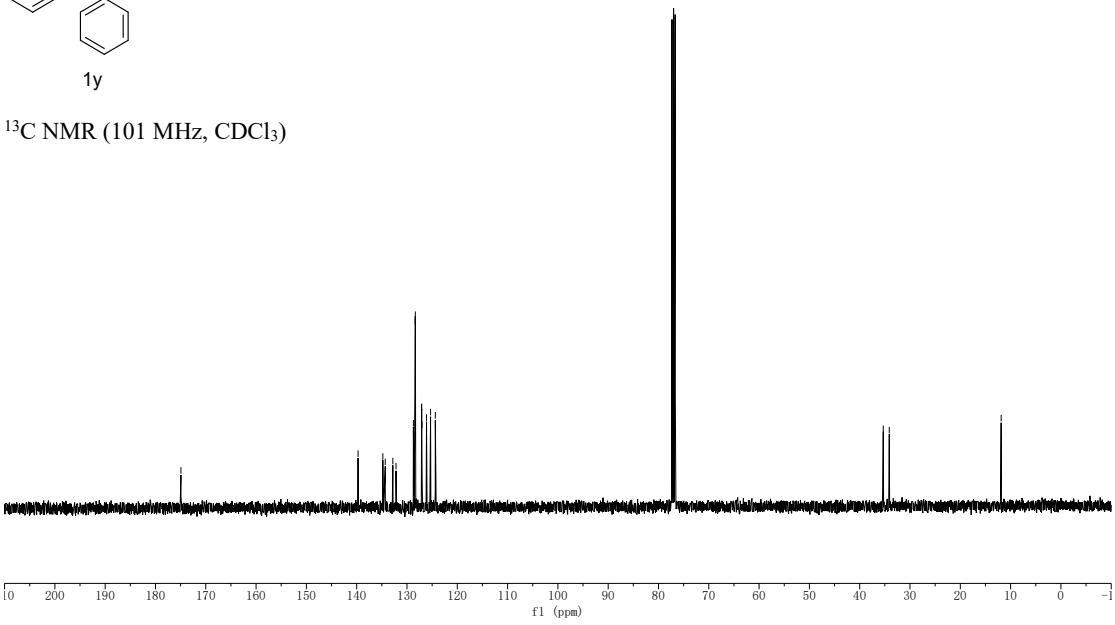
^{1}H NMR (400 MHz, $CDCl_3$)

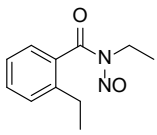




1y

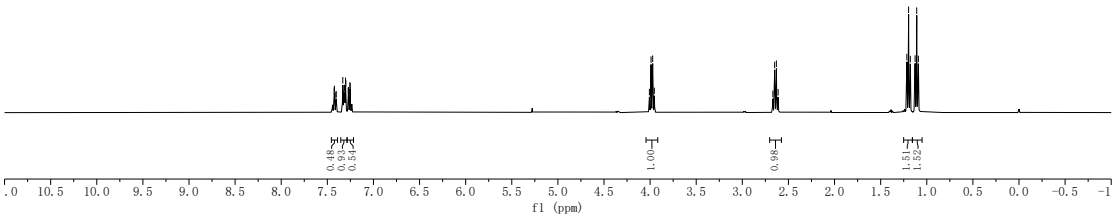
^{13}C NMR (101 MHz, $CDCl_3$)

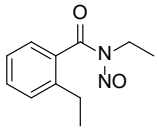




1z

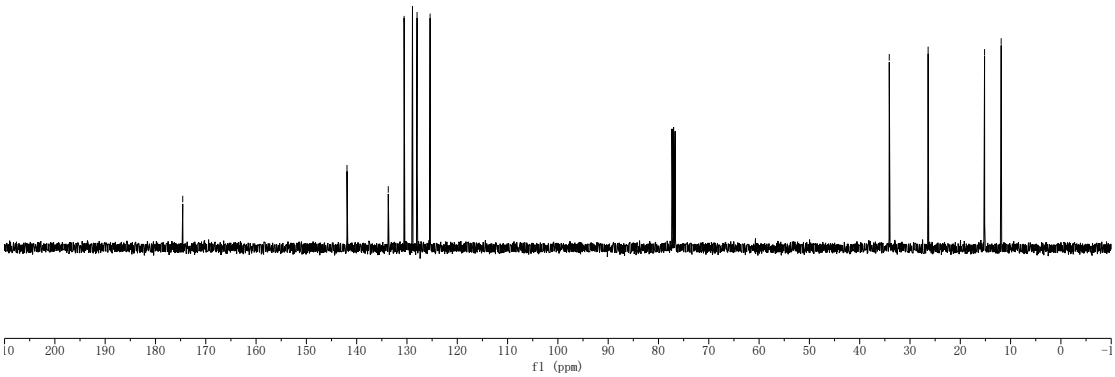
^{1}H NMR (400 MHz, $CDCl_3$)

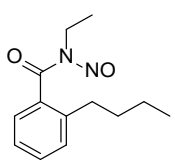




1z

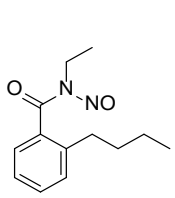
^{13}C NMR (101 MHz, $CDCl_3$)





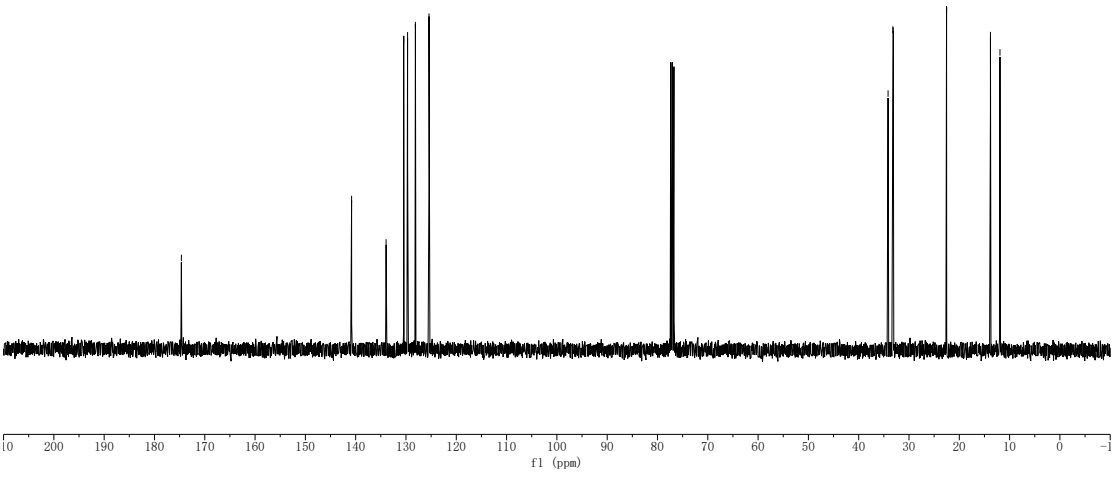
1aa

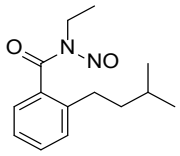
^{1}H NMR (400 MHz, $CDCl_3$)



1aa

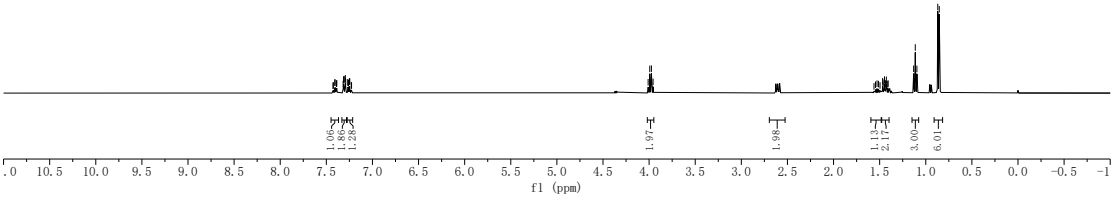
^{13}C NMR (101 MHz, $CDCl_3$)

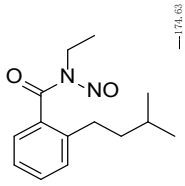




1ab

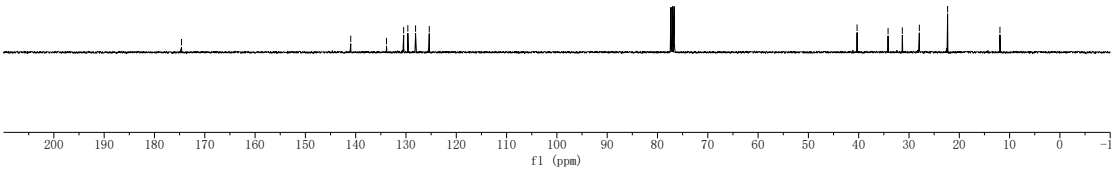
^{1}H NMR (400 MHz, $CDCl_3$)

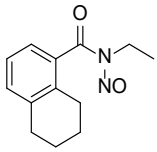




1ab

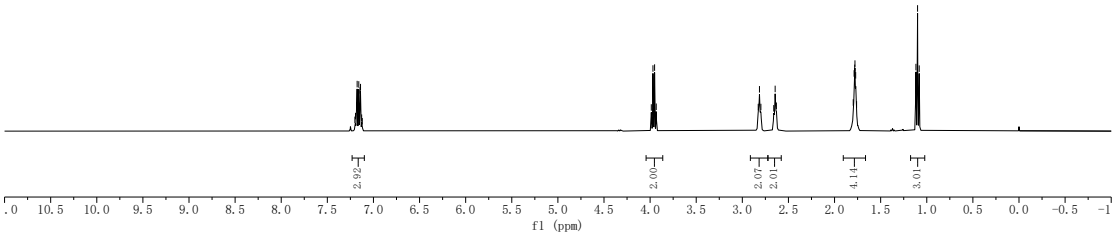
^{13}C NMR (101 MHz, $CDCl_3$)

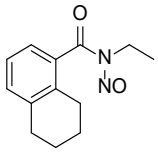




1ad

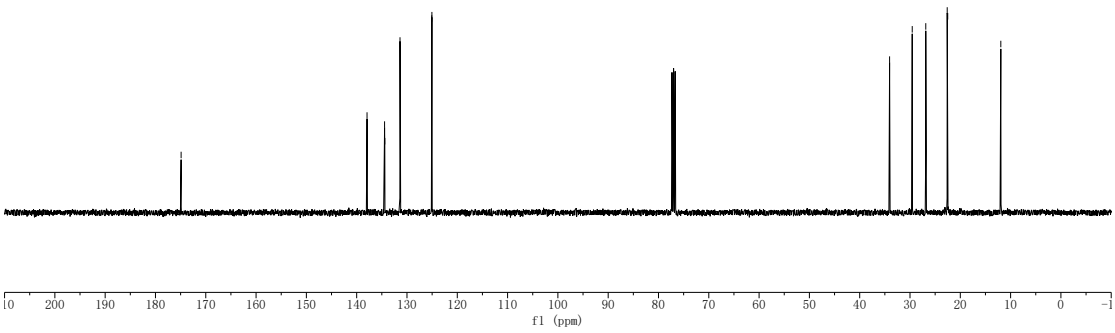
^{1}H NMR (400 MHz, $CDCl_3$)

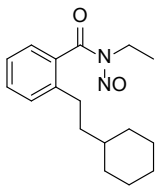




1ad

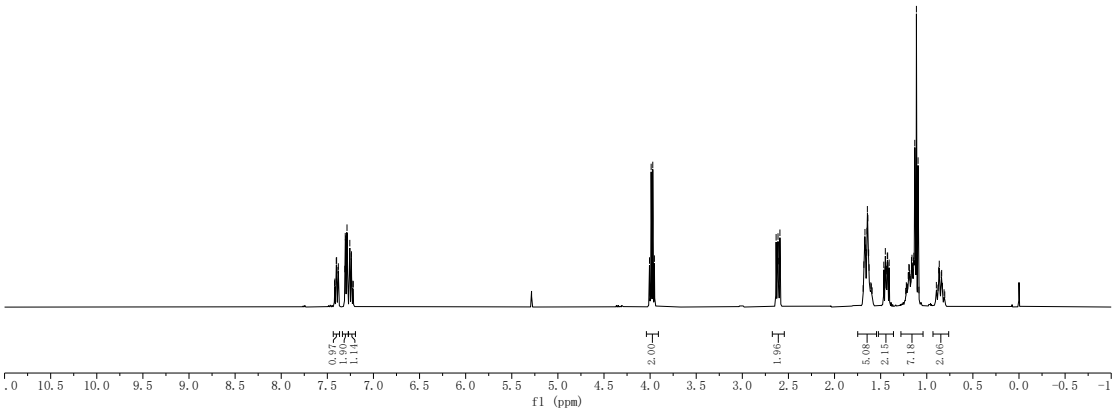
^{13}C NMR (101 MHz, $CDCl_3$)

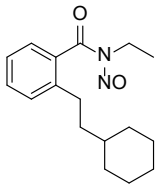




1ae

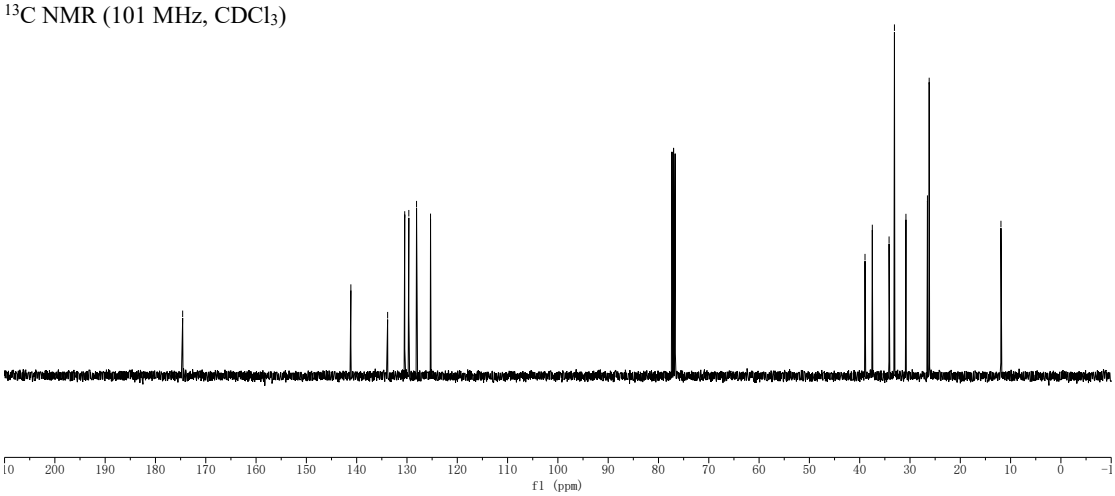
^{1}H NMR (400 MHz, $CDCl_3$)

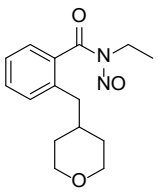




1ae

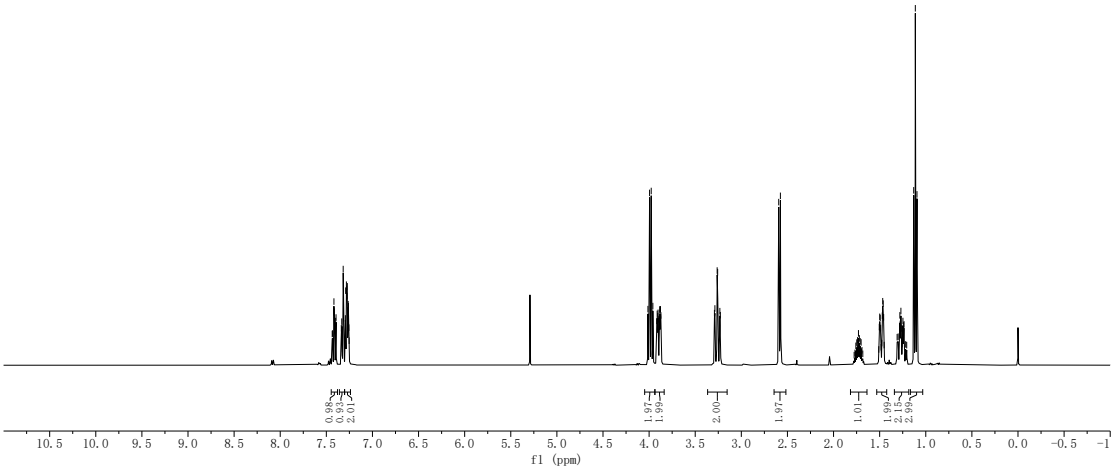
^{13}C NMR (101 MHz, $CDCl_3$)

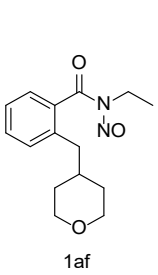




1af

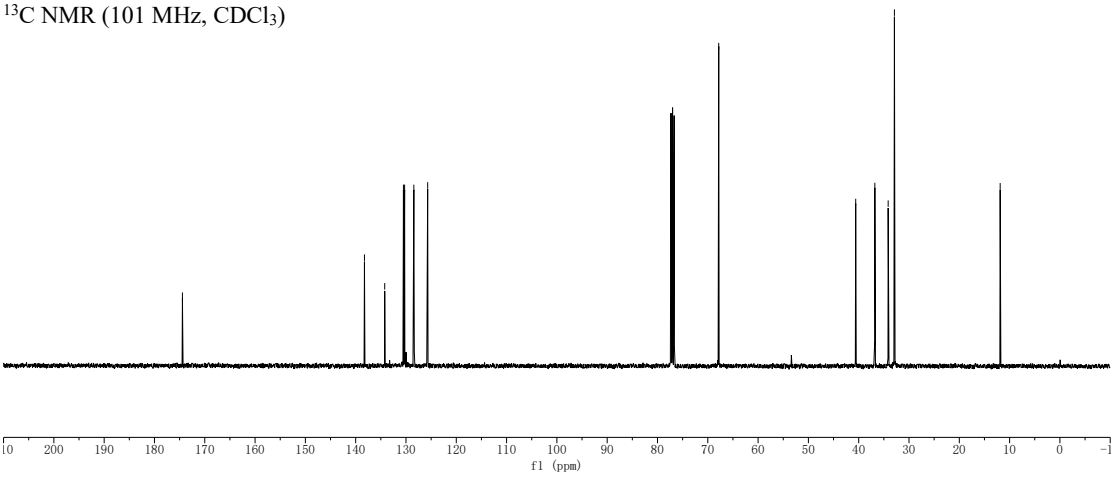
^{1}H NMR (400 MHz, $CDCl_3$)

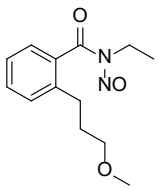




1af

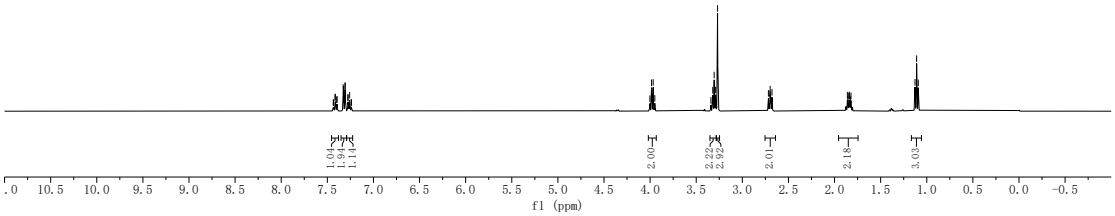
^{13}C NMR (101 MHz, $CDCl_3$)

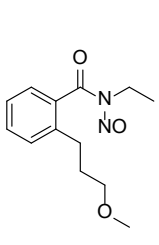




1ag

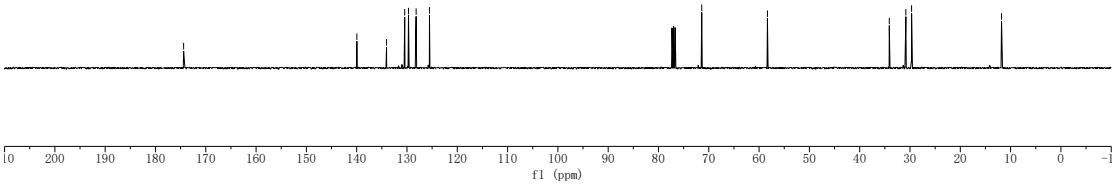
^{1}H NMR (400 MHz, $CDCl_3$)

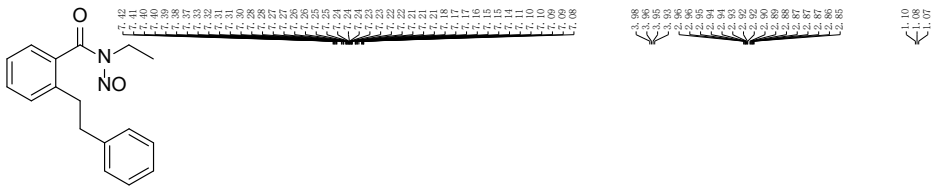




1ag

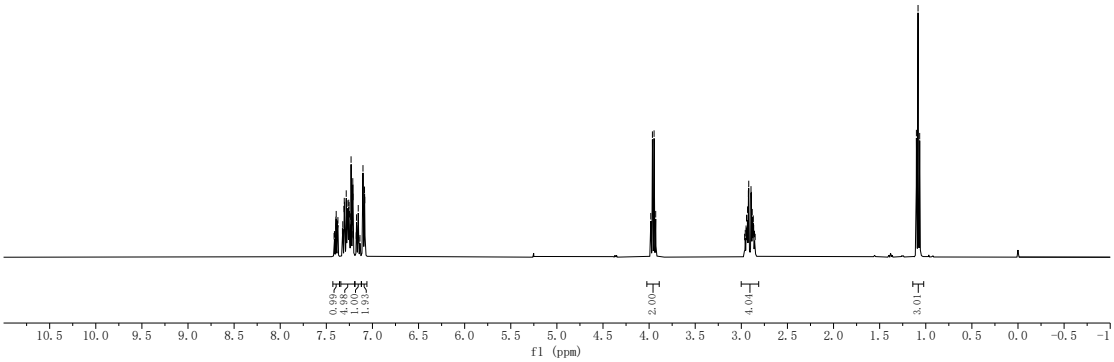
^{13}C NMR (101 MHz, $CDCl_3$)

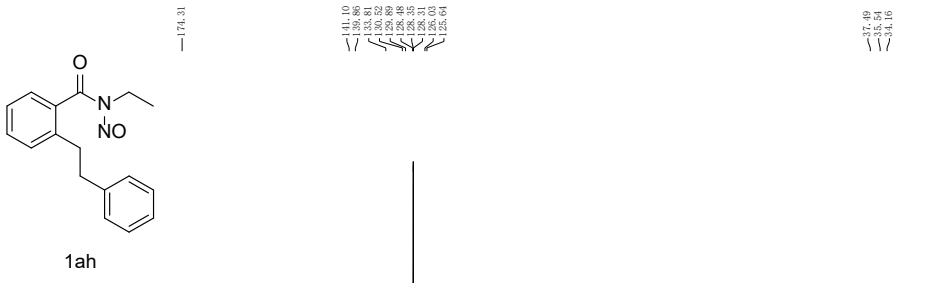




1ah

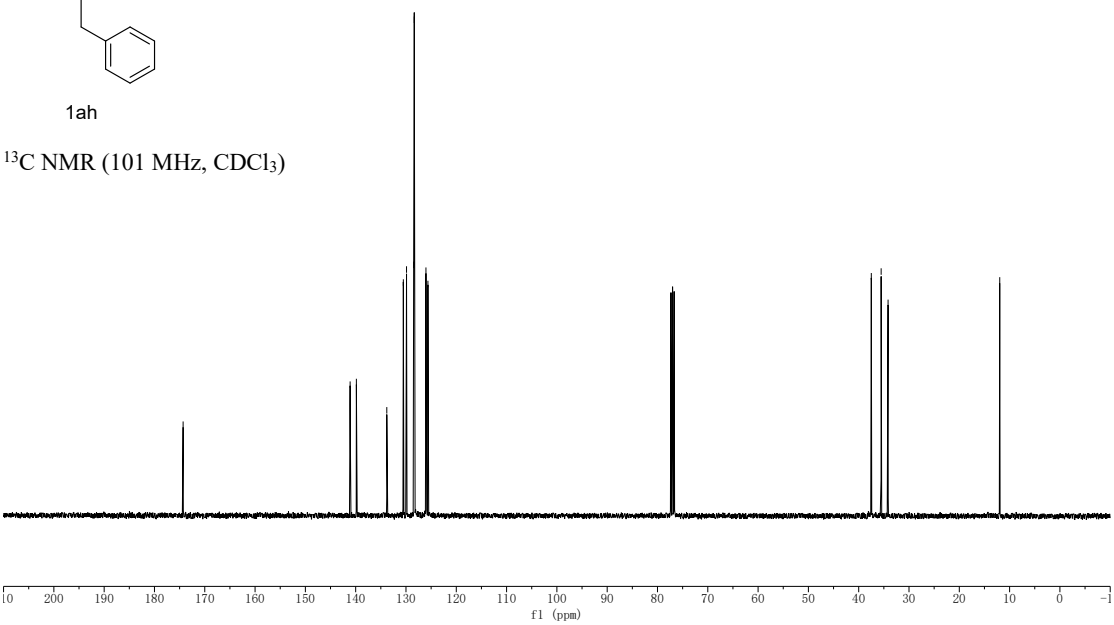
^{1}H NMR (400 MHz, $CDCl_3$)

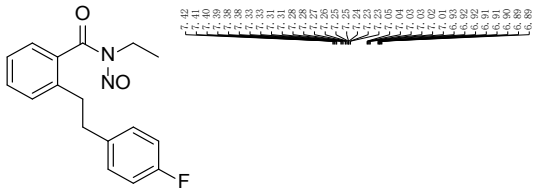




1ah

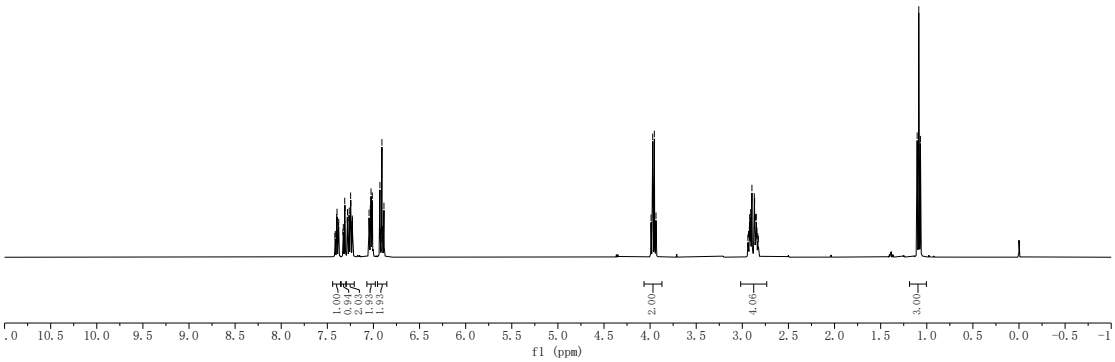
^{13}C NMR (101 MHz, $CDCl_3$)

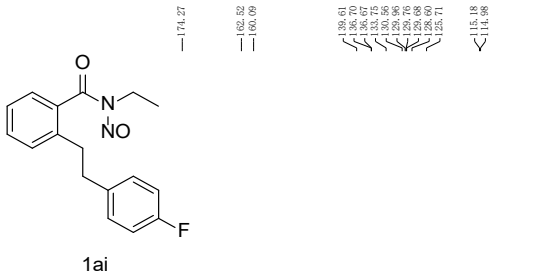




1ai

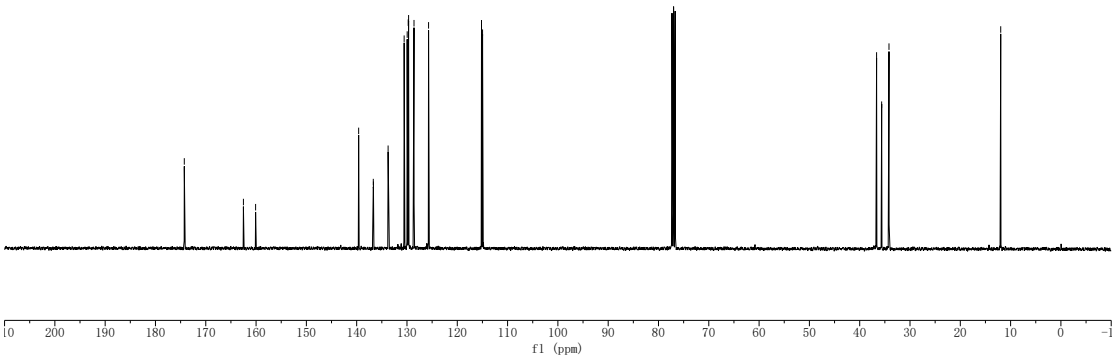
^{1}H NMR (400 MHz, $CDCl_3$)

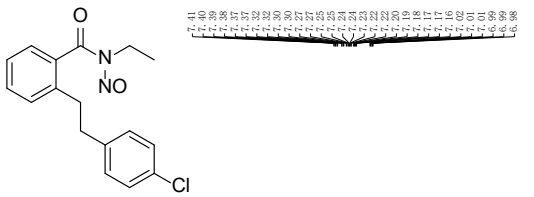




1ai

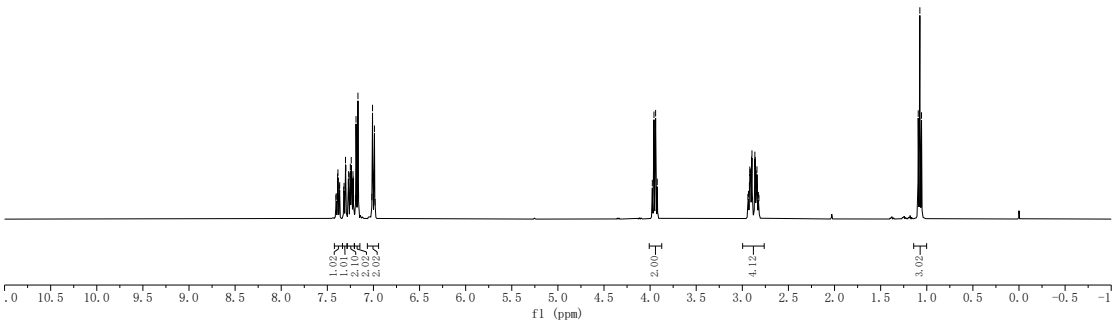
^{13}C NMR (101 MHz, $CDCl_3$)

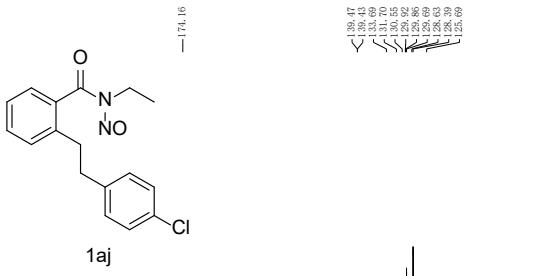




1aj

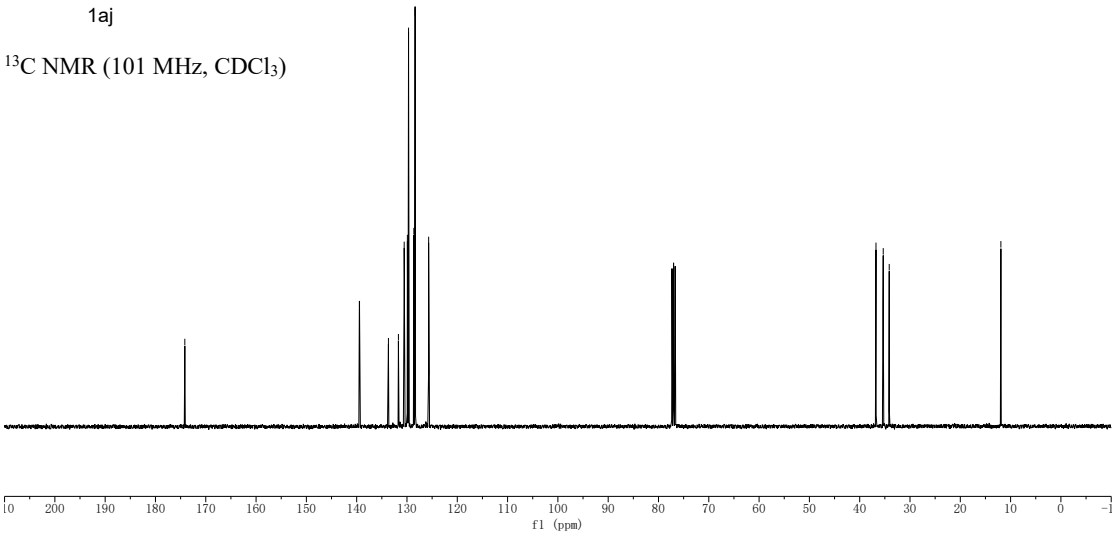
^{1}H NMR (400 MHz, $CDCl_3$)

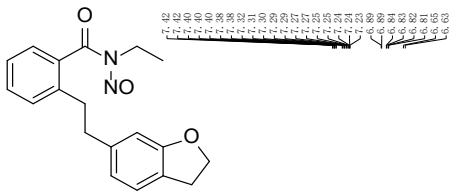




1aj

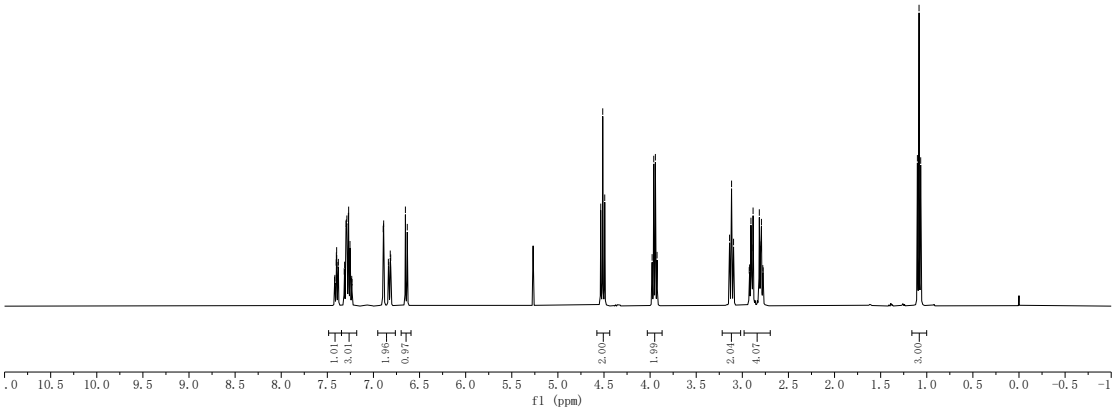
^{13}C NMR (101 MHz, $CDCl_3$)

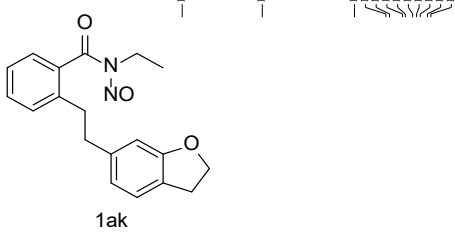




1ak

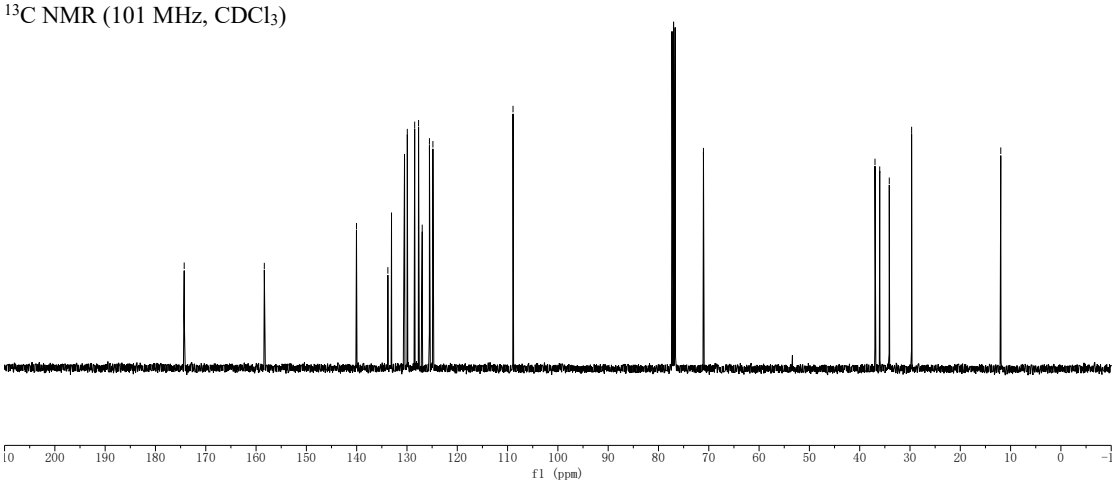
^{1}H NMR (400 MHz, $CDCl_3$)

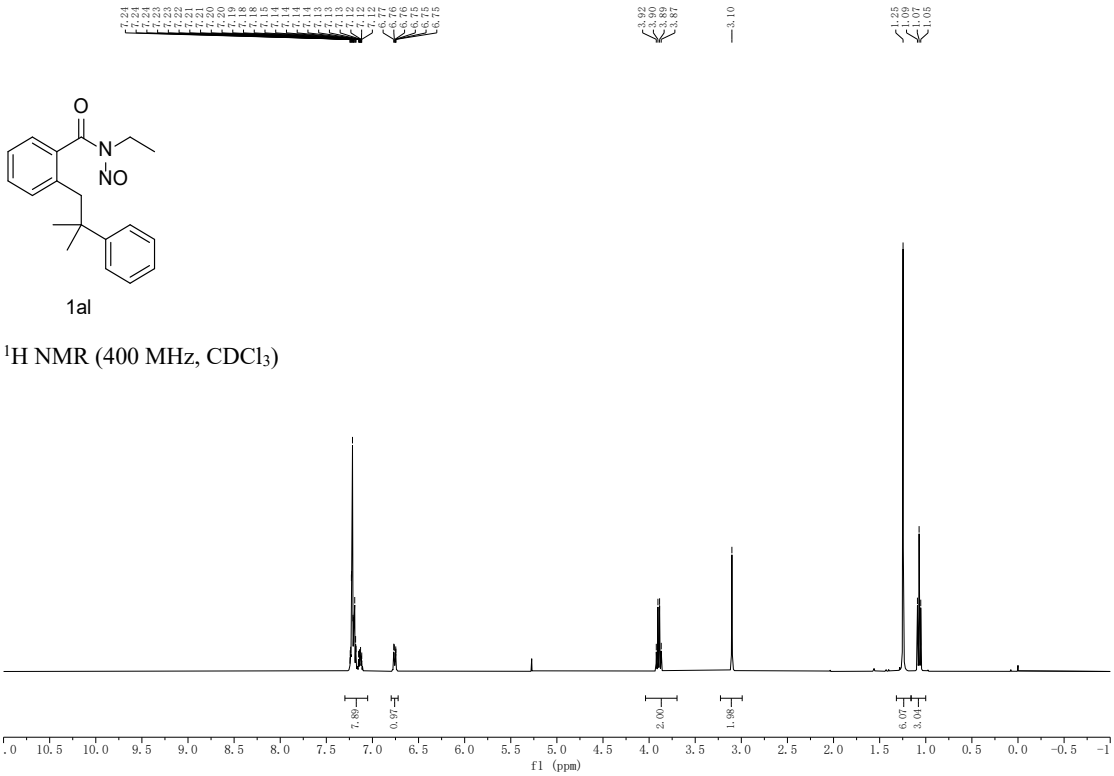




1ak

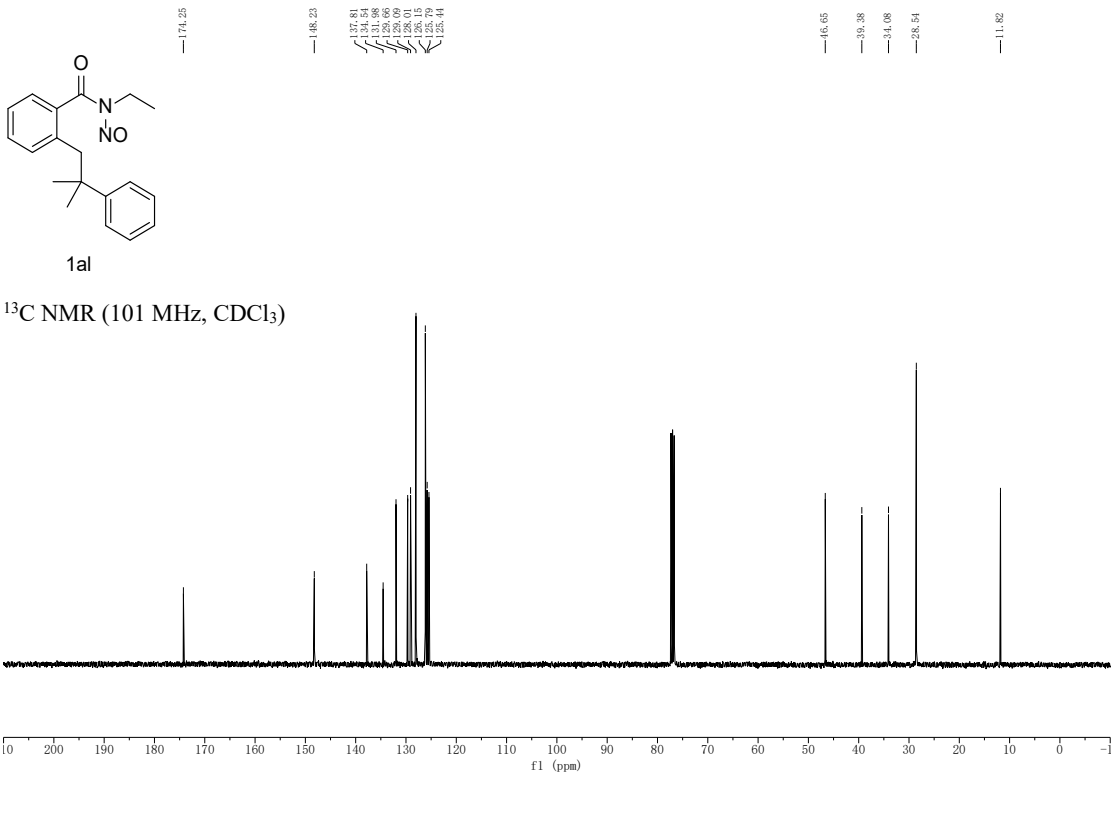
^{13}C NMR (101 MHz, $CDCl_3$)





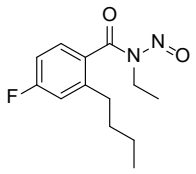
1al

^{1}H NMR (400 MHz, $CDCl_3$)



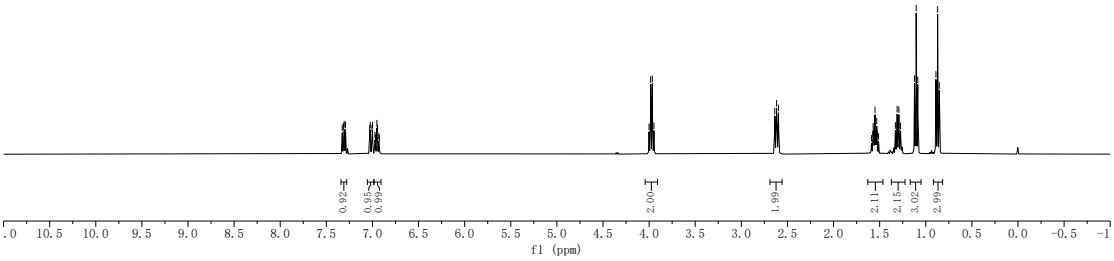
1al

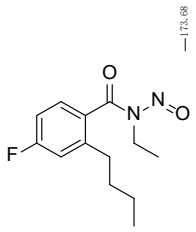
^{13}C NMR (101 MHz, $CDCl_3$)



1am

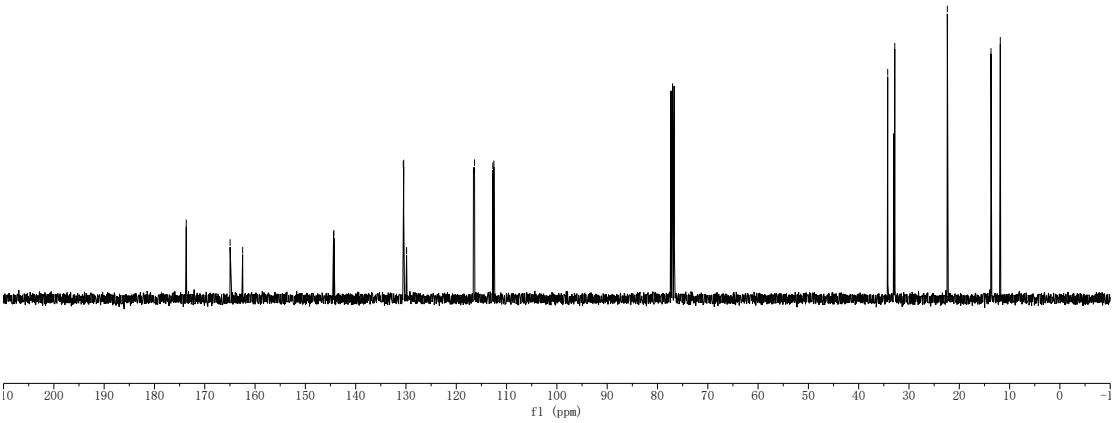
^{1}H NMR (400 MHz, $CDCl_3$)

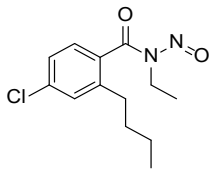




1am

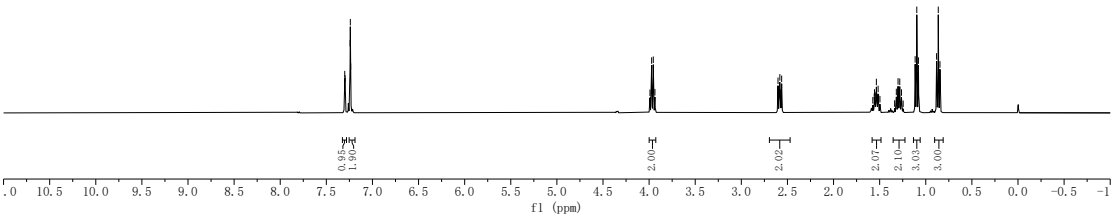
^{13}C NMR (101 MHz, $CDCl_3$)

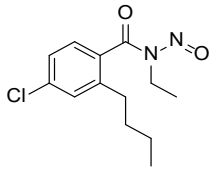




1an

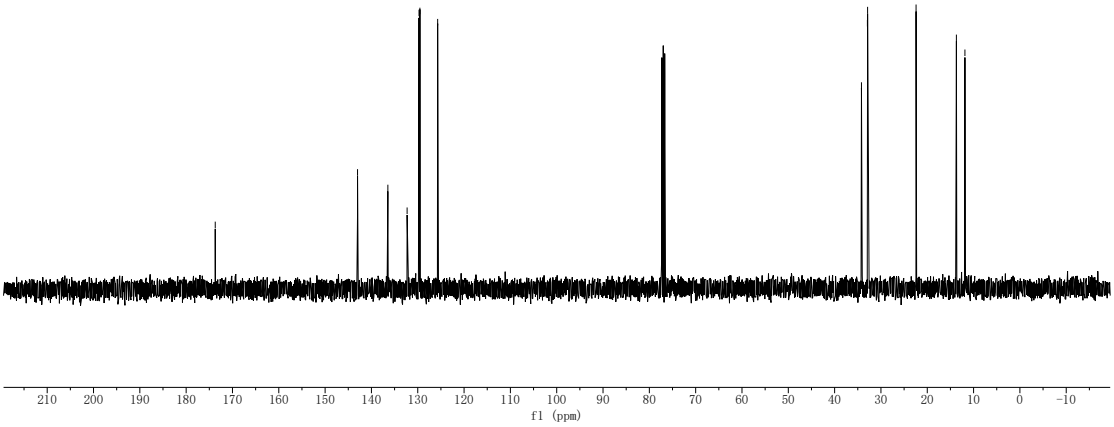
^{1}H NMR (400 MHz, $CDCl_3$)



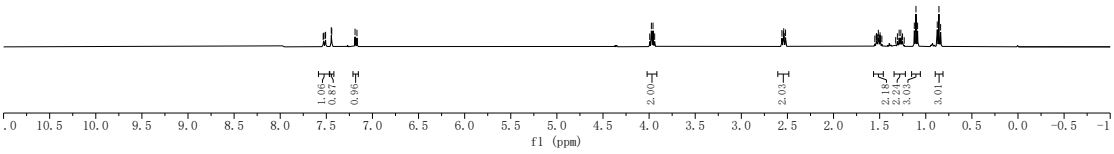


1an

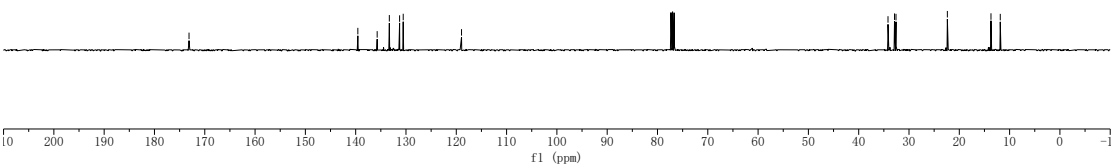
^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)

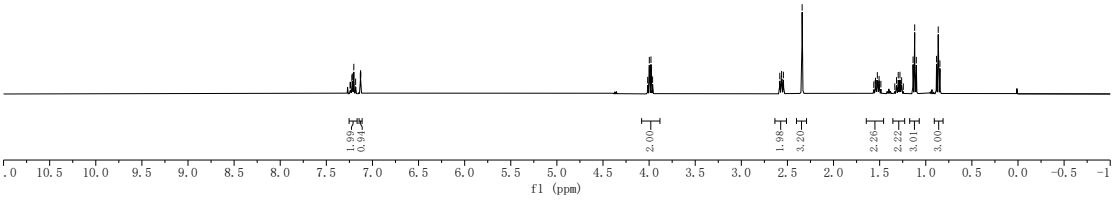


^{13}C NMR (101 MHz, $CDCl_3$)



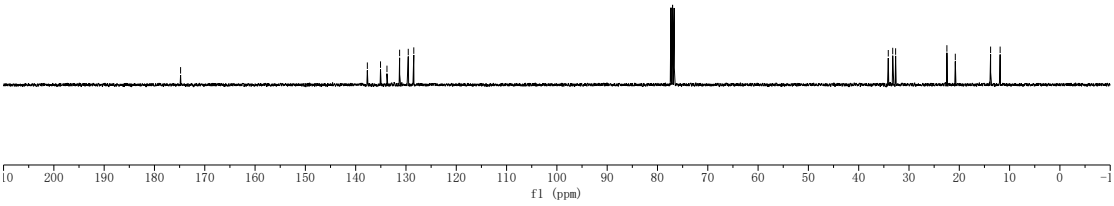
1ap

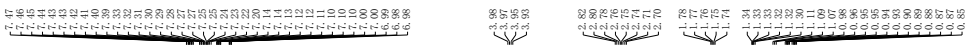
^{1}H NMR (400 MHz, $CDCl_3$)

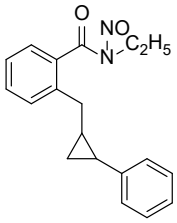


1ap

^{13}C NMR (101 MHz, $CDCl_3$)

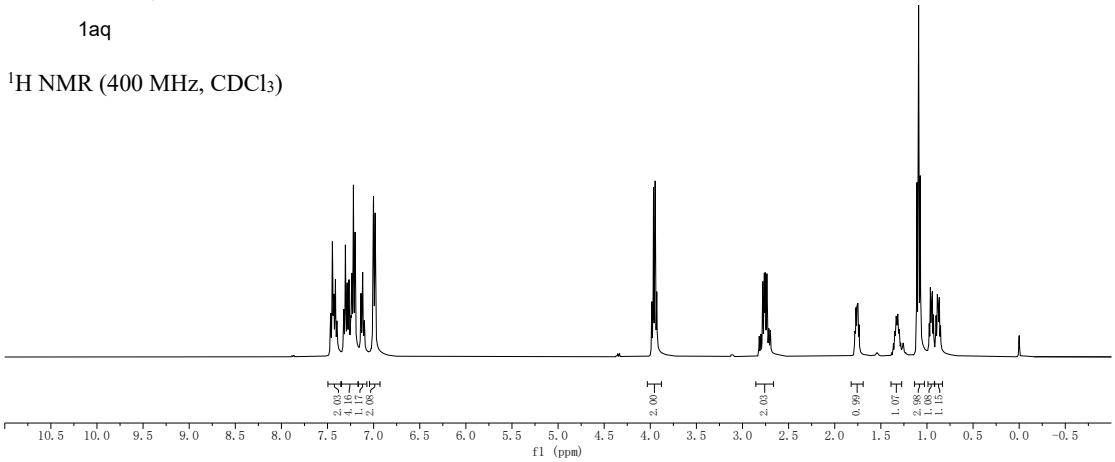


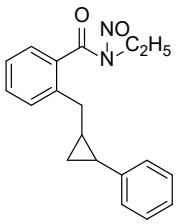




1aq

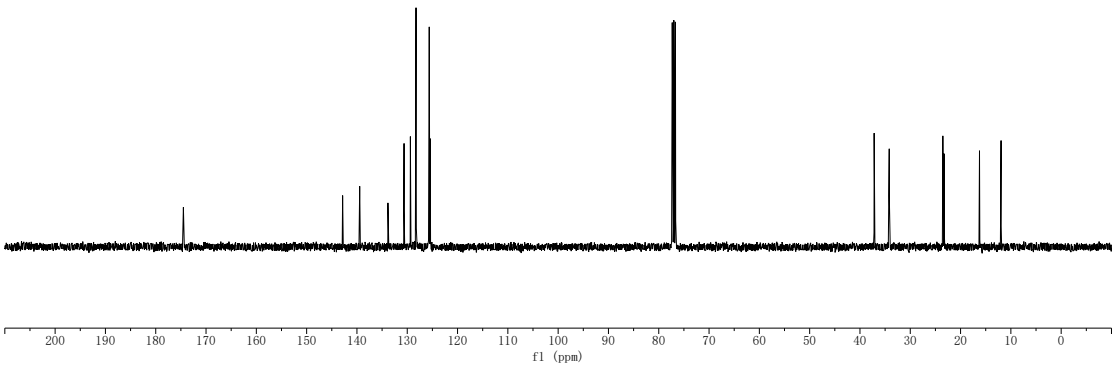
^{1}H NMR (400 MHz, $CDCl_3$)

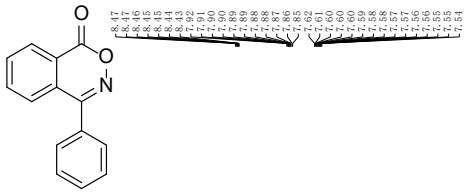




1aq

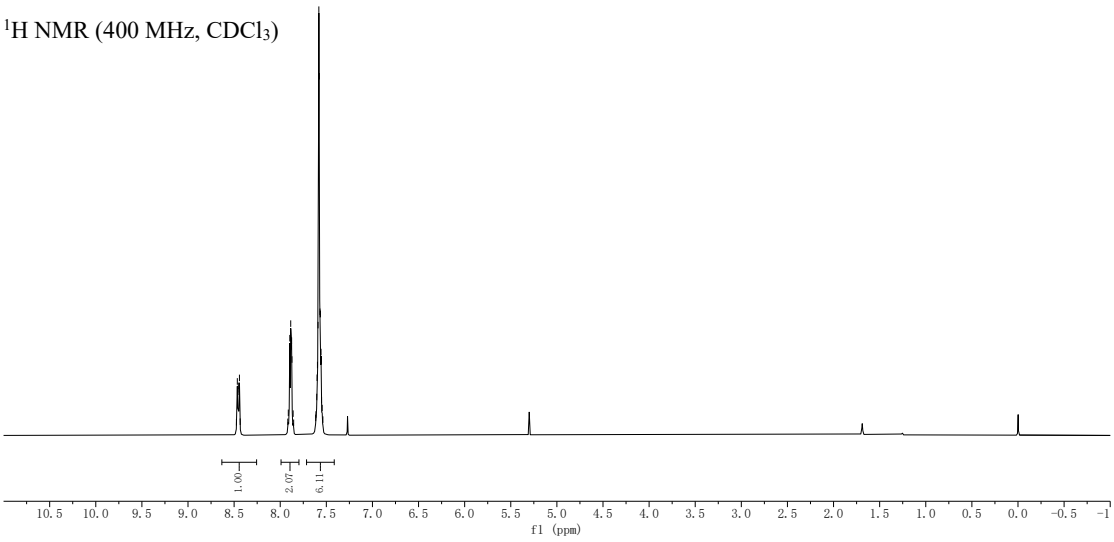
^{13}C NMR (101 MHz, $CDCl_3$)

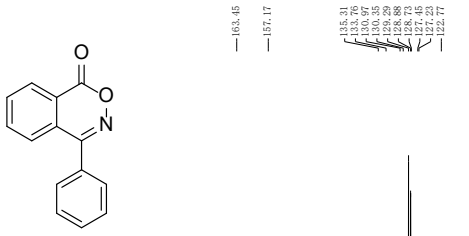




2a

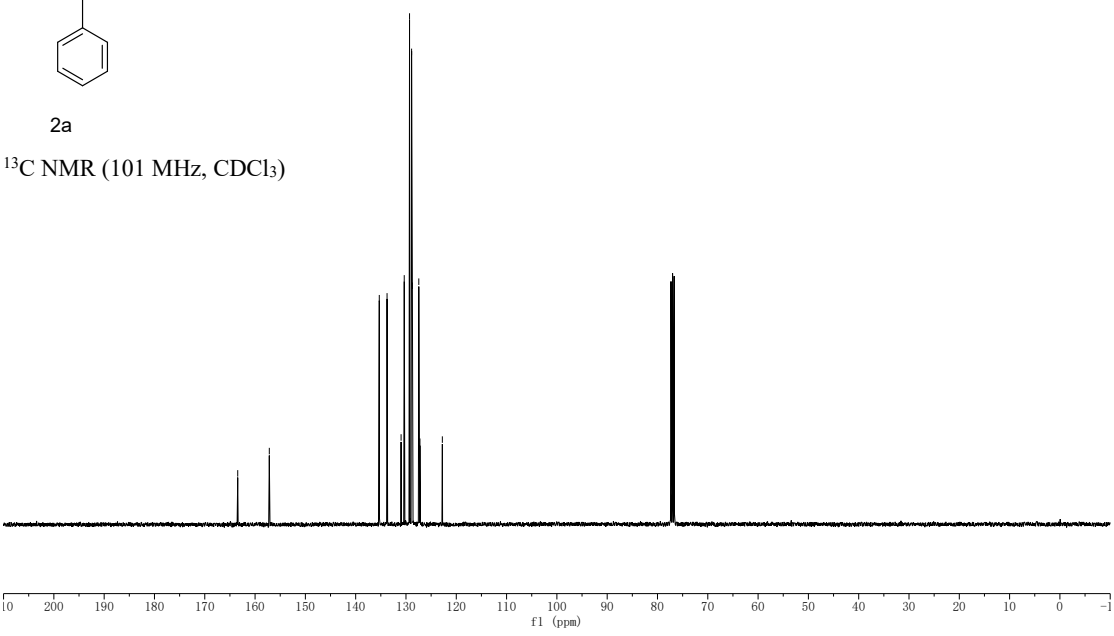
^{1}H NMR (400 MHz, $CDCl_3$)

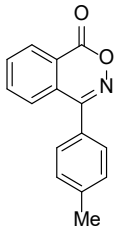




2a

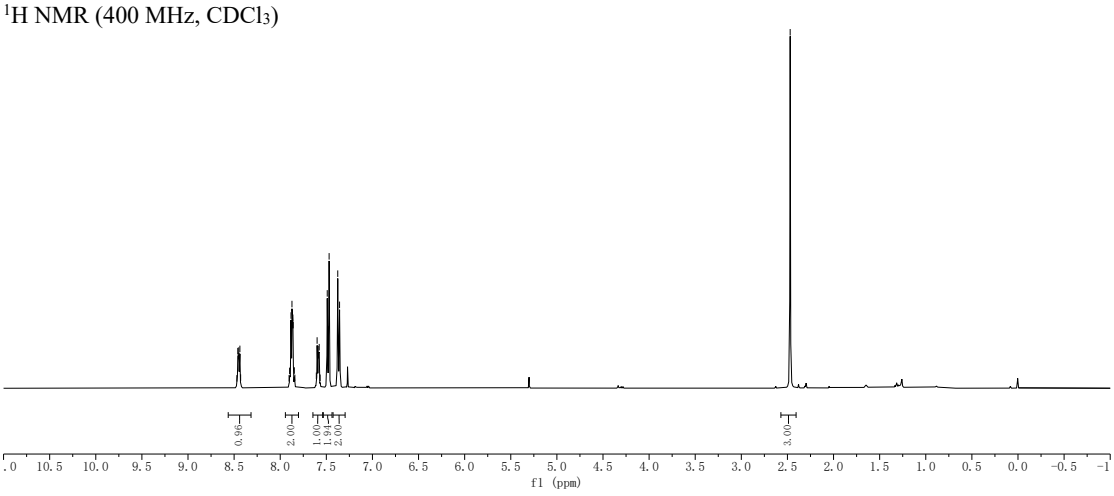
^{13}C NMR (101 MHz, $CDCl_3$)

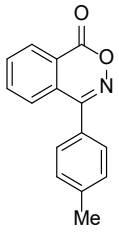




2b

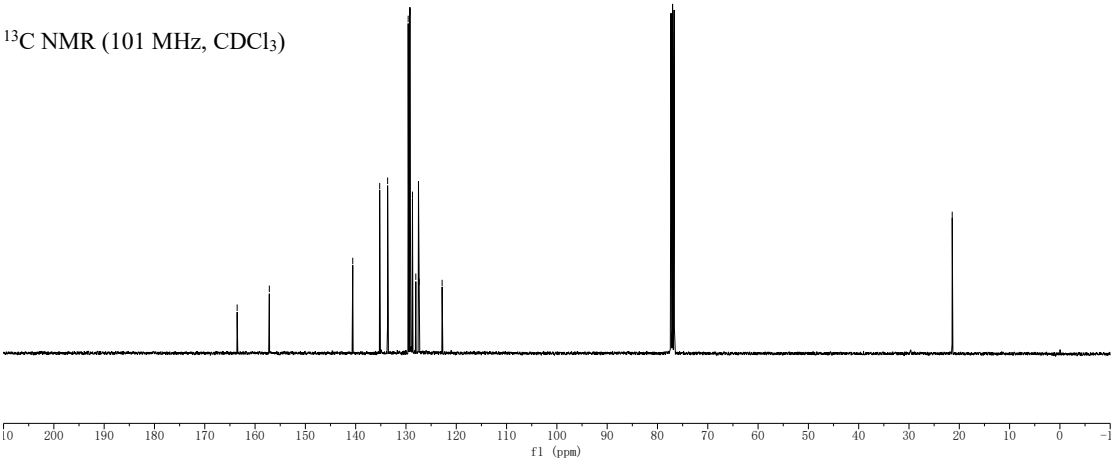
^{1}H NMR (400 MHz, $CDCl_3$)

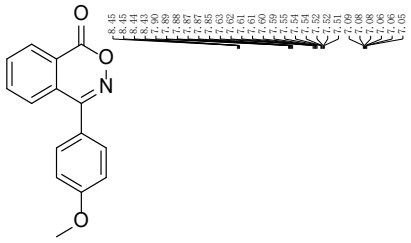




2b

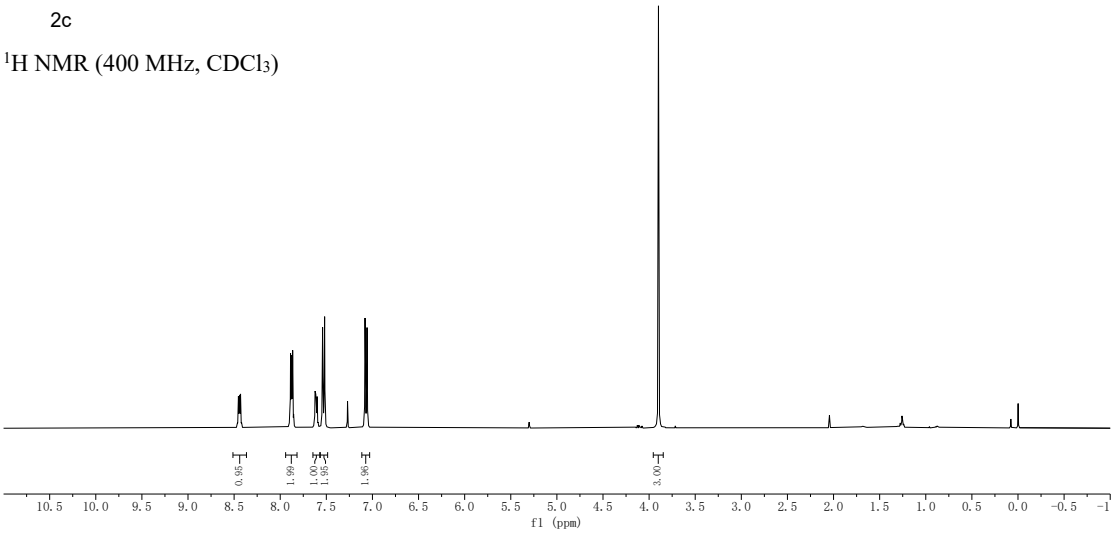
^{13}C NMR (101 MHz, $CDCl_3$)

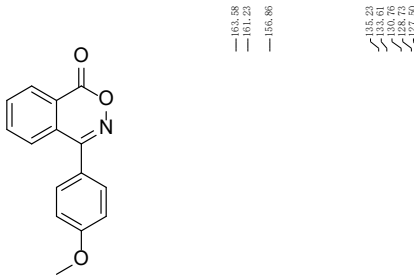




2c

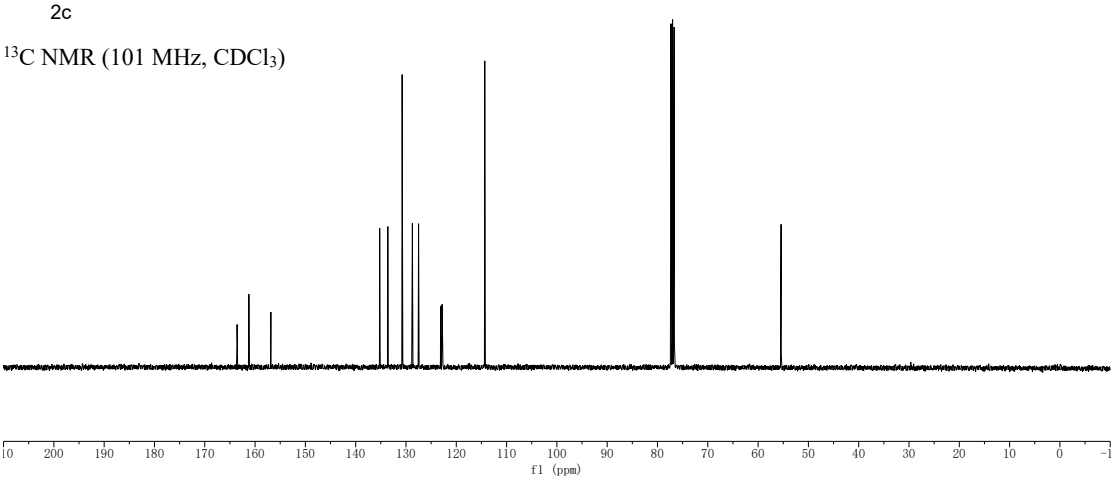
^{1}H NMR (400 MHz, $CDCl_3$)

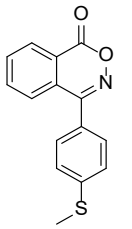




2c

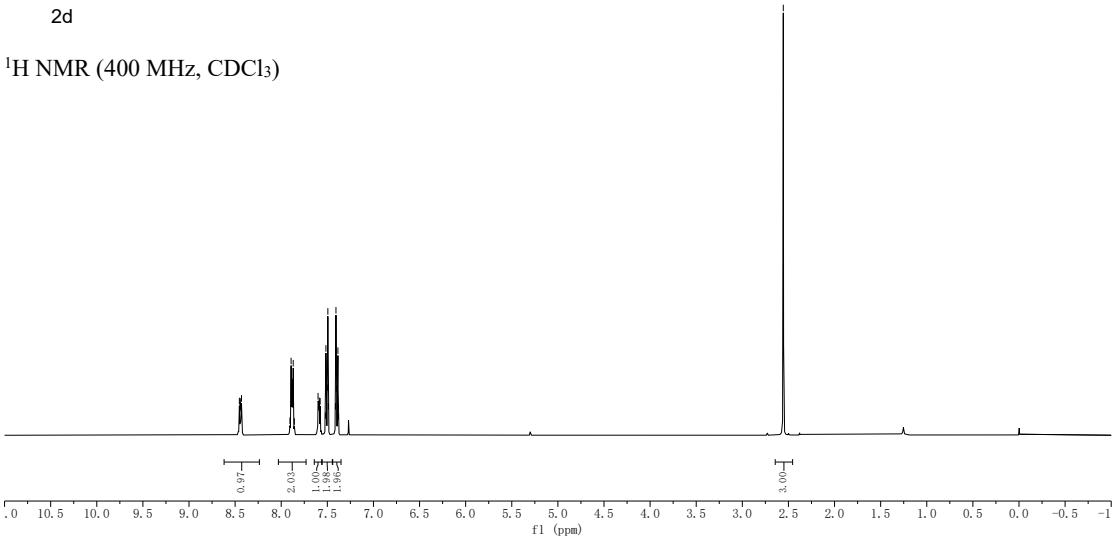
^{13}C NMR (101 MHz, $CDCl_3$)

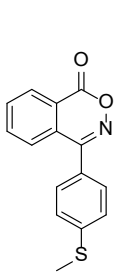




2d

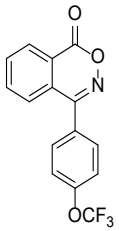
^{1}H NMR (400 MHz, $CDCl_3$)





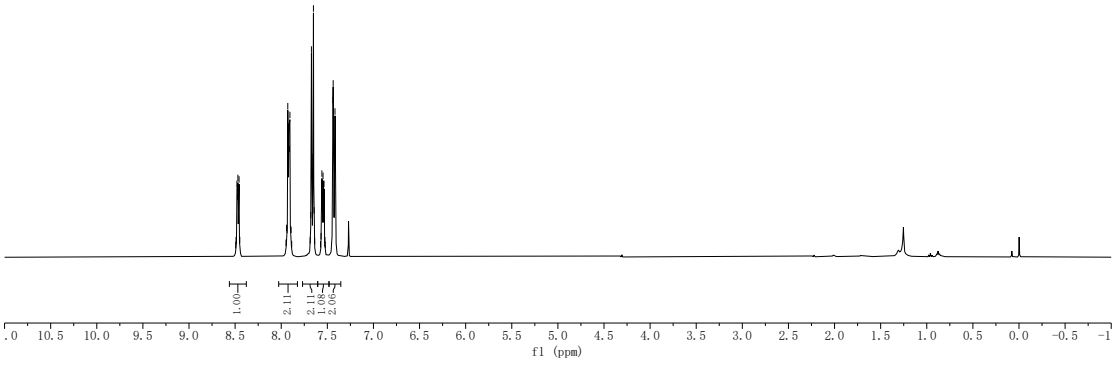
2d

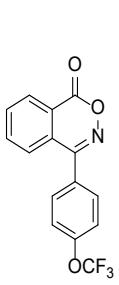
^{13}C NMR (101 MHz, $CDCl_3$)



2e

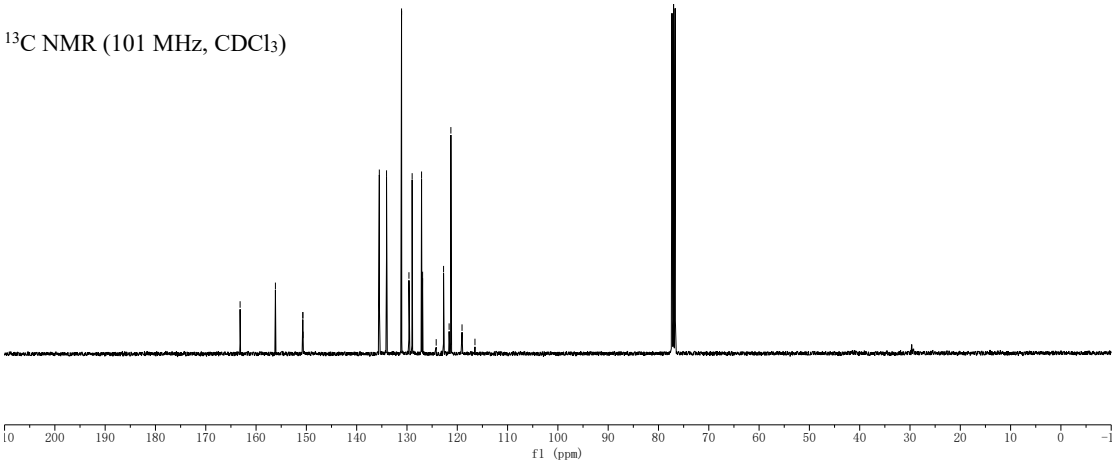
^{1}H NMR (400 MHz, $CDCl_3$)

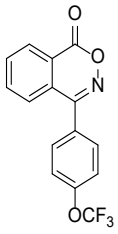




2e

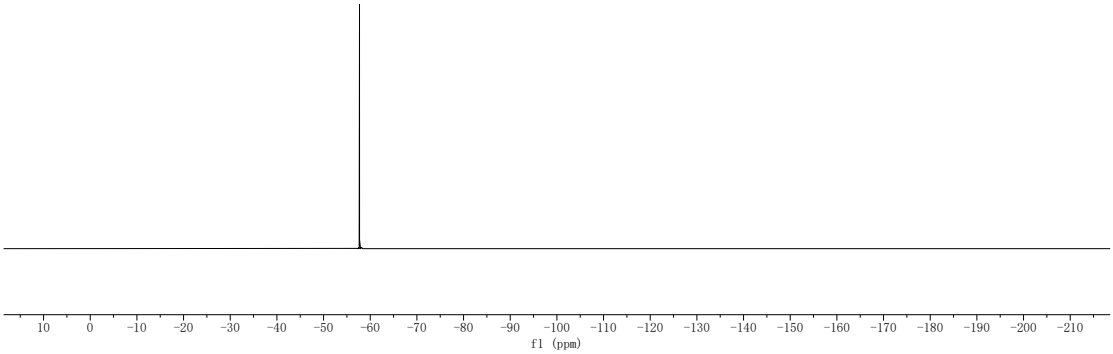
^{13}C NMR (101 MHz, $CDCl_3$)

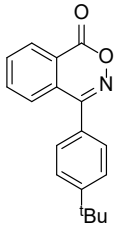




2e

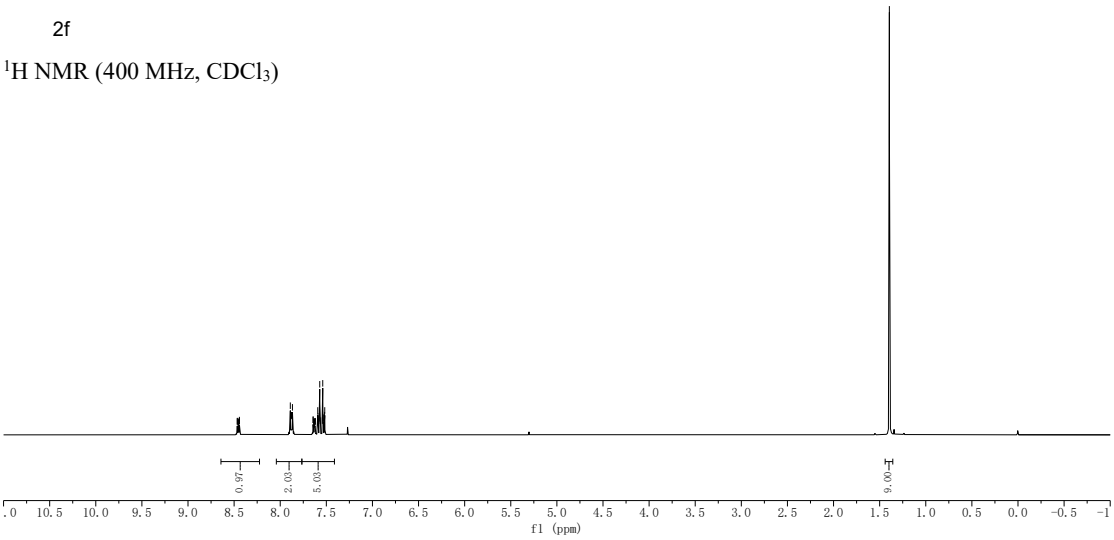
^{19}F NMR (376 MHz, $CDCl_3$)

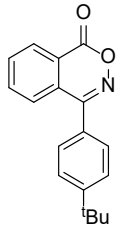




2f

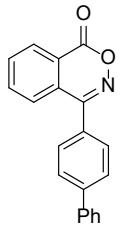
^{1}H NMR (400 MHz, $CDCl_3$)





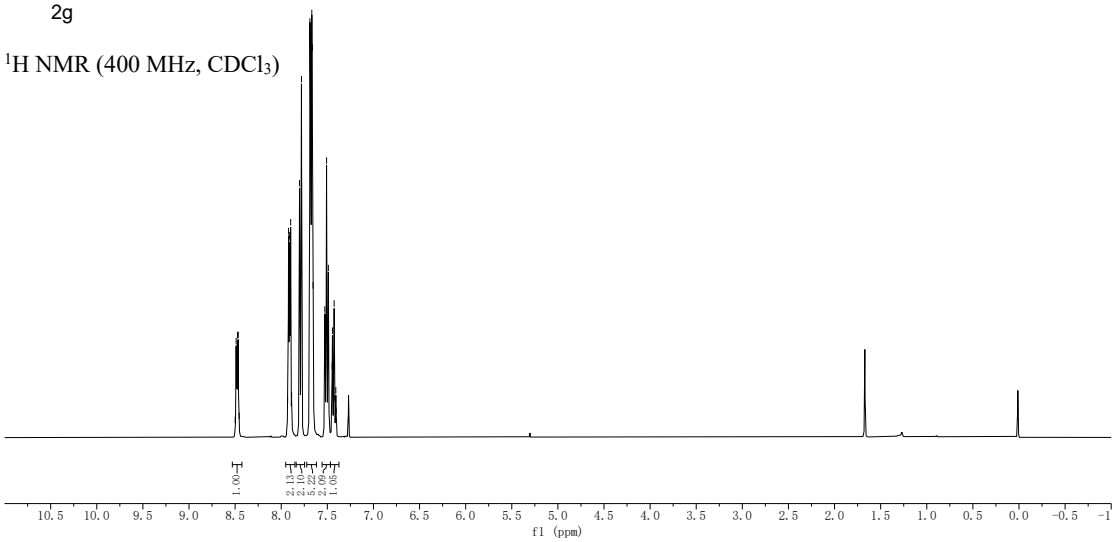
2f

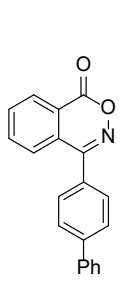
^{13}C NMR (101 MHz, $CDCl_3$)



2g

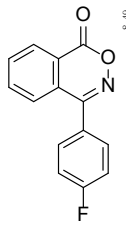
^{1}H NMR (400 MHz, $CDCl_3$)





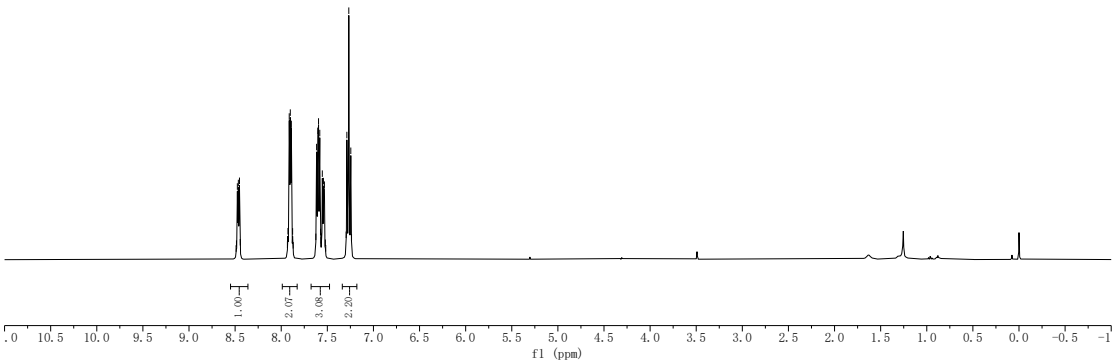
2g

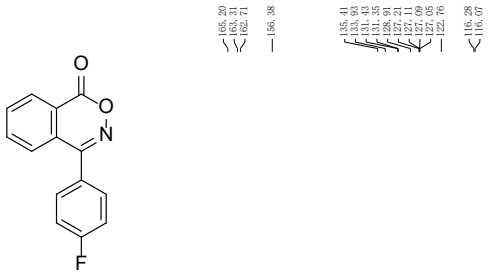
^{13}C NMR (101 MHz, $CDCl_3$)



2h

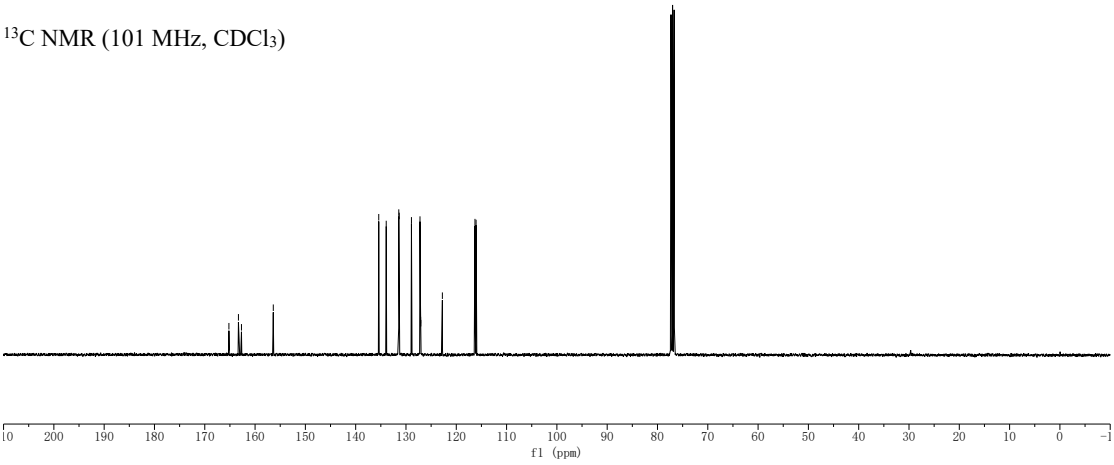
^{1}H NMR (400 MHz, $CDCl_3$)





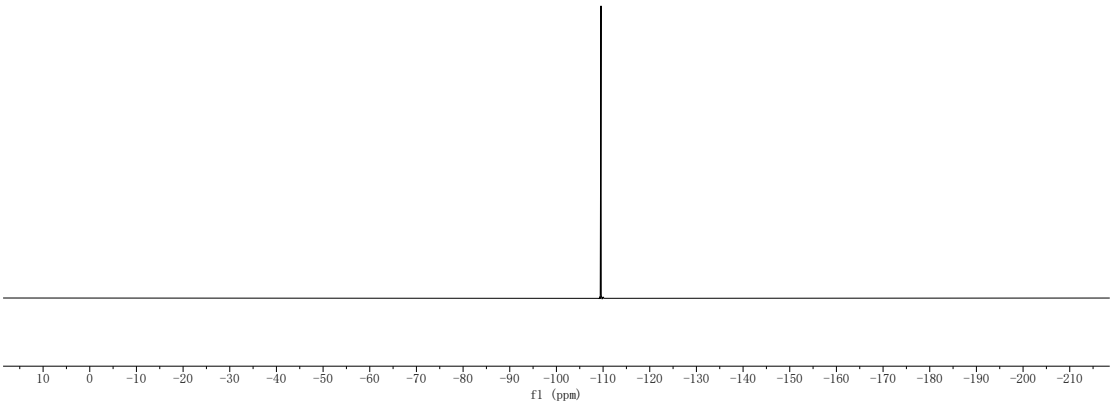
2h

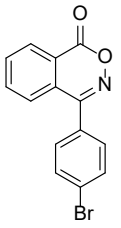
^{13}C NMR (101 MHz, $CDCl_3$)

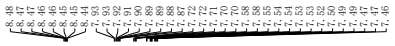


2h

^{19}F NMR (376 MHz, $CDCl_3$)

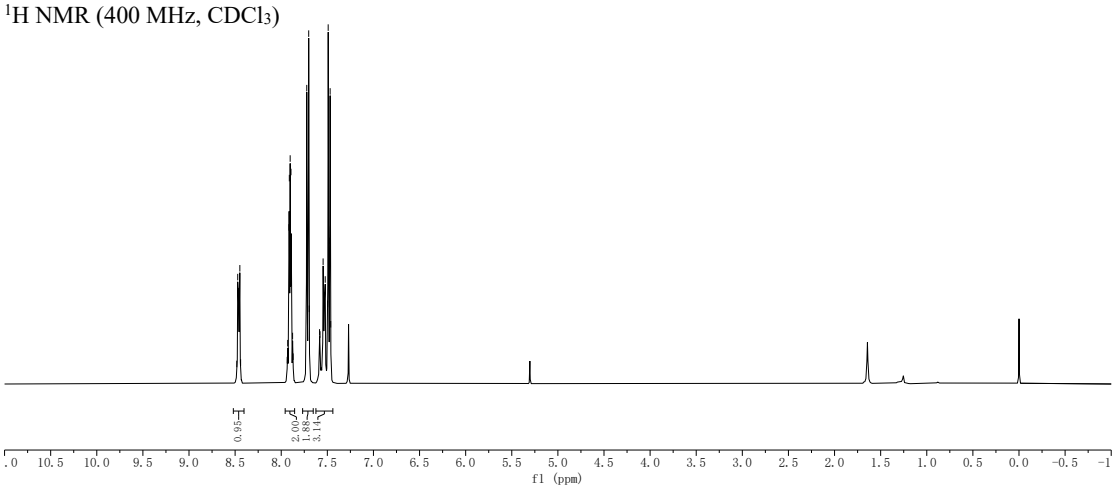


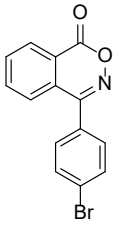


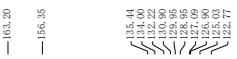


2i

^{1}H NMR (400 MHz, $CDCl_3$)

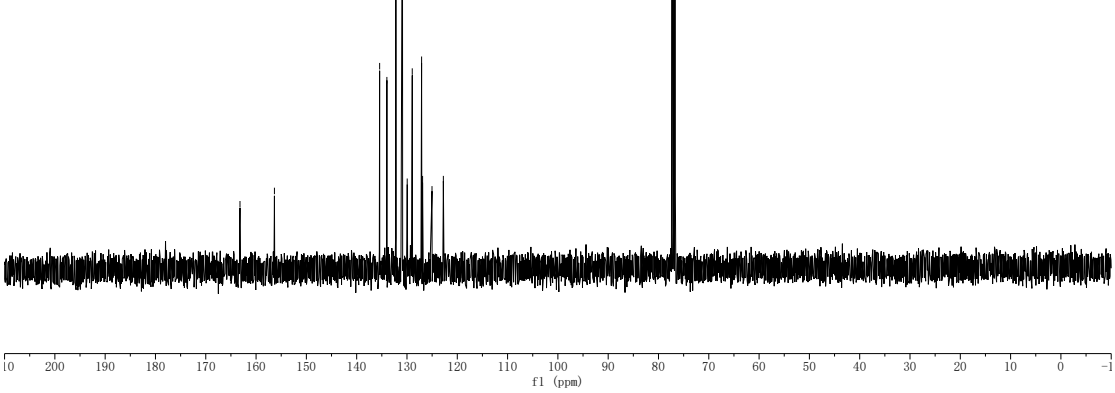






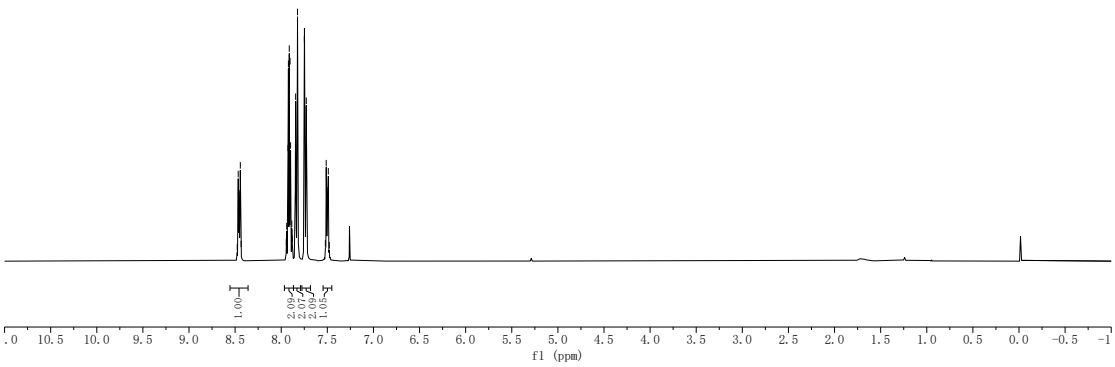
2i

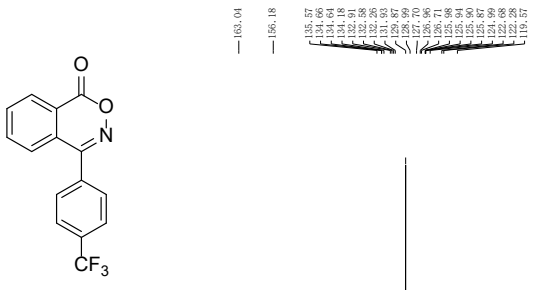
^{13}C NMR (101 MHz, $CDCl_3$)



2j

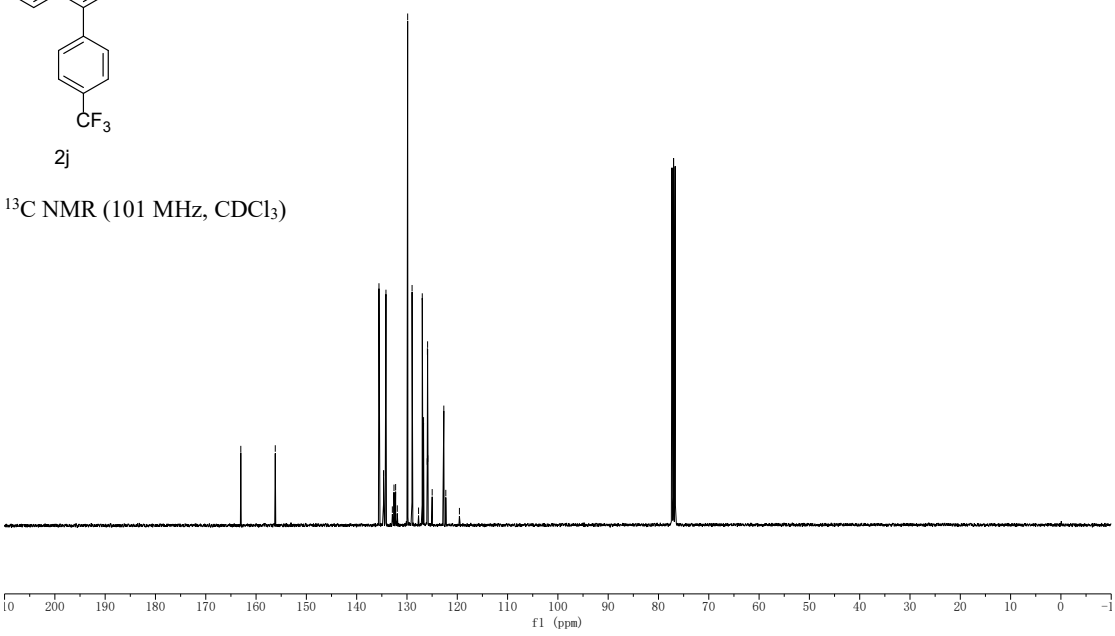
^{1}H NMR (400 MHz, $CDCl_3$)

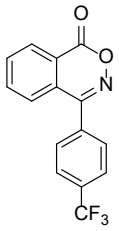




2j

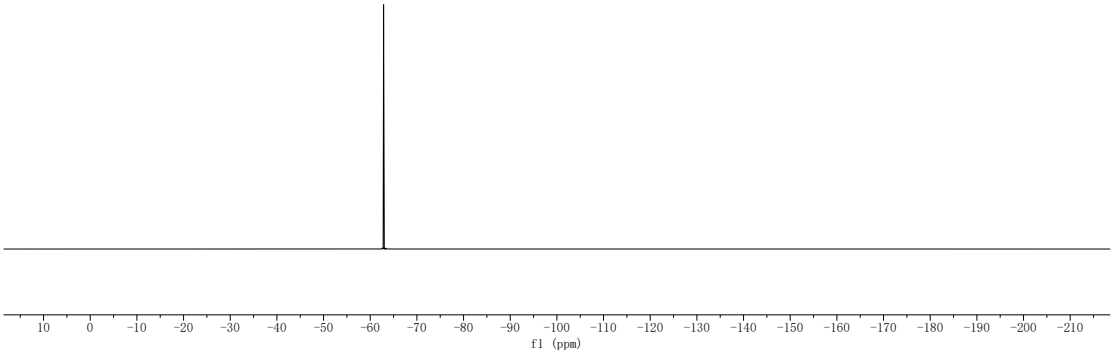
^{13}C NMR (101 MHz, $CDCl_3$)

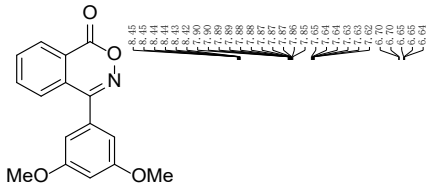




2j

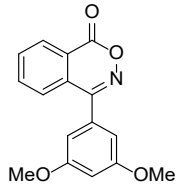
^{19}F NMR (376 MHz, $CDCl_3$)





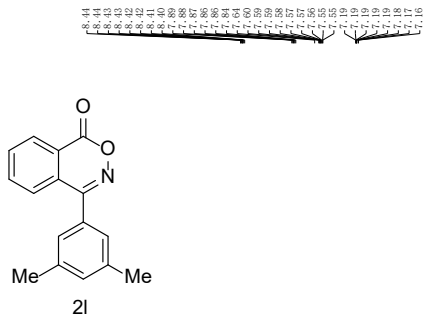
2k

^{1}H NMR (400 MHz, $CDCl_3$)



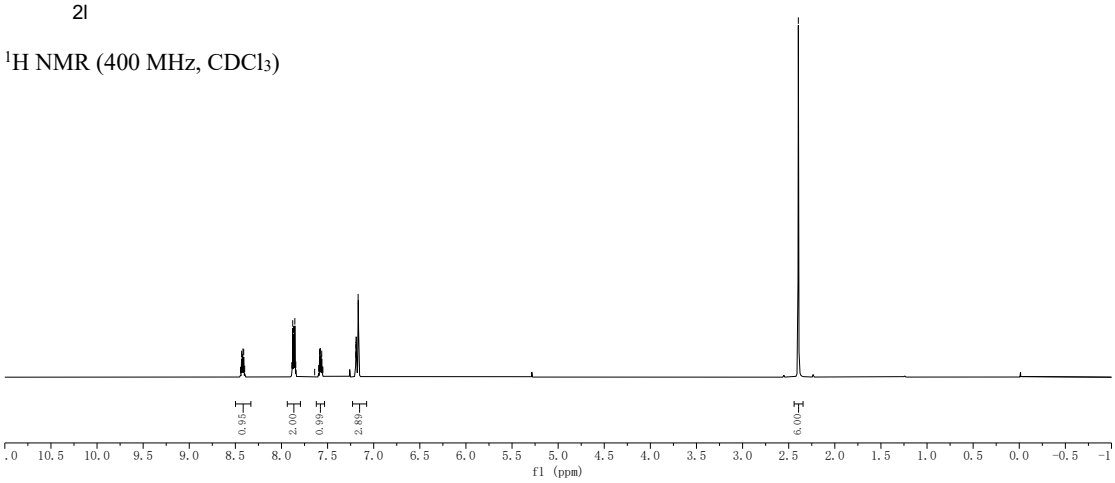
2k

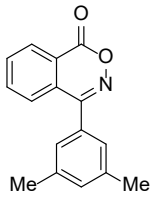
^{13}C NMR (101 MHz, $CDCl_3$)



2l

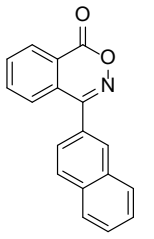
^{1}H NMR (400 MHz, $CDCl_3$)





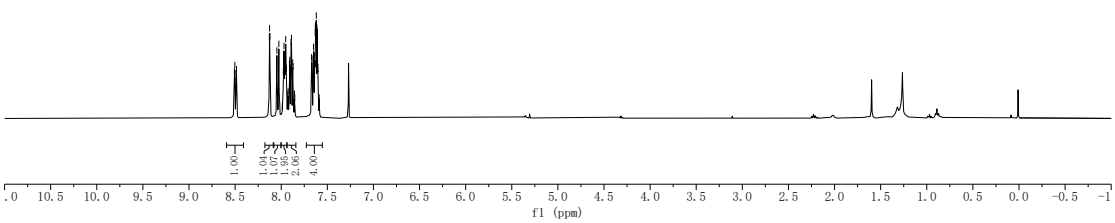
2l

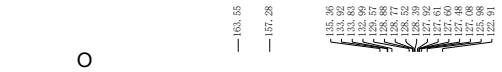
^{13}C NMR (101 MHz, $CDCl_3$)

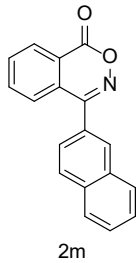


2m

^{1}H NMR (400 MHz, $CDCl_3$)

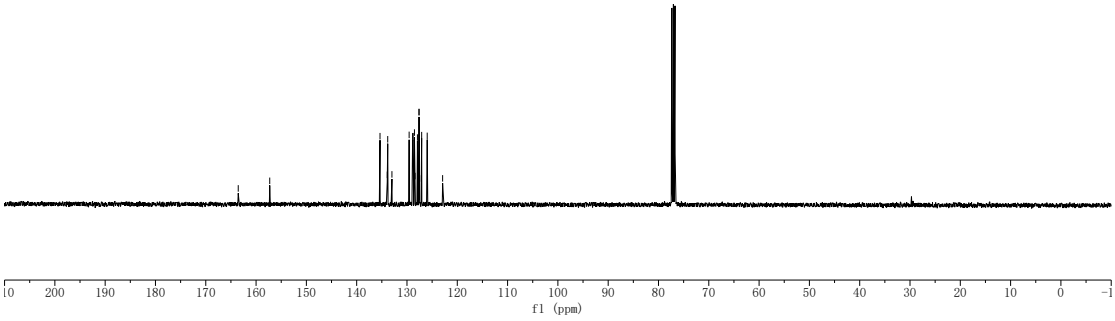


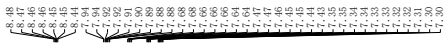


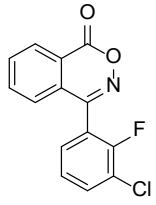


2m

^{13}C NMR (101 MHz, $CDCl_3$)

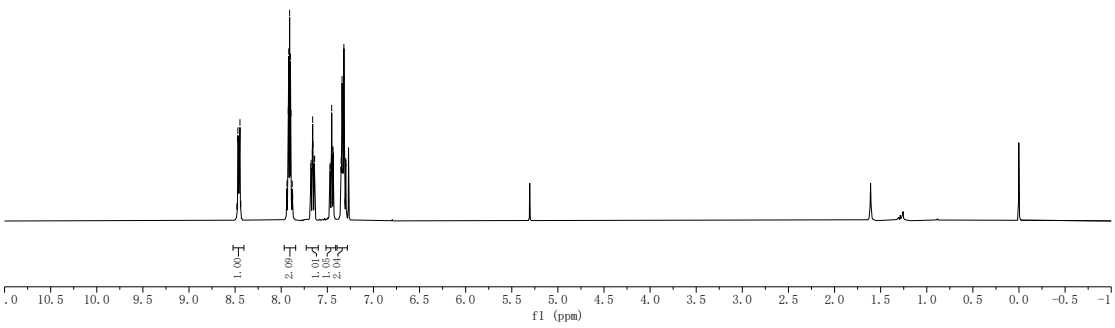


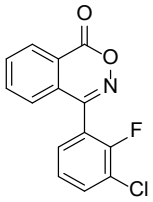




2n

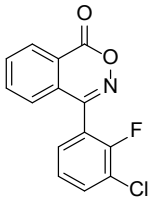
^{1}H NMR (400 MHz, $CDCl_3$)





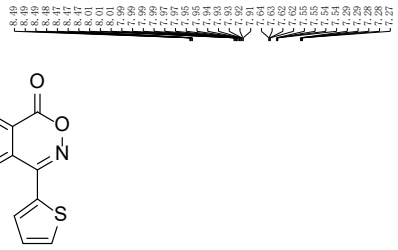
2n

^{13}C NMR (101 MHz, $CDCl_3$)



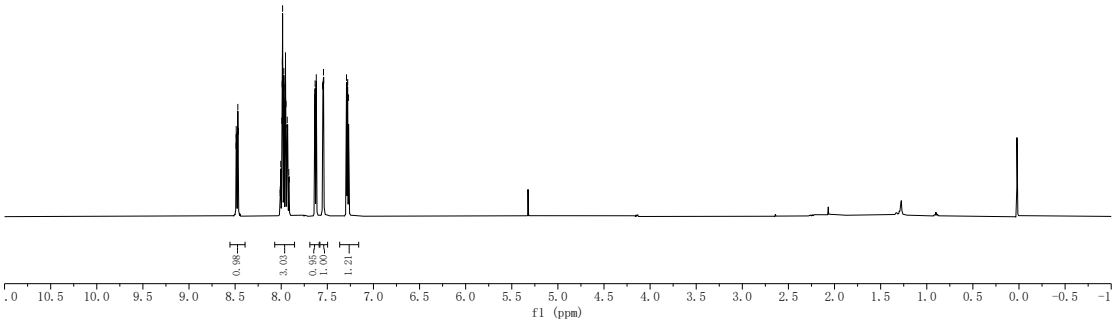
2n

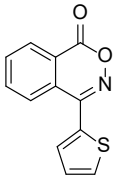
^{19}F NMR (376 MHz, $CDCl_3$)

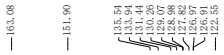


2o

^{1}H NMR (400 MHz, $CDCl_3$)

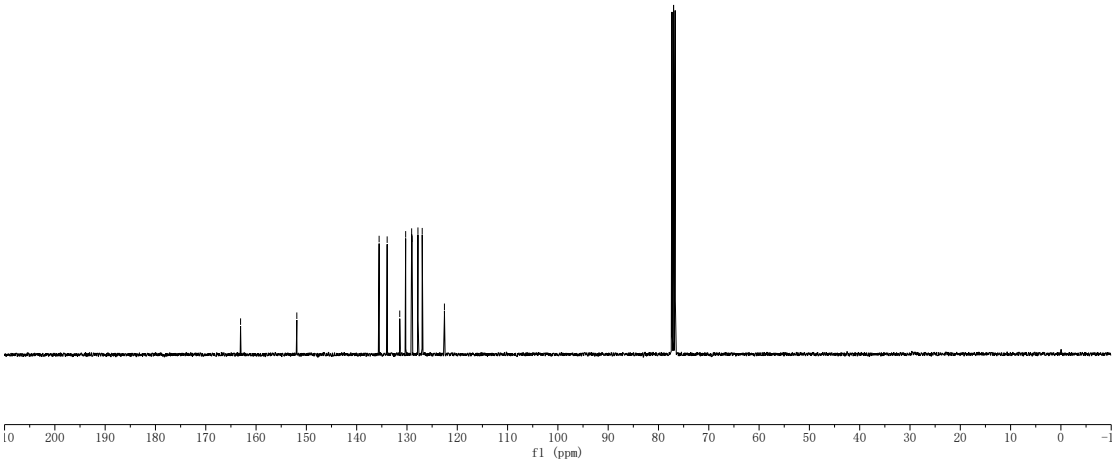


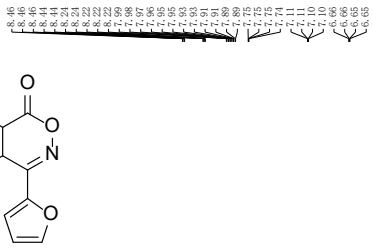




2o

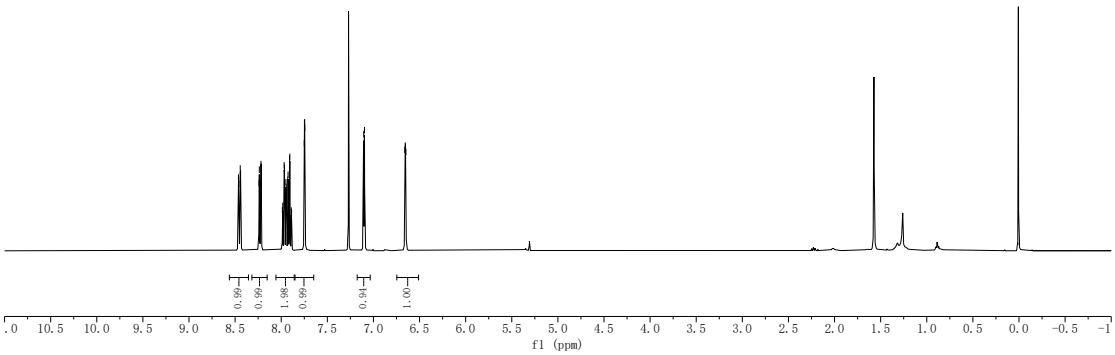
^{13}C NMR (101 MHz, $CDCl_3$)





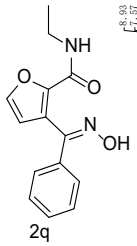
2p

^{1}H NMR (400 MHz, $CDCl_3$)



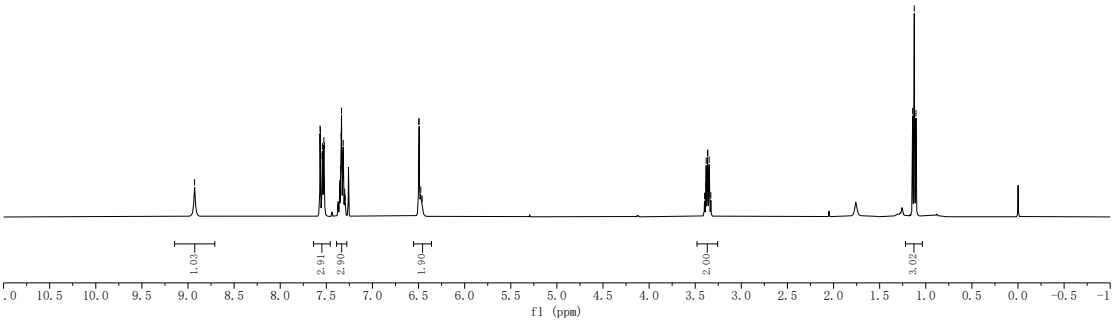
2p

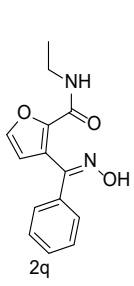
^{13}C NMR (101 MHz, $CDCl_3$)



2q

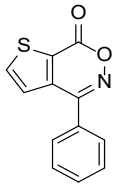
^{1}H NMR (400 MHz, $CDCl_3$)





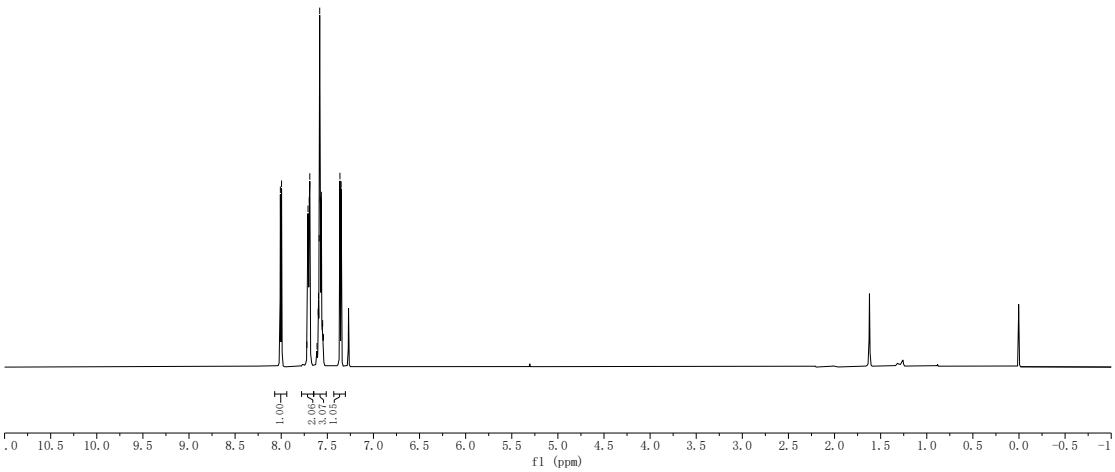
2q

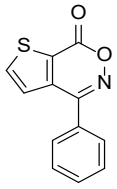
^{13}C NMR (101 MHz, $CDCl_3$)



2r

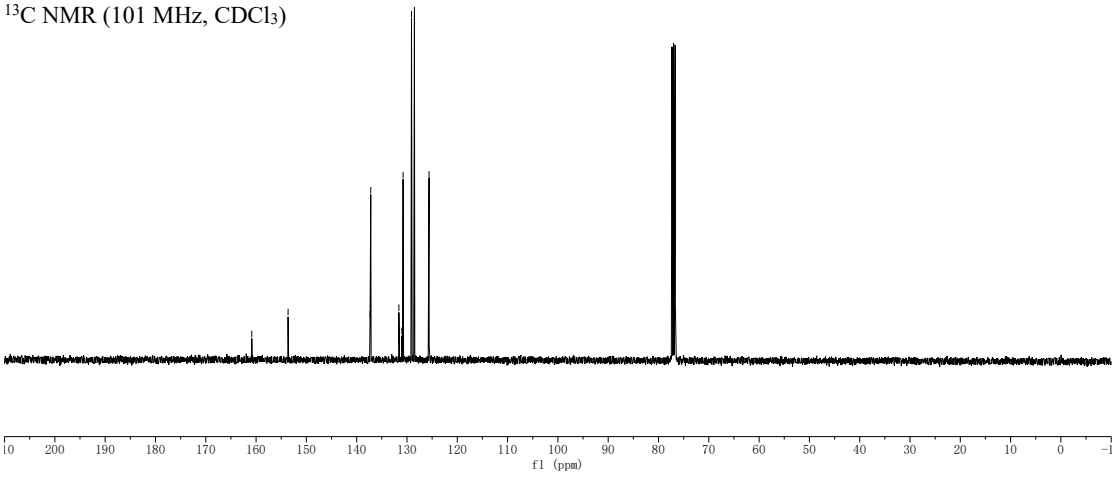
^{1}H NMR (400 MHz, $CDCl_3$)

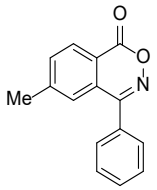




2r

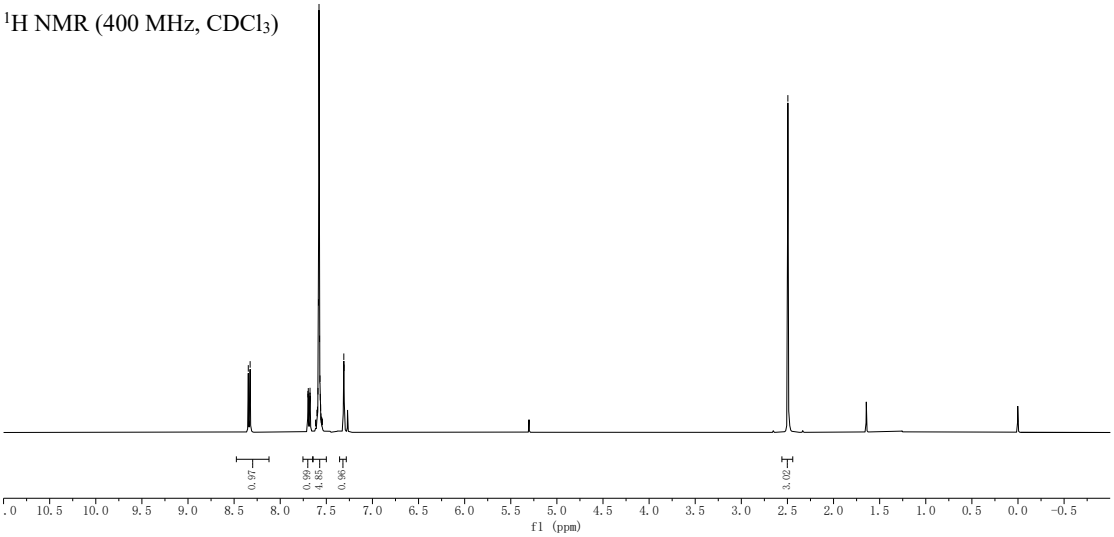
^{13}C NMR (101 MHz, $CDCl_3$)

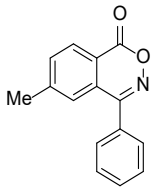




2s

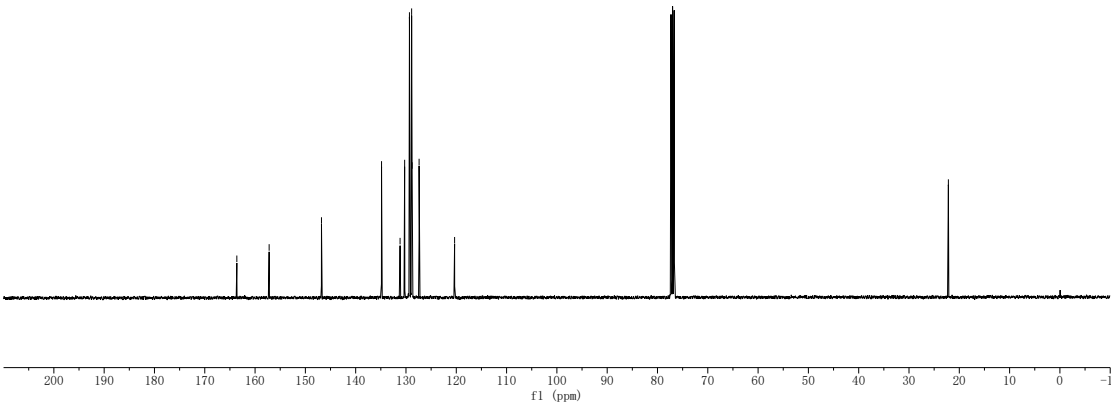
^{1}H NMR (400 MHz, $CDCl_3$)

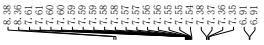


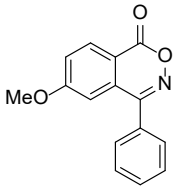


2s

^{13}C NMR (101 MHz, $CDCl_3$)

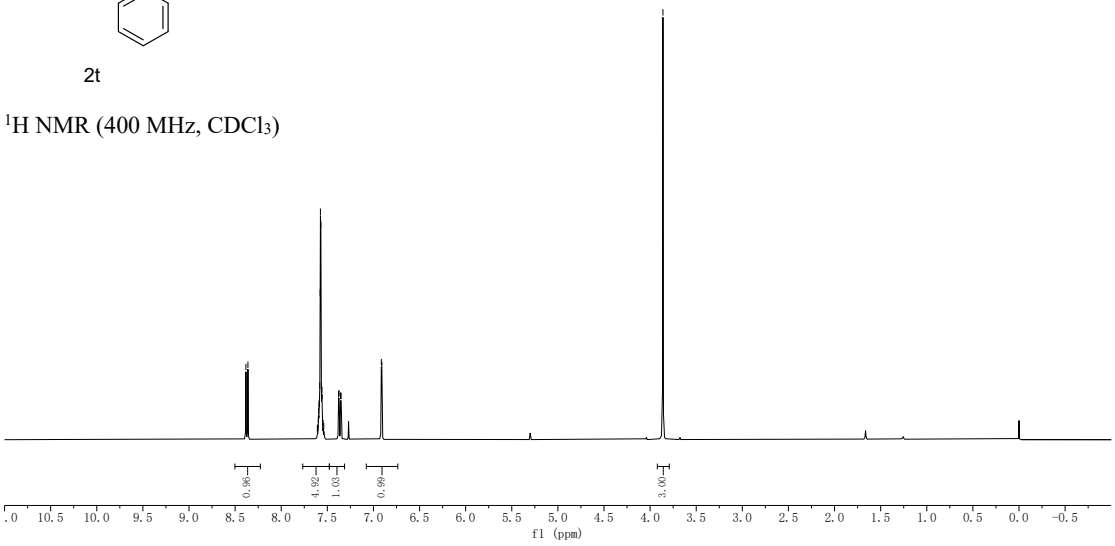


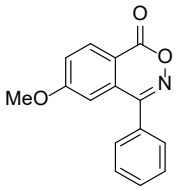


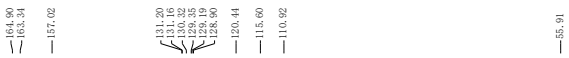


2t

^{1}H NMR (400 MHz, $CDCl_3$)

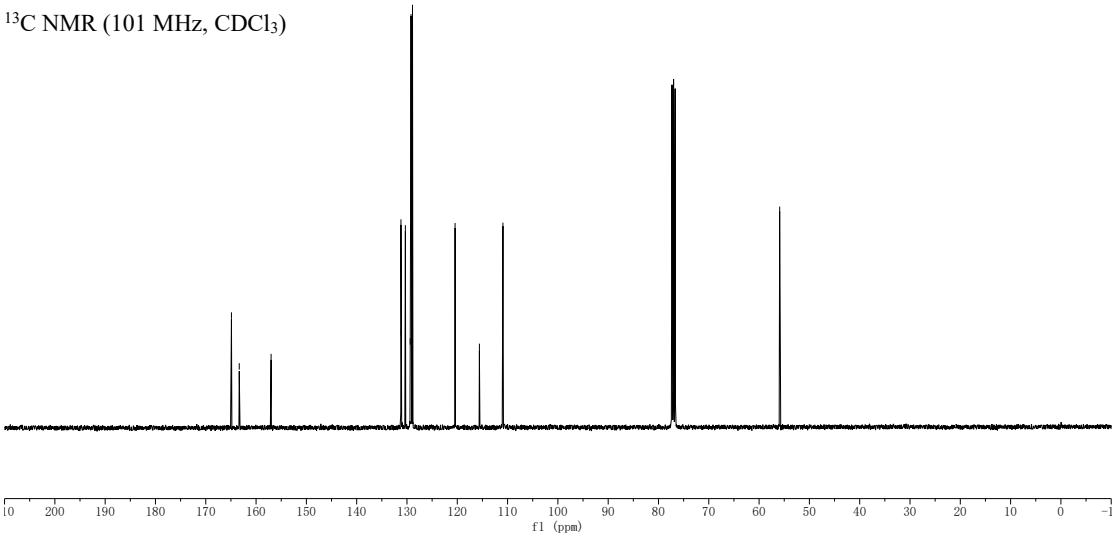


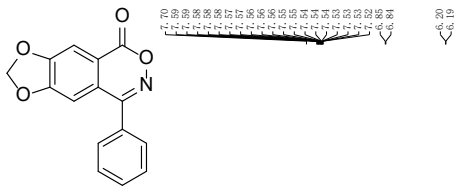




2t

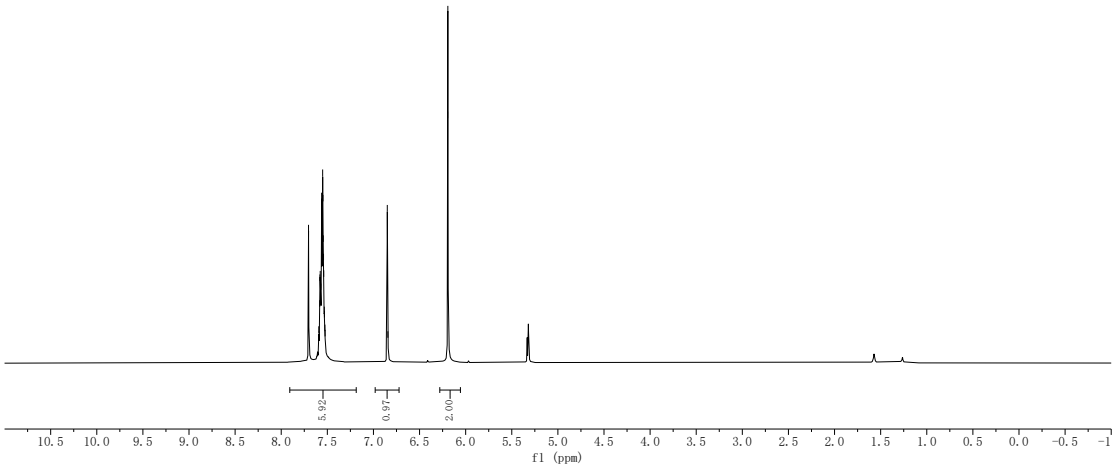
^{13}C NMR (101 MHz, $CDCl_3$)

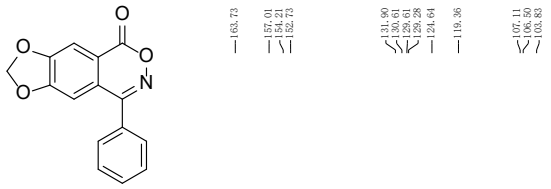




2u

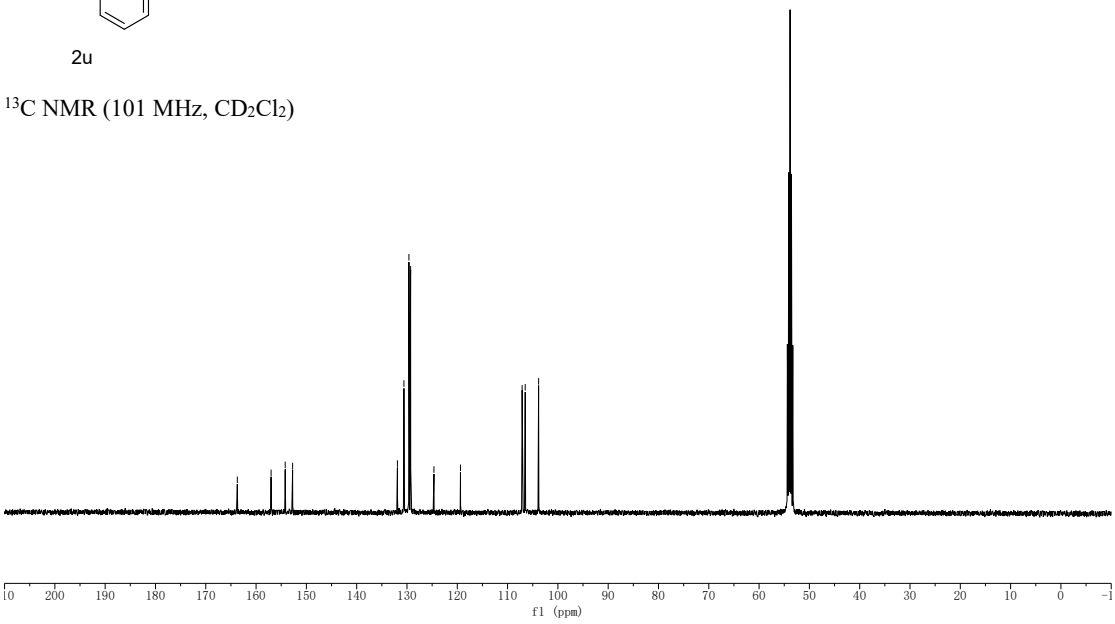
^{1}H NMR (400 MHz, CD_2Cl_2)

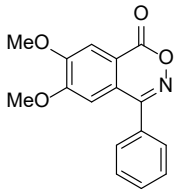




2u

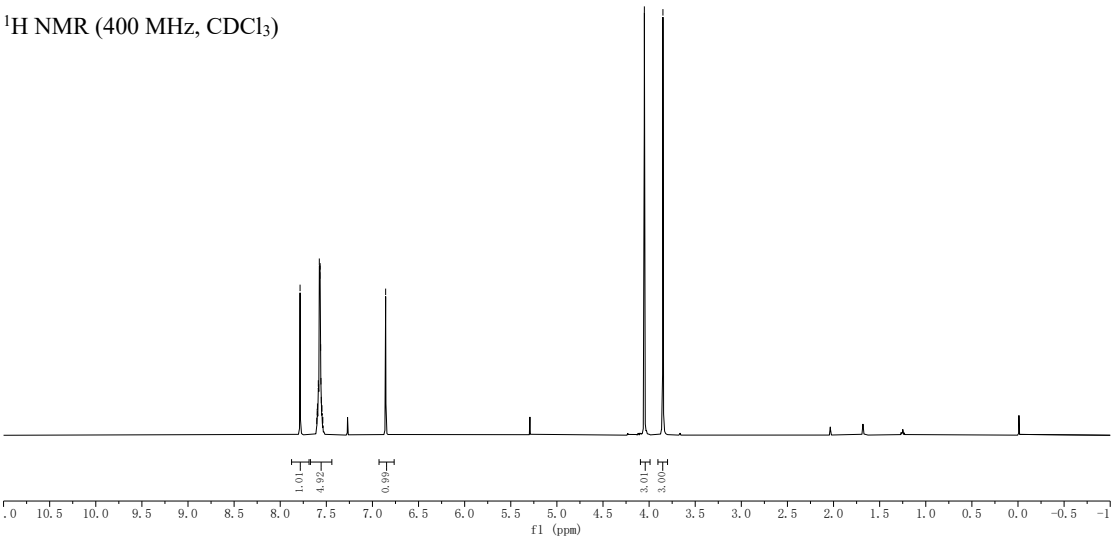
^{13}C NMR (101 MHz, CD_2Cl_2)

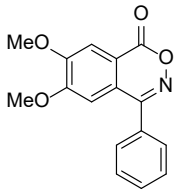




2v

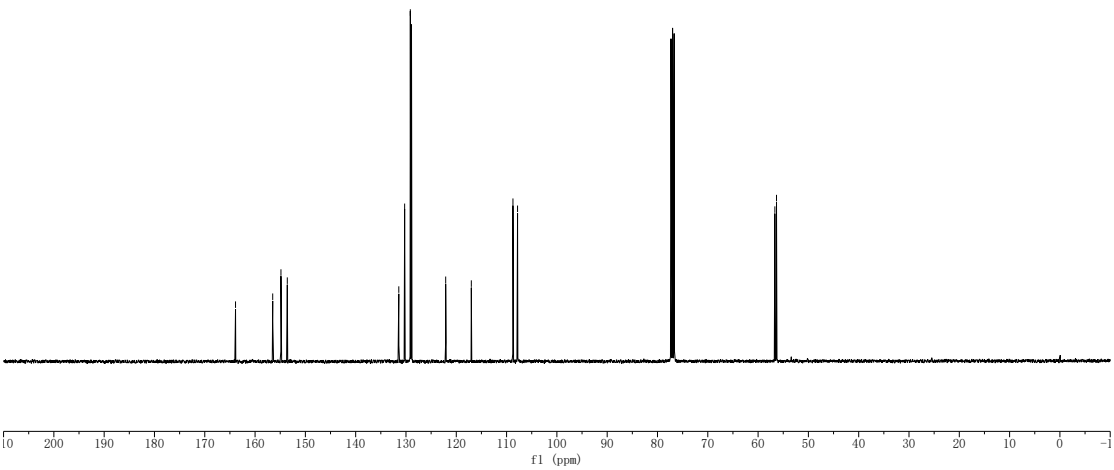
^{1}H NMR (400 MHz, $CDCl_3$)

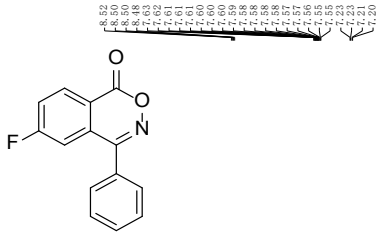




2v

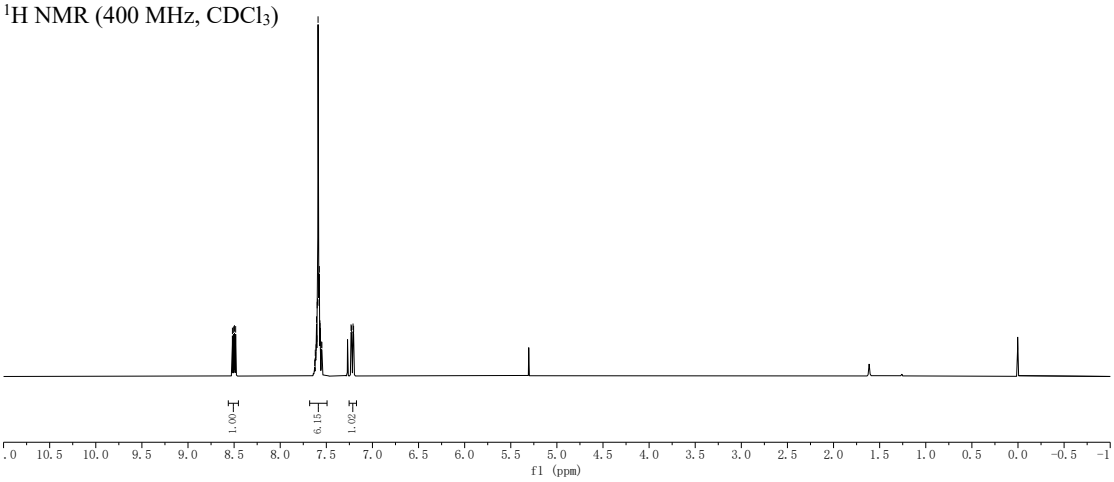
^{13}C NMR (101 MHz, $CDCl_3$)





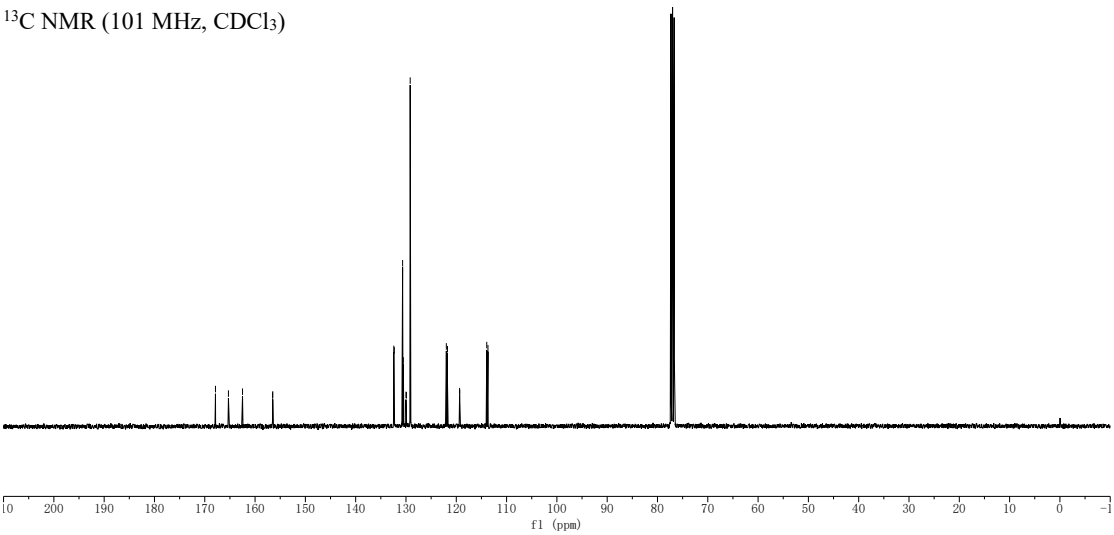
2w

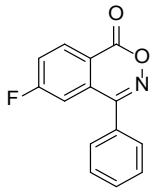
^{1}H NMR (400 MHz, $CDCl_3$)



2w

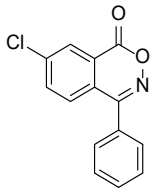
^{13}C NMR (101 MHz, $CDCl_3$)





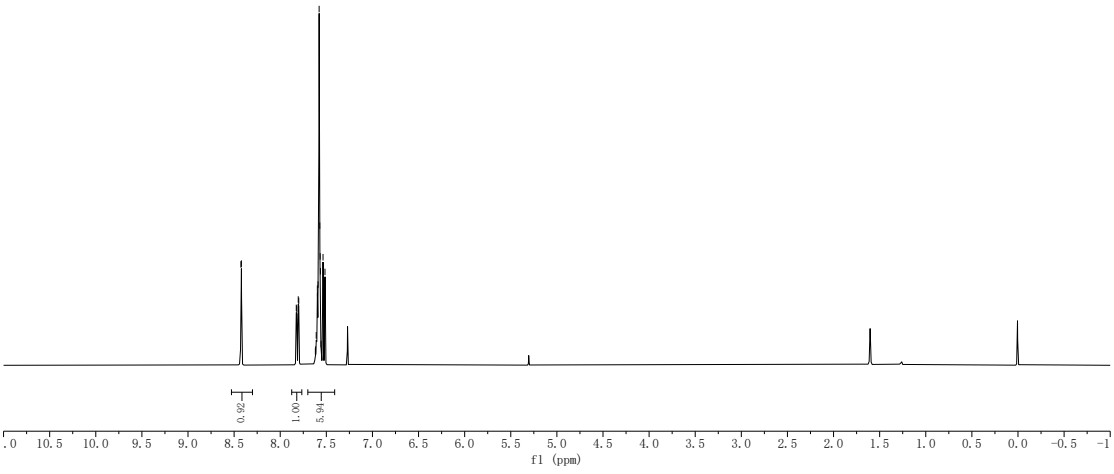
2w

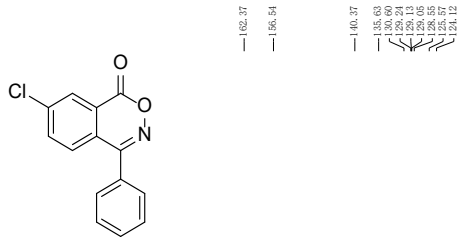
^{19}F NMR (376 MHz, $CDCl_3$)



2x

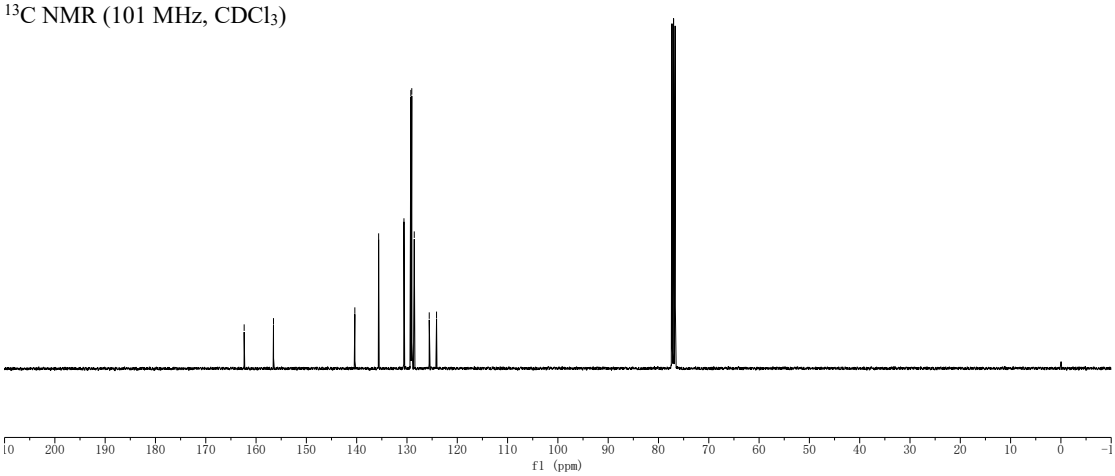
^{1}H NMR (400 MHz, $CDCl_3$)

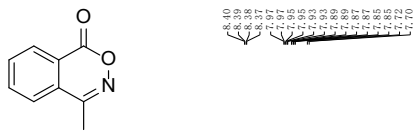




2x

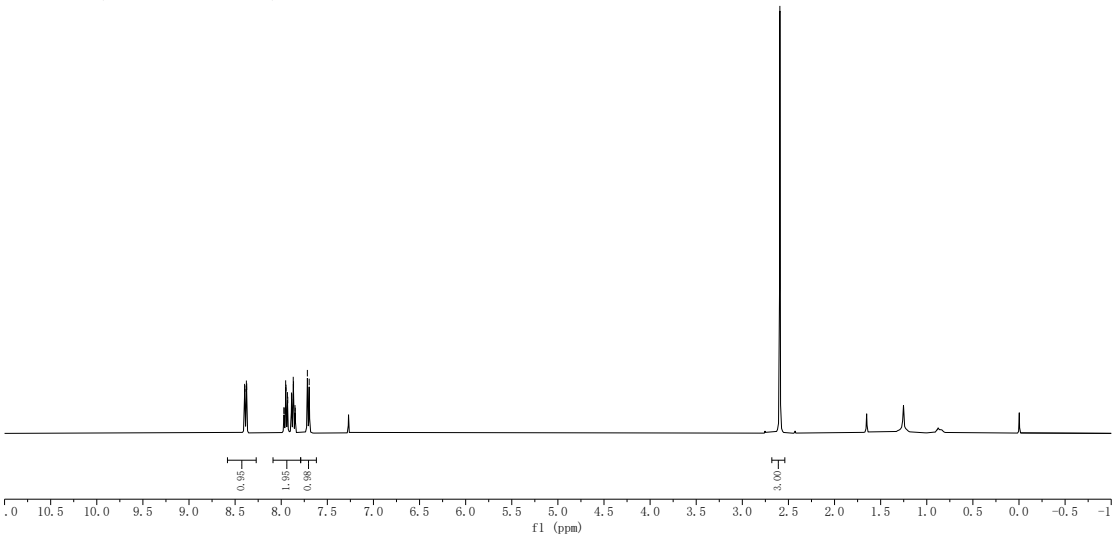
^{13}C NMR (101 MHz, $CDCl_3$)

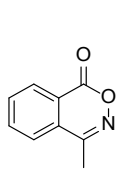




2z

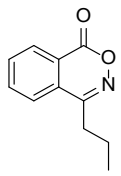
^{1}H NMR (400 MHz, $CDCl_3$)





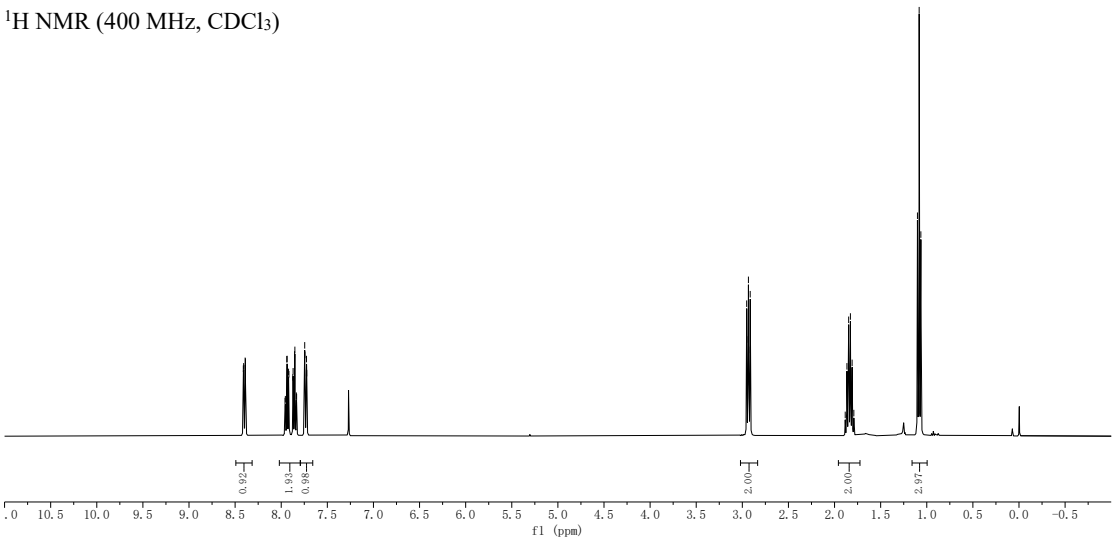
2z

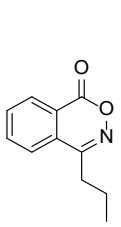
^{13}C NMR (101 MHz, $CDCl_3$)



2aa

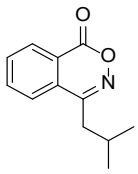
^{1}H NMR (400 MHz, $CDCl_3$)





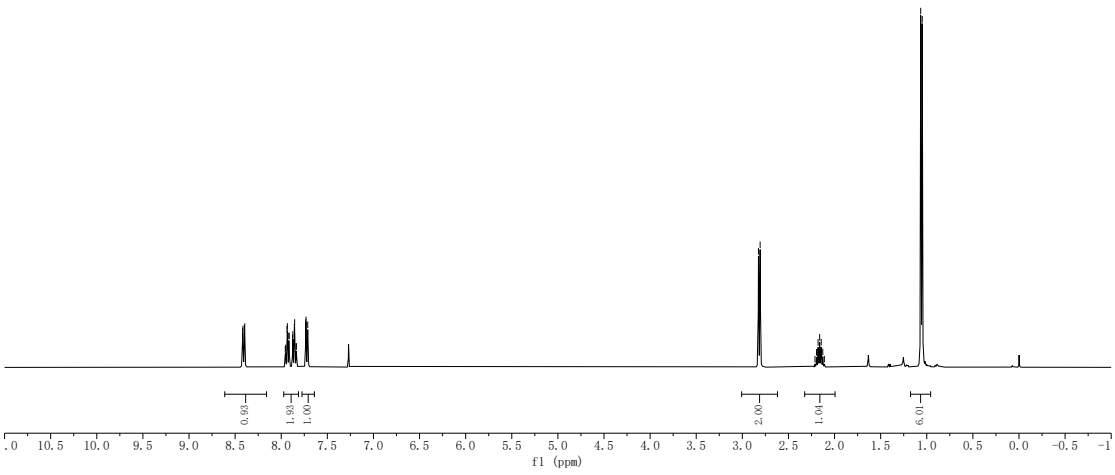
2aa

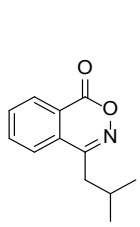
^{13}C NMR (101 MHz, $CDCl_3$)



2ab

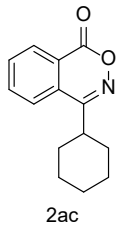
^{1}H NMR (400 MHz, $CDCl_3$)





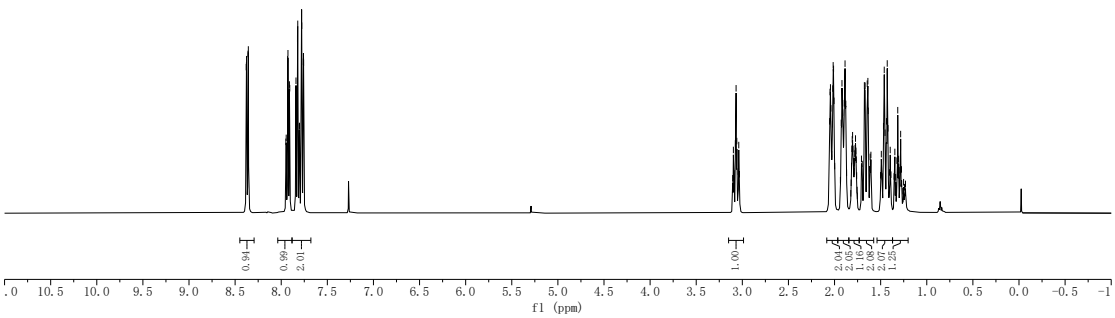
2ab

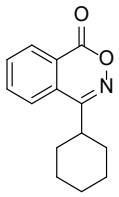
^{13}C NMR (101 MHz, $CDCl_3$)



2ac

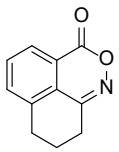
^{1}H NMR (400 MHz, $CDCl_3$)





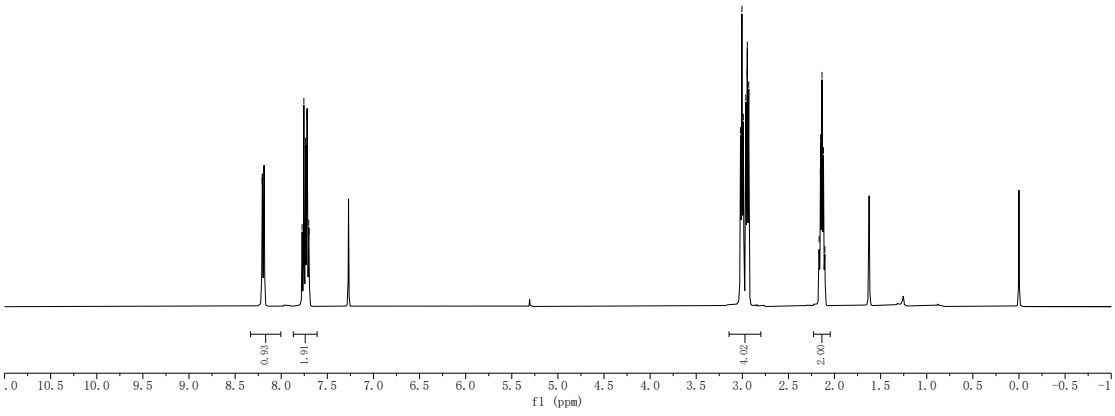
2ac

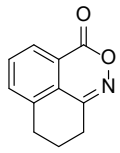
^{13}C NMR (101 MHz, $CDCl_3$)



2ad

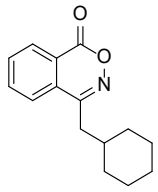
^{1}H NMR (400 MHz, $CDCl_3$)





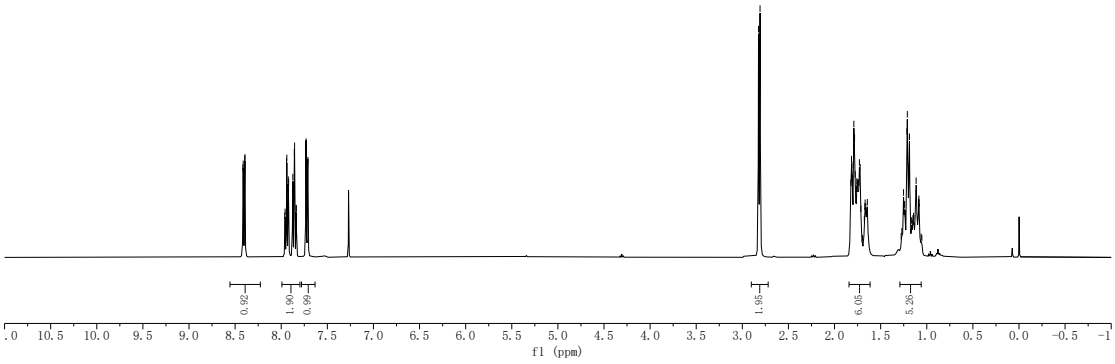
2ad

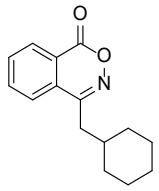
^{13}C NMR (101 MHz, $CDCl_3$)



2ae

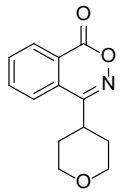
^{1}H NMR (400 MHz, $CDCl_3$)





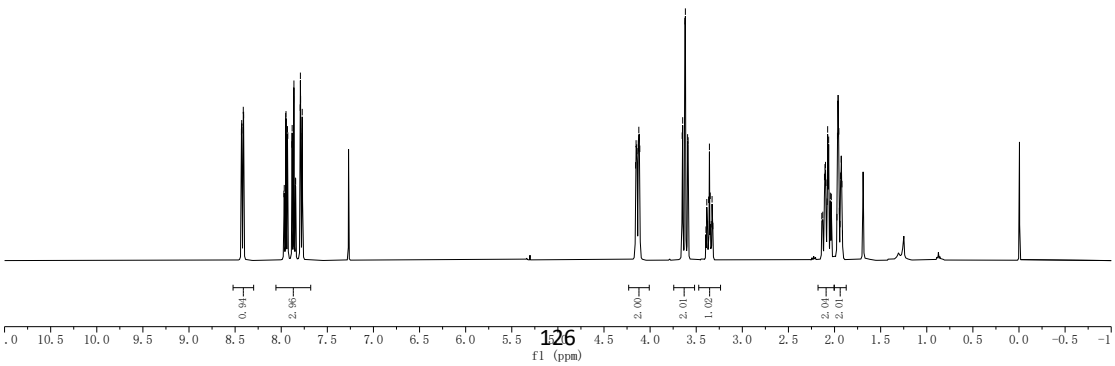
2ae

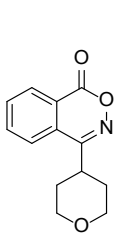
^{13}C NMR (101 MHz, $CDCl_3$)



2af

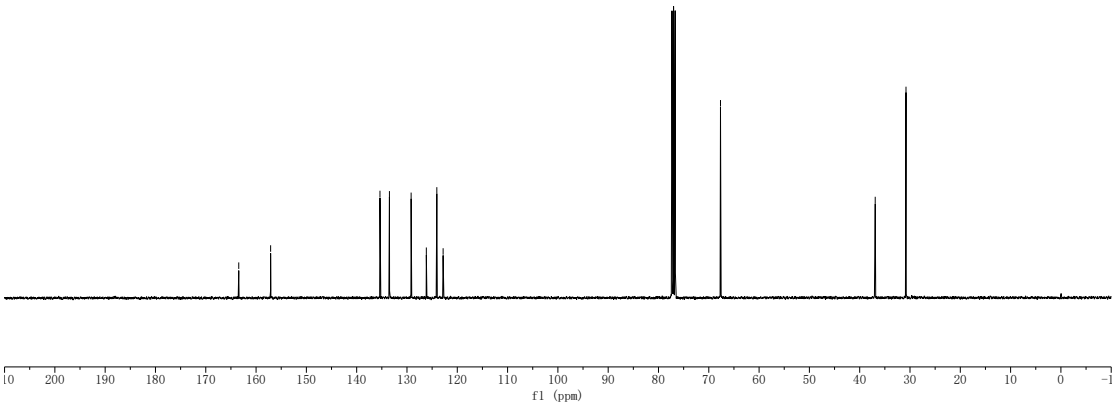
^{1}H NMR (400 MHz, $CDCl_3$)

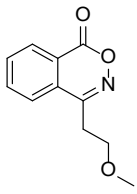




2af

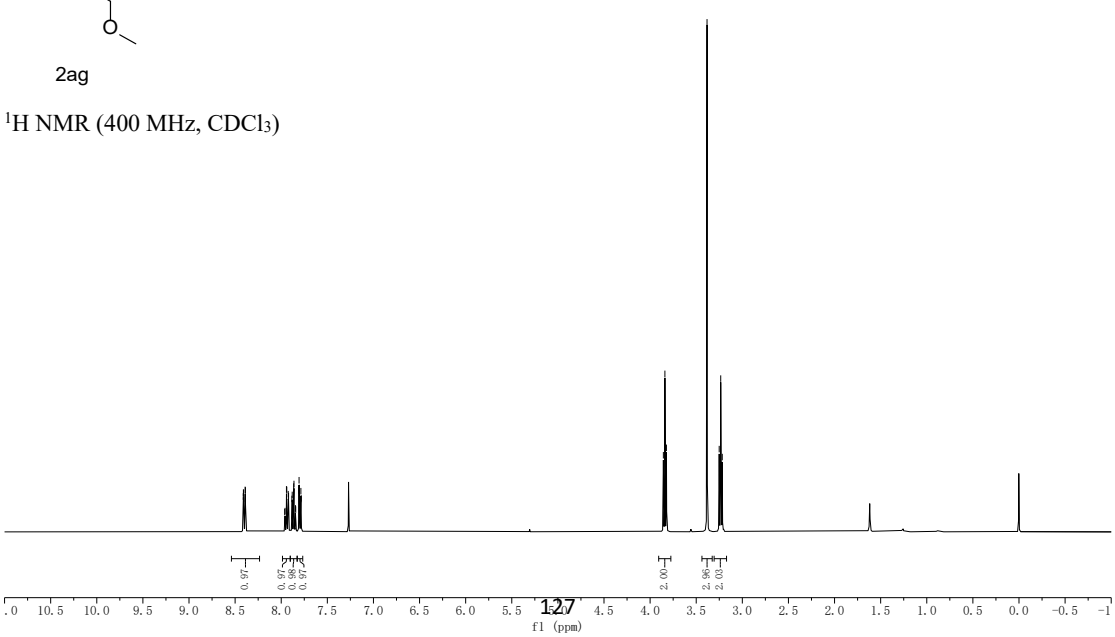
^{13}C NMR (101 MHz, $CDCl_3$)

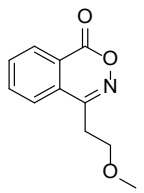




2ag

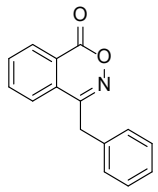
^{1}H NMR (400 MHz, $CDCl_3$)





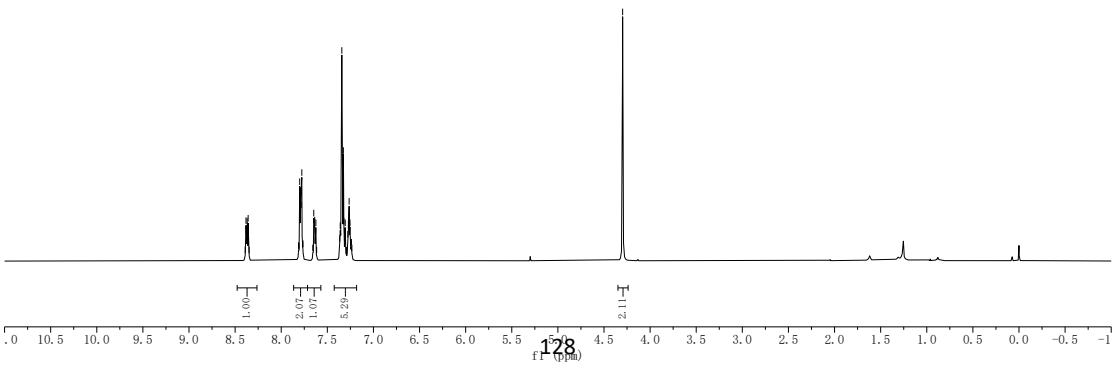
2ag

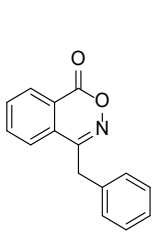
^{13}C NMR (101 MHz, $CDCl_3$)



2ah

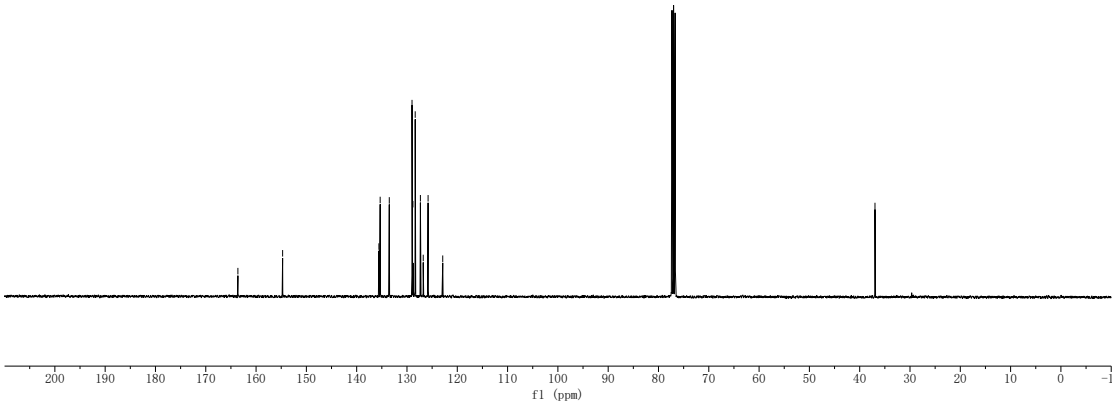
^{1}H NMR (400 MHz, $CDCl_3$)

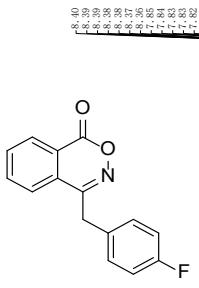




2ah

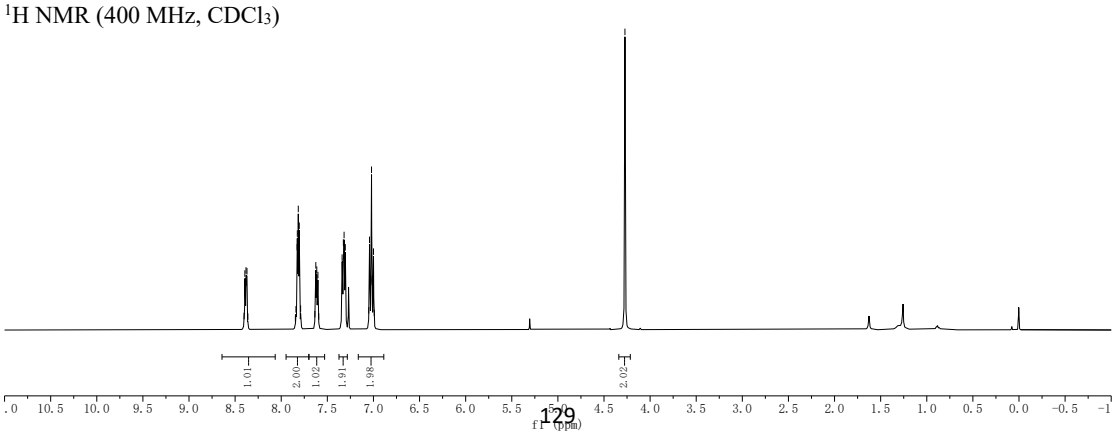
^{13}C NMR (101 MHz, $CDCl_3$)

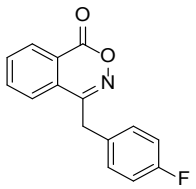




2ai

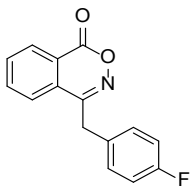
^{1}H NMR (400 MHz, $CDCl_3$)





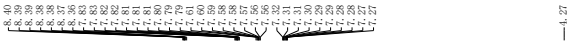
2ai

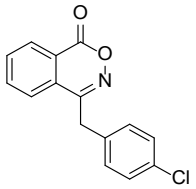
^{13}C NMR (101 MHz, $CDCl_3$)



2ai

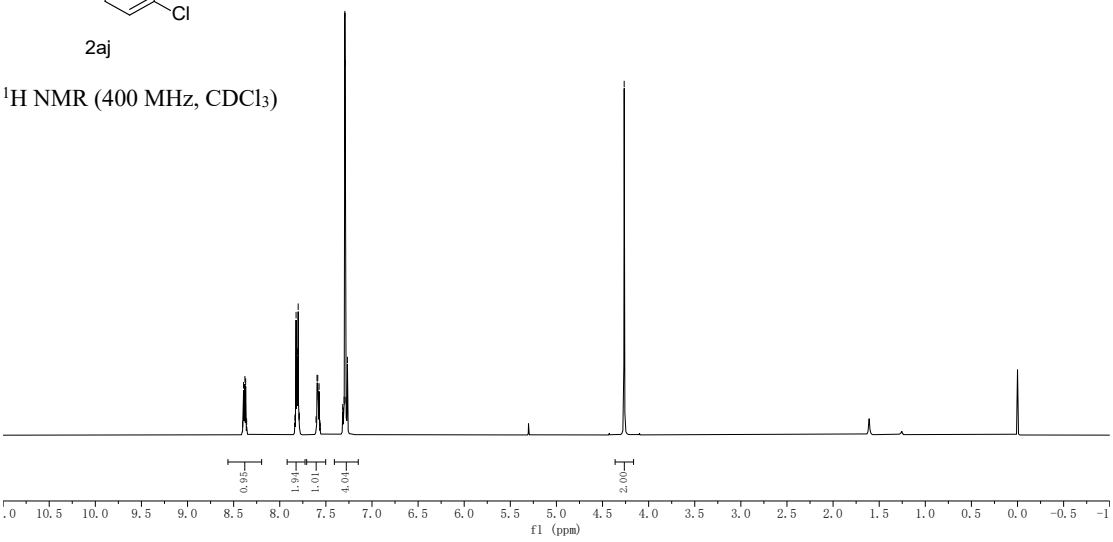
^{19}F NMR (376 MHz, $CDCl_3$)

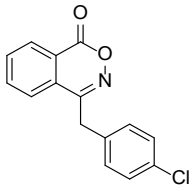




2aj

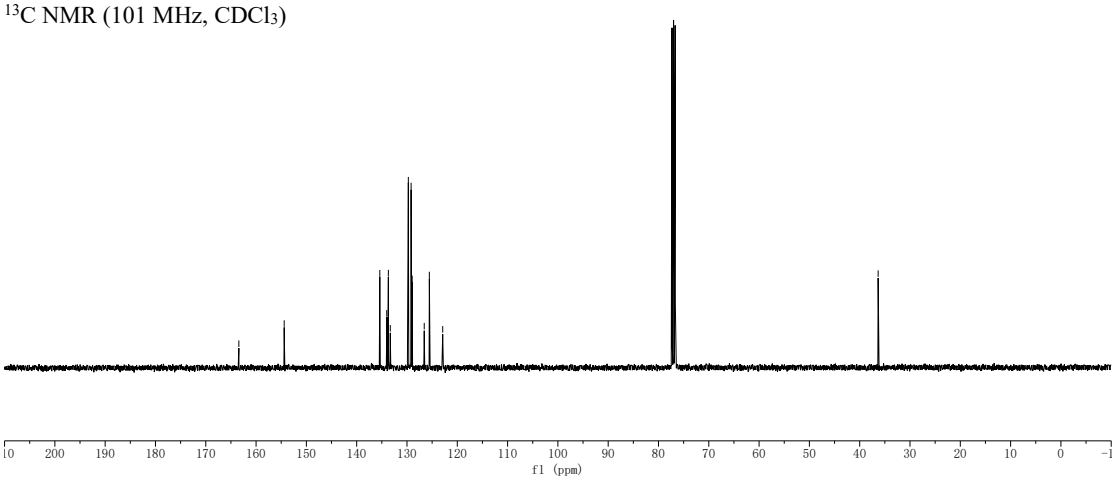
^{1}H NMR (400 MHz, $CDCl_3$)

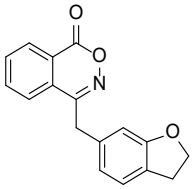




2aj

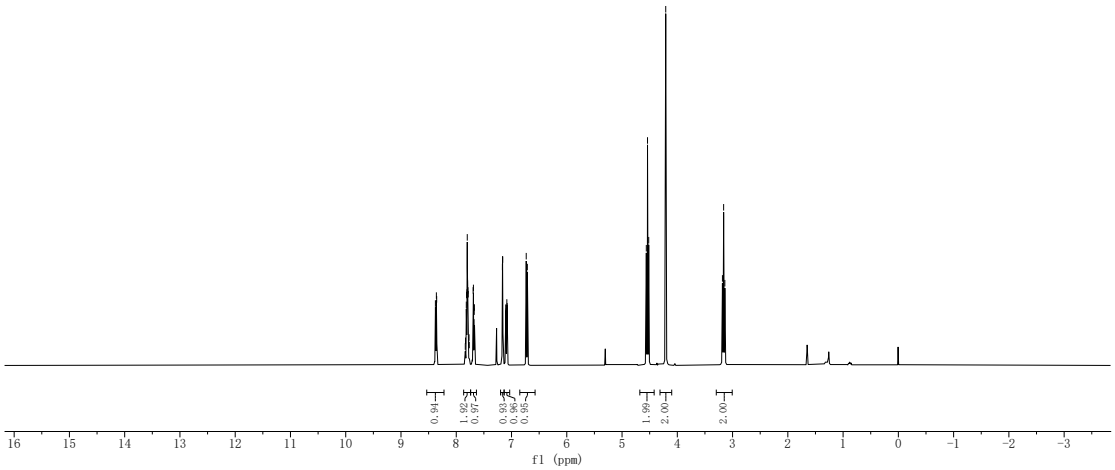
^{13}C NMR (101 MHz, $CDCl_3$)

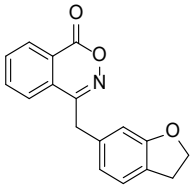




2ak

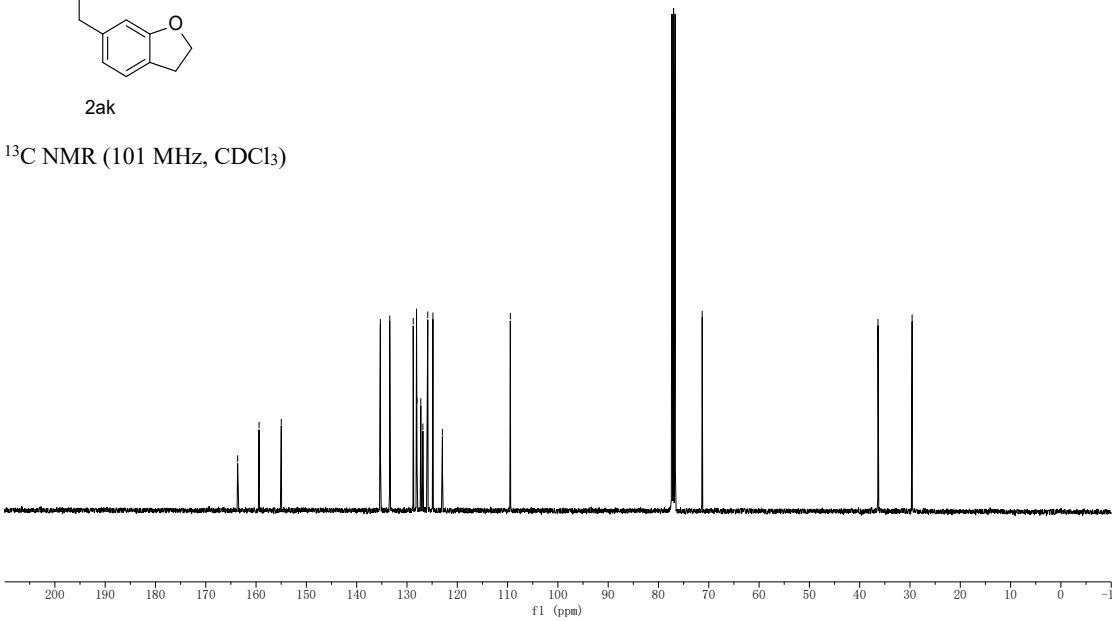
^{1}H NMR (400 MHz, $CDCl_3$)

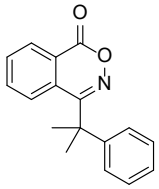




2ak

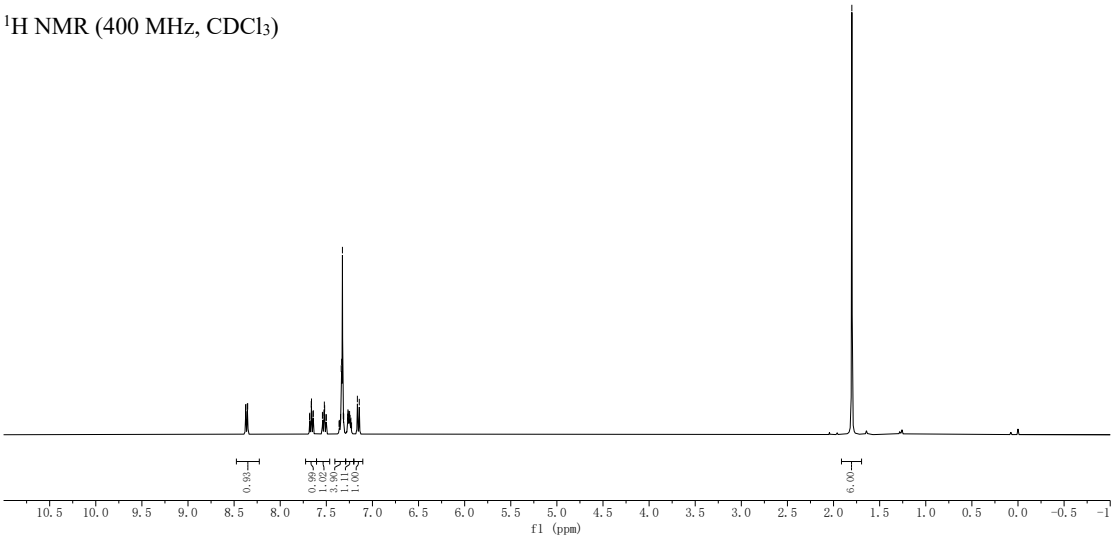
^{13}C NMR (101 MHz, $CDCl_3$)

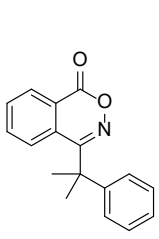




2al

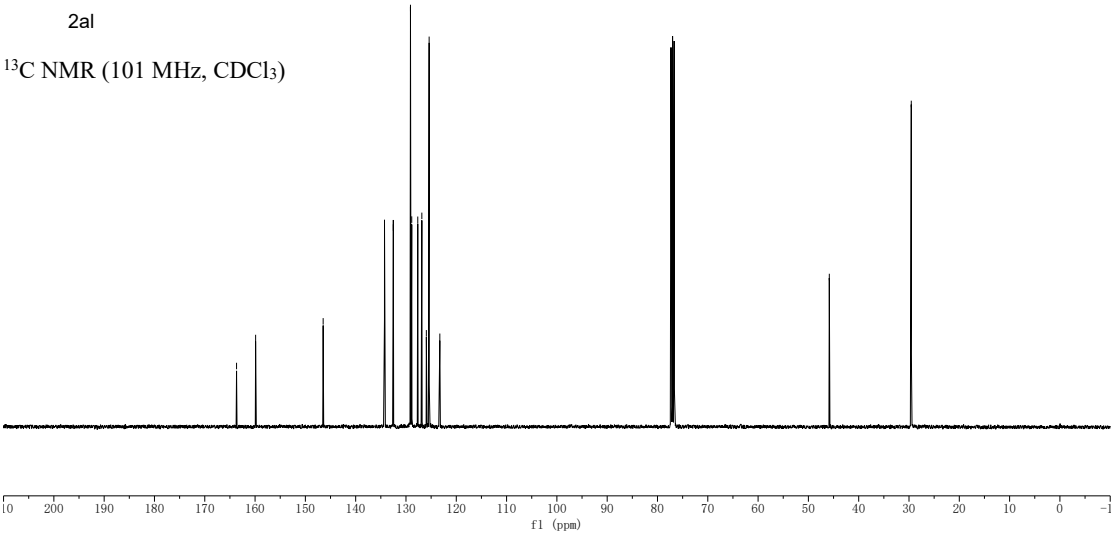
^{1}H NMR (400 MHz, $CDCl_3$)

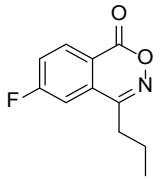




2al

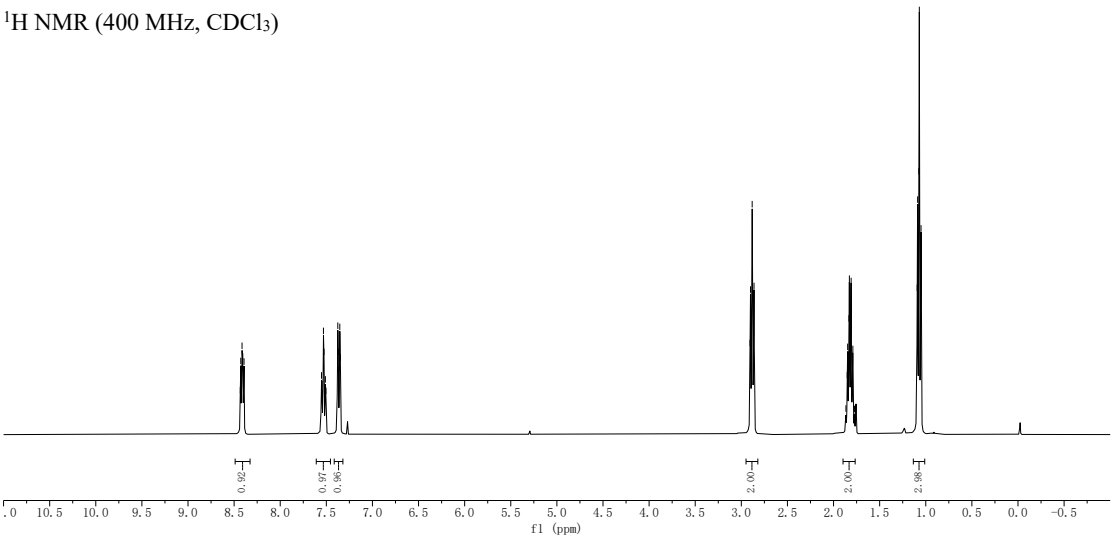
^{13}C NMR (101 MHz, $CDCl_3$)

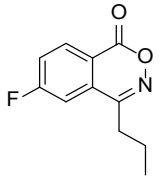




2am

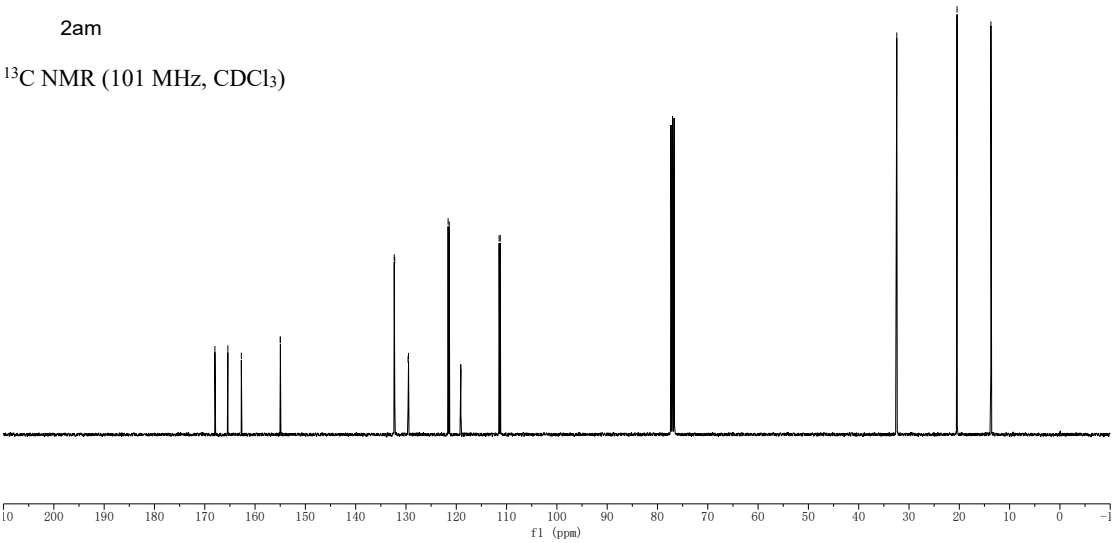
^{1}H NMR (400 MHz, $CDCl_3$)

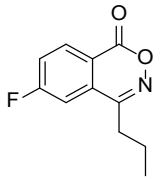




2am

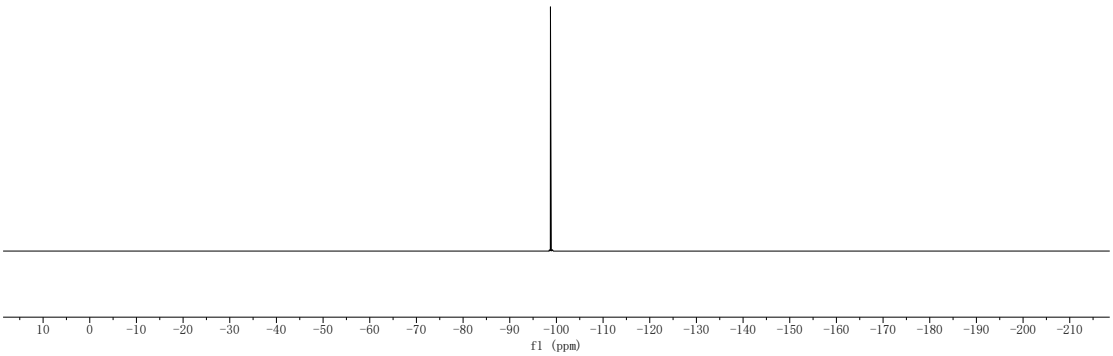
^{13}C NMR (101 MHz, $CDCl_3$)

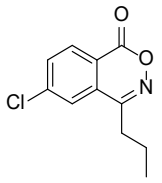




2am

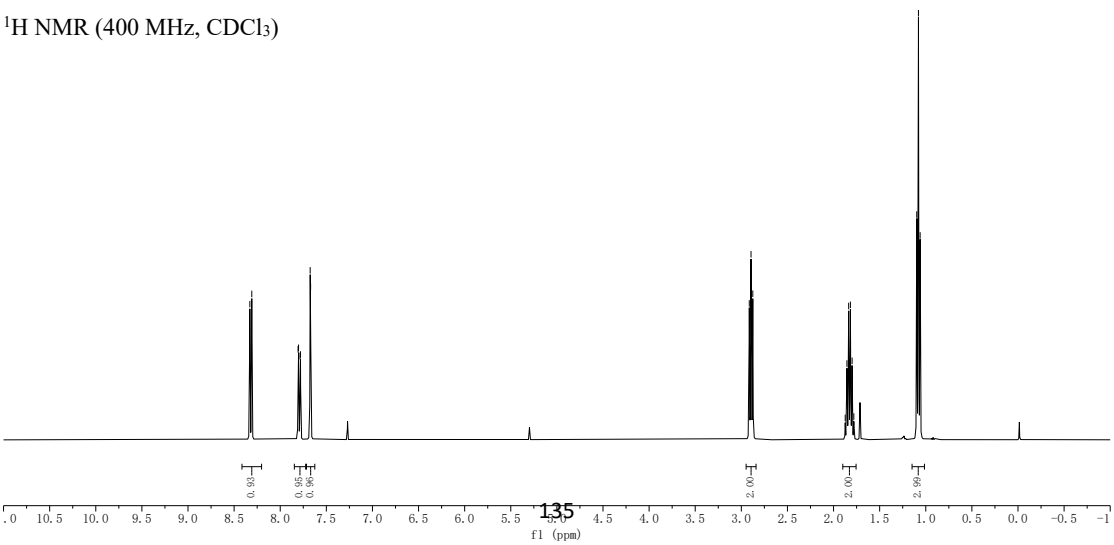
^{19}F NMR (376 MHz, $CDCl_3$)

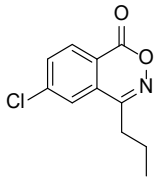




2an

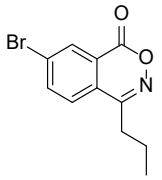
^{1}H NMR (400 MHz, $CDCl_3$)





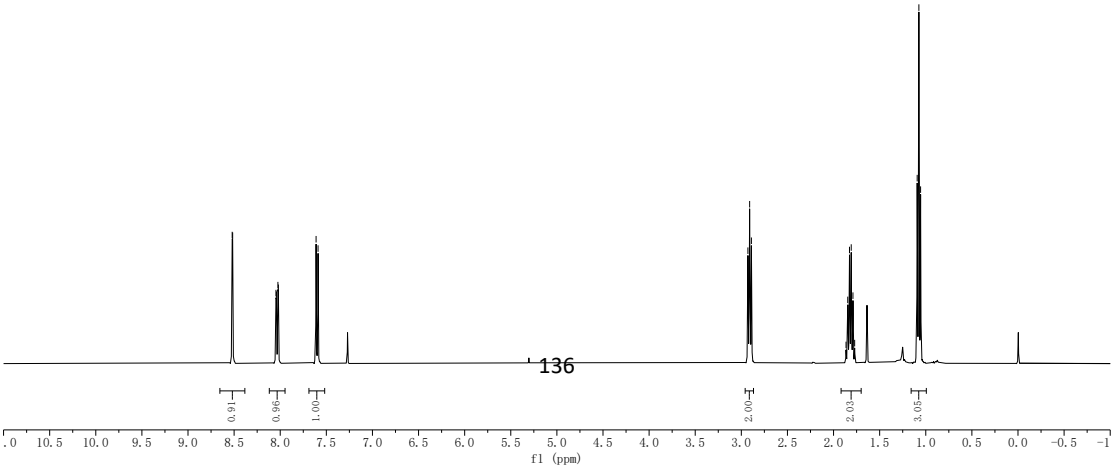
2an

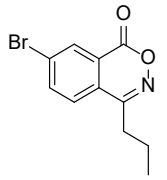
^{13}C NMR (101 MHz, $CDCl_3$)



2ao

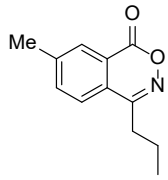
^{1}H NMR (400 MHz, $CDCl_3$)





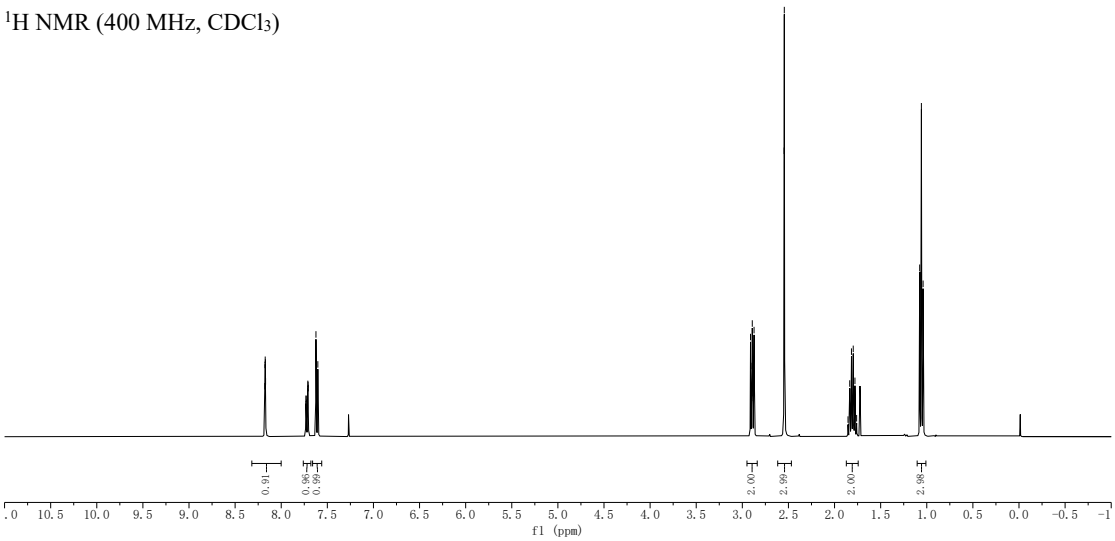
2ao

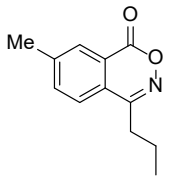
^{13}C NMR (101 MHz, $CDCl_3$)



2ap

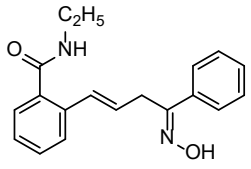
^{1}H NMR (400 MHz, $CDCl_3$)





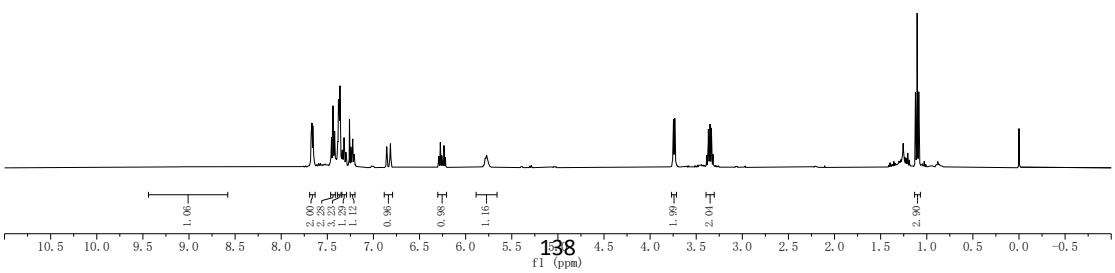
2ap

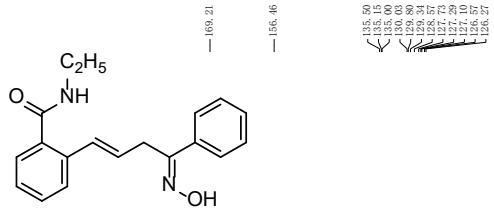
^{13}C NMR (101 MHz, $CDCl_3$)



2aq

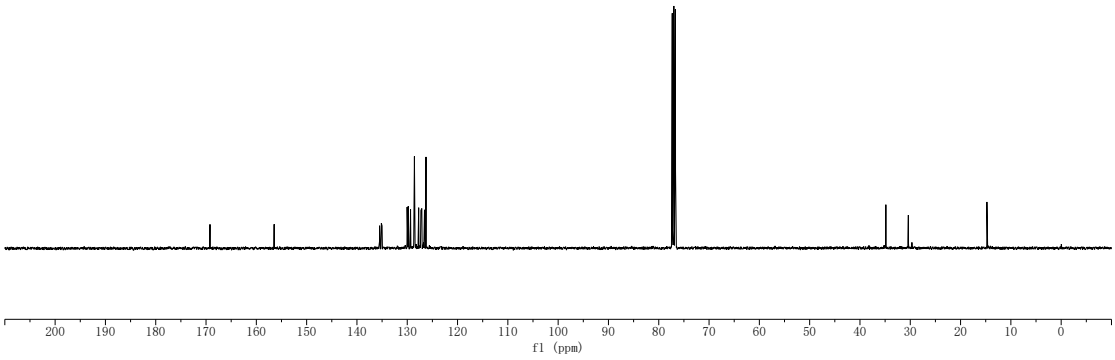
^{1}H NMR (400 MHz, $CDCl_3$)

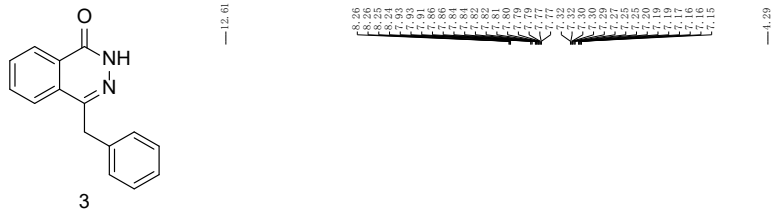




2aq

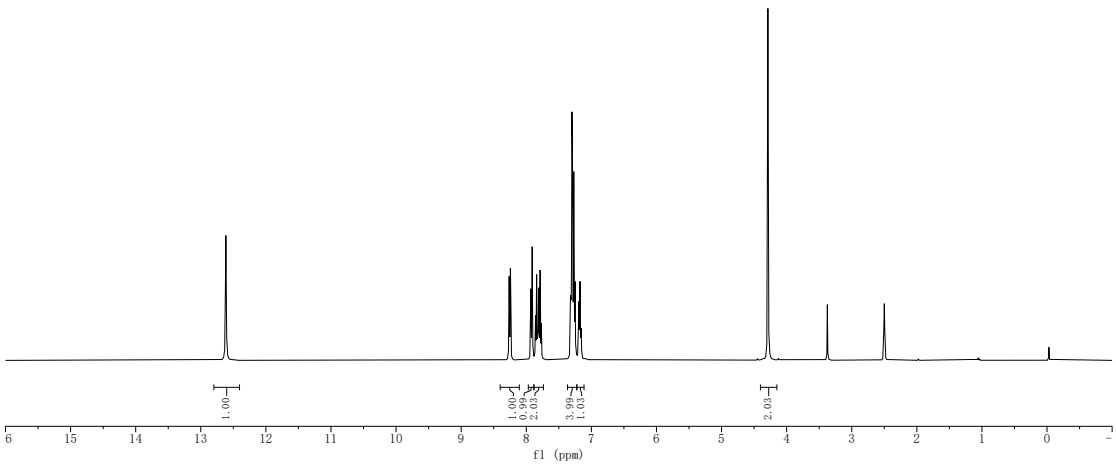
^{13}C NMR (101 MHz, $CDCl_3$)

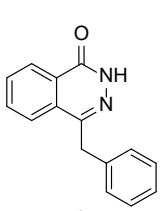




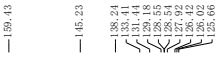
3

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

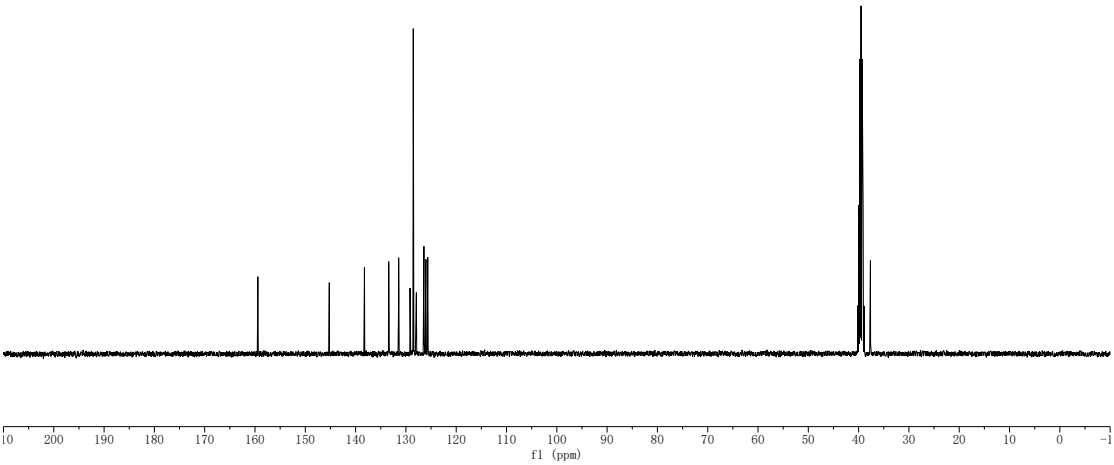


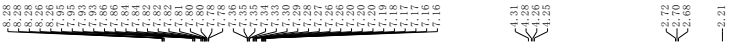


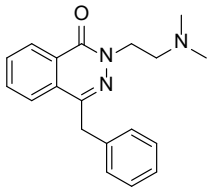
3



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

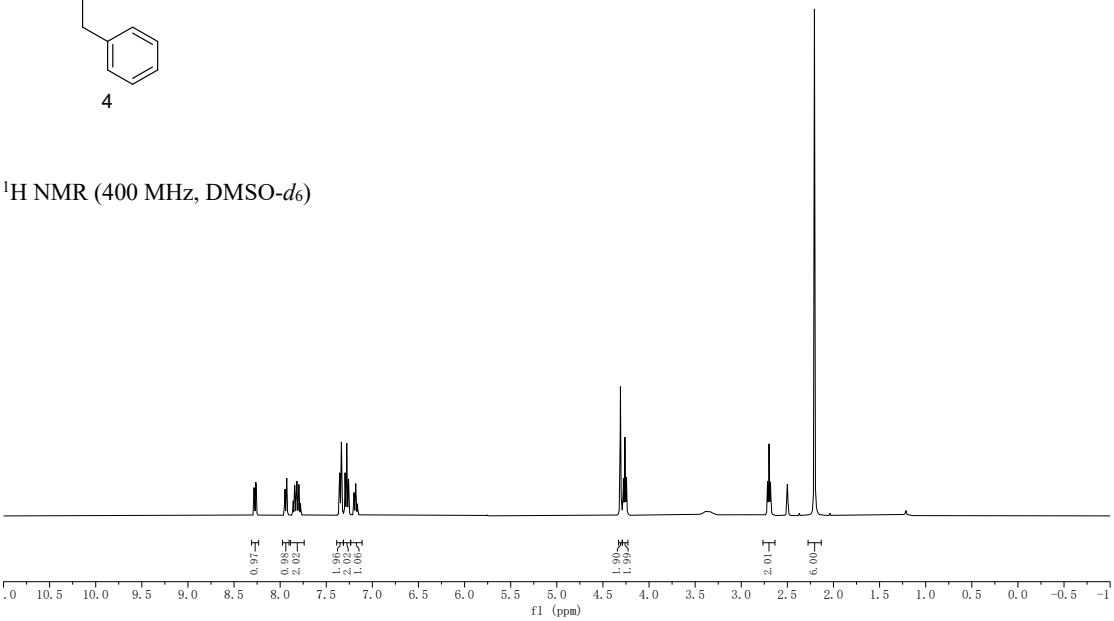


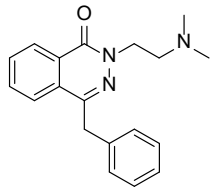




4

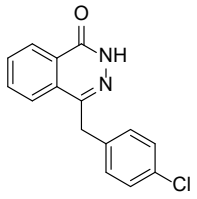
^{1}H NMR (400 MHz, DMSO-d_6)





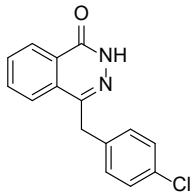
4

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



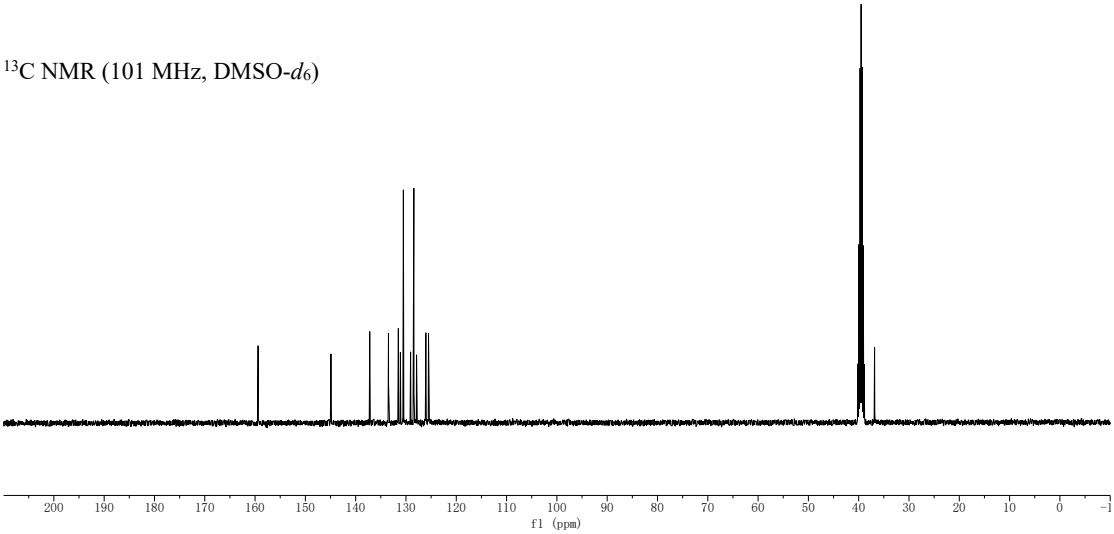
5

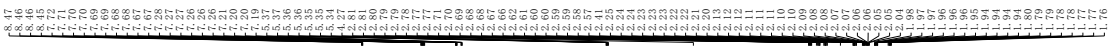
^{1}H NMR (400 MHz, DMSO-d_6)

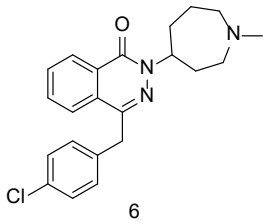


5

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

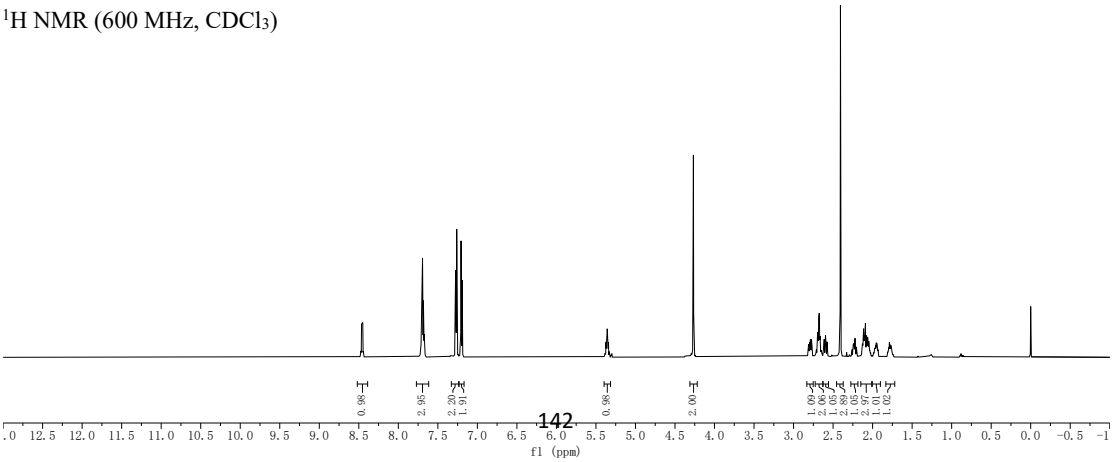


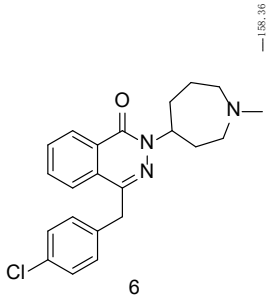




6

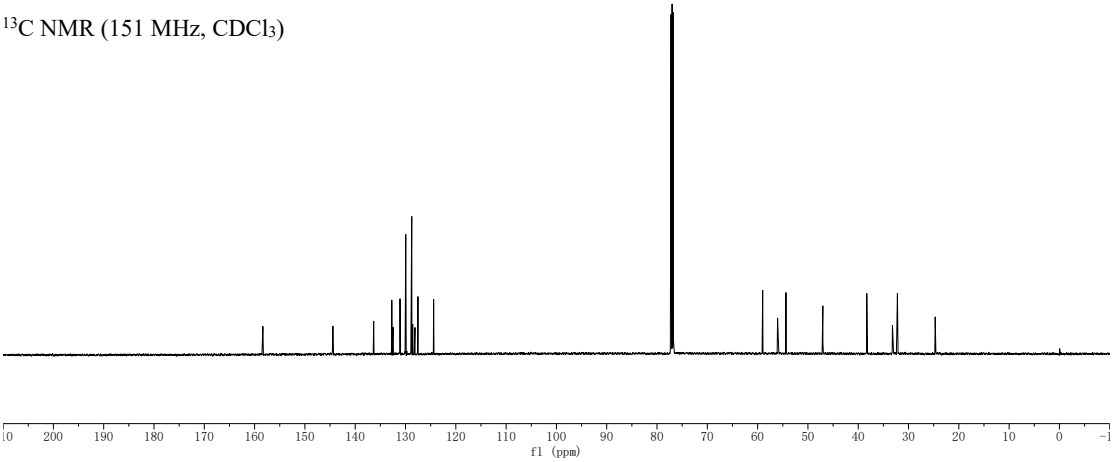
^{1}H NMR (600 MHz, $CDCl_3$)

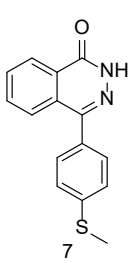




6

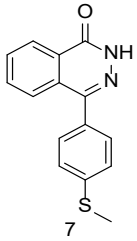
^{13}C NMR (151 MHz, $CDCl_3$)





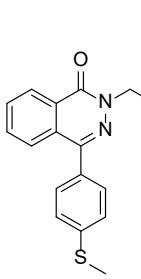
7

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



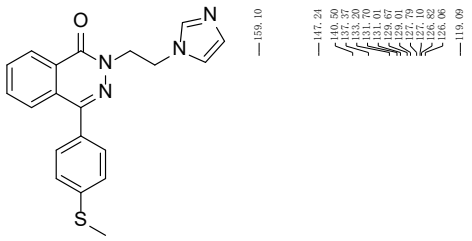
7

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



8

^{1}H NMR (400 MHz, $CDCl_3$)



8

^{13}C NMR (101 MHz, $CDCl_3$)