Supplementary Information

Transition-metal-free Photochemical Reductive Denitration of Nitroarenes

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1. General information

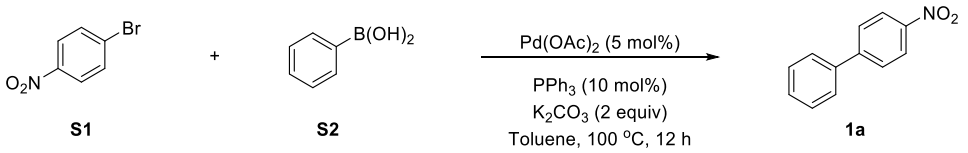
Unless otherwise specified, all materials were sourced from commercial suppliers and used without further purification. Eosin Y Disodium Salt and ^{t}BuONO were purchased from Bide (Shanghai, China), while ^{i}PrOH, D$_9$-^{i}PrOH (99% D) and B_2pin_2 were obtained from Energy Chemical (Shanghai, China). All reactions were conducted under a nitrogen atmosphere (99.999%) using dried glassware and standard Schlenk techniques. Unless otherwise noted, all reactions were performed in a 10-mL Schlenk tube (with a Teflon high-pressure valve and sidearm) and all work-up and purification procedures were carried out with reagent-grade solvents in the air.

Analytical thin-layer chromatography (TLC) was performed using Leyan plates (Shanghai Haohong Scientific Co., Ltd., China), with visualization under UV light (254 nm). Flash column chromatography was conducted with silica gel (200–300 mesh). Gas chromatography (GC) analysis was carried out using a Shimadzu GC-2030 instrument with an Rtx-1 column (30 m × 0.25 mm, Dell). GCMS analysis was performed on a Shimadzu GCMS-QP2010 instrument equipped with an Rtx-5MS column (30 m × 0.25 mm, Dell). Nuclear magnetic resonance (NMR) spectra were recorded on Bruker Advance III spectrometers (400 MHz) using tetramethylsilane as the internal standard. For ^{1}H NMR, chemical shifts are reported in parts per million (ppm) relative to the residual peak of $CDCl_3$ (δ 7.26 ppm), and for ^{13}C NMR, relative to $CDCl_3$ (δ 77.16 ppm). Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, m = multiplet, dt = doublet of triplets, td = triplet of doublets, q = quartet, v = virtual coupling, br = broad signal), coupling constant (Hz), and integration. High-resolution mass spectra (HRMS) were obtained on a Thermo Fisher LTQ Orbitrap LCMS system using electrospray ionization (ESI).

2. Synthesis of starting materials

All nitroarenes, except for **1a** and **1b**, were obtained from commercial sources.

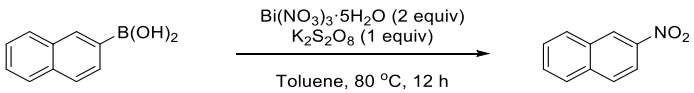
a) Synthesis of **1a**



S1 **S2** **1a**

Compound **1a** was synthesized following the procedure reported in the literature[1]. In an oven-dried Schlenk tube equipped with a stirring bar, **S1** (10 mmol, 2.0200 g), **S2** (12 mmol, 1.4630 g), $Pd(OAc)_2$ (5 mol%, 112.3 mg), PPh_3 (10 mol%, 262.3 mg), and K_2CO_3 (20 mmol, 2.7640 g) were sequentially added. Toluene (50.0 mL) was introduced under a nitrogen atmosphere, and the tube was sealed. The reaction mixture was then heated in a preheated oil bath at 100 °C and stirred for 12 hours. Afterward, the mixture was allowed to cool to room temperature, diluted with CH_2Cl_2, filtered through Celite, and concentrated. The crude product was purified by flash column chromatography on silica gel to yield the desired compound.

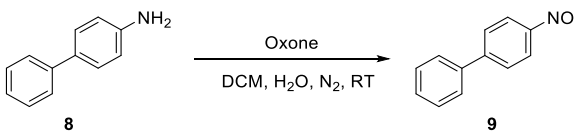
b) Synthesis of **1b**



S3 **1b**

Compound **1b** was synthesized according to the procedure reported in the literature[2]. An oven-dried Schlenk tube, equipped with a magnetic stir bar, was charged with bismuth(III) nitrate (20 mmol, 9.7000 g), potassium persulfate (10 mmol, 2.7000 g), and **S3** (10 mmol, 1.1720 g). Toluene (100.0 mL) was added under a nitrogen atmosphere, and the tube was sealed. The tube was then placed in a preheated oil bath at 80 ºC, and the reaction mixture was stirred vigorously for 12 hours. After cooling to room temperature, dichloromethane and ethyl acetate were added, and the mixture was stirred. The organic layer was filtered through a Celite bed, concentrated, and purified by column chromatography on silica gel to yield the desired compound.

c) Synthesis of **10**



8 **9**

Compound **9** was synthesized according to the procedure reported in the literature[3]. Substituted aniline (8.1 mmol, 1.00 equiv) was dissolved in 24 mL of DCM. To this solution Oxone (7.6 g, 12.1 mmol, 1.50 equiv) dissolved in 30 mL of water was added. The solution was stirred under nitrogen at room temperature until TLC monitoring indicated complete consumption of the starting material. After separation of the layers, the aqueous layer was extracted with DCM twice. The combined organic layers were washed with 1N HCl twice, saturated sodium bicarbonate solution, water, brine and dried (magnesium sulfate). The solution of mixture was concentrated and then purified by flash chromatography (PE:EA=100:1) to give the corresponding product.

3. Transition-metal-free photochemical reductive denitration of nitroarenes

***Reaction optimization*:** A 10-mL Schlenk tube equipped with a magnetic stirring bar was sequentially charged with the photocatalyst, $B_2(OH)_4$, and **1a** (0.2 mmol, 49.8 mg). Then *tert*-butyl nitrite and the solvent were added under a nitrogen atmosphere. After sealing the tube, it was placed in a photoreactor. The reaction mixture was stirred while being irradiated with LED light at room temperature for 12 hours. The yield of **2a** was determined by gas chromatography (GC), with dodecane as the internal standard for calibration.

***General procedure*:** A 10-mL Schlenk tube equipped with a magnetic stirring bar was sequentially charged with Eosin Y Disodium Salt (5 mol%, 6.9 mg), $B_2(OH)_4$ (0.8 mmol, 71.7 mg), and **1** (0.2 mmol). The tube was then added *tert*-butyl nitrite (0.4 mmol, 50.0 μL) and ^{i}PrOH (4.0 mL) under a nitrogen atmosphere. After sealing, the tube was placed in a photoreactor, and the reaction mixture was stirred while exposed to LED light (430 nm) at room temperature for 12 hours. Upon completion, the solvent was evaporated under reduced pressure, and the residue was purified by flash column chromatography, eluting with petroleum ether/ethyl acetate on silica gel, to afford the desired product.

Note: The reactions involving **1c**, **1h**, **1w**, **1x**, and **1z** were carried out using a solvent mixture of ^{i}PrOH (2.0 mL) and MeCN (2.0 mL). For all reactions, dodecane was used as the internal standard for determining GC yield, except for **1s**, which employed biphenyl as the internal standard.

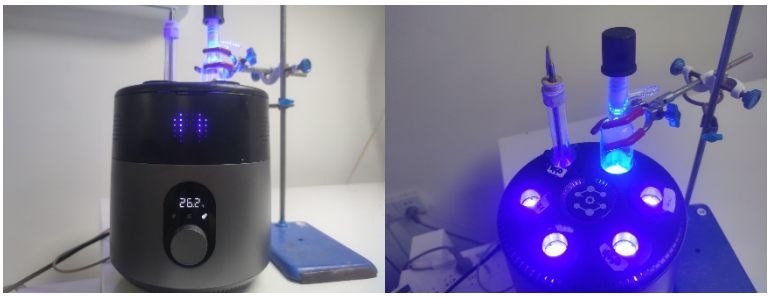
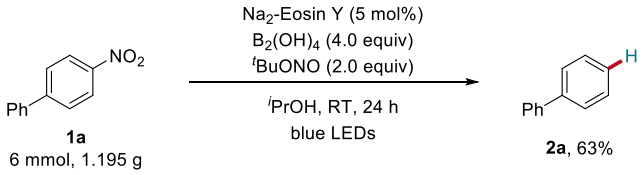


Figure S1. Photoreactor

Photoreactor with blue LED was obtained from SHANGHAI 3S TECHNOLOGY CO., LTD Type: SSSTECH-LAL1CV1.0 (Figure S1); Operating voltage range: 100-240 VAC 50/60 Hz; Unit luminous power: 0-12 W; Stirring speed: 300-1500 rpm, Operating temperature: 0-50 °C; Adjustable wavelength range: 365-450 nm.

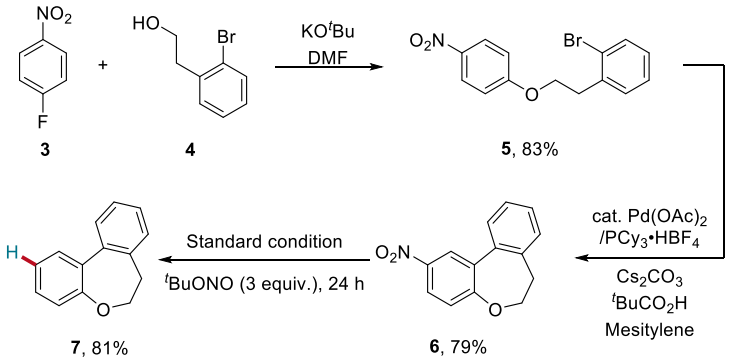
4. Synthetic application

a) *Gram-scale experiment*



A 100-mL Schlenk tube equipped with a magnetic stirring bar was sequentially charged with Eosin Y Disodium Salt (5 mol%, 207.0 mg), $B_2(OH)_4$ (24 mmol, 2.1600 g), and **1a** (6 mmol, 1.1950 g). Then *tert*-butyl nitrite (12 mmol, 1.5 mL) and ^{i}PrOH (60.0 mL) were added under a nitrogen atmosphere. After sealing the tube, the reaction mixture was stirred while exposed to LED light at room temperature for 24 hours. Upon completion, the mixture was diluted with ethyl acetate, and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography using a petroleum ether/ethyl acetate eluent on silica gel, yielding the desired product **2a** in 63% yield (0.5787 g).

b) *The synthesis of dibenzoxepane*



Compound **5** was synthesized following the procedure reported in the literature[4]. A 100-mL Schlenk tube equipped with a magnetic stirring bar. After the Schlenk tube was charged with nitrogen to replace air atmosphere, compound **3** (5 mmol, 705.5 mg) and DMF (20 mL) were then added using a syringe. A solution of compound **4** in DMF (10 mmol in 5 mL) was added to the Schlenk tube, which was subsequently cooled to 0 °C using an ice bath. A 1.0 M solution of *tert*-BuOK in THF (7.5 mL) was added dropwise over 5 minutes with stirring at 0 °C. After sealing the tube, the reaction mixture was stirred at 25 °C until TLC monitoring confirmed the reaction's completion. The reaction was quenched by adding saturated NH_4Cl aqueous solution, and the mixture was transferred to a separatory funnel and extracted with CH_2Cl_2 (3 times). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated

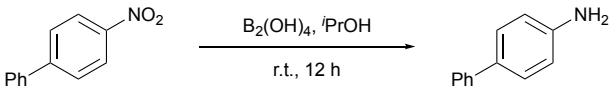
under reduced pressure. The crude product was purified by column chromatography on silica gel, yielding the desired compound **5** as a white solid (1.3360 g, 83%).

Compound **6** was synthesized according to the procedure reported in the literature[5]. A 10-mL Schlenk tube equipped with a magnetic stirring bar was sequentially charged with $Pd(OAc)_2$ (5 mol%, 5.6 mg), PCy_3-HBF_4 (10 mol%, 18.4 mg), compound **5** (0.5 mmol, 161.1 mg), and Cs_2CO_3 (0.55 mmol, 179.2 mg). Then ^{t}BuCOOH (30 mmol%, 15.3 mg) and Mesitylene (4.0 mL) were added under a nitrogen atmosphere. The tube was sealed and the reaction mixture was stirred at 135 °C for 12 hours. Following this, the mixture was transferred to a separatory funnel and extracted with CH_2Cl_2 (3 times). The combined organic extracts were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel to yield the desired product **6** as a white solid (95.2 mg, 79%).

A 10-mL Schlenk tube equipped with a magnetic stirring bar was sequentially charged with Eosin Y Disodium Salt (5 mol%, 6.9 mg), $B_2(OH)_4$ (0.8 mmol, 71.7 mg), and compound **6** (0.2 mmol, 48.2 mg). The tube was charged with nitrogen to replace air atmosphere, followed by the addition of *tert*-butyl nitrite (0.6 mmol, 75.0 μL), ^{i}PrOH (2.0 mL), and MeCN (2.0 mL). After sealing the tube, it was placed in a photoreactor. The reaction mixture was stirred and exposed to LED light (430 nm) at room temperature for 12 hours. The solvent was then evaporated under reduced pressure, and the residue was purified directly by flash column chromatography, eluting with a petroleum ether/ethyl acetate mixture on silica gel, to yield the desired product **7** as a white solid (32.3 mg, 81%).

5. Mechanistic investigations

a) *Control experiment: reduction of **1a** to **8***

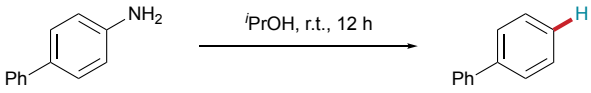


1a **8**

blue LEDs	Na_2-Eosin Y	yield of **8**
✘	✘	0%
✔	✘	55%
✔	✔	77%

A 10-mL Schlenk tube equipped with a magnetic stirring bar was sequentially charged with Eosin Y Disodium Salt (5 mol%, 7.0 mg), $B_2(OH)_4$ (0.8 mmol, 71.7 mg), and **1a** (0.2 mmol, 49.8 mg). Then ^{i}PrOH (4.0 mL) was added under a nitrogen atmosphere. After sealing the tube, it was placed in a photoreactor. The reaction mixture was stirred and exposed to LED light at room temperature for 12 hours. The yield of **8** was determined by gas chromatography (GC), with dodecane used as the internal standard for calibration.

b) *Control experiment: deamination of **8** to **2a***

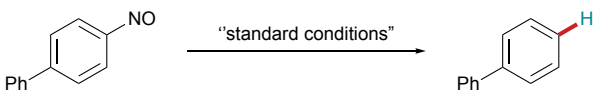


8 **2a**

^{t}BuONO	blue LEDs	Na_2-Eosin Y	yield of **2a**
✘	✘	✘	0%
✔	✘	✘	56%
✔	✔	✘	70%
✔	✔	✔	90%

A 10-mL Schlenk tube equipped with a magnetic stirring bar was sequentially charged with Eosin Y Disodium Salt (5 mol%, 7.0 mg) and **8** (0.2 mmol, 33.8 mg). Then *tert*-butyl nitrite (0.4 mmol, 50.0 μL) and ^{i}PrOH (4.0 mL) were added under a nitrogen atmosphere. After sealing the tube, it was placed in a photoreactor. The reaction mixture was stirred and exposed to LED light at room temperature for 12 hours. The yield of **2a** was determined by gas chromatography (GC), with dodecane used as the internal standard for calibration.

c) *Control experiment: the reaction employing nitrosobenzene **9***

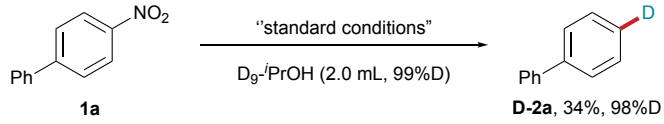


9 **2a**, 70%

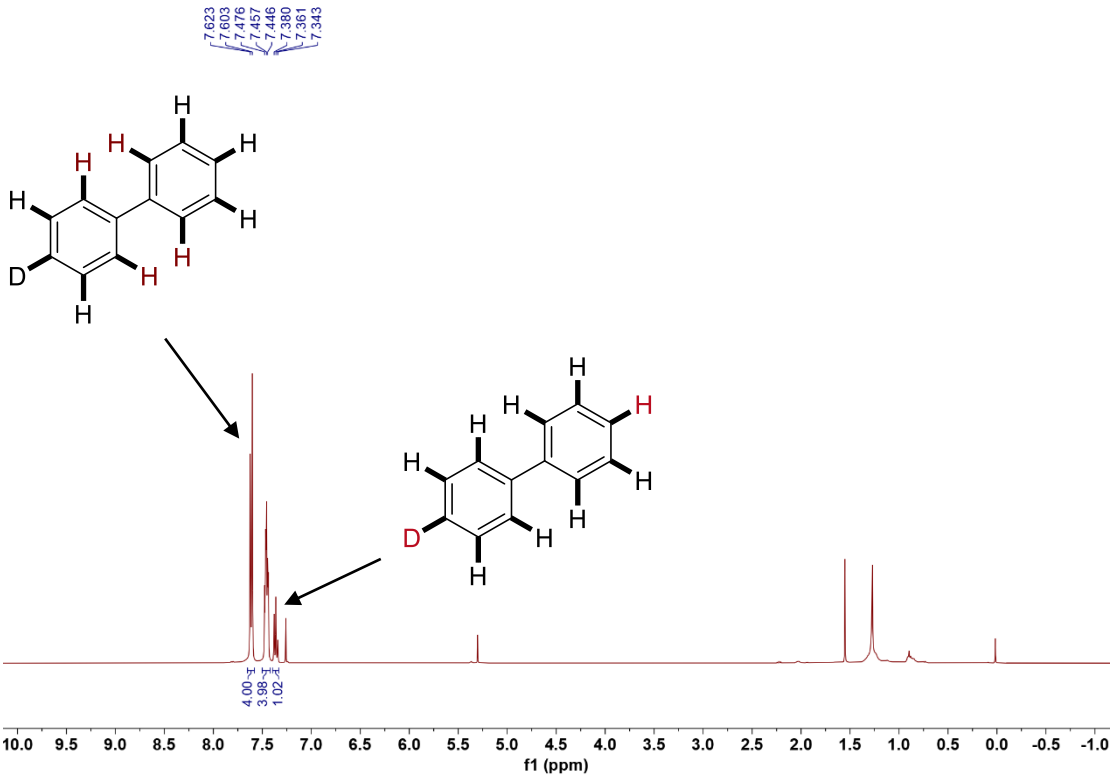
A 10-mL Schlenk tube equipped with a magnetic stirring bar was sequentially charged with Eosin Y Disodium Salt (5 mol%, 6.9 mg), $B_2(OH)_4$ (0.8 mmol, 71.7 mg), and **9** (0.2 mmol, 36.6 mg). The tube was then added *tert*-butyl nitrite (0.4 mmol, 50.0 μL) and ^{i}PrOH (4.0 mL) under

a nitrogen atmosphere. After sealing, the tube was placed in a photoreactor, and the reaction mixture was stirred while exposed to LED light (430 nm) at room temperature for 12 hours. Upon completion, the solvent was evaporated under reduced pressure, and the residue was purified by flash column chromatography, eluting with petroleum ether/ethyl acetate on silica gel, to afford the desired product **2a** (21.6 mg, 70%).

d) *Control experiment: the reaction in D_9-^{i}PrOH*



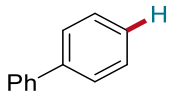
1a **D-2a**, 34%, 98%D



A 10-mL Schlenk tube equipped with a magnetic stirring bar was sequentially charged with Eosin Y Disodium Salt (5 mol%, 6.9 mg), $B_2(OH)_4$ (0.8 mmol, 71.7 mg), and **1a** (0.2 mmol, 39.8 mg). The tube was then added *tert*-butyl nitrite (0.4 mmol, 50.0 μL) and D_9-^{i}PrOH (4.0 mL) under a nitrogen atmosphere. After sealing, the tube was placed in a photoreactor, and the reaction mixture was stirred while exposed to LED light (430 nm) at room temperature for 12 hours. Upon completion, the solvent was evaporated under reduced pressure, and the residue was purified by flash column chromatography, eluting with petroleum ether/ethyl acetate on silica gel, to afford the desired product **D-2a** (10.4 mg, 34%).

6. Analytical data of products

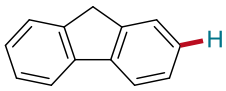
1,1'-Biphenyl (**2a**)[6]



2a

2a (24.3 mg, 79%) was obtained as a white solid after flash chromatography; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 7.5 Hz, 4H), 7.48 (t, J = 7.4 Hz, 4H), 7.38 (t, J = 7.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4, 128.9, 127.4, 127.3.

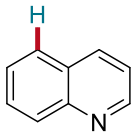
9*H*-fluorene (**2c**)[7]



2c

2c (24.9 mg, 75%) was obtained as a white solid after flash chromatography; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 7.5 Hz, 2H), 7.57 (d, J = 7.6 Hz, 2H), 7.40 (t, J = 7.2 Hz, 2H), 7.33 (td, J = 7.4, 1.2 Hz, 2H), 3.93 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 141.8, 126.9, 126.8, 125.2, 120.0, 37.1.

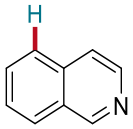
Quinoline (**2d**)[6]



2d

2d (20.1 mg, 78%) was obtained as a colorless liquid after flash chromatography; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (dd, J = 4.2, 1.6 Hz, 1H), 8.15-8.08 (m, 2H), 7.79 (d, J = 8.0 Hz, 1H), 7.74-7.64 (m, 1H), 7.51 (td, J = 8.0, 1.2 Hz, 1H), 7.37 (dd, J = 8.2, 4.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4, 148.3, 136.2, 129.6, 129.5, 128.4, 127.9, 126.6, 121.1.

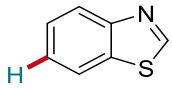
Isoquinoline (**2e**)[6]



2e

2e (11.6 mg, 45%) was obtained as a colorless crystal after flash chromatography; ^{1}H NMR(400 MHz, $CDCl_3$) δ 9.25 (s, 1H), 8.52 (dd, J = 5.6, 1.6 Hz, 1H), 7.96 (d, J = 8.4 Hz, 1H), 7.82 (d, J = 8.4 Hz, 1H), 7.73-7.55 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.6, 143.0, 135.9, 130.5, 128.8, 127.7, 127.4, 126.6, 120.6.

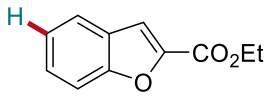
Benzothiazole **(2f)**[8]



2f

2f (14.3 mg, 53%) was obtained as a pale yellow liquid after flash chromatography; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (s, 1H), 8.15 (d, J = 8.2 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.56-7.48 (m, 1H), 7.48-7.40 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.0, 153.3, 133.8, 126.3, 125.7, 123.7, 122.0.

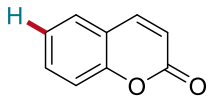
Ethyl benzofuran-2-carboxylate (**2g**)[9]



2g

2g (29.6 mg, 78%) was obtained as a colorless oil after flash chromatography; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 7.9 Hz, 1H), 7.59 (dd, J = 0.8, 8.4 Hz,, 1H), 7.53 (d, J = 0.8 Hz, 1H), 7.47-7.40 (m, 1H), 7.33-7.27 (m, 1H), 4.44 (q, J = 7.1 Hz, 2H), 1.42 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 155.8, 145.8, 127.7, 127.1, 123.9, 122.9, 113.9, 112.5, 61.6, 14.5.

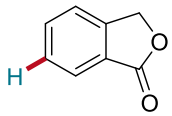
2*H*-chromen-2-one (**2h**)[10]



2h

2h (14.6 mg, 50%) was obtained as a white solid after flash chromatography; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 9.6 Hz, 1H), 7.56-7.45 (m, 2H), 7.35-7.24 (m, 2H), 6.42 (d, J = 9.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9, 154.1, 143.6, 131.9, 128.0,124.5, 118.9, 117.0, 116.8.

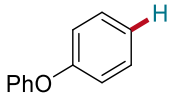
Isobenzofuran-1(3*H*)-one (**2i**)[11]



2i

2i (21.4 mg, 80%) was obtained as a white crystalline powder solid after flash chromatography; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 7.6 Hz, 1H), 7.68 (td, J = 7.4, 1.2 Hz, 1H), 7.54 (d, J = 7.5 Hz, 1H), 7.50 (d, J = 7.9 Hz, 1H), 5.32 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 146.6, 134.1, 129.1, 129.1, 125.8, 122.2, 69.8.

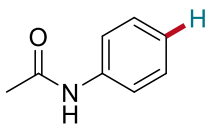
Oxydibenzene (**2l**)[12]



2l

2l (19.0 mg, 56%) was obtained as a colorless liquid after flash chromatography; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (t, J = 7.7 Hz, 4H), 7.11 (t, J = 7.4 Hz, 2H), 7.03 (d, J = 8.1 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 129.9, 123.4, 119.1.

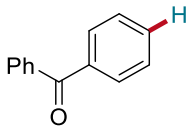
N-phenylacetamide (**2n**)[13]



2n

2n (21.3 mg, 79%) was obtained as a white crystalline powder after flash chromatography; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.50 (d, J = 8.2 Hz, 2H), 7.30 (t, J = 7.8 Hz, 2H), 7.13-7.06 (m, 1H), 2.16 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 138.1, 129.1, 124.4, 120.1, 24.6.

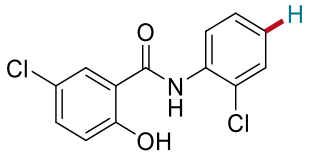
Benzophenone (**2r**)[6]



2r

2r (25.8 mg, 71%) was obtained as a white solid after flash chromatography; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.4 Hz, 4H), 7.59 (t, J = 7.4 Hz, 2H), 7.48 (t, J = 7.6 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.9, 137.7, 132.5, 130.2, 128.4.

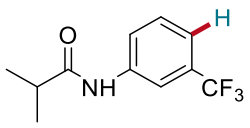
5-Chloro-N-(2-chlorophenyl)-2-hydroxybenzamide (**2v**)[14]



2v

2v (33.7 mg, 60%) was obtained as a white solid after flash chromatography; ^{1}H NMR (400 MHz, DMSO) δ 12.27 (s, 1H), 10.89 (s, 1H), 8.41 (dd, J = 8.2, 1.2 Hz, 1H), 7.98 (d, J = 2.8 Hz, 1H), 7.54 (dd, J = 8.0, 1.3 Hz, 1H), 7.48 (dd, J = 8.7, 2.8 Hz, 1H), 7.42-7.31 (m, 1H), 7.21-7.13 (m, 1H), 7.06 (d, J = 8.8 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ 162.6, 155.4, 135.1, 133.4, 129.8, 129.4, 127.8, 125.4, 123.5, 123.5, 122.8, 119.6, 119.1.

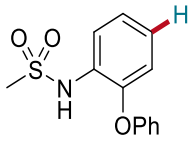
N-(3-(trifluoromethyl)phenyl)isobutyramide (**2w**)[15]



2w

2w (36.0 mg, 78%) was obtained as a white solid after flash chromatography; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.75 (bs, 1H), 7.71 (d, J = 8.1 Hz, 1H), 7.39 (t, J = 7.9 Hz, 1H), 7.33 (d, J = 7.8 Hz, 1H), 2.58-2.50 (m, 1H), 1.24 (d, J = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.1, 138.7, 131.4(q, J = 32 Hz), 129.6, 123.1(q, J = 270 Hz), 122.6, 120.8(q, J = 3 Hz), 116.8(q, J = 3 Hz), 36.7, 19.6.

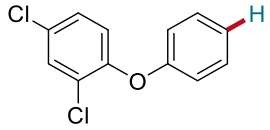
N-(2-phenoxyphenyl)methanesulfonamide (**2x**)[16]



2x

2x (30.0 mg, 57%) was obtained as a white crystalline after flash chromatography; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67-7.62 (m, 1H), 7.37 (t, J = 8.0 Hz, 2H), 7.20-7.07 (m, 3H), 7.00 (d, J = 7.9 Hz, 2H), 6.90 (s, 1H), 6.88 (d, J = 2.1 Hz, 1H), 2.99 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 147.4, 130.2, 128.3, 125.8, 124.4, 121.8, 118.7, 118.4, 39.6.

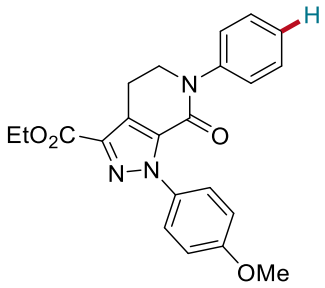
2,4-dichloro-1-phenoxybenzene (**2y**)[17]



2y

2y (30.4 mg, 64%) was obtained as a colorless liquid after flash chromatography; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 2.5 Hz, 1H), 7.35 (t, J = 8 Hz, 2H), 7.19 (dd, J = 8.8, 2.5 Hz, 1H), 7.13 (t, J = 7.4 Hz, 1H), 6.96 (d, J = 7.7 Hz, 2H), 6.91 (d, J = 8.8 Hz, 1H). ^{13}C NMR (101MHz,$CDCl_3$) δ 156.7, 151.6, 130.6, 130.0, 129.3, 128.2, 126.7, 123.9, 121.5, 118.1.

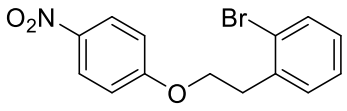
Ethyl-1-(4-methoxyphenyl)-7-oxo-6-phenyl-4,5,6,7-tetrahydro-1*H*-pyrazolo[3,4*c*]pyridine-3-carboxylate (**2z**)



2z

2z (59.4 mg, 76%) was obtained as a white solid after flash chromatography; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.44 (m, 2H), 7.39-7.33 (m, 2H), 7.30 (dd, J = 8.5, 1.2 Hz, 2H), 7.24-7.19 (m, 1H), 6.93-6.87 (m, 2H), 4.45 (q, J = 7.1 Hz, 2H), 4.11 (t, J = 6.7 Hz, 2H), 3.79 (s, 3H), 3.31 (t, J = 6.7 Hz, 2H), 1.42 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2, 159.9, 157.2, 141.8, 139.0, 133.2, 132.6, 129.0, 127.0, 126.9, 126.6, 125.5, 113.6, 61.2, 55.5, 51.1, 21.6, 14.5. HRMS (ESI, m/z) $[M + H]^+$ calcd. for $[C_{22}H_{22}O_4N_3]^+$: 392.1605； found: 392,1601.

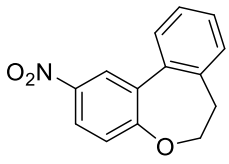
1-bromo-2-(2-(4-nitrophenoxy)ethyl)benzene (**5**)



5

5 (1.336 g, 83%) was obtained as a white solid after flash chromatography; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 9.3 Hz, 2H), 7.58 (dd, J = 8.0, 1.0 Hz, 1H), 7.33 (dd, J = 7.6, 1.8 Hz, 1H), 7.29 (dd, J = 7.3, 1.0 Hz, 1H), 7.13 (td, J = 7.8, 1.9 Hz, 1H), 6.95 (d, J = 9.3 Hz, 2H), 4.29 (t, J = 7.0 Hz, 2H), 3.28 (t, J = 6.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9, 141.7, 136.9, 133.2, 131.5, 128.8, 127.8, 126.0, 124.7, 114.7, 67.8, 35.9.HRMS (ESI, m/z) $[M + H]^+$ calcd. for $[C_{14}H_{13}O_3NBr]^+$: 322.0074; found: 322.0075.

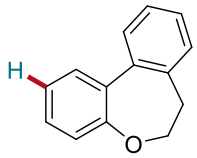
2-Nitro-6,7-dihydrodibenzo[b,d]oxepine (**6**)[18]



6

6 (95.2 mg, 79%) was obtained as a white solid after flash chromatography; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, J = 2.8 Hz, 1H), 8.19 (dd, J = 8.9, 2.8 Hz, 1H), 7.51 (dd, J = 7.6, 1.3 Hz, 1H), 7.44 (td, J = 7.4, 1.5 Hz, 1H), 7.39 (td, J = 7.4, 1.6 Hz, 1H), 7.30 (ddd, J = 7.4, 1.2, 0.3 Hz, 1H), 7.22 (d, J = 8.9 Hz, 1H), 4.68 (t, J = 6.1 Hz, 2H), 2.89 (t, J = 6.1 Hz, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 144.4, 137.7, 136.7, 135.3, 129.0, 128.6, 128.4, 128.0, 125.4, 124.5, 123.4, 79.3, 33.5.

6,7-Dihydrodibenzo[b,d]oxepine (**7**) [18]



7

7 (28.6 mg, 73%) was obtained as a white solid after flash chromatography; ^{1}H NMR (400 MHz, CDCl3) δ 7.48 (dd, J = 7.8,1.4 Hz,1H), 7.46 – 7.42 (m, 1H), 7.42 – 7.37 (m, 1H), 7.32 – 7.28 (m, 3H), 7.28 – 7.23 (m, 1H), 7.19 – 7.14 (m, 1H), 4.60 (t, J = 6.3 Hz,2H), 2.83 (t, J = 6.4 Hz, 2H). ^{13}C NMR (101 MHz, CDCl3) δ 154.5, 139.0, 137.5, 135.4, 129.4, 129.2, 128.3, 128.2, 127.8, 127.5, 124.7, 122.5, 78.6, 33.6.

7. Reference

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8. NMR spectra of products

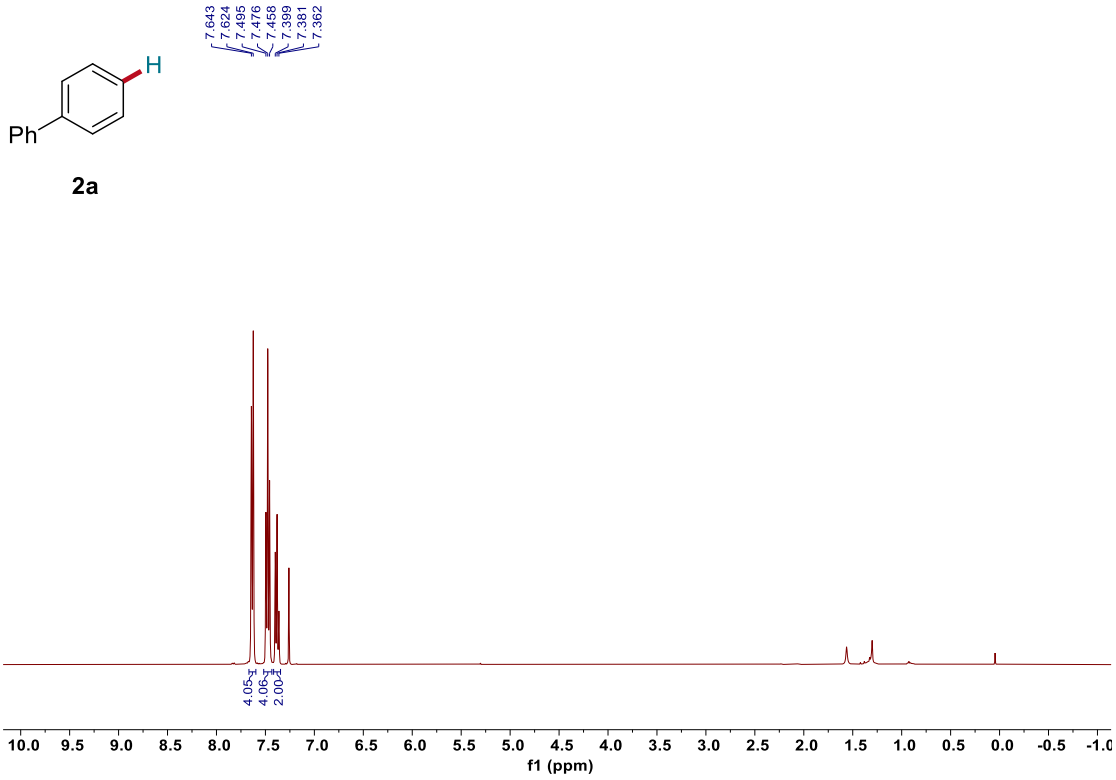


Figure S2. ^{1}H NMR Spectrum of **2a** (400 MHz, $CDCl_3$)

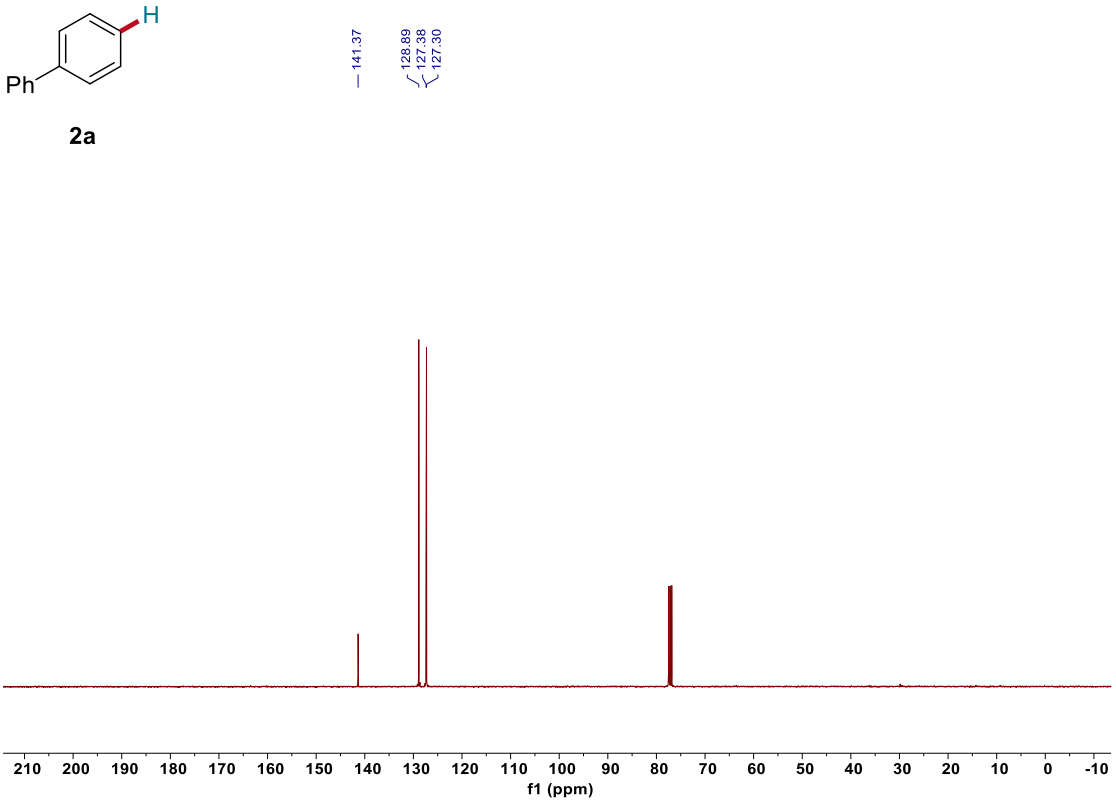


Figure S3. ^{13}C NMR Spectrum of **2a** (101 MHz, $CDCl_3$)

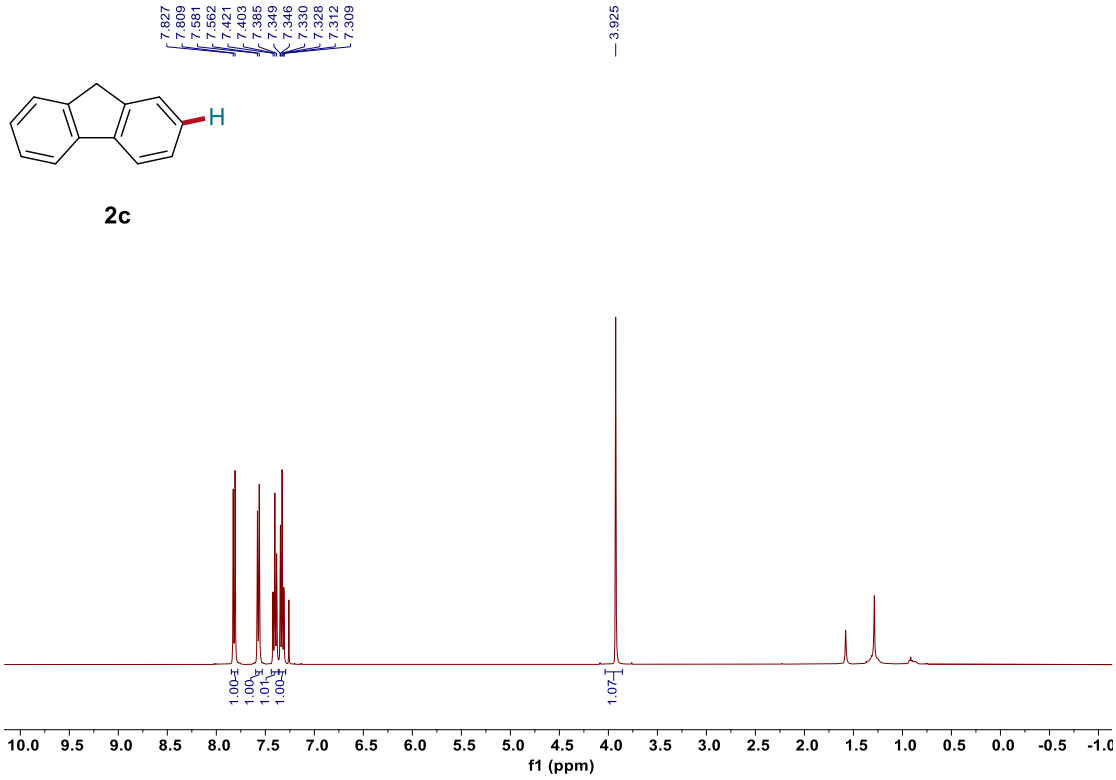


Figure S4. ^{1}H NMR Spectrum of **2c** (400 MHz, $CDCl_3$)

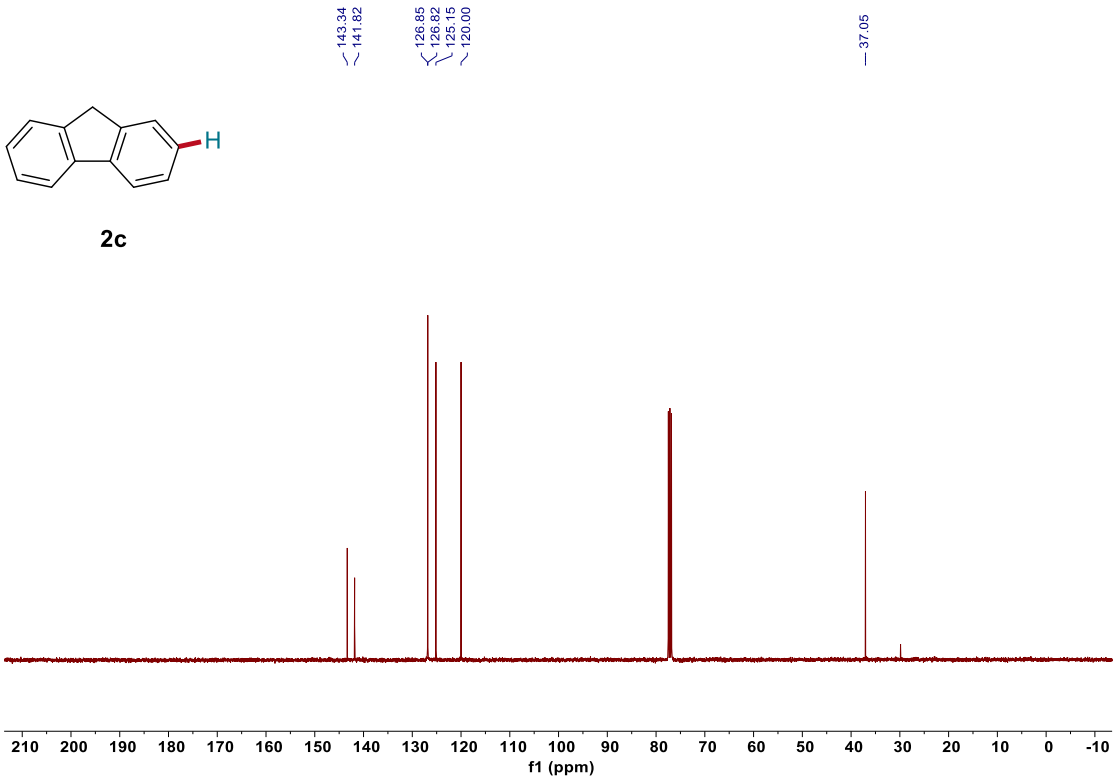


Figure S5. ^{13}C NMR Spectrum of **2c** (101 MHz, $CDCl_3$)

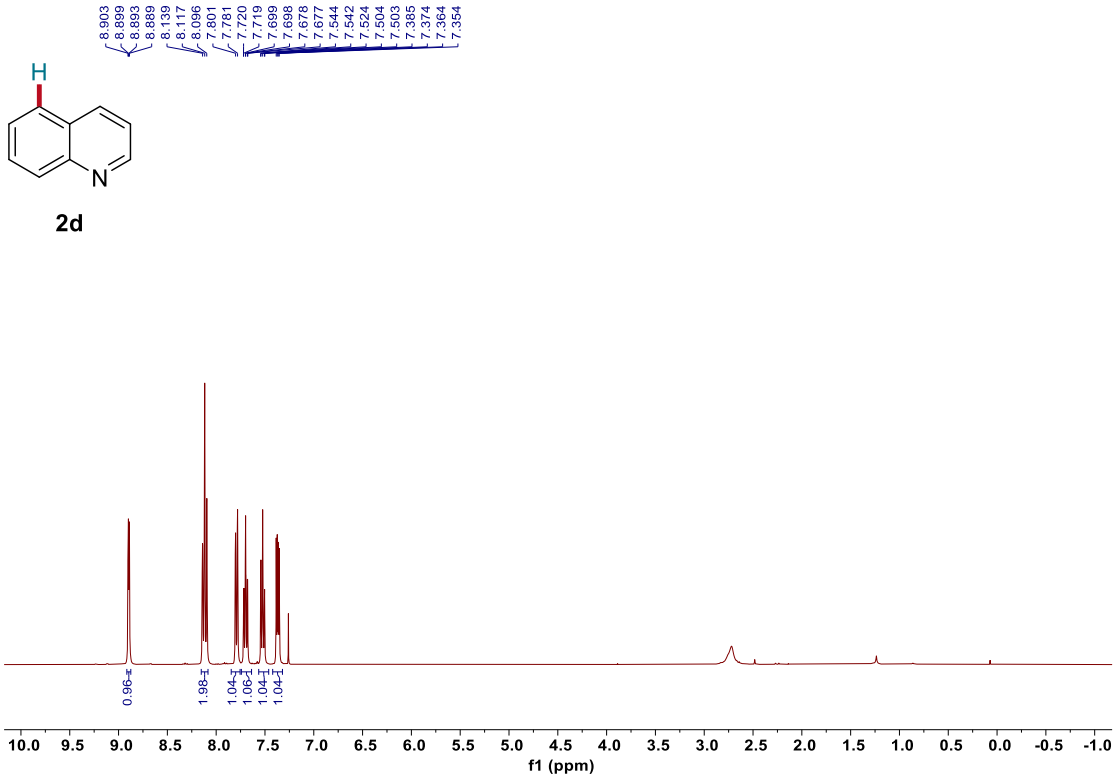


Figure S6. ^{1}H NMR Spectrum of **2d** (400 MHz, $CDCl_3$)

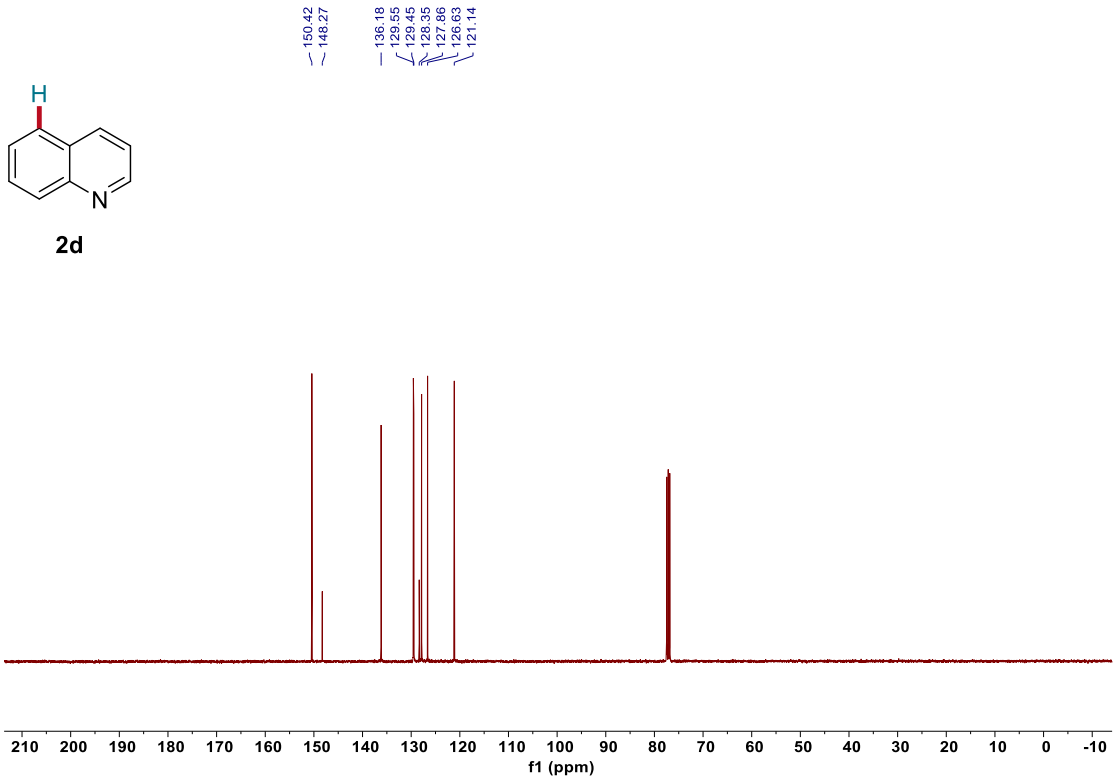


Figure S7. ^{13}C NMR Spectrum of **2d** (101 MHz, $CDCl_3$)

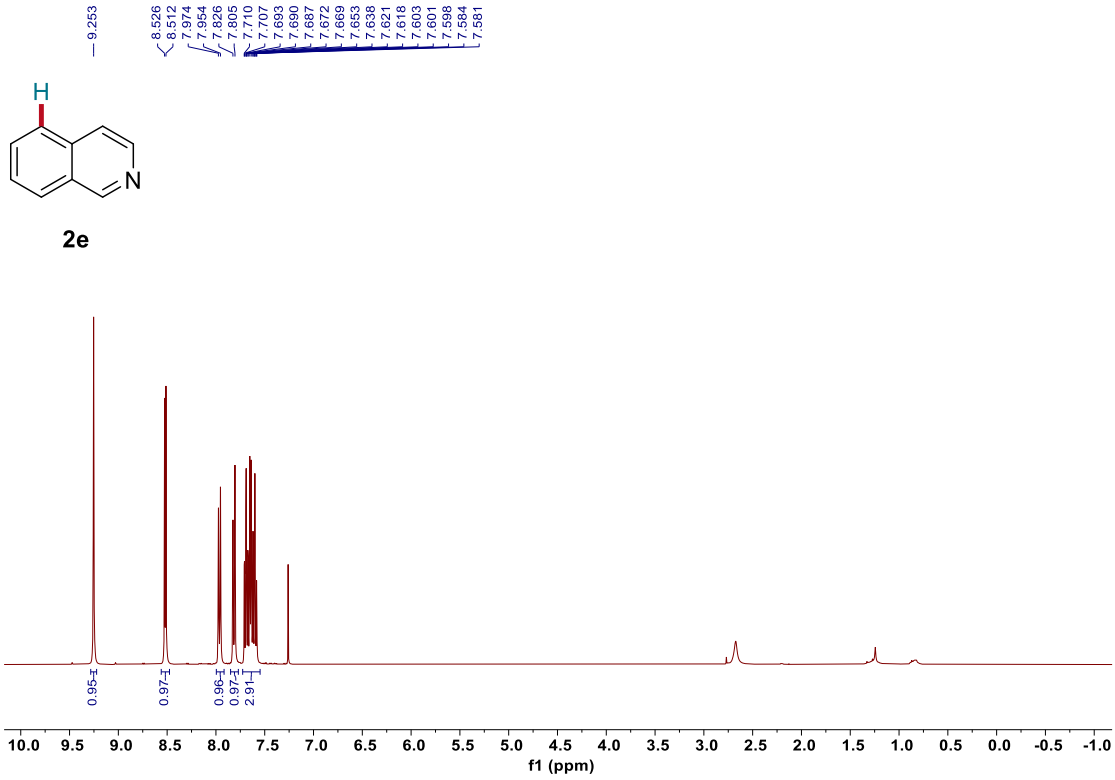


Figure S8. ^{1}H NMR Spectrum of **2e** (400 MHz, $CDCl_3$)

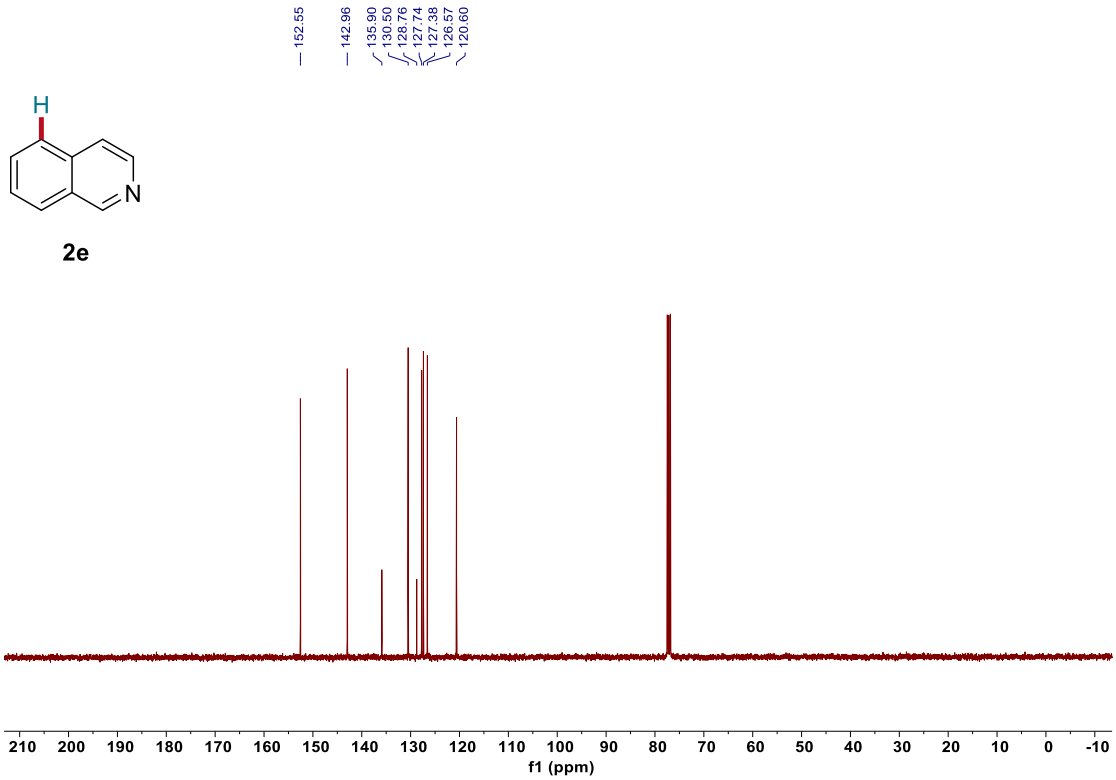


Figure S9. ^{13}C NMR Spectrum of **2e** (101 MHz, $CDCl_3$)

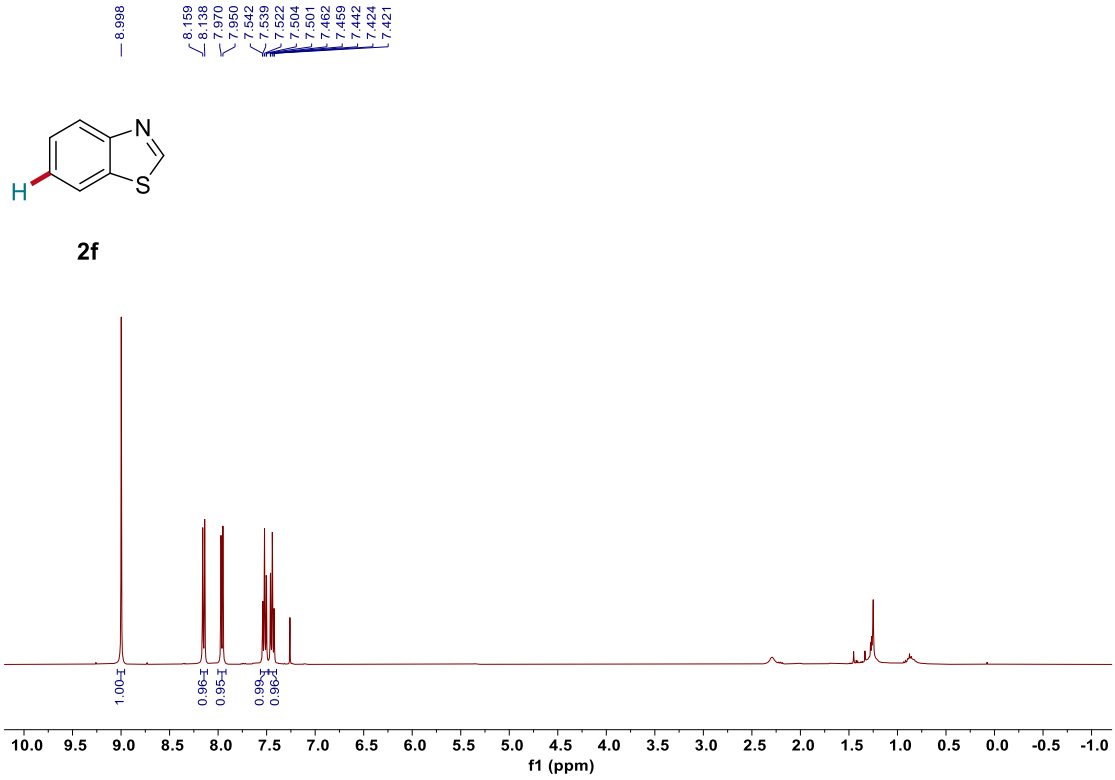


Figure S10. ^{1}H NMR Spectrum of **2f** (400 MHz, $CDCl_3$)

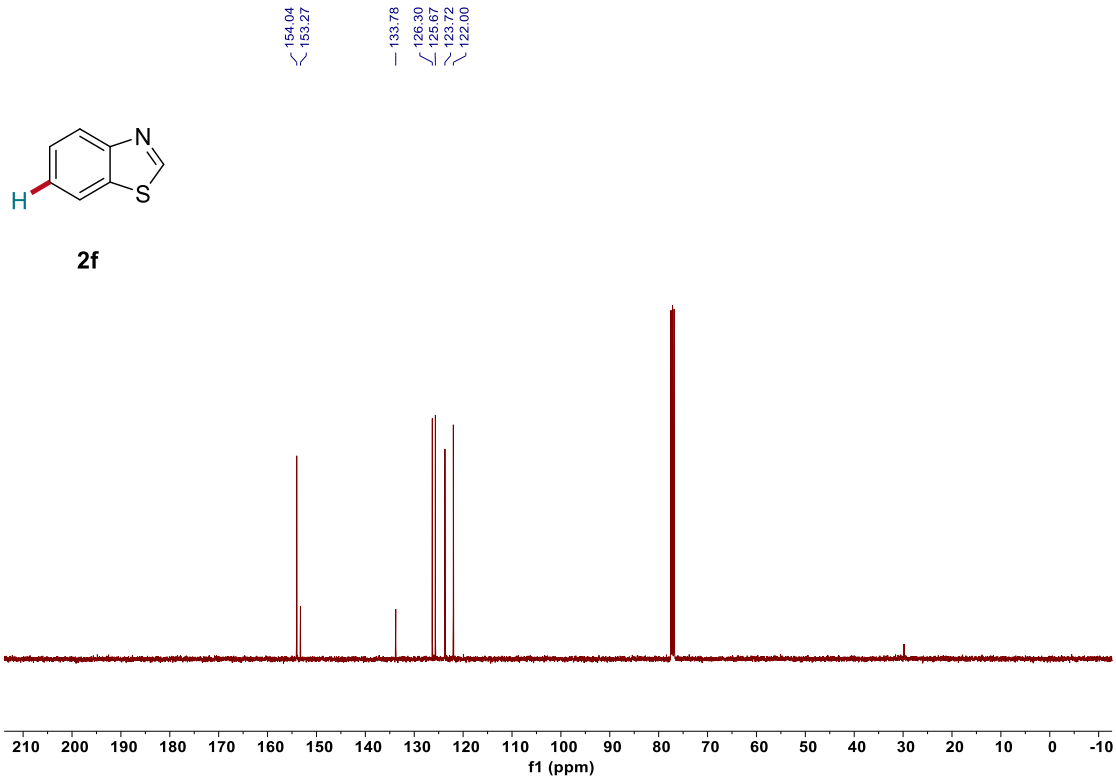


Figure S11. ^{13}C NMR Spectrum of **2f** (101 MHz, $CDCl_3$)

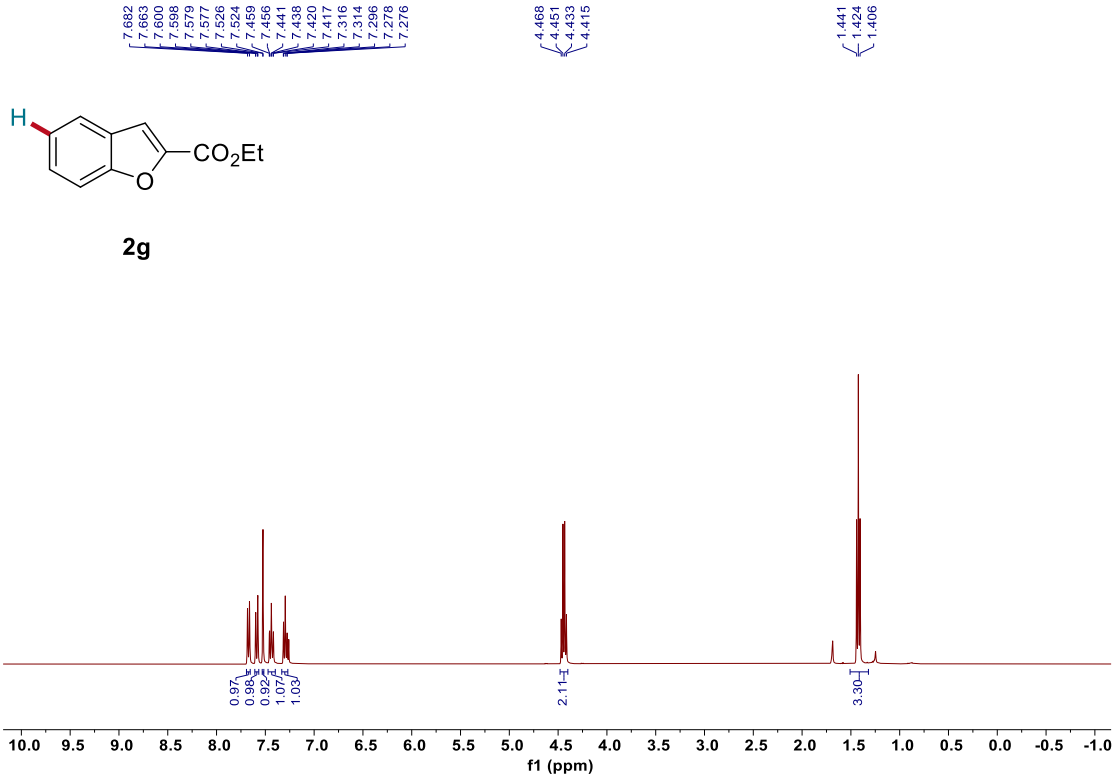


Figure S12. ^{1}H NMR Spectrum of **2g** (400 MHz, $CDCl_3$)

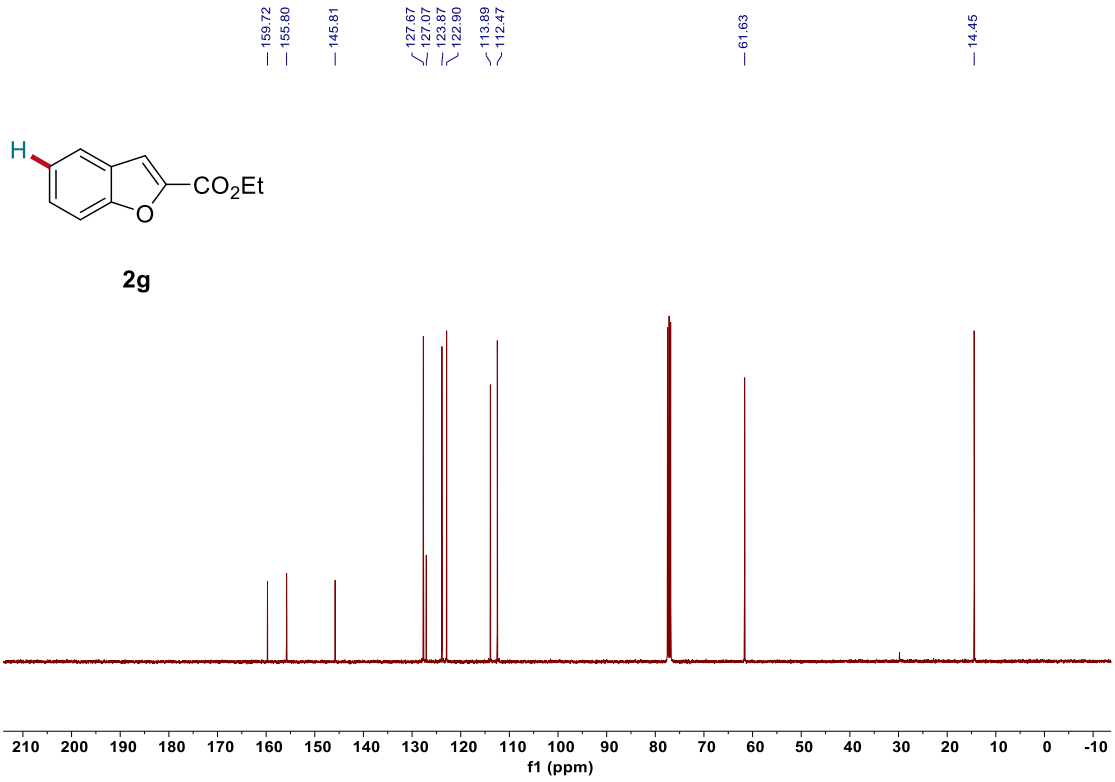


Figure S13. ^{13}C NMR Spectrum of **2g** (101 MHz, $CDCl_3$)

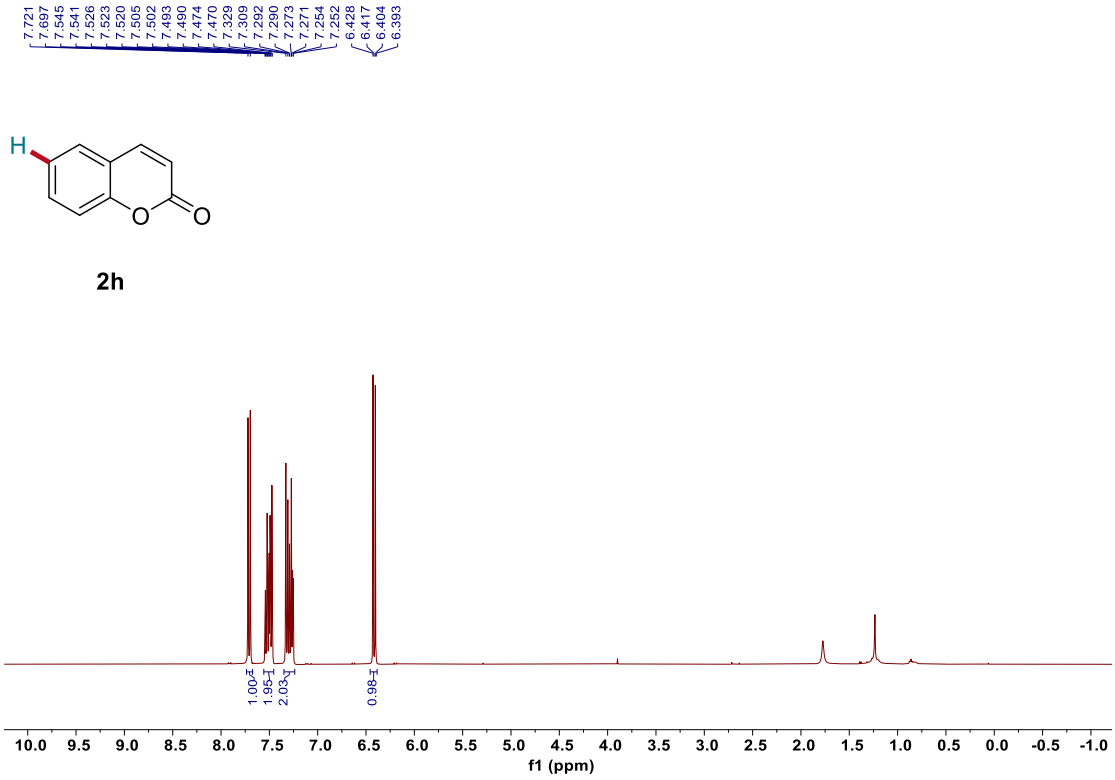


Figure S14. ^{1}H NMR Spectrum of **2h** (400 MHz, $CDCl_3$)

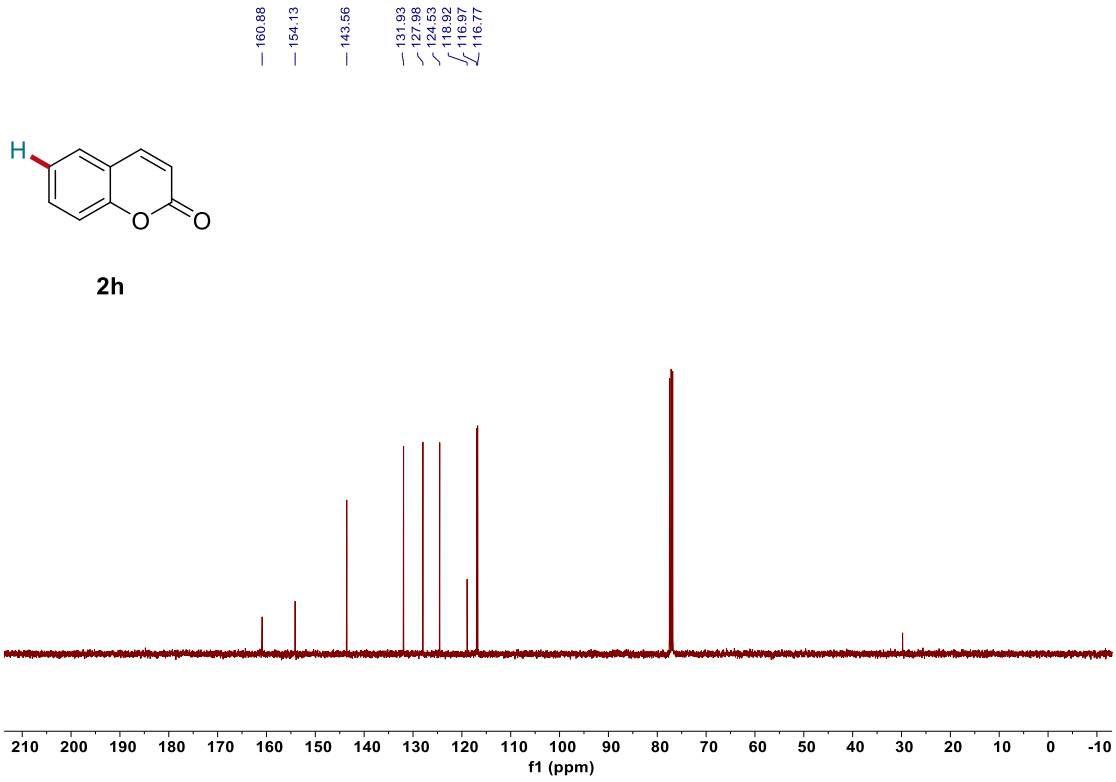


Figure S15. ^{13}C NMR Spectrum of **2h** (101 MHz, $CDCl_3$)

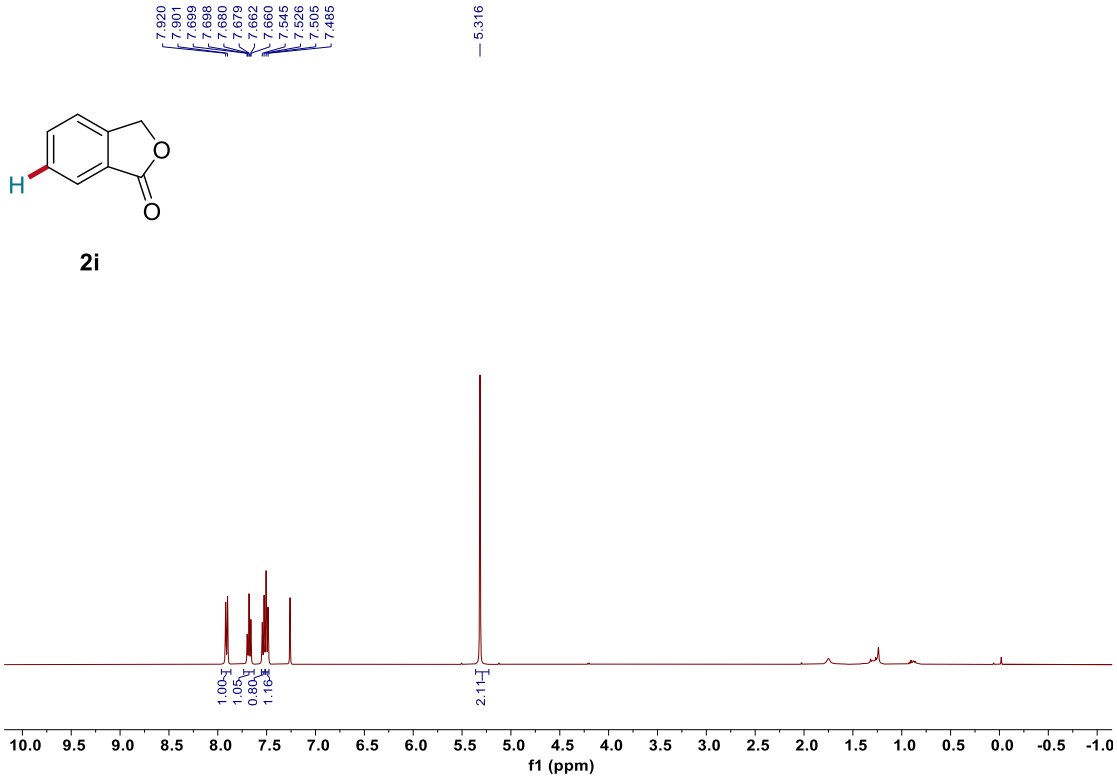


Figure S16. ^{1}H NMR Spectrum of **2i** (400 MHz, $CDCl_3$)

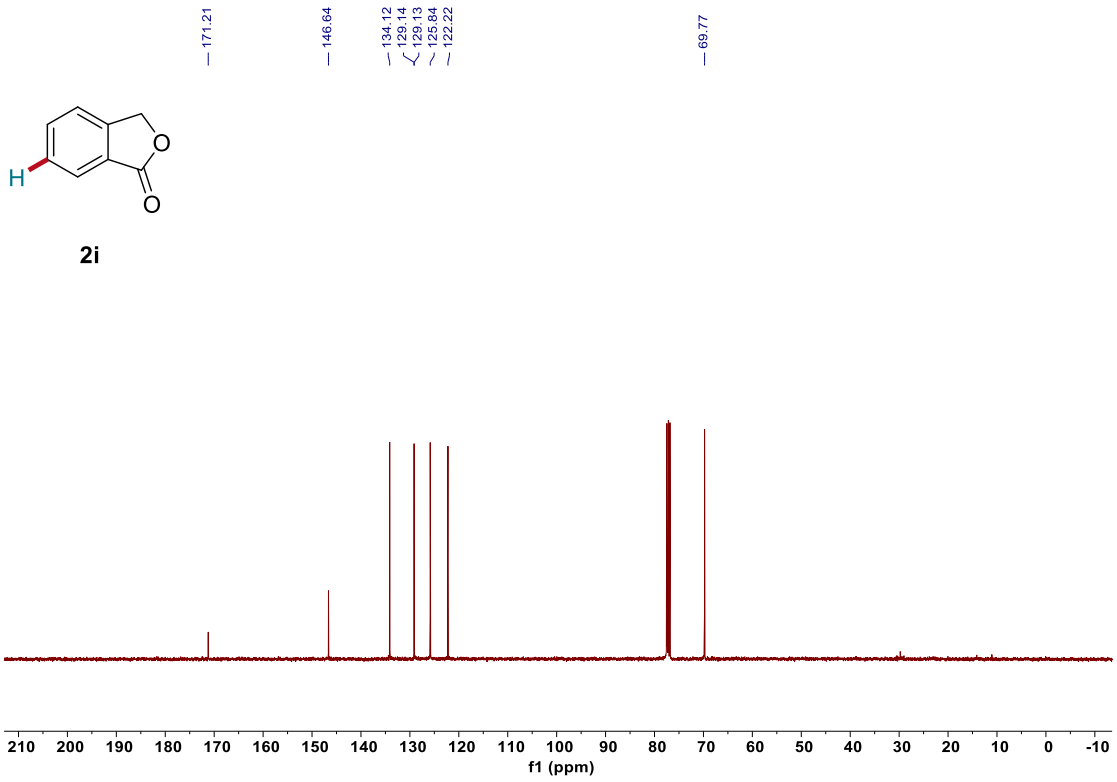


Figure S17. ^{13}C NMR Spectrum of **2i** (101 MHz, $CDCl_3$)

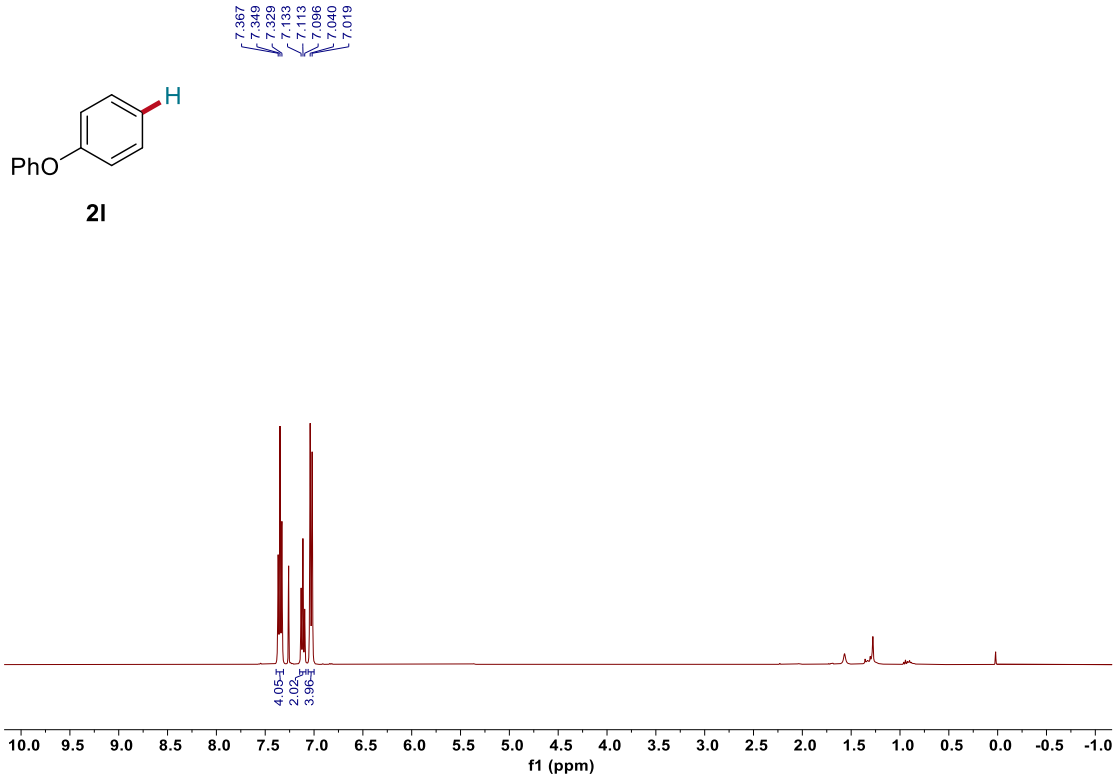


Figure S18. ^{1}H NMR Spectrum of **2l** (400 MHz, $CDCl_3$)

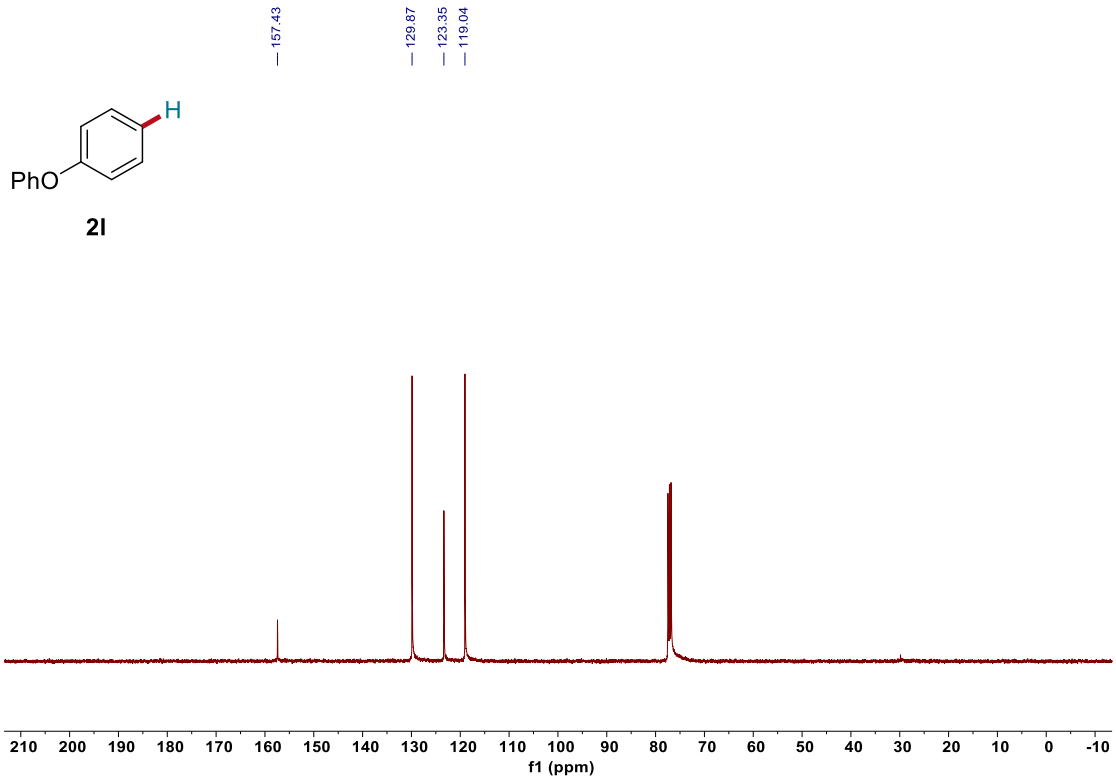


Figure S19. ^{13}C NMR Spectrum of **2l** (101 MHz, $CDCl_3$)

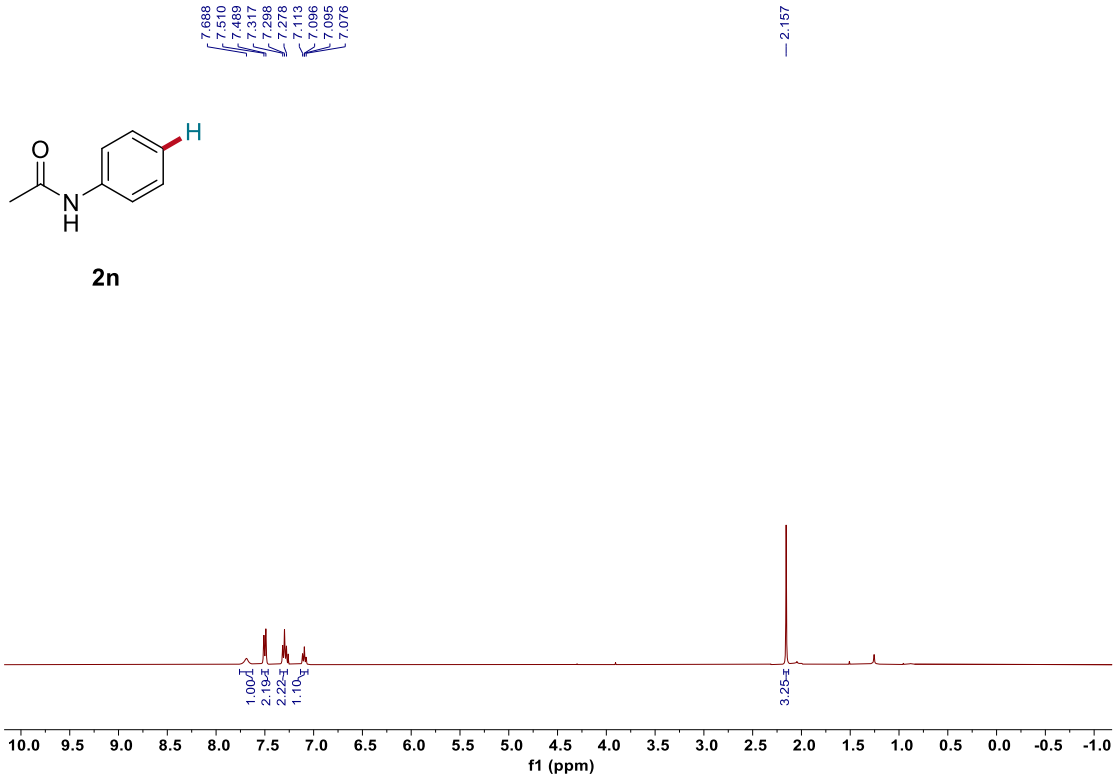


Figure S20. ^{1}H NMR Spectrum of **2n** (400 MHz, $CDCl_3$)

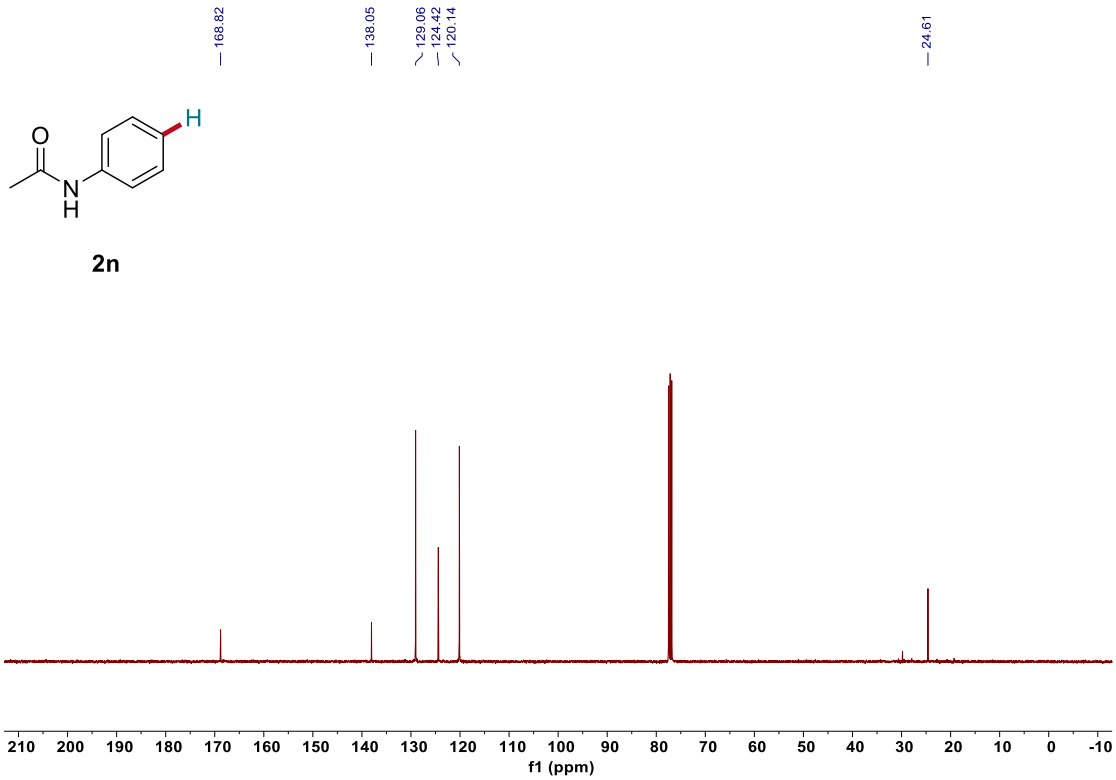


Figure S21. ^{13}C NMR Spectrum of **2n** (101 MHz, $CDCl_3$)

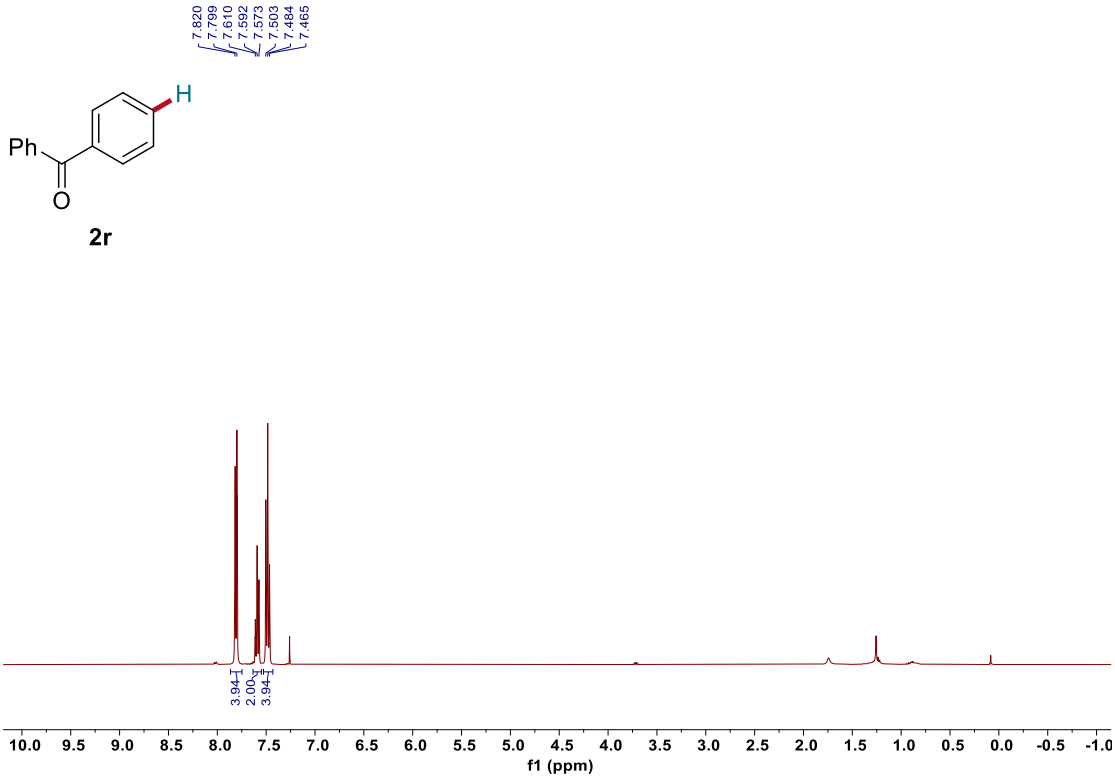


Figure S22. ^{1}H NMR Spectrum of **2r** (400 MHz, $CDCl_3$)

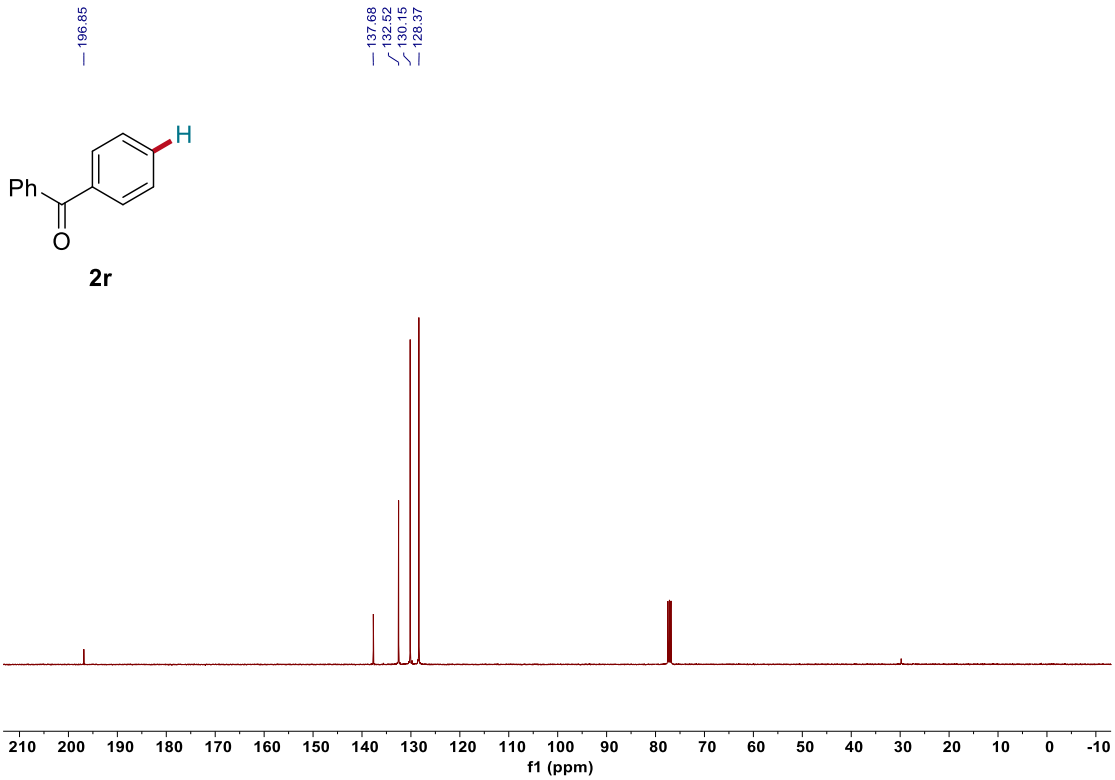


Figure S23. ^{13}C NMR Spectrum of **2r** (101 MHz, $CDCl_3$)

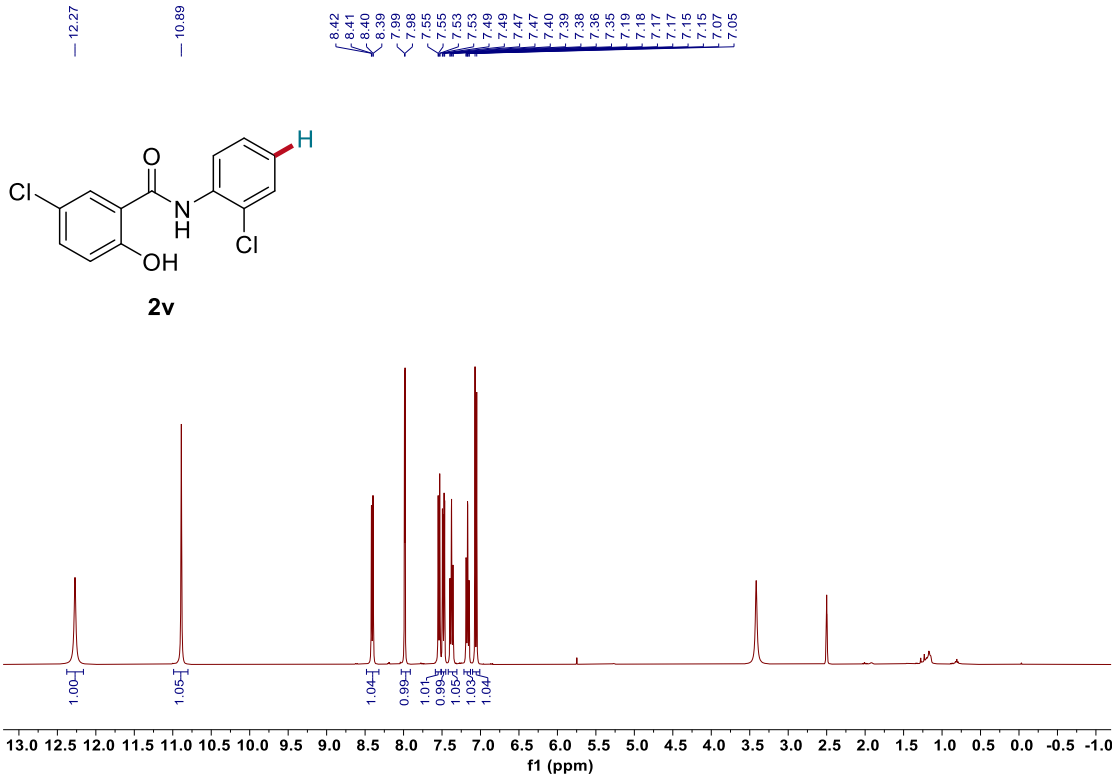


Figure S24. ^{1}H NMR Spectrum of **2v** (400 MHz, DMSO)

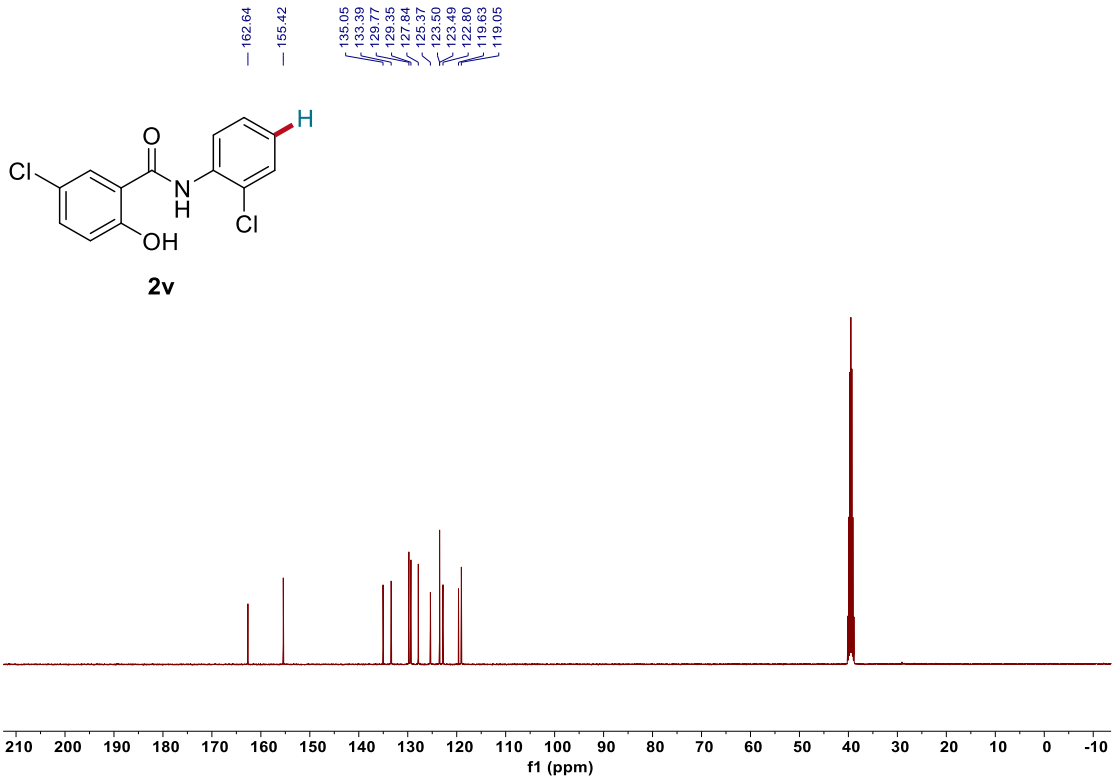


Figure S25. ^{13}C NMR Spectrum of **2v** (101 MHz, DMSO)

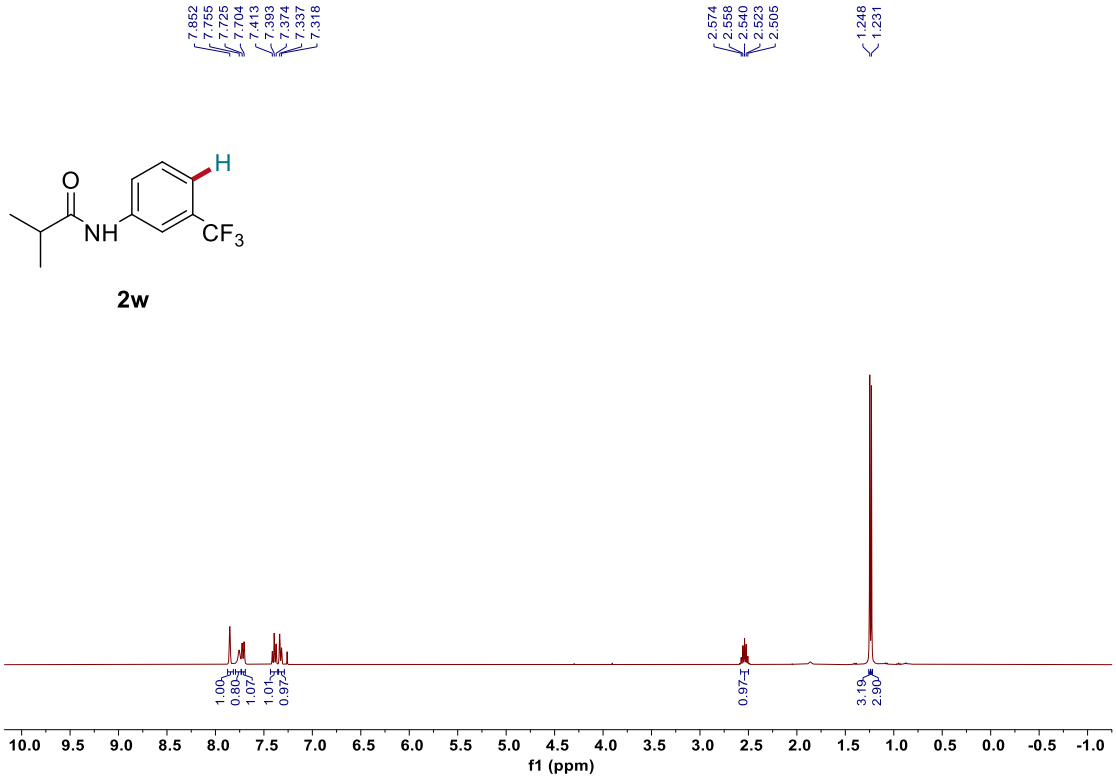


Figure S26. ^{1}H NMR Spectrum of **2w** (400 MHz, $CDCl_3$)

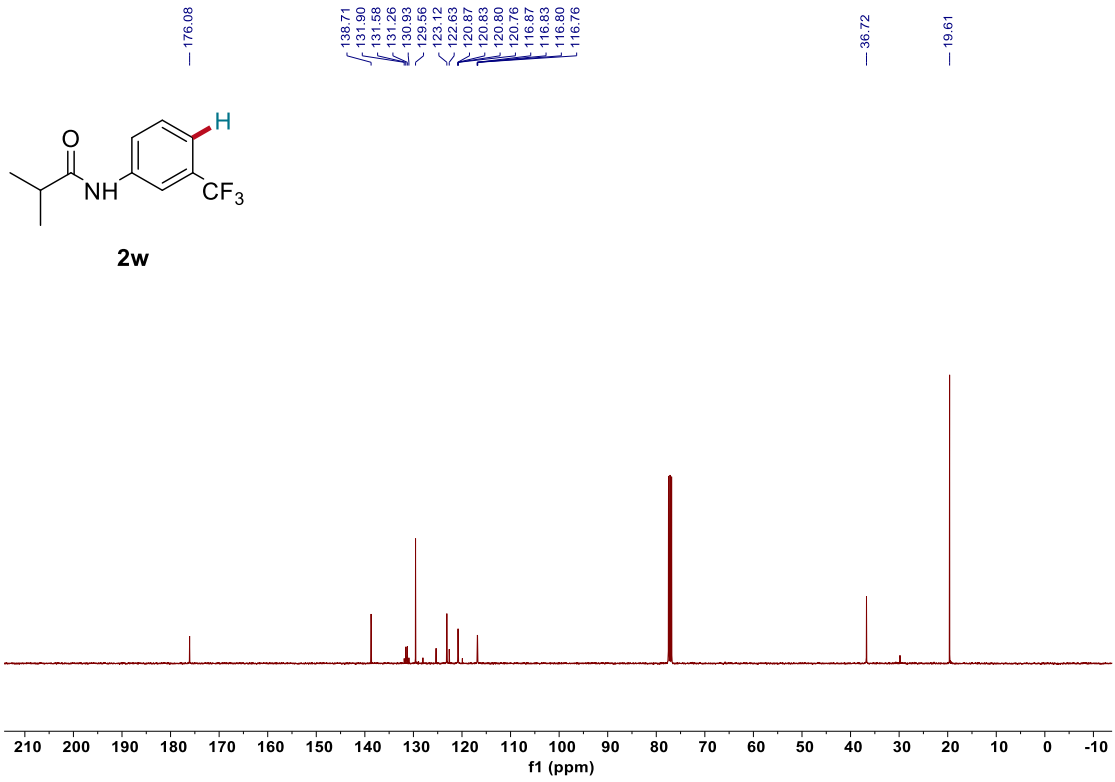


Figure S27. ^{13}C NMR Spectrum of **2w** (101 MHz, $CDCl_3$)

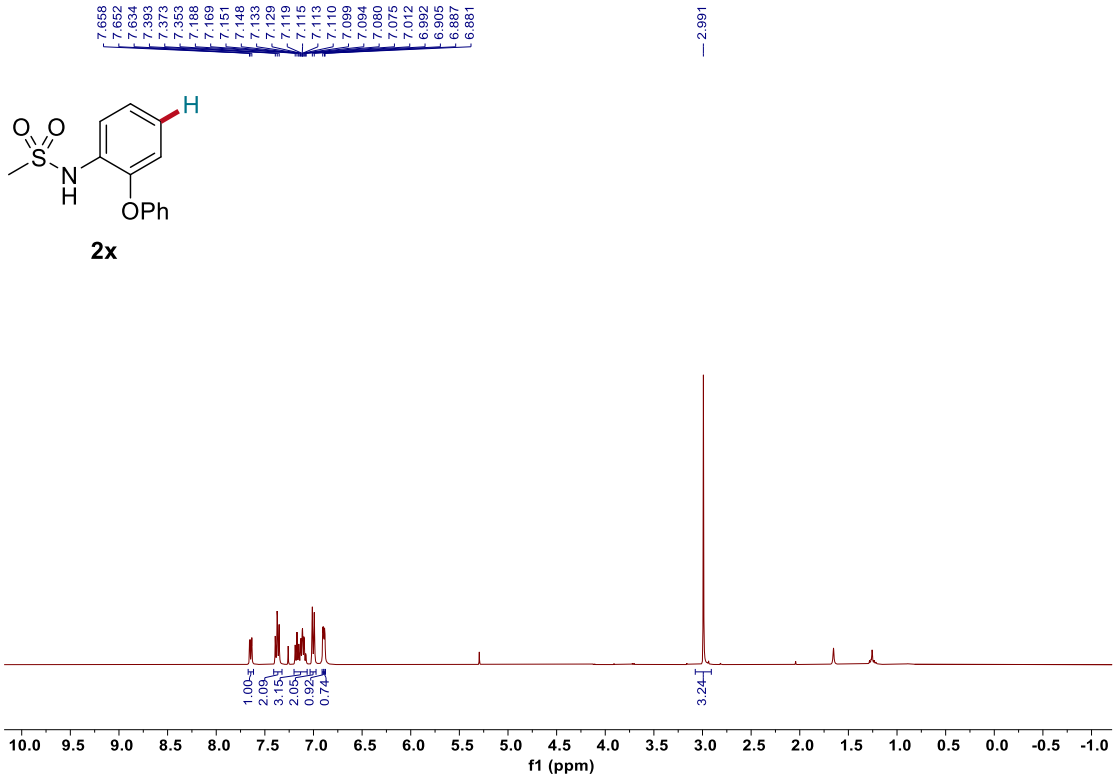


Figure S28. ^{1}H NMR Spectrum of **2x** (400 MHz, $CDCl_3$)

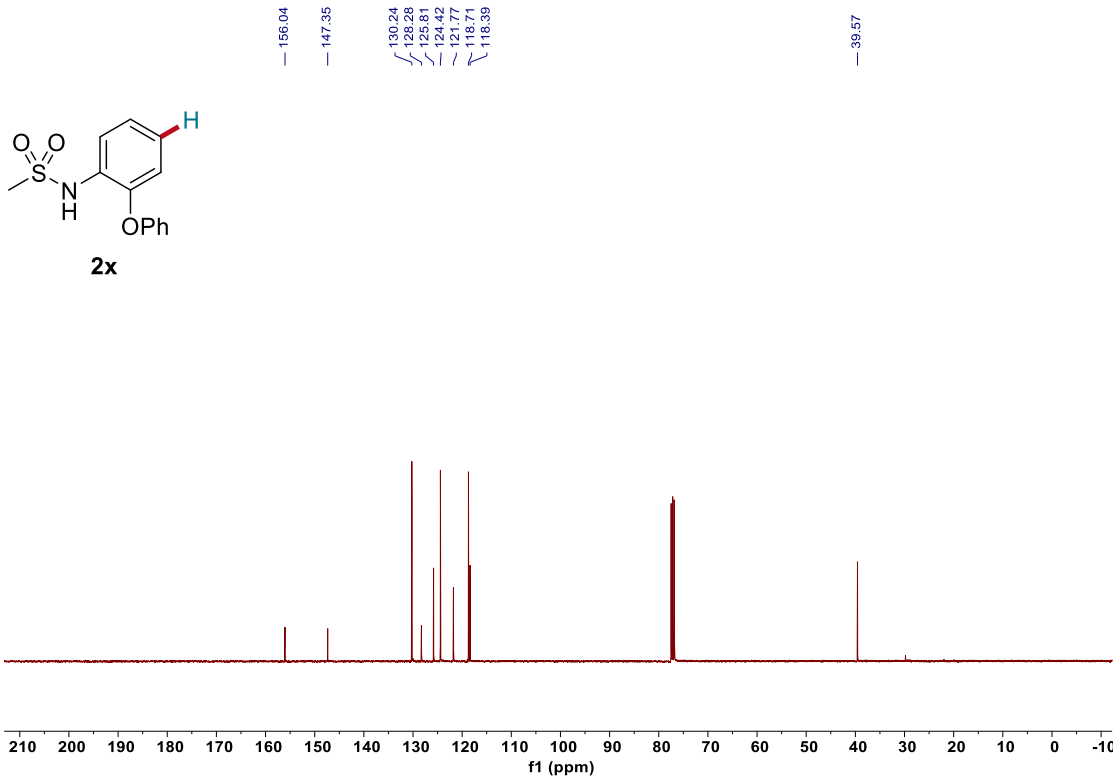


Figure S29. ^{13}C NMR Spectrum of **2x** (101 MHz, $CDCl_3$)

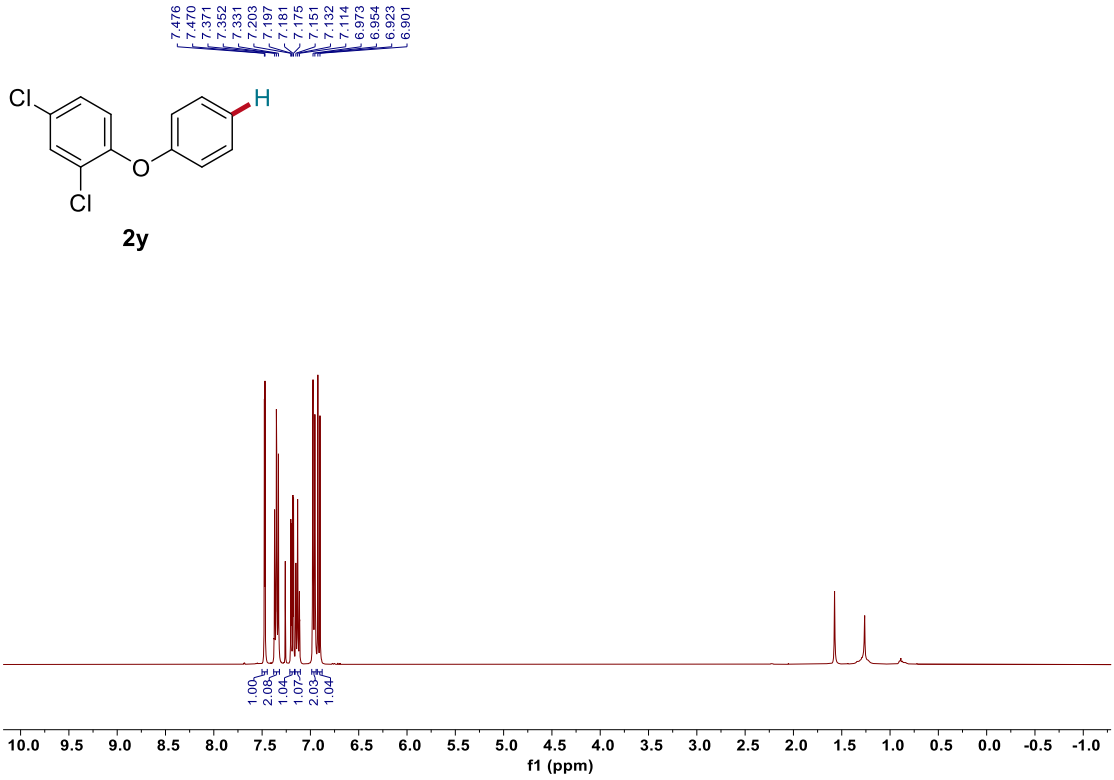


Figure S30. ^{1}H NMR Spectrum of **2y** (400 MHz, $CDCl_3$)

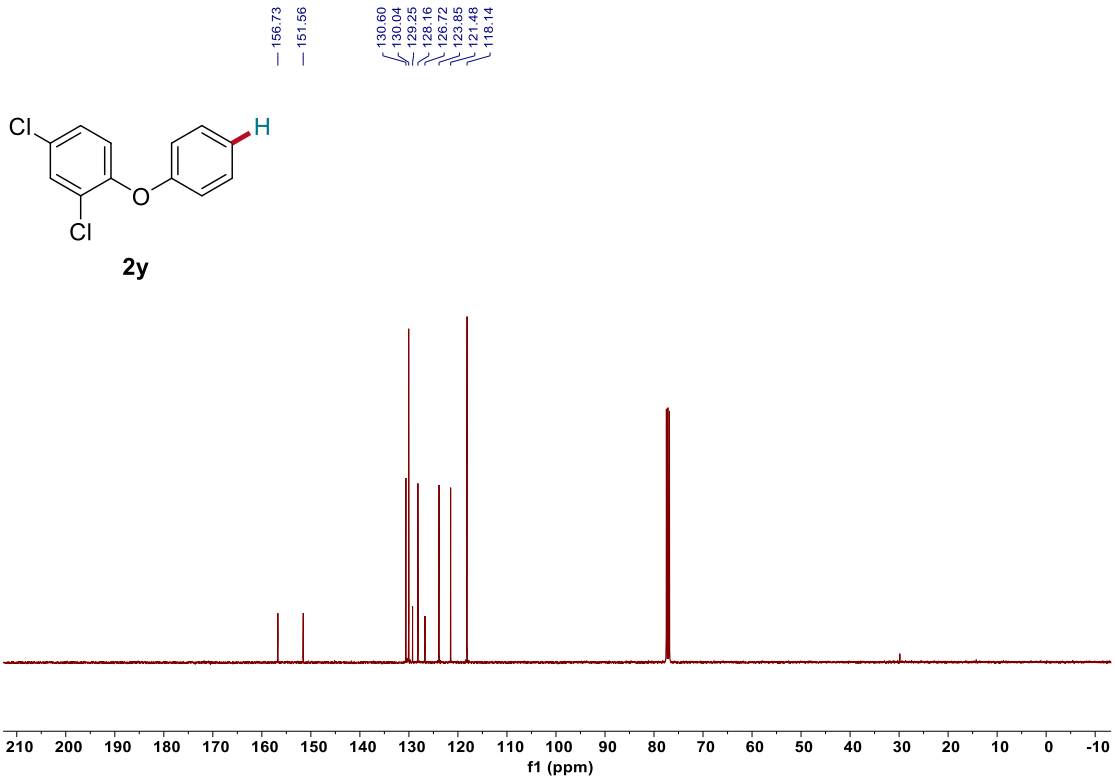


Figure S31. ^{13}C NMR Spectrum of **2y** (101 MHz, $CDCl_3$)

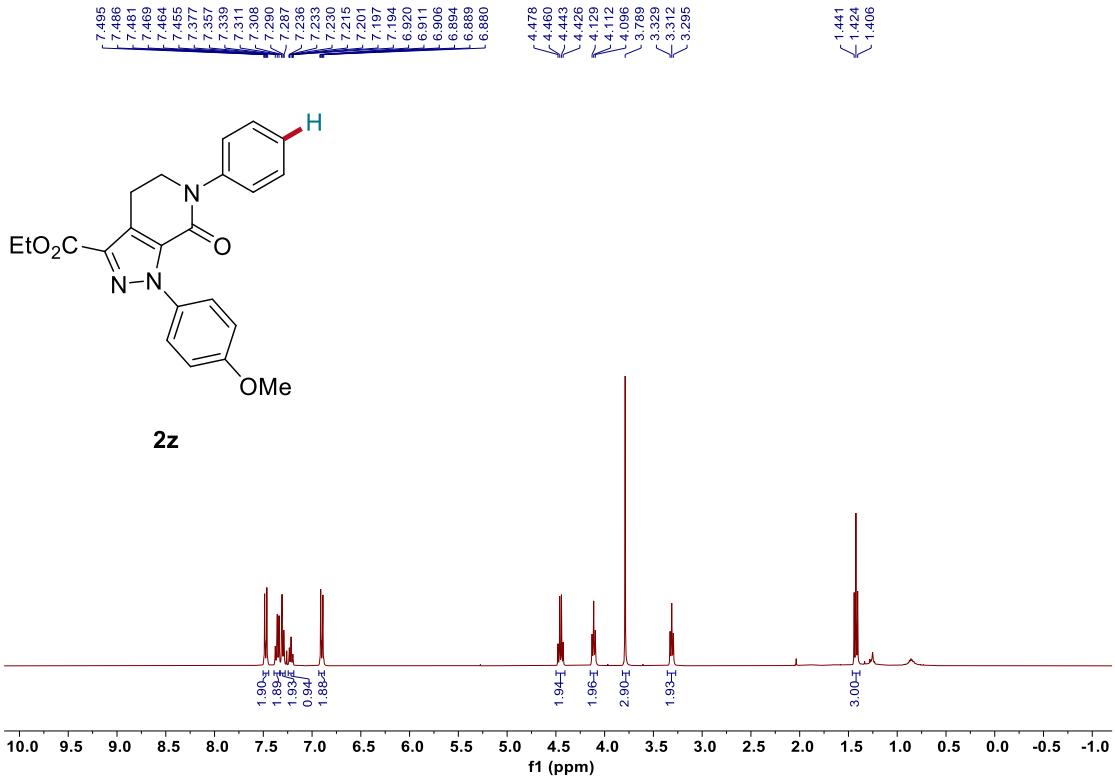


Figure S32. ^{1}H NMR Spectrum of **2z** (400 MHz, $CDCl_3$)

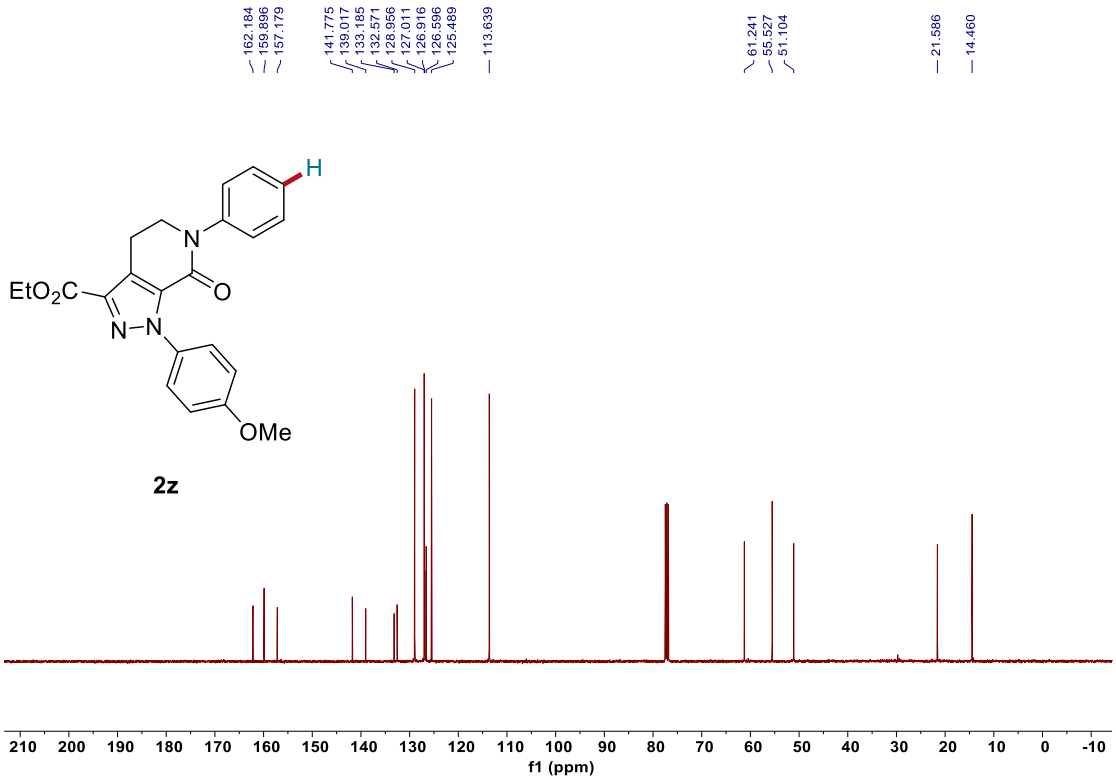


Figure S33. ^{13}C NMR Spectrum of **2z** (101 MHz, $CDCl_3$)

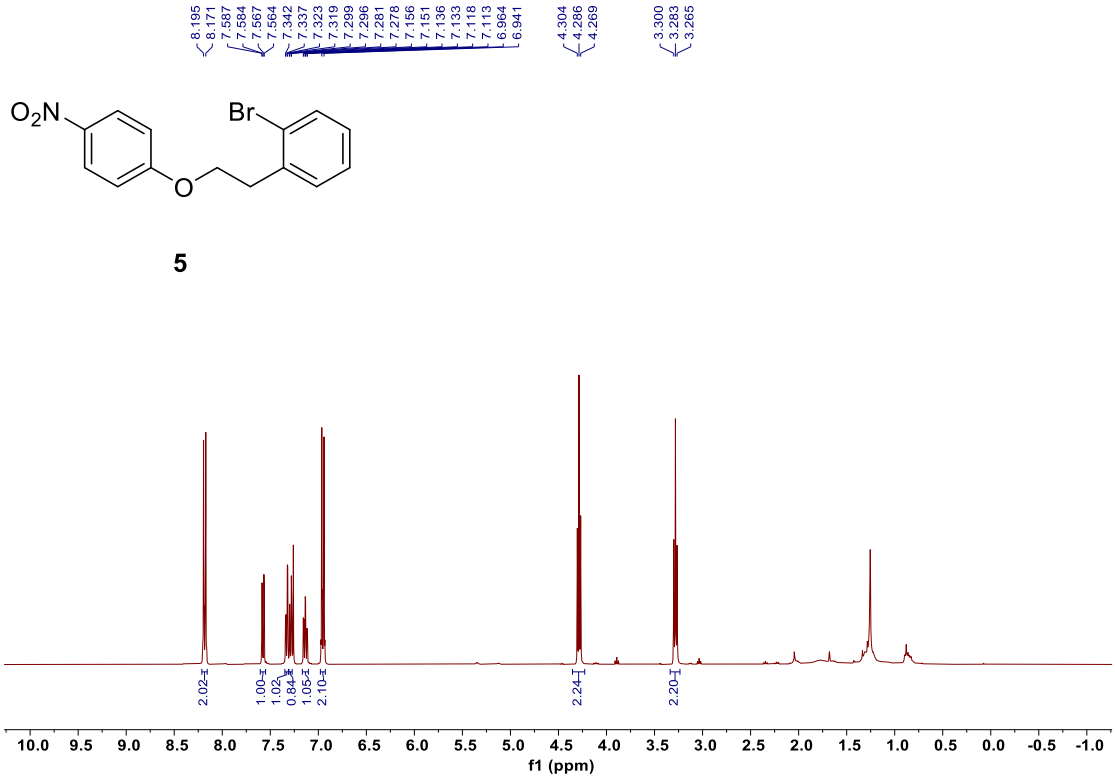


Figure S34. ^{1}H NMR Spectrum of **5** (400 MHz, $CDCl_3$)

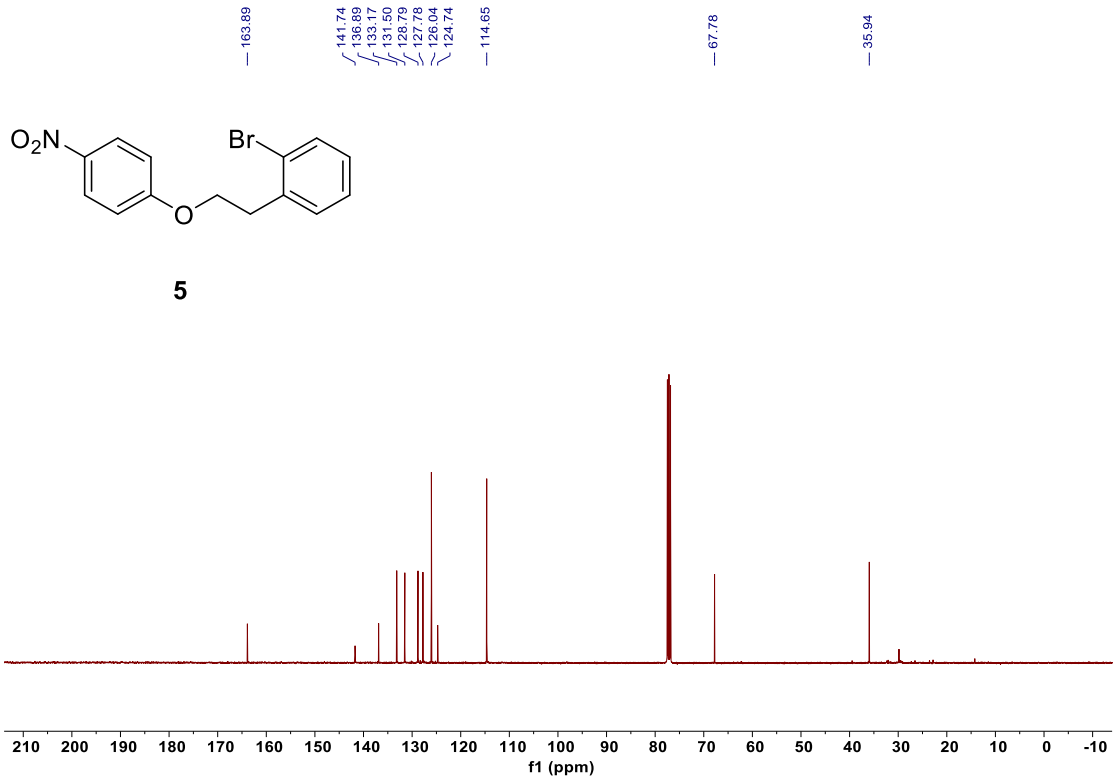


Figure S35. ^{13}C NMR Spectrum of **5** (101 MHz, $CDCl_3$)

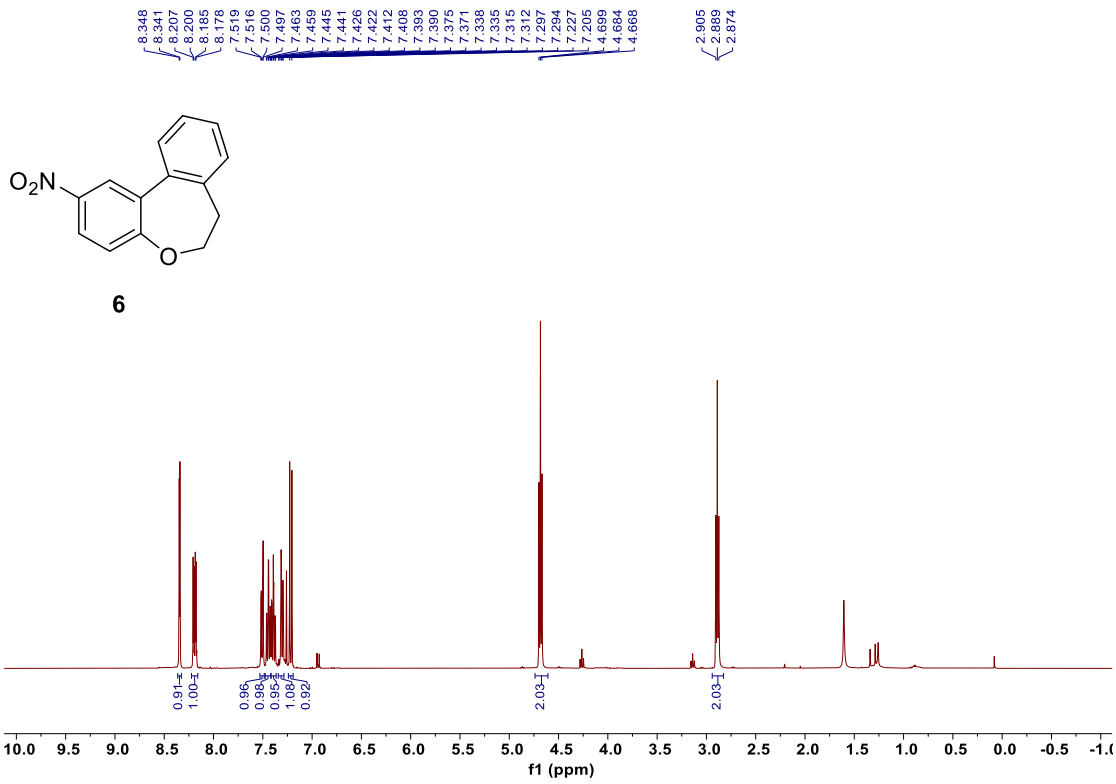


Figure S36. ^{1}H NMR Spectrum of **6** (400 MHz, $CDCl_3$)

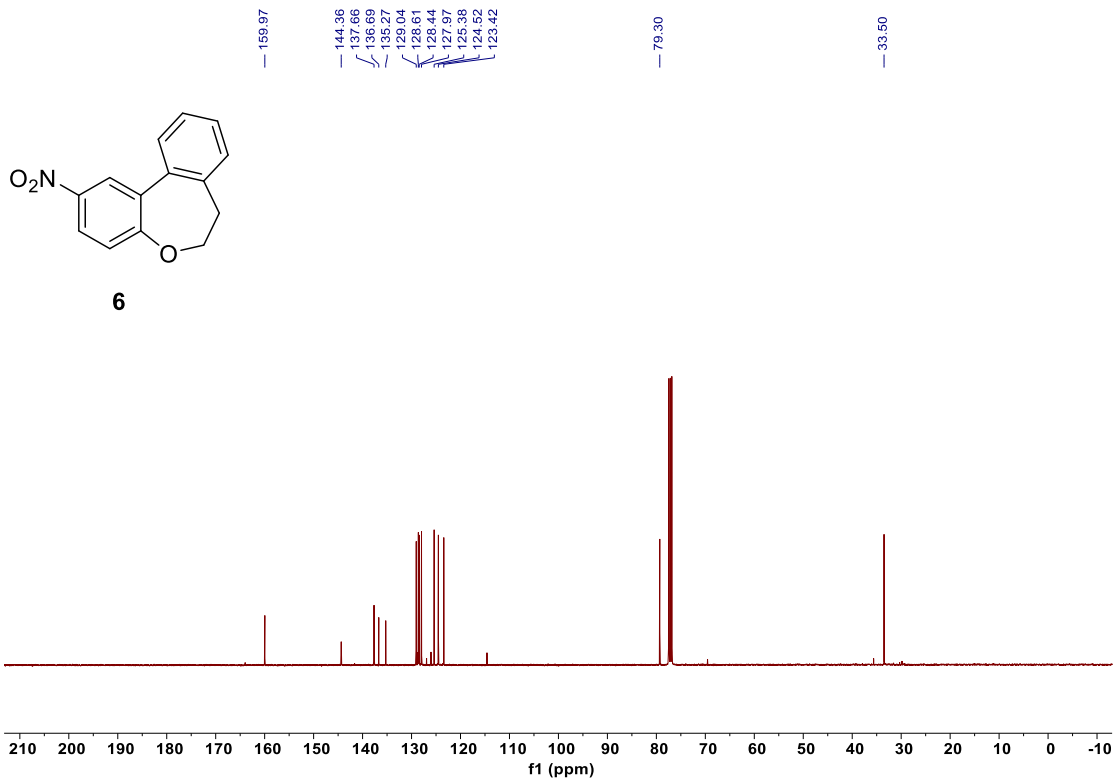


Figure S37. ^{13}C NMR Spectrum of **6** (101 MHz, $CDCl_3$)

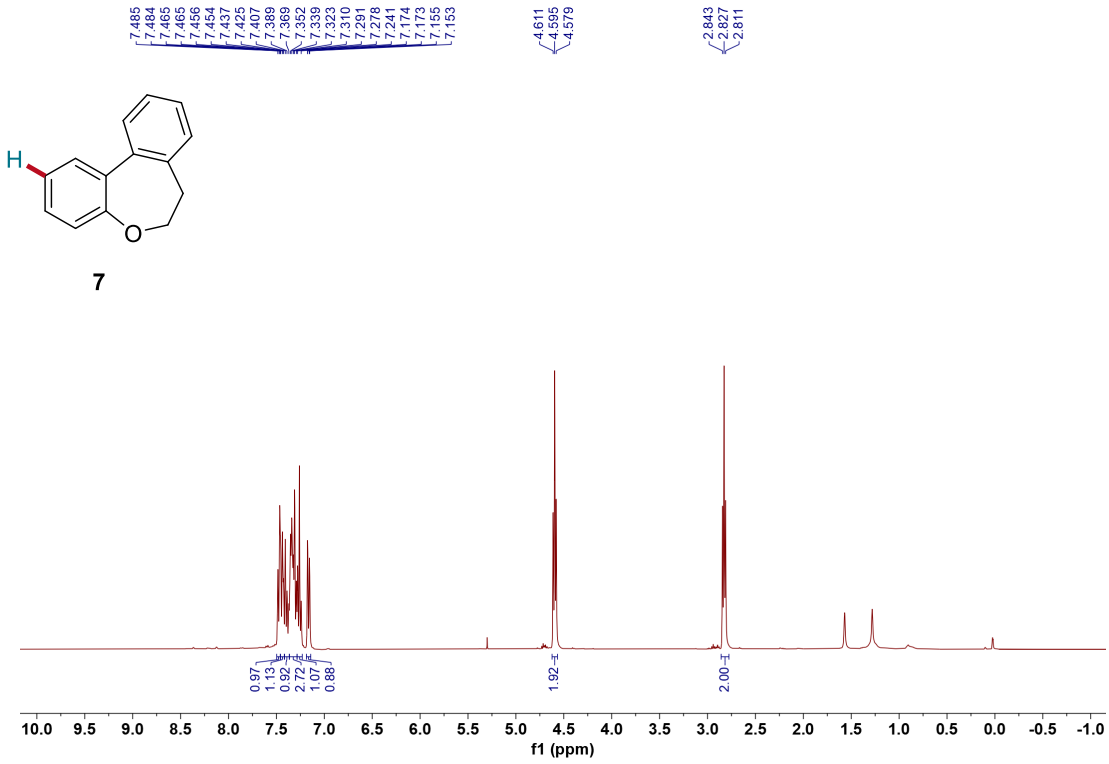


Figure S38. ^{1}H NMR Spectrum of **7** (400 MHz, $CDCl_3$)

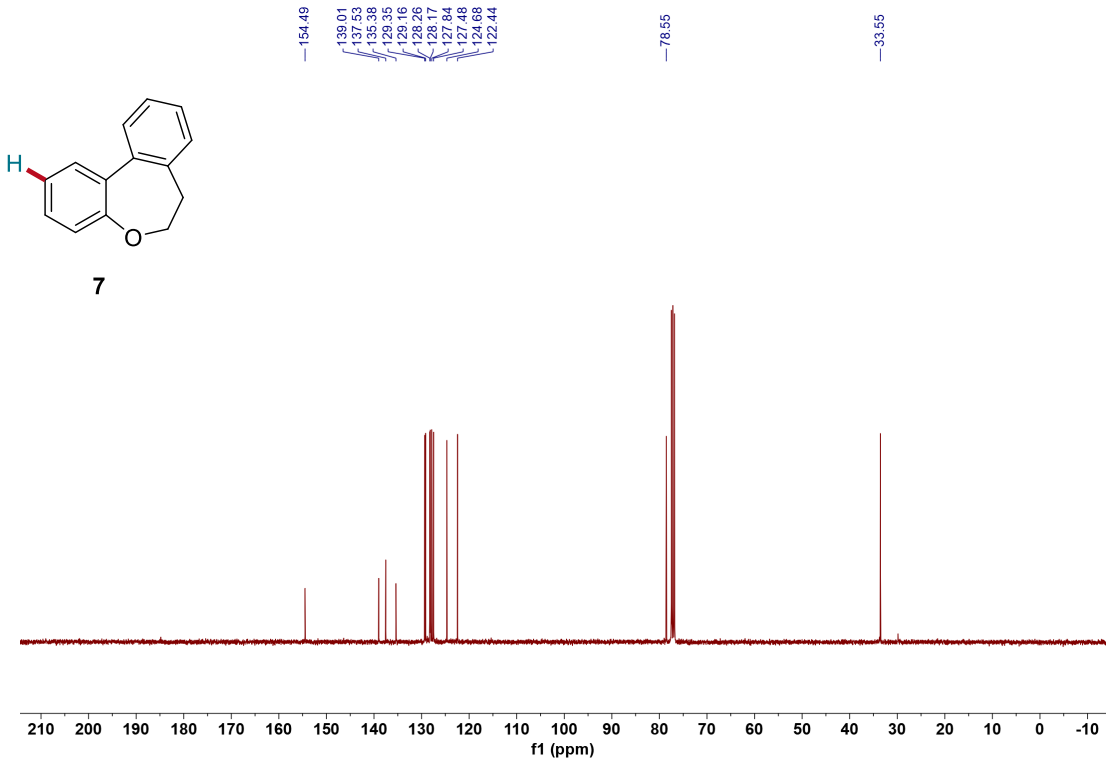


Figure S39. ^{13}C NMR Spectrum of **7** (101 MHz, $CDCl_3$)

9. GC/FID spectrum of products

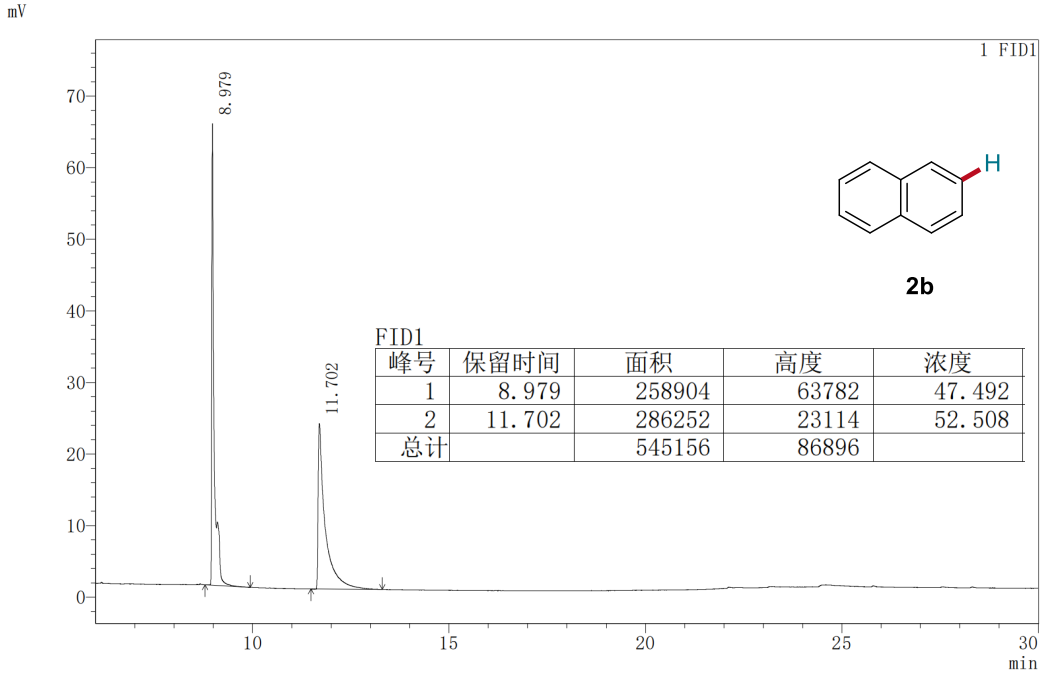


Figure S40: GC/FID spectrum: **2b** (8.979 min) and biphenyl (11.702 min) as internal standard.

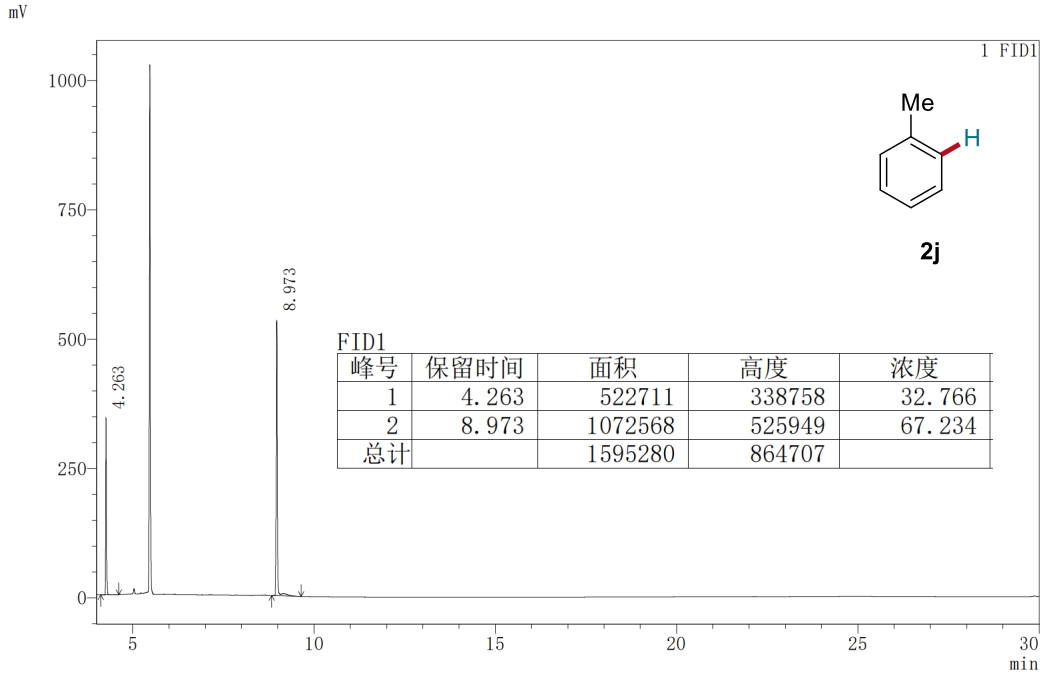
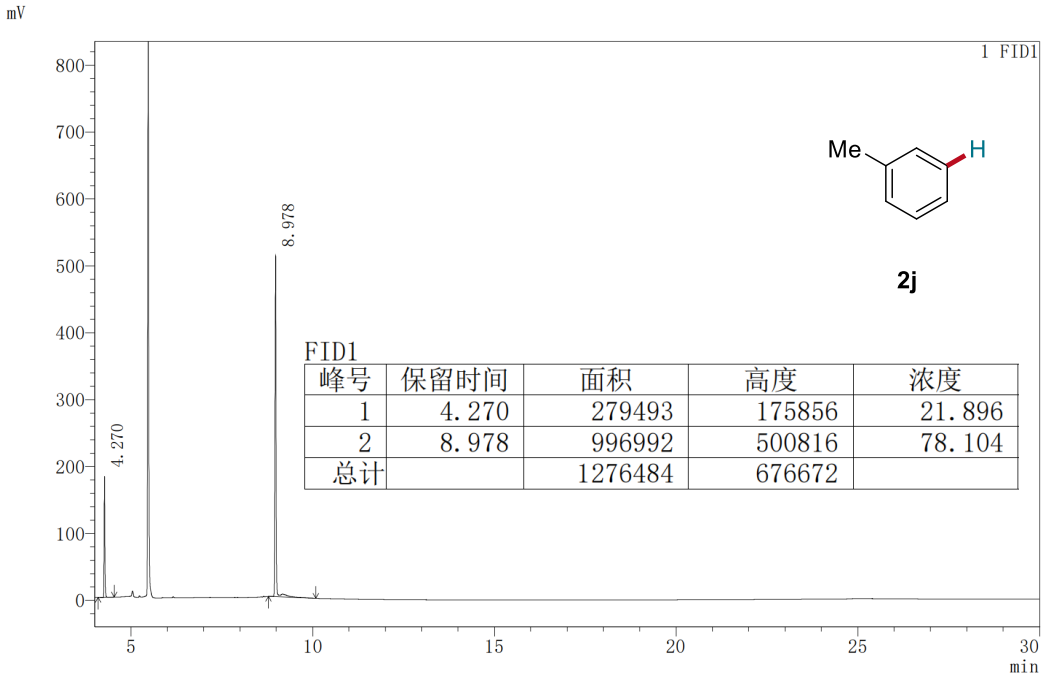


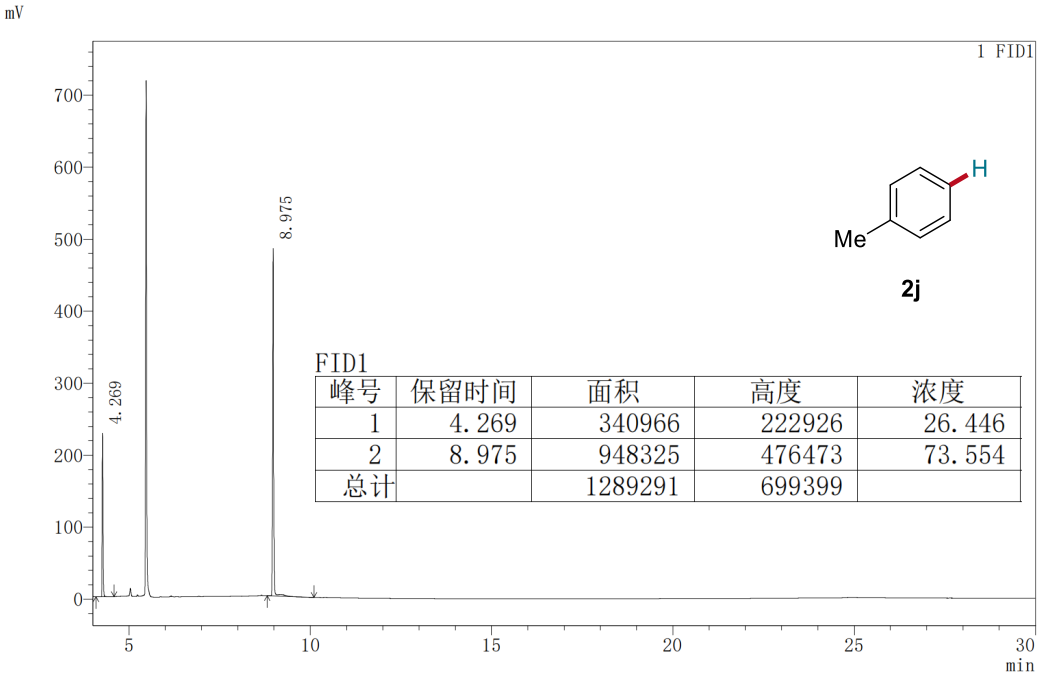
Figure S41: GC/FID spectrum: **2j** (4.263 min) and dodecane (8.973 min) as internal standard.



FID1

峰号	保留时间	面积	高度	浓度
1	4.270	279493	175856	21.896
2	8.978	996992	500816	78.104
总计		1276484	676672	

Figure S42: GC/FID spectrum: **2j** (4.270 min) and dodecane (8.978 min) as internal standard.



FID1

峰号	保留时间	面积	高度	浓度
1	4.269	340966	222926	26.446
2	8.975	948325	476473	73.554
总计		1289291	699399	

Figure S43**:** GC/FID spectrum: **2j** (4.269 min) and dodecane (8.975 min) as internal standard

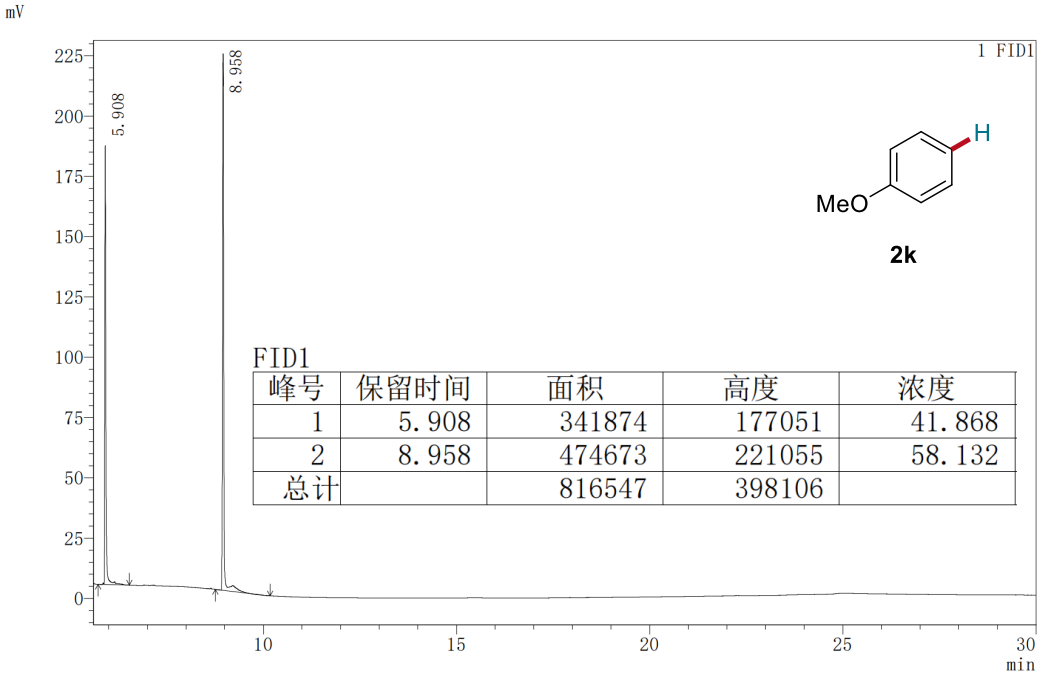


Figure S44: GC/FID spectrum: **2k** (5.908 min) and dodecane (8.958 min) as internal standard.

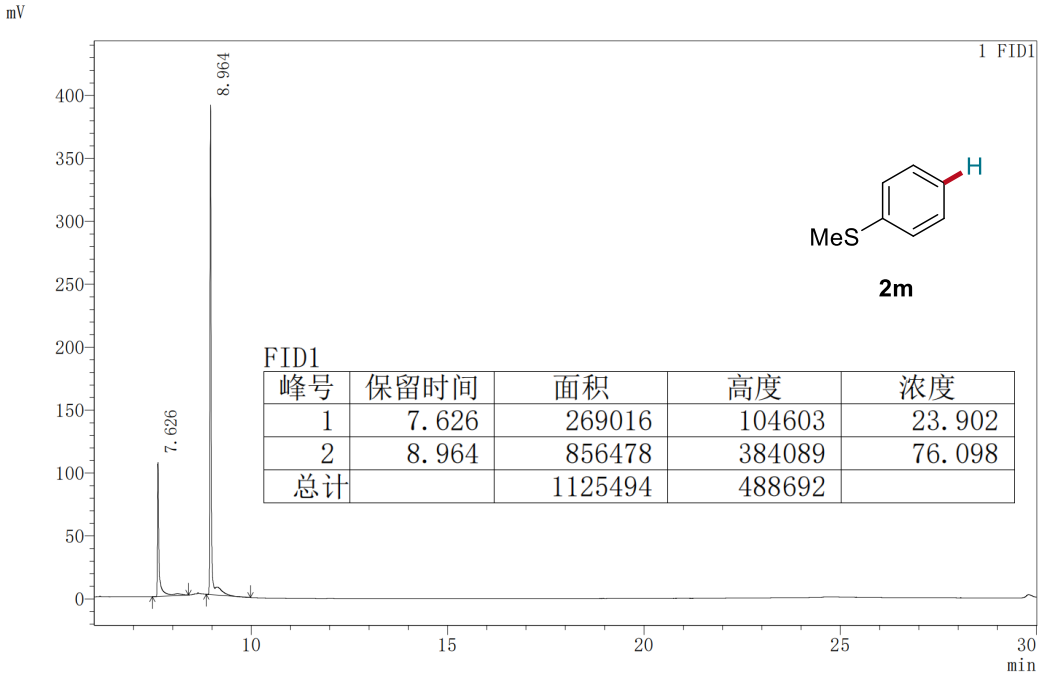
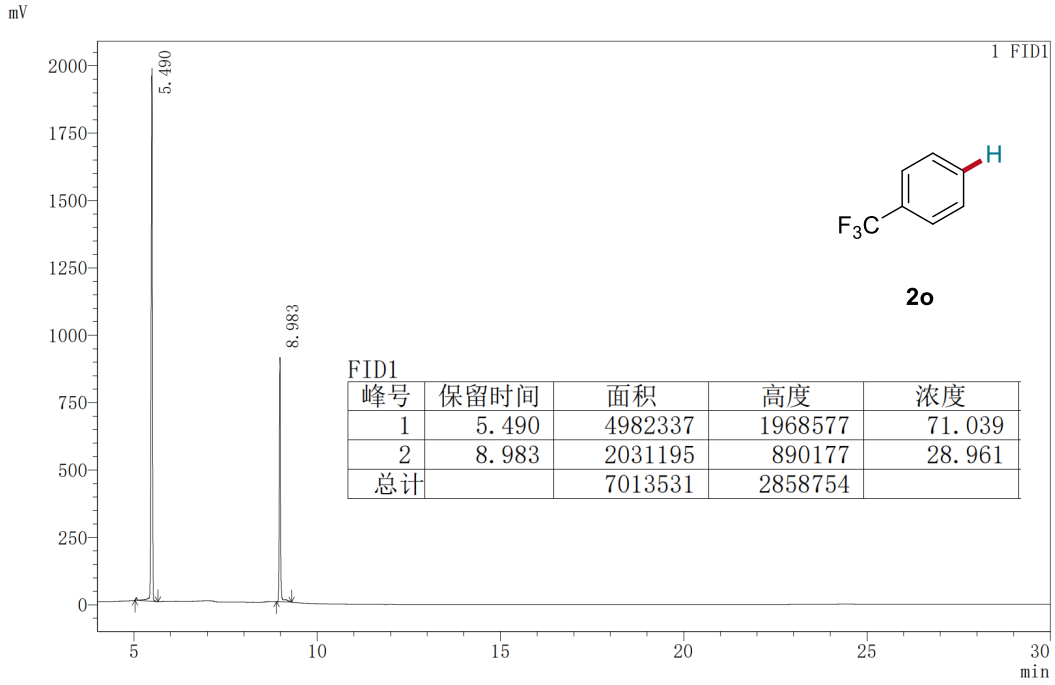


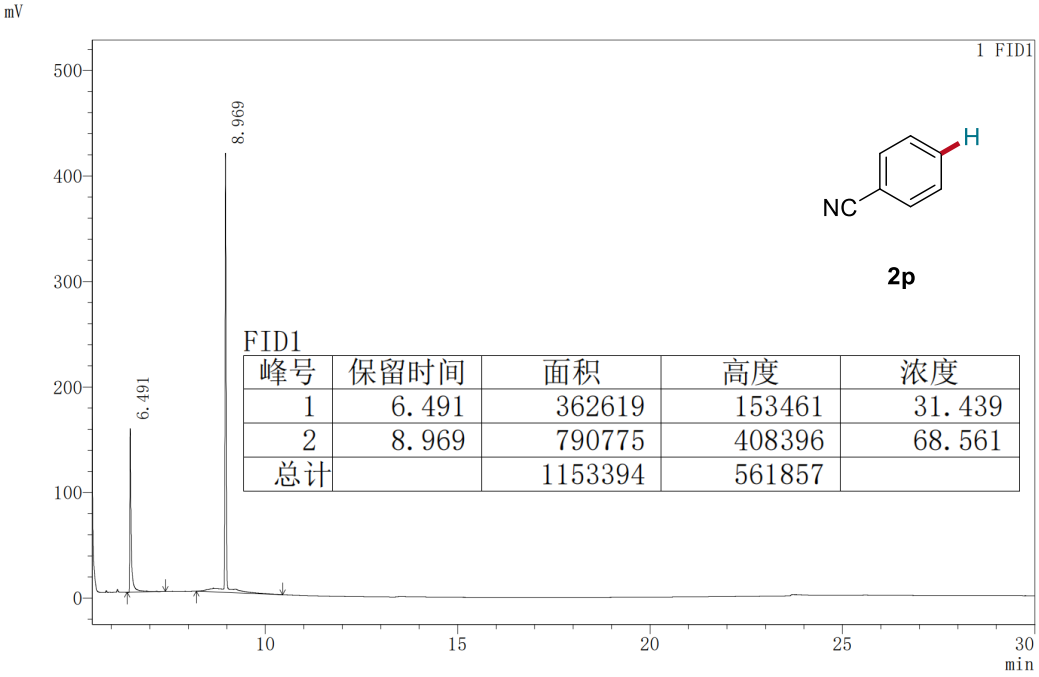
Figure S45: GC/FID spectrum: **2m** (7.626 min) and dodecane (8.964 min) as internal standard



FID1

峰号	保留时间	面积	高度	浓度
1	5.490	4982337	1968577	71.039
2	8.983	2031195	890177	28.961
总计		7013531	2858754	

Figure S46: GC/FID spectrum: **2o** (5.490 min) and dodecane (8.983 min) as internal standard.



FID1

峰号	保留时间	面积	高度	浓度
1	6.491	362619	153461	31.439
2	8.969	790775	408396	68.561
总计		1153394	561857	

Figure S47: GC/FID spectrum: **2p** (6.491 min) and dodecane (8.969 min) as internal standard.

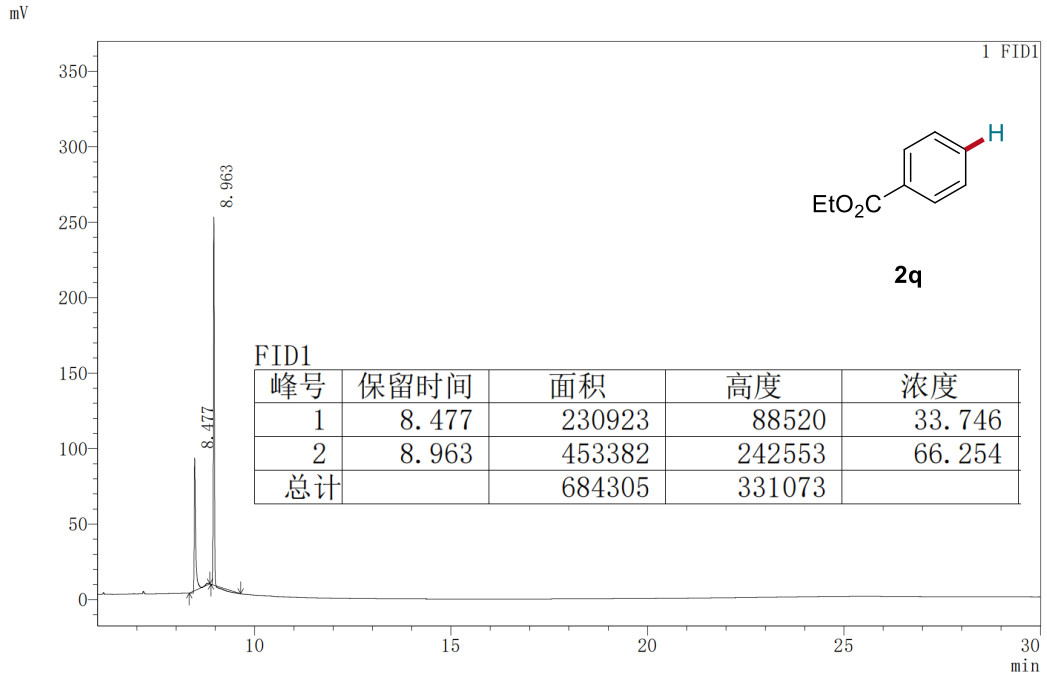


Figure S48: GC/FID spectrum: **2q** (8.477 min) and dodecane (8.963 min) as internal standard.

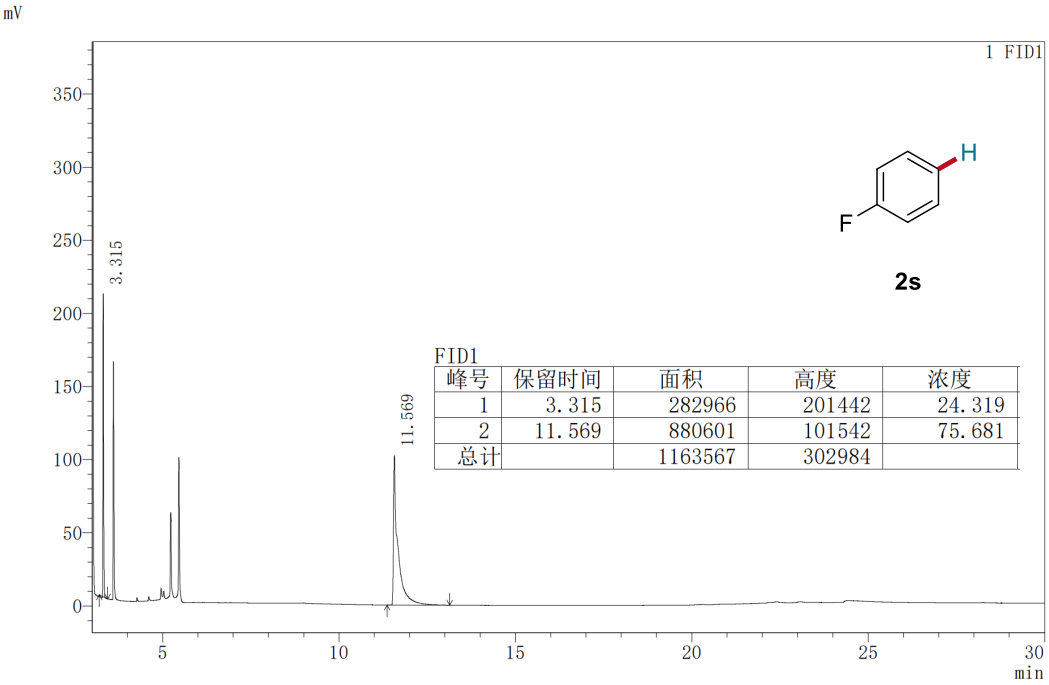
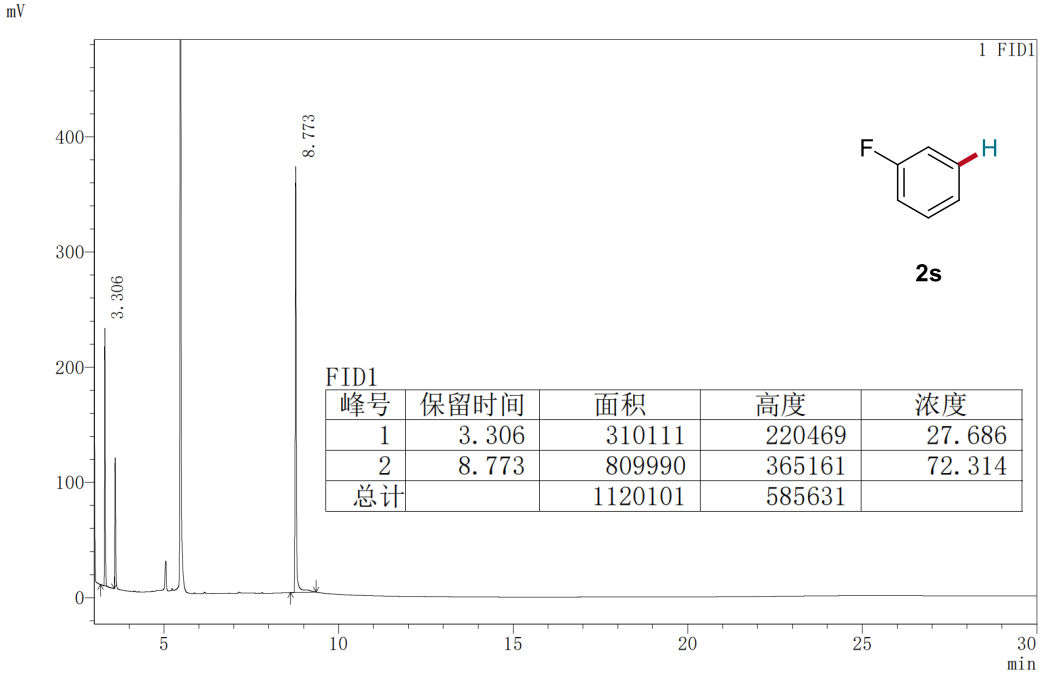


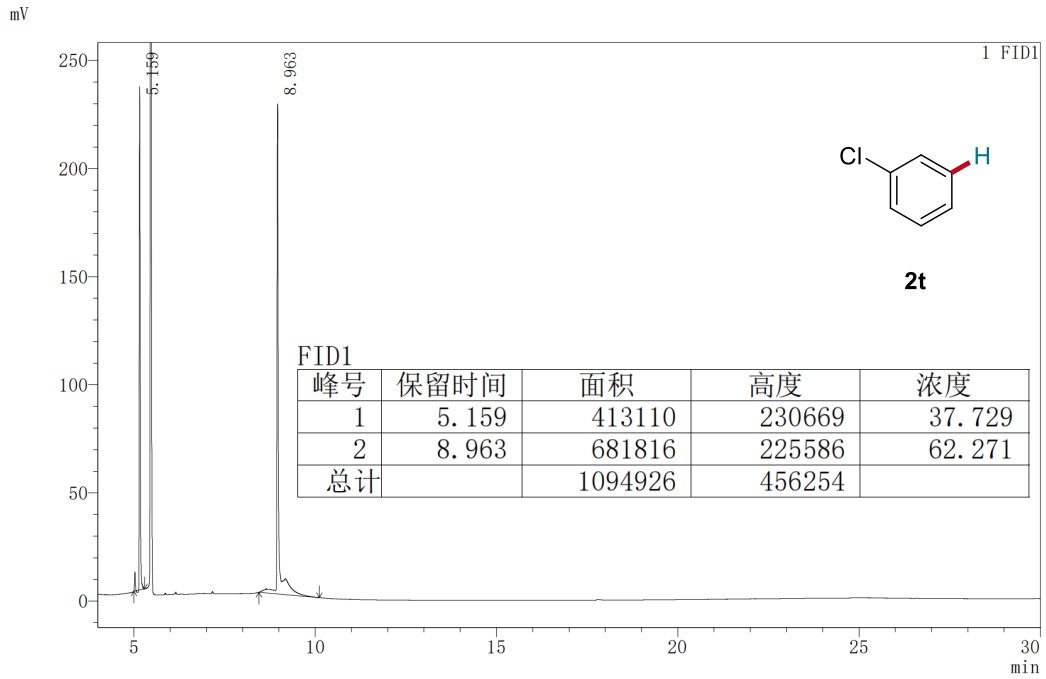
Figure S49: GC/FID spectrum: **2s** (3.315 min) and biphenyl (11.569 min) as internal standard.



FID1

峰号	保留时间	面积	高度	浓度
1	3.306	310111	220469	27.686
2	8.773	809990	365161	72.314
总计		1120101	585631	

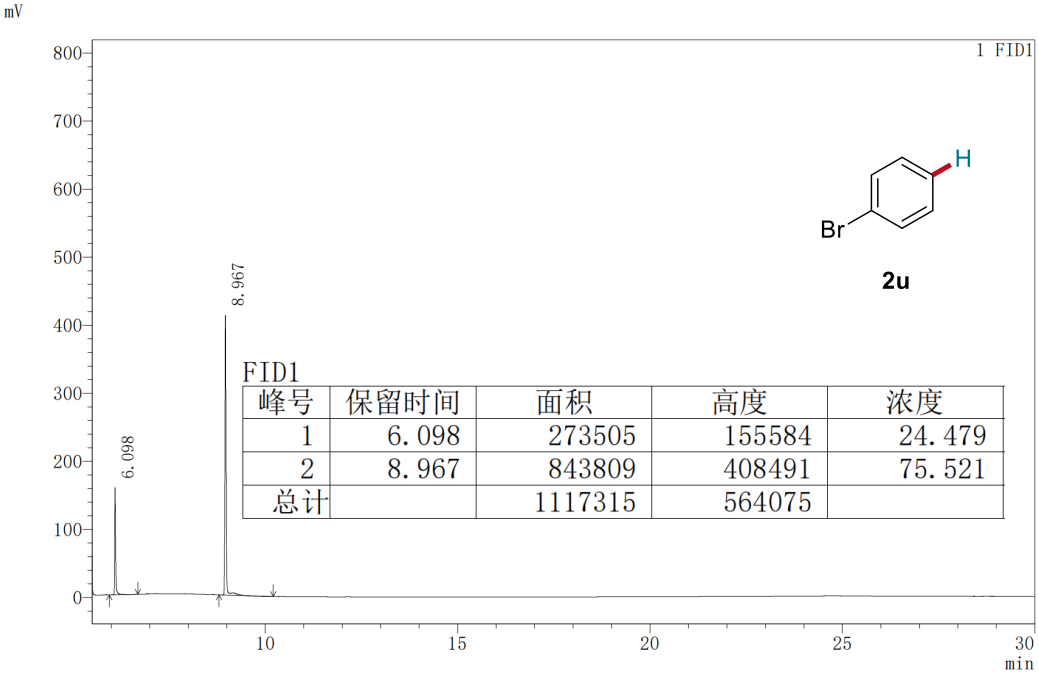
Figure S50: GC/FID spectrum: **2s** (3.306 min) and naphthalene (8.773 min) as internal standard.



FID1

峰号	保留时间	面积	高度	浓度
1	5.159	413110	230669	37.729
2	8.963	681816	225586	62.271
总计		1094926	456254	

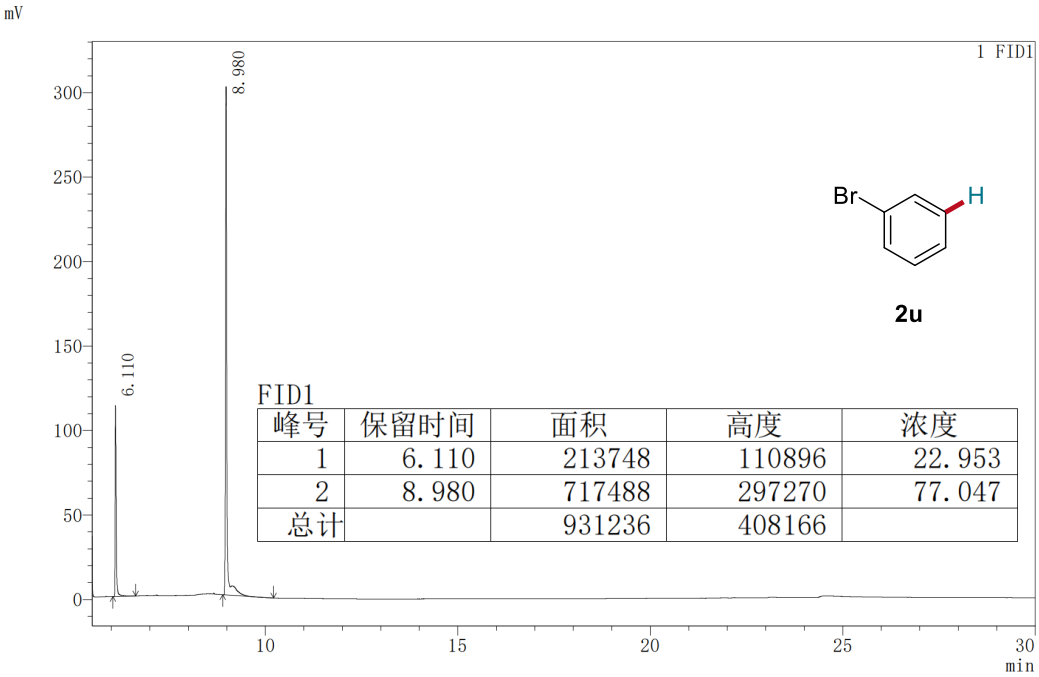
Figure S51: GC/FID spectrum: **2t** (5.159 min) and dodecane (8.963 min) as internal standard.



FID1

峰号	保留时间	面积	高度	浓度
1	6.098	273505	155584	24.479
2	8.967	843809	408491	75.521
总计		1117315	564075	

Figure S52: GC/FID spectrum: **2u** (6.098 min) and dodecane (8.967 min) as internal standard.



FID1

峰号	保留时间	面积	高度	浓度
1	6.110	213748	110896	22.953
2	8.980	717488	297270	77.047
总计		931236	408166	

Figure S53: GC/FID spectrum: **2u** (6.110 min) and dodecane (8.980 min) as internal standard.