Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Synthesis of Oxindole Fused 1,3-Oxazepanes via Hydride Transfer Initiated Ring Expansion of Pyrrolidine

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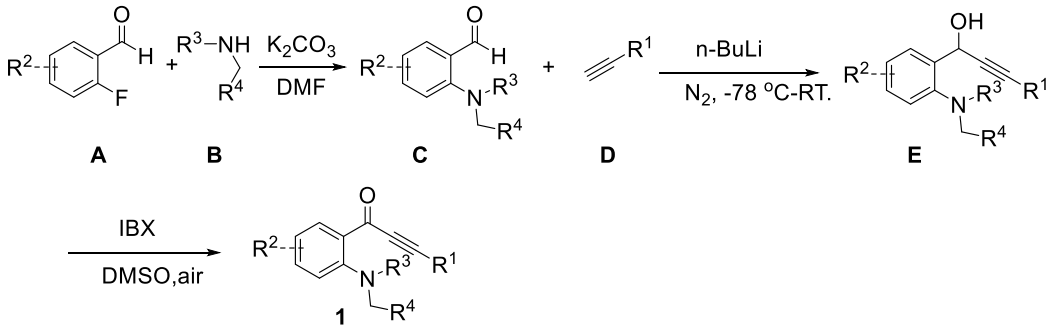
1. General methods

Unless noted, all commercial reagents were used without further purification. DCE is dried in calcium hydride and re-evaporated for use. THF and toluene are dried in sodium wire and re-evaporated for use. DMSO and DMF are re-evaporated for use. Reactions were monitored by thin layer chromatography. Purification of reaction products was carried out by flash chromatography on silica gel (200~300 mesh). ^{1}H NMR spectra were recorded at 500 MHz or 600 MHz, ^{13}C NMR spectra were recorded at 125 MHz or 150 MHz, and in $CDCl_3$ or d^6-DMSO (containing 0.03% TMS) solutions. ^{1}H NMR spectra were recorded with tetramethylsilane (δ= 0.00 ppm) as internal reference; ^{13}C NMR spectra were recorded with $CDCl_3$ (δ= 77.00 ppm) or d^6-DMSO (δ = 39.52 ppm) as internal reference. High-resolution mass spectra were performed on a mass spectrometer with a TOF (for EI or ESI) or FT-ICR (for MALDI) analyzer. Single crystal X-ray diffraction data was collected on a XtaLAB AFC11 (RCD3): quarter-chi single diffractometer with molybdenum cathodes.

The crystal preparation and measurement methods of **2a** as follows: Place 60.0 mg of **2a** in a 50 ml round bottom flask, dissolve **2a** with 4 mL of dichloromethane, then add 20 mL of petroleum ether and shake well, seal the flask with a sealing film, pierce a few holes, and let it stand still at room temperature until crystals precipitate out. The crystal was carefully picked out from the solvent with a spatula, and observed under a microscope to confirm that it was transparent for single crystal X-ray diffraction.

2. Synthesis of starting materials

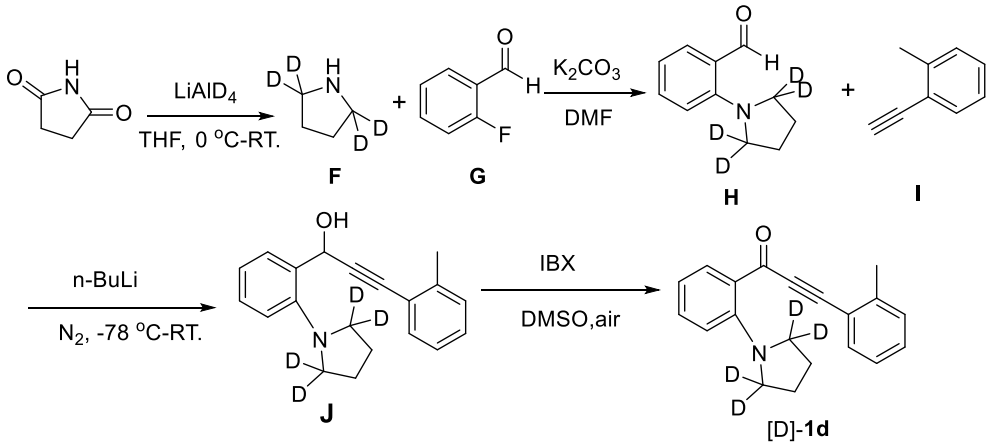
2.1 General Procedure for the Preparation of Ynones 1.



Potassium carbonate (12.0 mmol, 1.2 equiv,1.658 g) and amines **B** (12.0 mmol, 1.2 equiv) were added to a solution of the required o-fluorobenzaldehydes **A** (10.0 mmol, 1.0 equiv) in dimethylformamide (20 mL). The reaction mixture was heated to reflux for 3–6 h and then left to cool down to room temperature before being diluted with water. The aqueous layer was extracted with chloroform, and the organic layer was washed with water, dried over anhydrous $MgSO_4$, and evaporated in vacuo. The resulting oil was then eluted with 5% EtOAc in petrol through a silica plug to give the desired o-aminobenzaldehydes **C**.[1] To a solution of **C** (3.0 mmol, 1.0 equiv) in anhydrous THF (10 mL) was added n-BuLi (2.5 M in hexane, 3.6 mmol, 1.2 equiv) at -78 °C under N_2 atmosphere. The reaction was stirred at -78 °C for 1 h. **D** (3.9 mmol, 1.3 equiv) was added to the mixture, which was warmed up to room temperature gradually, and was stirred for an additional hour before being quenched with aqueous NH_4Cl. After extracting with ethyl acetate (3 × 20 mL), combined organic phases was washed with water and brine, dried over anhydrous $MgSO_4$. After filtration of $MgSO_4$, the filtrate was concentrated under reduced pressure to give the desired alcohol **E**. Without purification, **E** was added to a solution of IBX (3.6 mmol, 1.2 equiv, 1.008 g) in DMSO (10 mL) and the solution was heated to 35 °C (oil bath). for 1 h. The cooled reaction mixture was diluted with EtOAc (70 mL) and water (20 mL) and stirred vigorously for 10 min. Then it was filtered over celite. The organic layer was separated and the aqueous phase was extracted with DCM (3x10 mL). The combined extracts were sequentially washed with aq. sat. $NaHCO_3$ (10 mL) and NaCl solutions (10 mL),

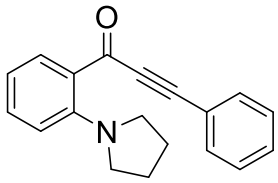
dried (Na_2SO_4) and evaporated in vacuo. The residue was subject to flash chromatography on silica gel (petroleum ether/ethyl acetate, 20:1) to afford pure alkynones **1**.

2.2 General procedure for the synthesis of deuterated 1-(2-(pyrrolidin-1-yl-2,2,5,5-d_4)phenyl)-3-(o-tolyl)prop-2-yn-1-one [D]-1d.



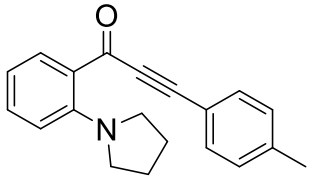
To a solution of pyrrolidine-2,5-dione (3.6 mmol, 357.0 mg) in THF (15 mL) was added $LiAlD_4$ (18 mmol, 756.0 mg) in portions in ice bath (0 °C). After stirring at 40 °C in oil bath for 12 h, $Na_2SO_4 \cdot 10H_2O$ was added until no bubbles appeared. Then DMF (15 mL), K_2CO_3 (4.5 mmol, 622.0 mg), and 2-fluorobenzaldehyde (3 mmol, 372.0 mg) were added in sequence. The mixture was heated to 120 °C in oil bath and monitored by TLC. After the consumption of 2-fluorobenzaldehyde, the mixture was cooled to room temperature and diluted with water (40 mL), and extracted with EtOAc (3 x 30 mL). The combined extracts were washed with brine (3 x 30 mL), dried by anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure and the residue was purified by flash column chromatography (eluent: EtOAc: petroleum ether, 1:20) to afford the deuterated substrate **H** as colorless oil in 76% yield (408 mg). To a solution of **H** (2.5 mmol, 1.0 equiv, 447.8 mg) in anhydrous THF (10 mL) was added n-BuLi (2.5 M in hexane, 3.0 mmol, 1.2 equiv) at -78 °C under N_2 atmosphere. The reaction was stirred at -78 °C for 1 h. **I** (3.25 mmol, 1.3 equiv, 377.2 mg) was added to the mixture, which was warmed up to room temperature gradually, and was stirred for an additional hour before being quenched with aqueous NH_4Cl. After extracting with ethyl acetate (3 × 20

mL), combined organic phases was washed with water and brine, dried over anhydrous $MgSO_4$. After filtration of $MgSO_4$, the filtrate was concentrated under reduced pressure to give the desired alcohol **J**. Without purification, **J** was added to a solution of IBX (3.0 mmol, 1.2 equiv, 840.0 g) in DMSO (10 mL) and the solution was heated to 35 °C (oil bath). for 1 h. The cooled reaction mixture was diluted with EtOAc (70 mL) and water (20 mL) and stirred vigorously for 10 min. Then it was filtered over celite. The organic layer was separated and the aqueous phase was extracted with DCM (3x10 mL). The combined extracts were sequentially washed with aq. sat. $NaHCO_3$ (10 mL) and NaCl solutions (10 mL), dried (Na_2SO_4) and evaporated in vacuo. The residue was subject to flash chromatography on silica gel (petroleum ether/ethyl acetate, 20:1) to afford pure alkynones [D]-**1d**. as yellow oil in 55% yield (403.2 mg).



1a

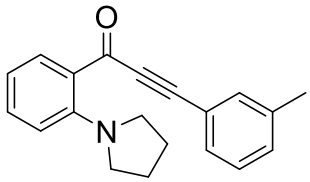
3-phenyl-1-(2-(pyrrolidin-1-yl)phenyl)prop-2-yn-1-one **(1a).** Yellow solid, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 20:1); yield: 50%, 412.70 mg, m.p. 71-73 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20-8.15 (m, 1H), 7.67-7.60 (m, 2H), 7.50-7.35 (m, 4H), 6.89-6.83 (m, 1H), 6.86 (d, J = 8.0 Hz, 1H), 3.24-3.19 (m, 4H), 2.02-1.95 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.6, 148.3, 133.4, 133.2, 132.8, 130.2, 128.5, 123.8, 120.7, 115.2, 114.3, 90.8, 88.7, 52.0, 25.9. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{18}NO$: 276.1383, found 276.1385.



1b

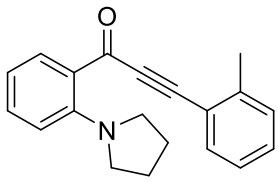
1-(2-(pyrrolidin-1-yl)phenyl)-3-(p-tolyl)prop-2-yn-1-one **(1b).** Yellow solid, purified

by chromatography on silica gel (petroleum ether/ethyl acetate = 20:1); yield: 75%, 648.0 mg, m.p. 119-121 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18-8.14 (m, 1H), 7.53 (d, *J* =8.0 Hz, 2H), 7.41-7.36 (m, 1H), 7.20 (d, *J* =8.0 Hz, 2H), 6.85 (d, *J* =8.0 Hz, 1H),6.81-6.76 (m, 1H), 3.24-3.19 (m, 4H), 2.39 (s, 3H), 2.00-1.95 (m,4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.9, 148.3, 140.8, 133.3, 133.2, 132.9, 129.3, 124.0, 117.6, 115.1, 114.3, 91.4, 88.5, 52.0, 25.9, 21.7. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{20}NO$ 290.1539, found 290.1539.



1c

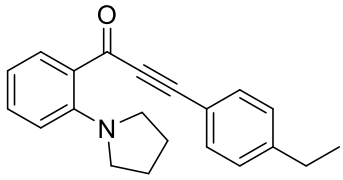
1-(2-(pyrrolidin-1-yl)phenyl)-3-(m-tolyl)prop-2-yn-1-one **(2c).** Yellow solid, purified by chromatography on silica gel (petroleum ether/ethyl acetate =20:1); yield: 48%, 416.0 mg, m.p. 115-117 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20-8.14 (m, 1H), 7.47-7.43 (m, 2H), 7.42-7.35 (m 1H), 7.32-7.22 (m, 2H), 6.85(d, *J* =8.5 Hz, 1H), 6.81-6.75 (m, 1H), 3.24-3.18 (m, 4H), 2.37(s, 3H), 2.02-1.96 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ176.7, 148.3, 138.3, 133.33, 133.31, 133.2, 131.1, 129.9, 128.4, 123.9, 120.5, 115.1, 114.3, 91.1, 88.4, 52.0, 25.9, 21.2. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{20}NO$ 290.1539, found 290.1537.



1d

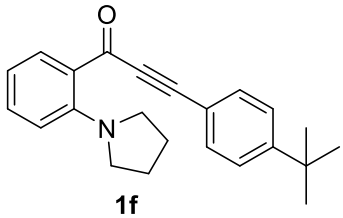
1-(2-(pyrrolidin-1-yl)phenyl)-3-(o-tolyl)prop-2-yn-1-one **(1d).** Yellow oil, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 20:1); yield: 58%, 503.1 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18-8.14 (m, 1H), 7.53 (d, *J* =8 Hz, 2H), 7.42-7.36 (m, 1H), 7.20 (d, *J* =8.0 Hz, 2H), 6.85 (d, *J* = 7.5 Hz, 1H), 6.81-6.76 (m, 1H), 3.24-3.19

(m, 4H), 2.39 (s,3 H), 2.00-1.90 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.8, 148.3, 141.9, 133.4, 133.3, 133.1, 130.3, 129.7, 125.8, 124.1, 120.6, 115.1, 114.3, 92.6, 89.9, 52.0, 25.9, 20.8. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{20}NO$ 290.1539, found 290.1542.



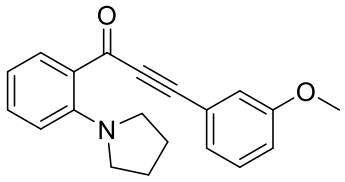
1e

3-(4-ethylphenyl)-1-(2-(pyrrolidin-1-yl)phenyl)prop-2-yn-1-one **(1e).** Yellow solid, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 20:1); yield: 55%, 498.7 mg, m.p. 80-82 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18-8.14 (m, 1H), 7.58-7.54 (m, 2H), 7.41-7.36 (m, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.85 (d, *J* = 7.5 Hz, 1H), 6.80-6.76 (m, 1H) 3.23-3.19 (m, 4H) 2.68 (q, *J* = 7.5Hz, 2H), 2.00-1.96 (m, 4H), 1.25 (t, *J* = 7.5Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.9, 148.3, 147.1, 133.25, 133.16, 133.0, 128.1, 124.0, 117.8, 115.1, 114.3, 91.5, 88.5, 52.0, 29.0, 25.9, 15.2. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{22}NO$ 304.1696, found 304.1697.



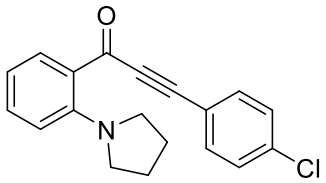
1f

3-(4-(tert-butyl)phenyl)-1-(2-(pyrrolidin-1-yl)phenyl)prop-2-yn-1-one **(1f).** Yellow oil, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 20:1); yield: 61%, 607.7 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18-8.14 (m, 1H), 7.60-7.55 (m, 2H), 7.44-7.36 (m, 3H), 6.86 (d, *J* = 7.5 Hz, 1H), 6.82-6.75 (m, 1H), 3.24-3.20 (m, 4H), 2.00-1.95 (m, 4H), 1.33 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.0, 153.9, 148.3, 133.3, 133.2, 132.7, 125.6, 124.0, 117.6, 115.1, 114.3, 91.4, 88.5, 52.0, 35.0, 31.1, 25.9. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{26}NO$ 332.2009, found 332.2006.



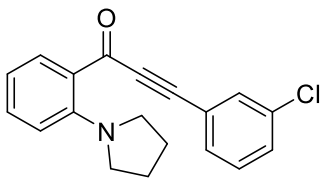
1g

3-(3-methoxyphenyl)-1-(2-(pyrrolidin-1-yl)phenyl)prop-2-yn-1-one **(2g).** Yellow oil, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 20:1); yield: 42%, 384.5 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18-8.16 (m, 1H), 7.42-7.37 (m, 1H), 7.32-7.27 (m, 1H), 7.26-7.22 (m, 1H), 7.17-7.14 (m, 1H), 7.02-6.97 (m, 1H), 6.86 (d, *J* = 7.5 Hz, 1H), 6.82-6.76 (m, 1H), 3.83 (s, 3H), 3.23-3.20 (m, 4H), 2.02-1.96 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.6, 159.4, 148.4, 133.4, 133.2, 129.6, 125.3, 123.8, 121.7, 117.3, 117.1, 115.2, 114.3, 90.7, 88.4, 55.4, 52.0, 25.9. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{20}NO$ 306.1489, found 306.1486.



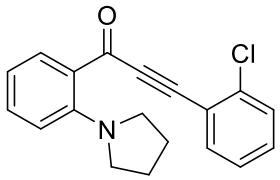
1h

3-(4-chlorophenyl)-1-(2-(pyrrolidin-1-yl)phenyl)prop-2-yn-1-one **(2h).** Yellow solid, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 20:1); yield: 67%, 624.0 mg, m.p. 84-86 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16-8.12 (m, 1H), 7.59-7.54 (m, 2H), 7.42-7.35 (m, 3H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.81-6.76 (m, 1H), 3.24-3.18 (m, 4H), 2.00-1.96 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.2, 148.4, 136.5, 134.0, 133.5, 133.2, 129.0, 123.5, 119.3, 115.2, 114.4, 89.4, 89.3, 52.1, 25.9. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{17}ClNO$ 310.0993, found 310.0997.



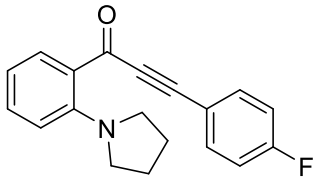
1i

3-(3-chlorophenyl)-1-(2-(pyrrolidin-1-yl)phenyl)prop-2-yn-1-one **(1i).** Yellow solid, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 20:1); yield: 45%, 417.0 mg, m.p. 89-91 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16-8.12 (m, 1H), 7.63-7.31 (m, 1H), 7.54-7.50 (m, 1H), 7.43-7.38 (m, 2H), 7.36-7.31 (m, 1H), 6.87 (d, *J* = 8.5 Hz, 1H), 6.81-6.77 (m, 1H), 3.24-3.19 (m, 4H), 2.01-1.97 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.0, 148.5, 134.4, 133.6, 133.3, 132.4, 130.9, 130.4, 129.8, 123.5, 122.5, 115.2, 114.4, 89.2, 88.7, 52.1, 25.9. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{17}ClNO$ 310.0993, found 310.0995.



1j

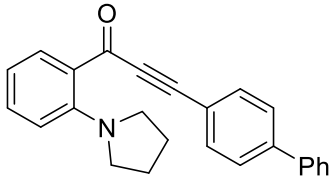
3-(2-chlorophenyl)-1-(2-(pyrrolidin-1-yl)phenyl)prop-2-yn-1-one **(1j).** yellow oil, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 20:1); yield: 44%, 407.8 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32-8.28 (m, 1H), 7.67-7.66 (m, 1H) 7.48-7.44 (m, 1H), 7.42-7.34 (m, 2H),7.31-7.27 (m, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.82-6.77 (m, 1H), 3.24-3.20 (m, 4H), 2.05-1.95 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.0, 148.5, 137.2, 134.6, 133.7, 133.6, 131.1, 129.5, 126.7, 123.6, 121.0, 115.3, 114.3, 92.8, 86.8, 52.1, 25.9. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{17}ClNO$ 310.0993, found 310.0996.



1k

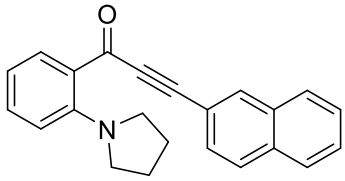
3-(4-fluorophenyl)-1-(2-(pyrrolidin-1-yl)phenyl)prop-2-yn-1-one **(1k).** Yellow solid, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 20:1); yield: 64%, 562.9 mg, m.p. 88-90 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16-8.13 (m, 1H), 7.67-7.60 (m, 2H), 7.42-7.36 (m, 1H), 7.12-7.06 (m, 2H), 6.86 (d, *J* = 7.5 Hz, 1H), 6.81-6.75

(m, 1H), 3.23-3.19 (m, 4H), 2.00-1.96 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.4, 163.7 (d, J = 251.4 Hz), 148.4, 134.6 (d, J = 8.8 Hz), 113.4, 133.2, 123.7, 116.9 (d, J = 3.5 Hz), 116.0 (d, J = 22.3 Hz), 115.2, 114.4, 89.7, 88.5, 52.0, 25.9. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{17}FNO$ 294.1289, found 294.1287.



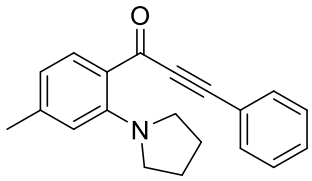
1l

3-([1,1'-biphenyl]-4-yl)-1-(2-(pyrrolidin-1-yl)phenyl)prop-2-yn-1-one **(1l).** Yellow oil, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 20:1); yield: 45%, 476.0 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21-8.18 (m, 1H), 7.73-7.69 (m, 2H), 7.65-7.59 (m, 4H), 7.49-7.44 (m, 2H), 7.41-7.37 (m, 2H), 6.87 (d, J = 8.0 Hz, 1H), 6.82-6.78 (m, 1H), 3.25-3.21 (m, 4H), 2.01-1.97 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.6, 148.4, 143.0, 139.9, 133.4, 133.3, 133.2, 128.9, 128.0, 127.2, 127.1, 123.8, 119.5, 115.2, 114.3, 90.8, 89.4, 52.1, 25.9. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{22}NO$ 352.1696, found 352.1699.



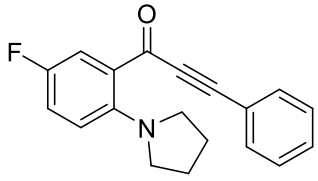
1m

3-(naphthalen-2-yl)-1-(2-(pyrrolidin-1-yl)phenyl)prop-2-yn-1-one **(1m).** Yellow solid, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 20:1); yield: 42%, 409.6 mg, m.p. 104-106 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25-8.19 (m, 2H), 7.90-7.83 (m, 3H), 7.67-7.62 (m, 1H), 7.59-7.51 (m, 2H), 7.43-7.38 (m, 1H), 6.87 (d, J = 7.5 Hz, 1H), 6.84-6.79 (m, 1H), 3.26-3.22 (m, 4H), 2.01-1.97 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.6, 148.4, 133.8, 133.7, 133.4, 133.3, 132.7, 128.5, 128.3, 128.1, 127.9, 127.7, 126.9, 123.9, 118.0, 115.2, 114.3, 91.3, 89.0, 52.1, 25.9. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{20}NO$ 326.1539, found 326.1530.



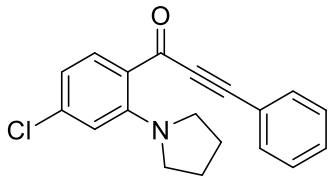
1n

1-(4-methyl-2-(pyrrolidin-1-yl)phenyl)-3-phenylprop-2-yn-1-one **(1n).** Yellow solid, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 20:1); yield: 49%, 421.1 mg, m.p. 118-120 ºC.. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.0 Hz, 1H), 7.65-7.62 (m, 2H), 7.44-7.36 (m, 3H), 6.66 (s, 1H), 6.63-6.60 (m, 1H), 3.24-3.21 (m, 4H), 2.37 (s, 3H), 2.00-1.96 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.9, 148.7, 144.3, 133.6, 132.8, 130.1, 128.5, 121.8, 120.9, 116.7, 114.5, 90.2, 88.8, 52.0, 25.9, 22.1. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{20}NO$ 290.1539, found 290.1542.



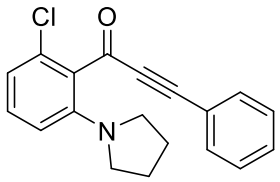
1o

1-(5-fluoro-2-(pyrrolidin-1-yl)phenyl)-3-phenylprop-2-yn-1-one **(1o).** Yellow oil, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 20:1); yield: 76%, 668.1 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88-7.83 (m, 1H), 7.67-7.63 (m, 2H), 7.48-7.38 (m, 3H), 7.19-7.14 (m, 1H), 6.84-6.80 (m, 1H), 3.20-3.17 (m, 4H), 2.01-1.97 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.6, 153.5 (d, *J* =233.8 Hz),145.4, 132.9, 130.5, 128.6, 123.4 (d, *J* = 5.3 Hz), 121.2 (d, *J* = 23.1 Hz), 120.4, 117.8 (d, *J* = 22.9 Hz), 115.5 (d, *J* = 7.0 Hz), 91.4, 88.2, 52.3, 25.9. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{17}FNO$ 294.1289, found 294.1279.



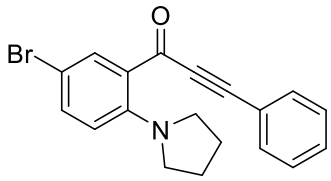
1p

1-(4-chloro-2-(pyrrolidin-1-yl)phenyl)-3-phenylprop-2-yn-1-one **(1p).** Yellow solid, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 20:1); yield: 76%, 704.5 mg, m.p. 72-76 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.5 Hz, 1H), 7.65-7.62 (m, 2H), 7.46-7.38 (m, 3H), 6.84 (d, *J* = 2.0 Hz, 1H), 6.76-6.72 (m, 1H), 3.22-3.19 (m, 4H), 2.01-1.97 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.6, 148.9, 139.6, 134.5, 132.9, 130.4, 128.6, 122.4, 120.5, 115.5, 114.0, 91.2, 88.3, 52.1, 25.9. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{17}ClNO$ 310.0993, found 310.0989.



1q

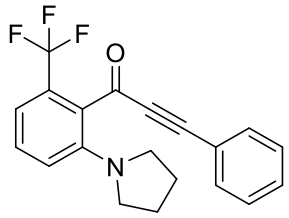
1-(2-chloro-6-(pyrrolidin-1-yl)phenyl)-3-phenylprop-2-yn-1-one **(1q).** Yellow solid, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 20:1); yield: 70%, 648.9 mg, m.p. 75-77 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61-7.57 (m, 2H), 7.47-7.42 (m, 1H), 7.40-7.36 (m, 2H), 7.19-7.14 (m, 1H), 6.76-6.73 (m, 1H), 6.68-6.65 (m, 1H), 3.30-3.26 (m, 4H), 1.97-1.93 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.5, 147.5, 133.1, 132.1, 130.8, 130.7, 128.6, 124.1, 120.4, 117.4, 112.8, 94.5, 90.0, 51.3, 25.9. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{17}ClNO$ 310.0993 found 310.0986.



1r

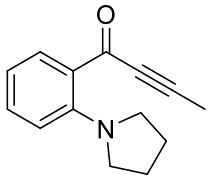
1-(5-bromo-2-(pyrrolidin-1-yl)phenyl)-3-phenylprop-2-yn-1-one **(1r).** Yellow oil, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 20:1); yield:

66%, 700.0 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 2.0 Hz, 1H), 7.67-7.64 (m, 2H), 7.49-7.39 (m, 4H), 6.75 (d, *J* = 9.0 Hz, 1H), 3.20-3.16 (m, 4H), 2.01-1.97 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.4, 147.2, 135.8, 134.8, 133.0, 130.5, 128.6, 125.0, 120.4, 116.2, 106.4, 91.7, 88.1, 52.2, 25.9. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{17}BrNO$ 354.0488, found 354.0485.



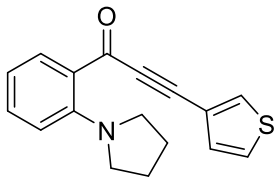
1s

3-phenyl-1-(2-(pyrrolidin-1-yl)-6-(trifluoromethyl)phenyl)prop-2-yn-1-one **(1s).** Yellow oil, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 20:1); yield: 53%, 546.6 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57-7.54(m, 2H), 7.45-7.42 (m, 1H), 7.39-7.34 (m, 3H), 7.08 (d, *J* = 7.5 Hz, 1H), 7.01 (d, *J* = 8.5 Hz, 1H), 3.38-3.34 (m, 4H), 2.00-1.93 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 181.4, 147.6, 133.0, 130.8, 130.0, 128.59 (d, *J* =30.6 Hz), 128.57, 124.6, 123.9 (q, *J* = 272.8 Hz), 120.2, 118.7, 114.6 (q, *J* = 5.6 Hz), 94.1, 89.7, 51.6, 25.9. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{17}F_3NO$ 344.1257, found 344.1250.



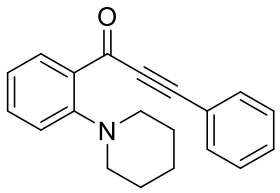
1t

1-(2-(pyrrolidin-1-yl)phenyl)but-2-yn-1-one **(1t).** Yellow oil, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 20:1); yield: 47%, 300.2 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08-8.05 (m, 1H), 7.38-7.25 (m, 1H), 6.83-6.80 (m, 1H), 6.77-6.72 (m, 1H), 3.18-3.15 (m, 4H), 2.11 (s, 3H), 1.98-1.94 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.1, 148.2, 133.3, 133.2, 123.7, 115.0, 114.2, 89.9, 80.6, 51.9, 25.9, 4.3. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{16}NO$ 214.1226, found 214.1219.



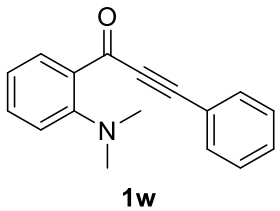
1u

1-(2-(pyrrolidin-1-yl)phenyl)-3-(thiophen-3-yl)prop-2-yn-1-one **(1u).** Yellow oil, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 20:1); yield: 68%, 573.8 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17-8.11 (m, 1H), 7.80-7.74 (m, 1H), 7.42-7.32 (m, 2H), 7.31-7.27 (m, 1H), 6.85 (d, *J* = 8.5 Hz, 1H), 6.80-6.76 (m, 1H), 3.24-3.17 (m, 4H), 2.00-1.96 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.7, 148.3, 133.3, 133.1, 132.9, 130.2, 125.9, 123.7, 120.0, 115.1, 114.3, 88.8, 86.2, 52.0, 25.9. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{16}NOS$ 282.0947, found 282.0951.



1v

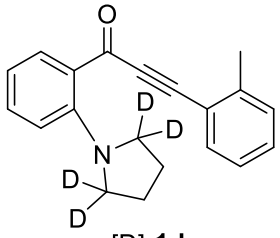
3-phenyl-1-(2-(piperidin-1-yl)phenyl)prop-2-yn-1-one **(1v).** Yellow oil, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 20:1); yield: 65%, 563.9 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00-7.90 (m, 1H), 7.66-7.60 (m, 2H), 7.48-7.36 (m, 4H), 7.07 (d, *J* = 8.5 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H) 3.13-3.06 (m, 4H), 1.79-1.74 (m, 4H), 1.58-1.54 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.9, 154.0, 133.7, 132.9, 132.8, 130.2, 130.1, 128.6, 120.8, 120.5, 118.6, 90.0, 89.3, 54.4, 25.9, 24.1. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{20}NO$ 290.1539, found 290.1540.



1w

3-phenyl-1-(2-(piperidin-1-yl)phenyl)prop-2-yn-1-one **(1v).** Yellow oil, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 20:1); yield: 20%, 149.4

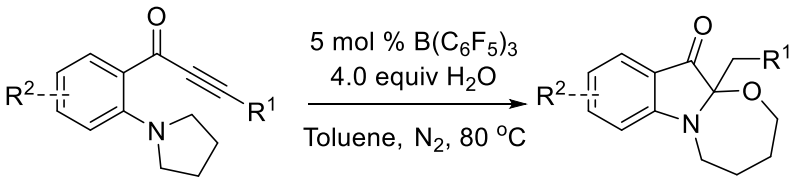
mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18-8.10 (m, 1H), 7.63 (d, *J* = 7.0 Hz, 2H), 7.47-7.37 (m, 4H), 7.00 (d, *J* = 8.5 Hz, 1H), 6.89 (t, *J* = 7.5 Hz, 1H) 2.95 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.5, 152.7, 133.9, 133.7, 132.9, 130.3, 128.6, 126.2, 120.8, 117.8, 116.4, 90.4, 88.7, 44.0. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{16}NO$ 250.1226, found 250.1226.



[D]-**1d**

1-(2-(pyrrolidin-1-yl-2,2,5,5-d$_4$)phenyl)-3-(o-tolyl)prop-2-yn-1-one **(**[D]-**1d).** Yellow oil, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 20:1); yield: 55%,403.2 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24-7.16 (m, 1H), 7.64-7.57 (m, 1H), 7.42-7.36 (m, 1H), 7.35-7.30 (m, 1H), 7.26 (d, *J* = 7.0 Hz, 1H), 7.23-7.17 (m, 1H), 6.85 (d, *J* = 9.0 Hz, 1H), 6.78 (t, *J* = 7.5 Hz, 1H), 2.95 (s, 0.14H), 2.57 (s, 3H), 1.97 (s, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.9, 148.4, 141.9, 133.4, 133.3, 133.1, 130.2, 129.7, 125.8, 124.0, 120.6, 115.1, 114.3, 92.6, 89.9, 51.4, 44.1, 25.7, 20.8. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{16}D_4NO$ 294.1791, found 294.1794.

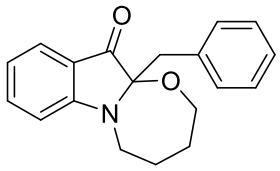
3. Synthesis of 2



1 **2**

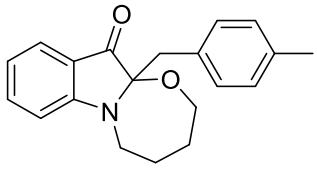
In a 10 mL dry schlenk tube, alkynones **1** (0.1 mmol, 1.0 equiv), $B(C_6F_5)_3$ (0.005 mmol, 2.6 mg, 0.05 equiv), H_2O (0.4 mmol, 7.2 mg, 4.0 equiv) and Toluene (1.0 mL) were stirred under N_2 at 80 ℃ (oil bath). After 1.5-15 h, the reaction mixture was cooled to room temperature and quenched with NH_4Cl aqueous solution (4 mL). Then the filtrate was extracted with DCM (5 mL × 3). The organic layers were combined, washed with

brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification by column chromatography with petroleum ether/ethyl acetate = 15:1-10:1 as the eluent to afford **2a-2u**.



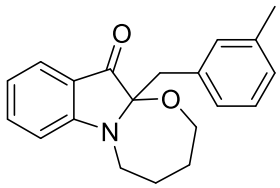
2a

11a-benzyl-2,3,4,5-tetrahydro-[1,3]oxazepino[3,2-a]indol-11(11aH)-one **(2a).** Yellow solid, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: 82%, 24.0 mg, m.p. 130-132 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.41 (m, 1H), 7.38-7.33 (m, 1H), 7.16-7.13 (m, 5H), 6.65-6.58 (m, 2H), 3.83-3.77 (m, 1H), 3.73-3.68 (m, 1H), 3.10-2.97 (m, 4H), 1.61-1.56 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.2, 160.4, 138.1, 134.4, 130.6, 127.8, 126.7, 124.6, 120.0, 117.5, 109.0, 94.7, 66.5, 41.4, 40.7, 30.1, 24.6. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{20}NO_2$ 294.1489, found 294.1486.



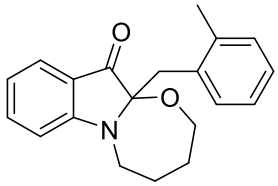
2b

11a-(4-methylbenzyl)-2,3,4,5-tetrahydro-[1,3]oxazepino[3,2-a]indol-11(11aH)-one **(2b).** Yellow solid, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: 70%, 21.5 mg, m.p. 117-119 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.41 (m, 1H), 7.38-7.34 (m, 1H), 7.03 (d, J = 8.0 Hz, 2H), 6.94 (d, J = 8.0 Hz, 2H), 6.65-6.57 (m, 2H), 3.81-3.76 (m, 1H), 3.73-3.67 (m, 1H), 3.07-2.93 (m, 4H), 2.22 (s, 3H), 1.62-1.56 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.3, 160.4, 138.0, 136.1, 131.2, 130.3, 128.5, 124.5, 120.0, 117.4, 109.0, 94.6, 66.4, 41.4, 40.2, 30.1, 24.5, 21.0. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{22}NO_2$ 308.1645, found 308.1644.



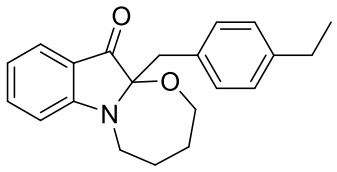
2c

11a-(3-methylbenzyl)-2,3,4,5-tetrahydro-[1,3]oxazepino[3,2-a]indol-11(11aH)-one **(2c).** yellow solid, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: 71%, 21.7 mg, m.p. 113-115 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45-7.42 (m, 1H), 7.39-7.34 (m, 1H), 7.05-7.01 (m, 1H), 6.96-6.91 (m, 3H), 6.65-6.57 (m, 2H), 3.82-3.78 (m, 1H), 3.70-3.66 (m, 1H), 3.01-2.90 (m, 4H), 2.23 (s, 3H), 1.60-1.58 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.3, 160.4, 138.0, 137.2, 134.3, 131.3, 127.60, 127.56, 127.4, 124.6, 120.0, 117.4, 109.0, 94.6, 66.4, 41.4, 40.6, 30.1, 24.6, 21.3. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{22}NO_2$ 308.1645, found 308.1647.



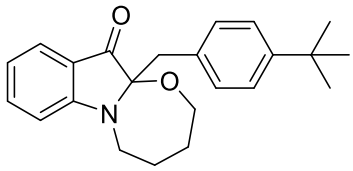
2d

11a-(2-methylbenzyl)-2,3,4,5-tetrahydro-[1,3]oxazepino[3,2-a]indol-11(11aH)-one **(2d).** yellow oil, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 15:1); yield: 56%, 17.1 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51-7.48 (m, 1H), 7.44-7.39 (m, 1H), 7.22 (d, J = 7.5 Hz, 1H), 7.08-7.02 (m, 3H), 6.70-6.64 (m, 2H), 3.84-3.79 (m, 1H), 3.62-3.57 (m, 1H), 3.11 (d, J = 14.0 Hz, 1H), 2.98 (d, J = 14.0 Hz, 1H), 2.91-2.84 (m, 1H), 2.78-2.71 (m, 1H), 2.31 (s, 3H), 1.58-1.49 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.8, 160.2, 138.2, 137.6, 133.2, 131.9, 130.0, 126.8, 125.2, 124.8, 119.9, 117.7, 109.3, 94.9, 66.7, 41.8, 37.2, 30.0, 24.7, 20.0. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{22}NO_2$ 308.1645, found 308.1640.



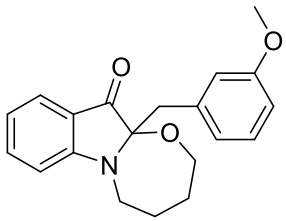
2e

11a-(4-ethylbenzyl)-2,3,4,5-tetrahydro-[1,3]oxazepino[3,2-a]indol-11(11aH)-one **(2e).** Yellow oil, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: 62%, 19.9 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45-7.42 (m, 1H), 7.39-7.34 (m, 1H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.66-6.58 (m, 2H), 3.82-3.78 (m, 1H), 3.72-3.67 (m, 1H), 3.07-2.91 (m, 4H), 2.53 (q, *J* = 7.5 Hz, 2H), 1.60-1.57 (m, 4H), 1.14 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.4, 160.4, 142.5, 138.0, 131.5, 130.5, 127.3, 124.6, 120.0, 117.4, 109.0, 94.7, 66.4, 41.4, 40.3, 30.1, 28.4, 24.6, 15.4. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{24}NO_2$ 322.1802, found 322.1794.



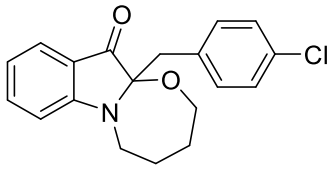
2f

11a-(4-(tert-butyl)benzyl)-2,3,4,5-tetrahydro-[1,3]oxazepino[3,2-a]indol-11(11aH)-one **(2f).** Yellow oil, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: 64%, 22.3 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.42 (m, 1H), 7.39-7.34 (m, 1H), 7.18-7.15 (m, 2H), 7.09-7.06 (m, 2H), 6.66-6.58 (m, 2H), 3.82-3.78 (m, 1H), 3.72- 3.68 (m, 1H), 3.07-2.93 (m, 4H), 1.63-1.57 (m, 4H), 1.23 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.4, 160.4, 149.4, 138.0, 131.3, 130.2, 124.64, 124.60, 120.0, 117.4, 109.0, 94.7, 66.5, 41.4, 40.2, 34.3, 31.3, 30.1, 24.6. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{28}NO_2$ 350.2115, found 350.2120.



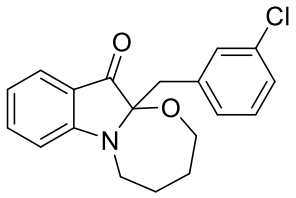
2g

11a-(3-methoxybenzyl)-2,3,4,5-tetrahydro-[1,3]oxazepino[3,2-a]indol-11(11aH)-one **(2g).** Yellow oil, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: 68%, 22.1 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46-7.43 (m, 1H), 7.40-7.35 (m, 1H), 7.08-7.05 (m, 1H), 6.76-6.70 (m, 2H), 6.69-6.60 (m, 3H),3.82-3.76 (m, 1H), 3.71 (s, 3H), 3.70-3.66 (m, 1H), 3.10-2.90 (m, 4H), 1.63-1.57 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.2, 160.4, 159.0, 138.1, 136.0, 128.7, 124.6, 123.1, 120.0, 117.5, 116.0, 112.4, 109.0, 94.5, 66.4, 55.1, 41.4, 40.8, 30.1, 24.6. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{22}NO_3$ 324.1594, found 324.1593.



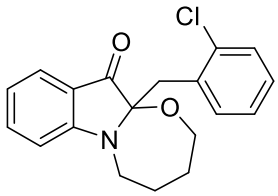
2h

11a-(4-chlorobenzyl)-2,3,4,5-tetrahydro-[1,3]oxazepino[3,2-a]indol-11(11aH)-one **(2h).** yellow oil, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: 84%, 27.6 mg. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, J = 6.0 Hz, 1H), 7.41-7.37 (m, 1H), 7.14-7.11 (m, 2H), 7.09-7.06 (m, 2H), 6.68-6.62 (m, 2H), 3.83-3.80 (m, 1H), 3.73-3.70 (m, 1H), 3.07-2.87 (m, 4H), 1.66-1.55 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 201.9, 160.4, 138.3, 132.9, 132.6, 131.8, 127.9, 124.6, 120.0, 117.8, 109.2, 94.4, 66.5, 41.5, 40.0, 30.1, 24.5. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{19}ClNO_2$ 328.1099, found 328.1098.



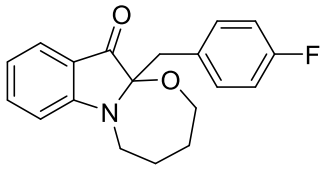
2i

11a-(3-chlorobenzyl)-2,3,4,5-tetrahydro-[1,3]oxazepino[3,2-a]indol-11(11aH)-one **(2i).** Yellow oil, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: 86%, 28.0 mg. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.8 Hz, 1H), 7.41-7.37(m, 1H), 7.16-7.14 (m, 1H), 7.13-7.02 (m, 3H), 6.69-6.62 (m, 2H), 3.84-3.79 (m, 1H), 3.75-3.71 (m, 1H), 3.08-2.91 (m, 4H), 1.66-1.56 (m, 4H). ^{13}C NMR (150MHz, $CDCl_3$) δ 201.8, 160.3, 138.3, 136.5, 133.5, 130.5, 129.0, 128.8, 126.9, 124.6, 119.9, 117.8, 109.2, 94.3, 66.5, 41.5, 40.4, 30.1, 24.6. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{19}ClNO_2$ 328.1099, found 328.1094.



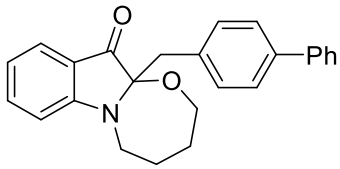
2j

11a-(2-chlorobenzyl)-2,3,4,5-tetrahydro-[1,3]oxazepino[3,2-a]indol-11(11aH)-one **(2j).** Yellow oil, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 15:1); yield: 72%, 23.6 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47-7.43 (m, 1H), 7.39-7.35 (m, 1H), 7.30-7.26 (m, 1H), 7.25-7.22 (m, 1H), 7.08-7.04 (m, 2H), 6.66-6.59 (m, 2H), 3.84-3.79 (m, 1H), 3.73-3.68 (m, 1H), 3.32 (d, *J* = 13.5 Hz, 1H), 3.21 (d, *J* = 13.5 Hz, 1H), 3.11-3.07 (m, 1H), 2.93-2.88 (m, 1H), 1.59-1.55 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.5, 160.4, 138.2, 135.1, 133.0, 132.3, 129.2, 128.1, 126.1, 124.5, 120.0, 117.5, 109.3, 94.4, 66.6, 41.9, 37.3, 30.1, 24.7. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{18}ClNO_2Na$ 350.0918, found 350.0922.



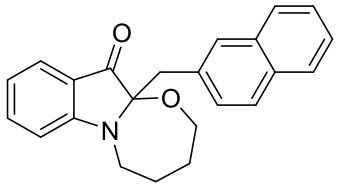
2k

11a-(4-fluorobenzyl)-2,3,4,5-tetrahydro-[1,3]oxazepino[3,2-a]indol-11(11aH)-one **(2k).** Yellow oil, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: 85%, 26.5 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.41 (m, 1H), 7.40-7.35 (m, 1H), 7.13-7.07 (m, 2H), 6.86-6.80 (m, 2H), 6.66-6.60 (m, 2H), 3.83-3.77 (m, 1H), 3.75-3.70 (m, 1H), 3.09-2.96 (m, 4H), 1.62-1.53 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ202.1, 161.8 (d, J = 243.4 Hz), 160.4, 138.2, 132.0 (d, J = 7.8 Hz), 130.1 (d, J = 3.3 Hz), 124.6, 120.0, 117.7, 114.6 (d, J = 20.9 Hz), 109.1, 94.5, 66.5, 41.4, 39.8, 30.1, 24.6. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{19}FNO_2$ 312.1394, found 312.1391.



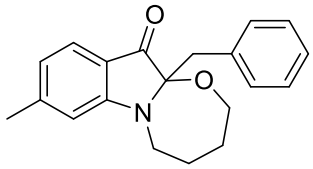
2l

11a-([1,1'-biphenyl]-4-ylmethyl)-2,3,4,5-tetrahydro-[1,3]oxazepino[3,2-a]indol-11(11aH)-one **(2l).** Yellow oil, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: 65%, 24.0 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54-7.51 (m, 2H), 7.46-7.43 (m, 1H), 7.42-7.34 (m, 5H), 7.32-7.27 (m, 1H), 7.24-7.21 (m, 2H), 6.66 (d, J = 8.5 Hz, 1H), 6.63-6.59 (m, 1H), 3.84-3.80 (m, 1H), 3.76-3.71 (m, 1H), 3.15-3.01 (m, 3H), 2.97-2.90 (m, 1H), 1.62-1.57 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.2, 160.4, 140.7, 139.3, 138.1, 133.6, 131.0, 128.7, 127.1, 126.9, 126.4, 124.6, 120.0, 117.6, 109.1, 94.6, 66.5, 41.5, 40.4, 30.1, 24.6. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{24}NO_2$ 370.1802, found 370.1805.



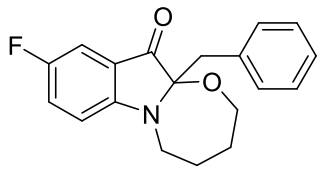
2m

***11a-(naphthalen-2-ylmethyl)-2,3,4,5-tetrahydro-[1,3]oxazepino[3,2-a]indol-11(11aH)-one* (2m).** Yellow oil, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 15:1); yield: 57%, 20.8 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75-7.71 (m, 2H), 7.66-7.57 (m, 2H), 7.45-7.36 (m, 3H), 7.35-7.30 (m, 2H), 6.63 (d, *J* = 8.0 Hz, 1H), 6.60-6.55 (m, 1H), 3.86-3.78 (m, 1H), 3.72-3.65 (m, 1H), 3.25 (d, *J* = 13.5 Hz 1H), 3.14 (d, *J* = 13.5 Hz, 1H), 3.05-2.92 (m, 2H), 1.61-1.50 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.2, 160.4, 138.1, 133.1, 132.3, 132.2, 129.3, 128.9, 127.7, 127.4, 127.2, 125.7, 125.4, 124.6, 120.0, 117.6, 109.2, 94.6, 66.5, 41.6, 40.9, 30.1, 24.5. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{21}NO_2Na$ 366.1465 found 366.1460.



2n

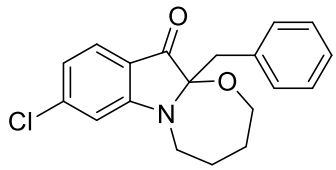
***11a-benzyl-8-methyl-2,3,4,5-tetrahydro-[1,3]oxazepino[3,2-a]indol-11(11aH)-one* (2n).** Yellow oil, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 15:1); yield: 64%, 19.6 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.0 Hz, 1H), 7.17-7.10 (m, 5H), 6.43 (d, *J* = 8.0 Hz, 2H), 3.82-3.77 (m, 1H), 3.72-3.65 (m, 1H), 3.10-2.88 (m, 4H), 2.30 (s, 3H), 1.63-1.53 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.2, 160.8, 149.9, 134.6, 130.6, 127.7, 126.6, 124.4, 119.3, 117.8, 109.2, 95.0, 66.3, 41.3, 40.7, 30.1, 24.6, 22.7. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{22}NO_2$ 308.1645, found 308.1639.



2o

11a-benzyl-9-fluoro-2,3,4,5-tetrahydro-[1,3]oxazepino[3,2-a]indol-11(11aH)-one

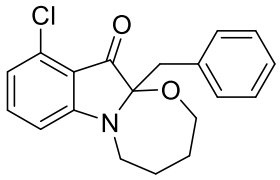
(2o). Yellow oil, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: 70%, 21.7 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17-7.06 (m, 7H), 6.60-6.56 (m, 1H), 3.84-3.79 (m, 1H), 3.71-3.66 (m, 1H), 3.10-2.97 (m, 3H), 2.94-2.88 (m, 1H), 1.61-1.57 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.1 (d, J = 3.1 Hz), 157.1, 155.4 (d, J = 237.4 Hz), 134.1, 130.5, 127.8, 126.8, 125.8 (d, J = 25.1 Hz), 120.1 (d, J = 6.9 Hz), 109.9 (d, J = 7.0 Hz), 109.6 (d, J = 22.5 Hz), 95.4, 66.6, 41.5, 40.8, 30.0, 24.5. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{18}FNO_2Na$ 334.1214, found 334.1208.



2p

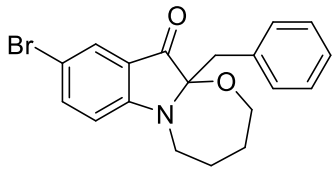
11a-benzyl-8-chloro-2,3,4,5-tetrahydro-[1,3]oxazepino[3,2-a]indol-11(11aH)-one

(2p). Yellow oil, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: 83%, 27.2 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, J = 8.0 Hz, 1H),7.16-7.09 (m, 5H), 6.63 (d, J = 1.5 Hz, 1H), 6.58-6.55 (m, 1H), 3.85-3.79 (m, 1H), 3.68-3.63 (m, 1H), 3.10-2.98 (m, 3H), 2.94-2.88 (m, 1H), 1.63-1.59 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.8, 160.5, 144.7, 133.9, 130.5, 127.9, 126.8, 125.5, 118.5, 118.3, 108.9, 95.1, 66.5, 41.5, 40.7, 30.0, 24.6. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{19}ClNO_2$ 328.1099, found 328.1091.



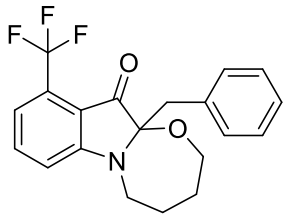
2q

11a-benzyl-10-chloro-2,3,4,5-tetrahydro-[1,3]oxazepino[3,2-a]indol-11(11aH)-one **(2q).** Yellow solid, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: 81%, 26.5 mg, m.p. 156-158 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (t, *J* = 8.0 Hz, 1H),7.18-7.10 (m, 5H), 6.53-6.50 (m, 2H), 3.86-3.80 (m, 1H), 3.71-3.65 (m, 1H), 3.10-2.89 (m, 4H), 1.63-1.54 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.4, 161.2, 138.0, 134.1, 132.3, 130.5, 127.8, 126.8, 118.5, 116.6, 107.1, 94.7, 66.5, 41.5, 40.9, 30.0, 24.6. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{19}ClNO_2$ 328.1099, found 328.1095.



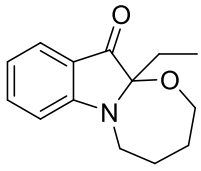
2r

11a-benzyl-9-bromo-2,3,4,5-tetrahydro-[1,3]oxazepino[3,2-a]indol-11(11aH)-one **(2r).** Yellow oil, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: 67%, 24.8 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 2.0 Hz, 1H),7.43-7.40 (m, 1H), 7.18-7.08 (m, 5H), 6.55 (d, *J* = 8.5 Hz, 1H), 3.84-3.78 (m, 1H), 3.72-3.66 (m, 1H), 3.10-2.97 (m, 3H), 2.92-2.85 (m, 1H), 1.62-1.56 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.0, 158.9, 140.4, 133.9, 130.5, 127.9, 126.9, 126.8, 121.5, 110.6, 109.7, 95.0, 66.6, 41.5, 40.7, 30.0, 24.5. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{19}BrNO_2$ 372.0594, found 372.0590.



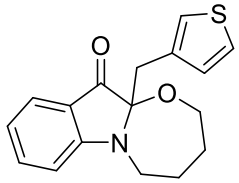
2s

11a-benzyl-10-(trifluoromethyl)-2,3,4,5-tetrahydro-[1,3]oxazepino[3,2-a]indol-11(11aH)-one **(2s).** Yellow solid, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: 68%, 24.8 mg, m.p. 113-115 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (t, *J* = 8.0 Hz, 1H),7.15-7.08 (m, 5H), 6.82 (t, *J* = 7.5 Hz, 2H), 3.87-3.82 (m, 1H), 3.78-3.72 (m, 1H), 3.19-3.12 (m, 1H), 3.06 (s, 2H), 2.96-2.90 (m, 1H), 1.65-1.59 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.7, 161.0, 137.0, 133.7, 130.4, 127.8, 127.1(d, *J* = 34.6 Hz), 126.8, 122.3 (q, *J* = 272.1 Hz), 115.5, 114.7 (q, *J* = 5.8 Hz), 94.7, 66.6, 41.4, 41.0, 30.0, 24.8. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{21}NO_2Na$ 366.1465, found 366.1460.



2t

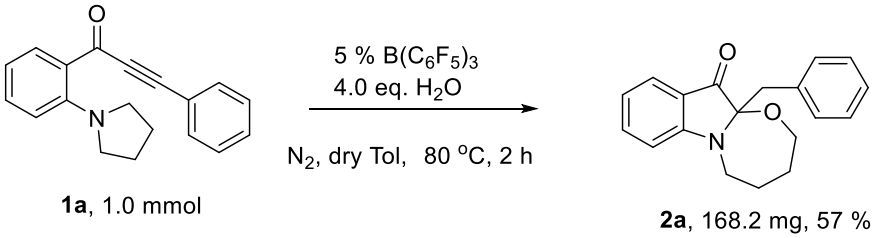
11a-ethyl-2,3,4,5-tetrahydro-[1,3]oxazepino[3,2-a]indol-11(11aH)-one **(2t).** Yellow oil, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 15:1); yield: 41%, 9.5 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56-7.52 (m, 1H),7.49-7.44 (m, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 6.72-6.68 (m, 1H), 3.87-3.79 (m, 1H), 3.77-3.70 (m, 1H), 3.33-3.25 (m, 1H), 2.97-2.90 (m, 1H), 1.98-1.89 (m, 1H), 1.79-1.72 (m, 1H), 1.71-1.58 (m, 4H), 0.73 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.7, 160.8, 138.2, 124.6, 120.4, 117.4, 109.0, 95.1, 66.1, 40.7, 30.2, 27.7, 24.4, 7.2. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{18}NO_2$ 232.1332, found 232.1329.



2u

11a-(thiophen-3-ylmethyl)-2,3,4,5-tetrahydro-[1,3]oxazepino[3,2-a]indol-11(11aH)-one (**2u**). Yellow oil, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 15:1); yield: 68%, 20.3 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.111-7.07 (m, 1H), 6.96 (d, *J* = 3.0 Hz, 1H), 6.90 (d, *J* = 5.0 Hz, 1H), 6.68-6.61 (m, 2H), 3.83-3.77 (m, 1H), 3.74-3.68 (m, 1H), 3.13-3.00 (m, 3H), 2.97-2.89 (m, 1H), 1.65-1.57 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.1, 160.4, 138.1, 134.5, 129.7, 124.60, 124.55, 123.7, 120.0, 117.6, 109.0, 94.1, 66.5, 41.2, 35.2, 30.2, 24.6. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{17}H_{17}NO_2SNa$ 322.0872, found 322.0872.

4. 1.0 mmol scale reaction for the preparation of 2a.



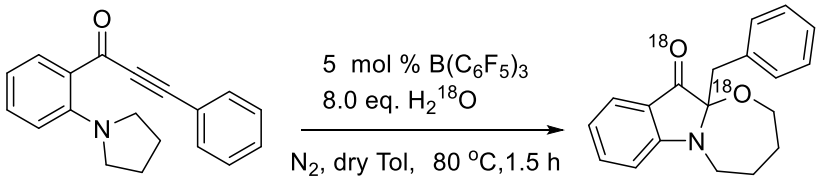
1a, 1.0 mmol

2a, 168.2 mg, 57 %

In a 25 mL dry high-pressure sealed reaction tube, alkynone **1a** (1.0 mmol, 275.1 mg, 1.0 equiv), $B(C_6F_5)_3$ (0.05 mmol, 2.6 mg, 0.05 equiv), H_2O (4.0 mmol, 72.0 mg, 4.0 equiv) and toluene (10 mL) were stirred under N_2 at 80 °C (oil bath). After 2 h, the reaction mixture was cooled to room temperature and quenched with NH_4Cl aqueous solution (30 mL). Then the filtrate was extracted with DCM (40 mL × 3). The organic layers were combined, washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification by column chromatography with petroleum ether/ethyl acetate = 10:1 as the eluent to afford **2a** (168.2 mg, 57%).

5. Mechanistic study by isotopically label

5.1 ^{18}O isotopic labeling experiment



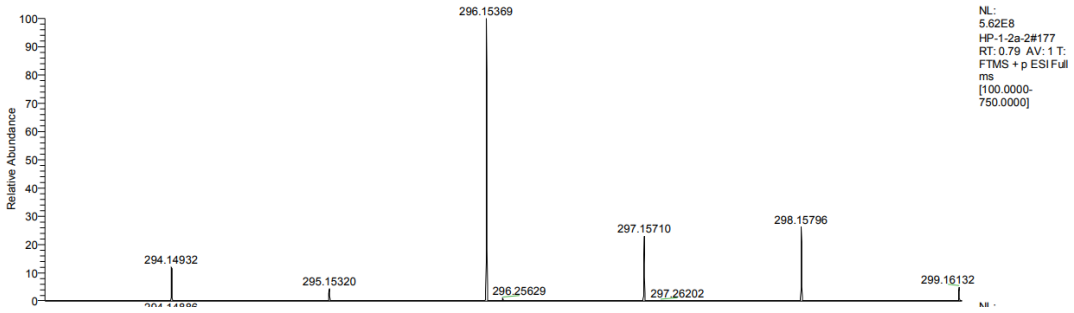
1a

^{18}O-**2a**, 78 %

$C_{19}H_{19}NO_2$	9%
$C_{19}H_{19}NO^{18}O$	72%
$C_{19}H_{19}N^{18}O_2$	19%

In a 25 mL dry high-pressure sealed reaction tube, alkynone **1a** (0.1 mmol, 27.5 mg, 1.0 equiv), $B(C_6F_5)_3$ (0.005 mmol, 2.6 mg, 0.05 equiv), $H_2{}^{18}O$ (0.8 mmol, 16.0 mg, 8.0 equiv) and toluene (1.0 mL) were stirred under N_2 at 80 °C (oil bath). After 1.5 h, the reaction mixture was cooled to room temperature and quenched with NH_4Cl aqueous solution (4 mL). Then the filtrate was extracted with DCM (5 mL × 3). The organic layers were combined, washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification by column chromatography with petroleum ether/ethyl acetate = 10:1 as the eluent to afford ^{18}O-**2a** (23.1 mg, 78%).

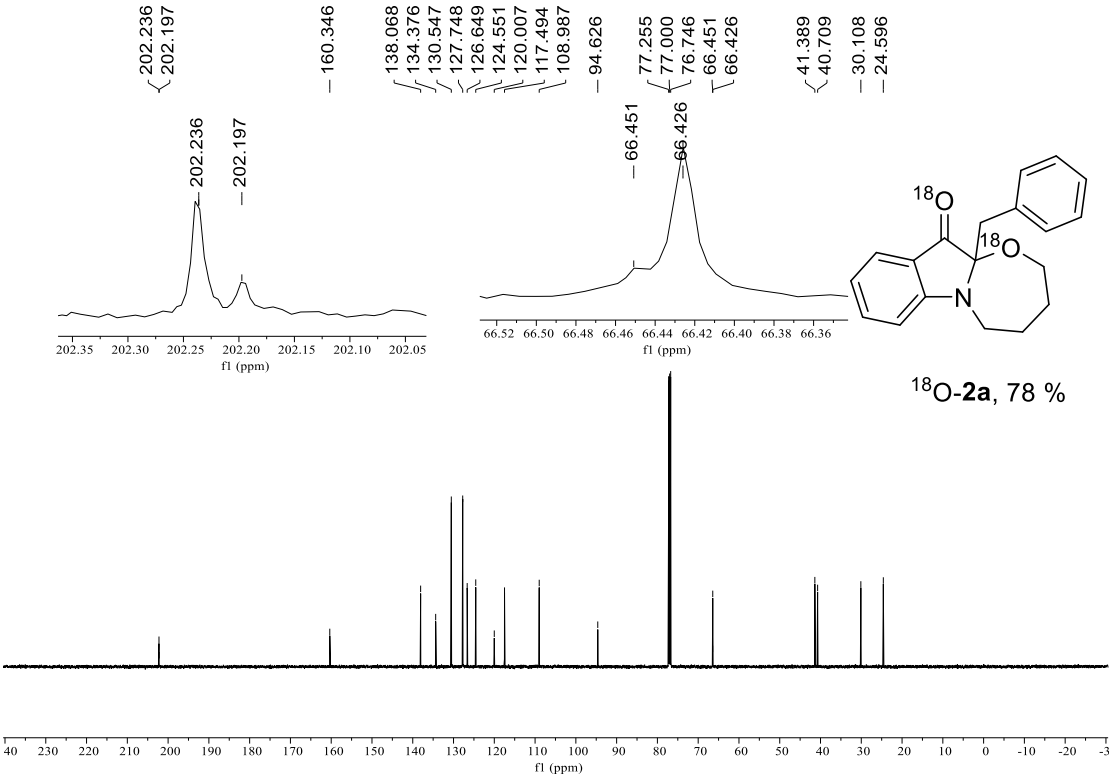
^{18}O-**2a**: ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.24, 202.20, 160.3, 138.1, 134.4, 130.5, 127.7, 126.6, 124.6, 120.0, 117.5, 109.0, 94.6, 66.5, 66.4, 41.4, 40.7, 30.1, 24.6. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{20}NO_2$ 294.1489, found 294.1493; $[M+H]^+$ calcd for $C_{19}H_{20}NO^{18}O$ 296.1531, found 296.1537; $[M+H]^+$ calcd for $C_{19}H_{20}N^{18}O_2$ 298.1574, found 298.1580.



HP-1-2a-2#177 RT: 0.79
T: FTMS + p ESI Full ms [100.0000-750.0000]
m/z= 293.79219-298.64861

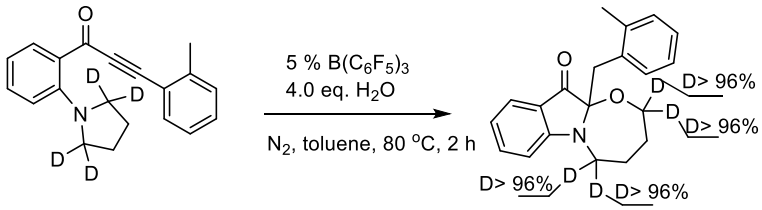
m/z	Intensity	Relative
294.14932	70021472.0	12.42
295.15320	25504008.0	4.52
296.15369	563844608.0	100.00
296.25629	4599975.0	0.82
297.15710	132497728.0	23.50
297.26202	1147435.0	0.20
298.15796	147349248.0	26.13

^{13}C NMR (125 MHz, $CDCl_3$)



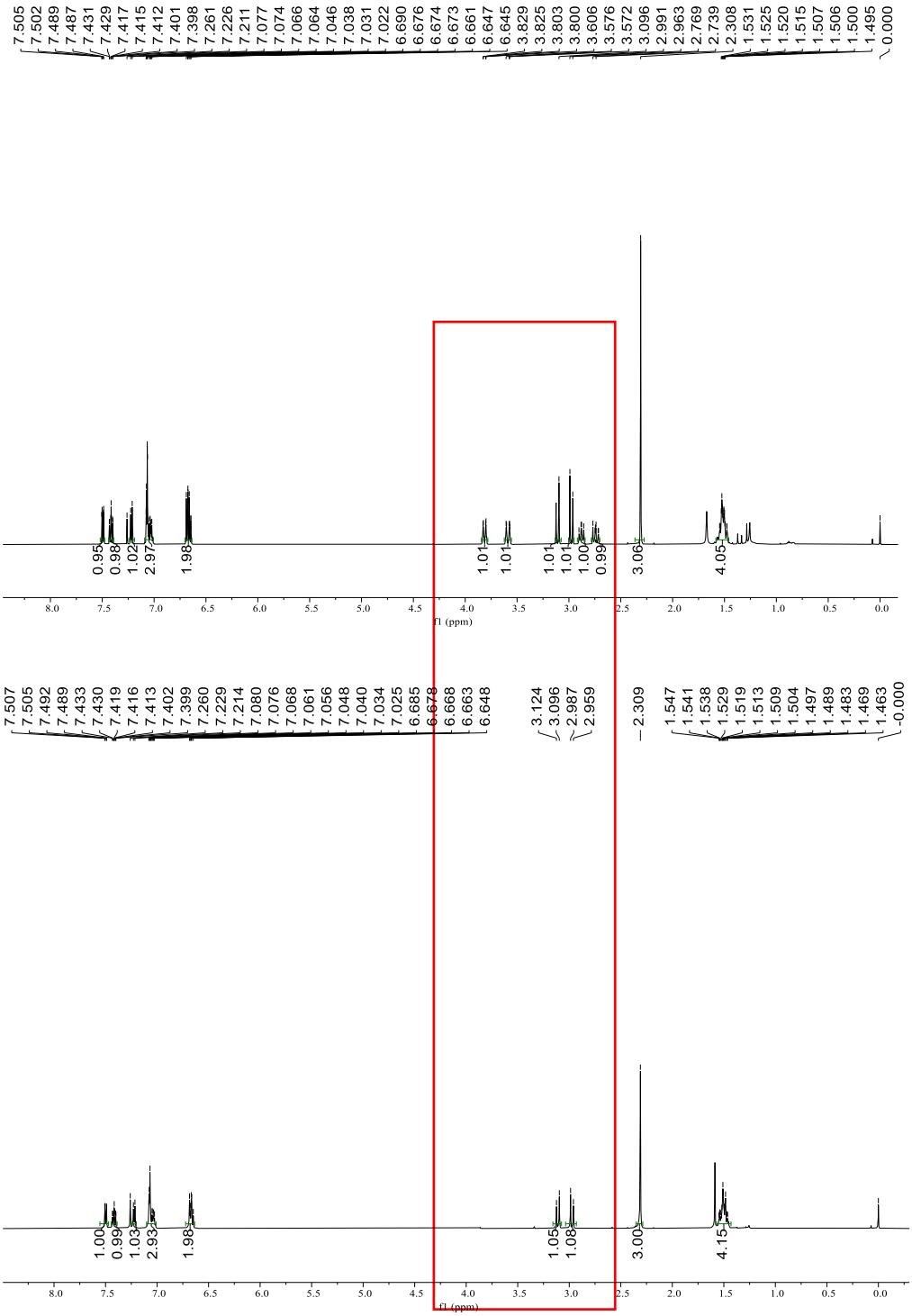
5.2 Deuterium Labelling Experiment

In a 25 mL dry high-pressure sealed reaction tube, alkynone [D]-**1d** (0.1 mmol, 29.3 mg, 1.0 equiv), $B(C_6F_5)_3$ (0.005 mmol, 2.6 mg, 0.05 equiv), H_2O (0.4 mmol, 7.2 mg, 4.0 equiv) and toluene (1.0 mL) were stirred under N_2 at 80 ℃ (oil bath). After 2 h, the reaction mixture was cooled to room temperature and quenched with NH_4Cl aqueous solution (4 mL). Then the filtrate was extracted with DCM (5 mL × 3). The organic layers were combined, washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification by column chromatography with petroleum ether/ethyl acetate = 10:1 as the eluent to afford [D]-**2d** (17.1 mg, 55%).



[D]-**1d**,D> 96%

[D]-**2d**, 55 %



6. Figure S1. Possible pathway to ^{18}O-2a

First, **1a** undergoes 1,5-hydride transfer to furnish intermediate **C**. $H_2{}^{18}O$ serves as a nucleophile attacking imine ions to form intermediate **D**-2. Under the action of Lewis acid $B(C_6F_5)_3$, **D**-2 transforms into **M**, $H_2{}^{18}O$ serves as a nucleophile again attacking **M** to form intermediate **N**. The target product ^{18}O-**2a** could be obtained from **N** through path a or path b (see Scheme 3 in the manuscript).

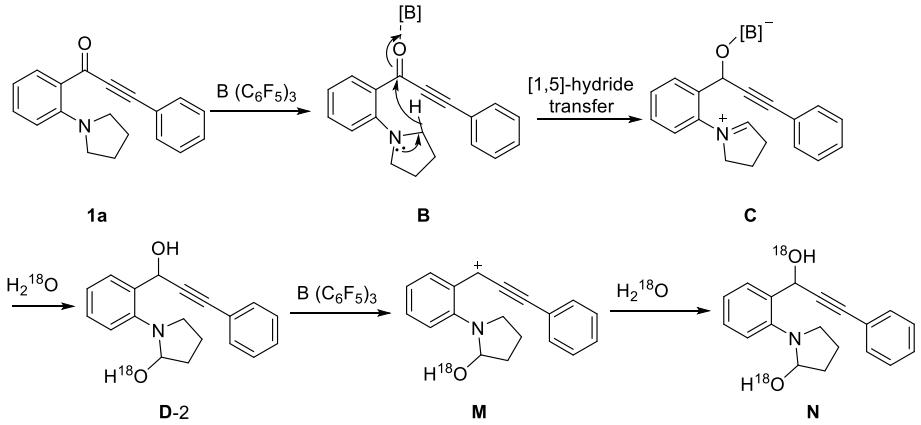


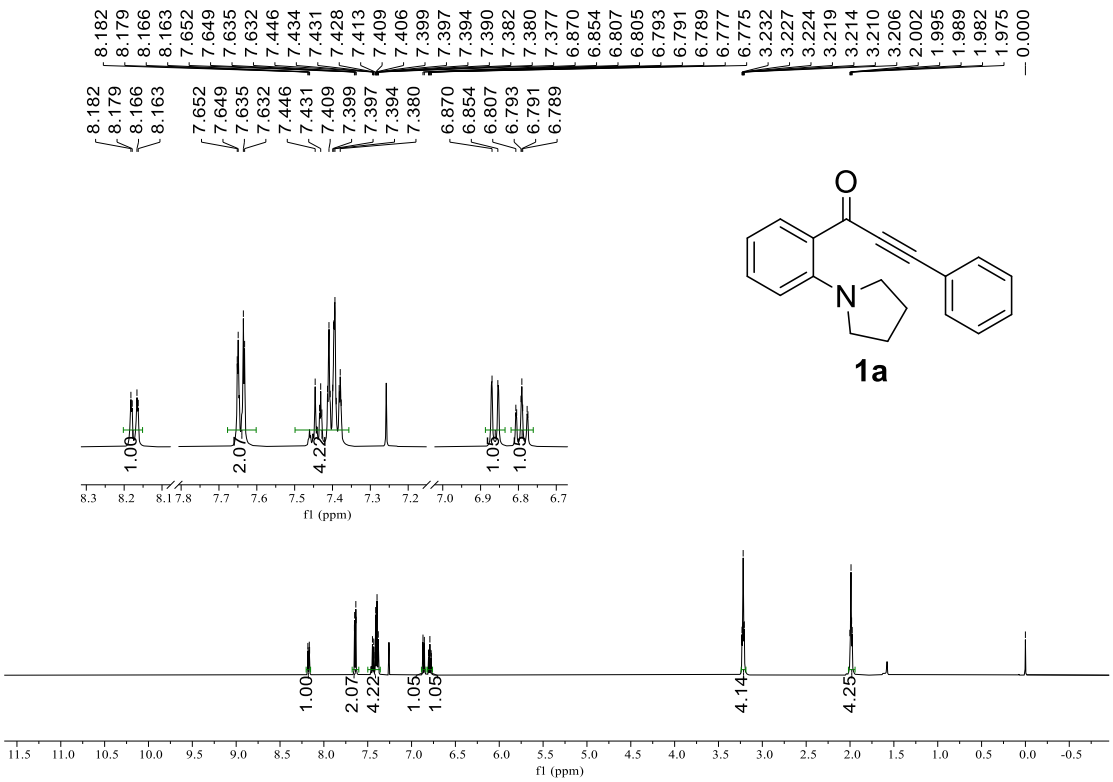
Figure S1. Possible pathway to ^{18}O-**2a**

7. References

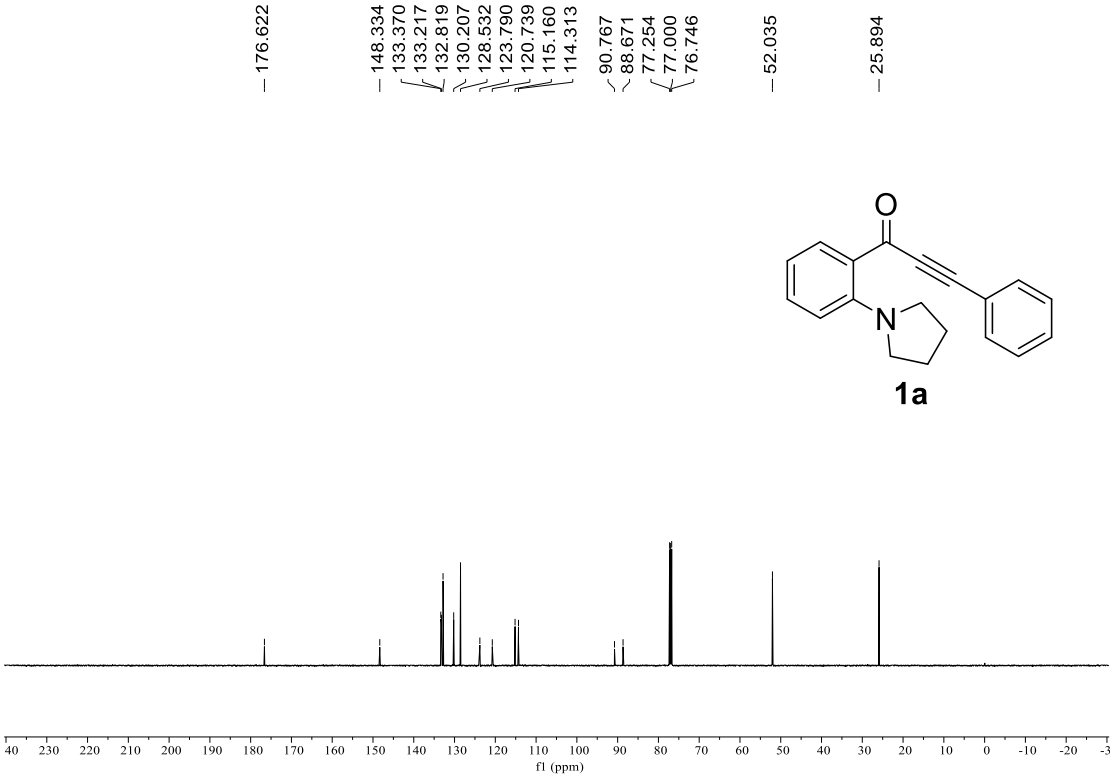
(1) (a) Han, Y.-Y.; Han, W.-Y.; Hou, X.; Zhang, X.-M.; Yuan, W.-C., FeCl3-Catalyzed Stereoselective Construction of Spirooxindole Tetrahydroquinolines via Tandem 1,5-Hydride Transfer/Ring Closure. *Org. Lett*. **2012**, 14, 4054-4057; (b) Wang, S.; Shen, Y.-B.; Li, L.-F.; Qiu, B.; Yu, L.; Liu, Q.; Xiao, J., N-Alkylation-Initiated Redox-Neutral [5 + 2] Annulation of 3-Alkylindoles with o-Aminobenzaldehydes: Access to Indole-1,2-Fused 1,4-Benzodiazepines. *Org. Lett*. **2019**, 21, 8904-8908

8. Copies of spectra of products

^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)



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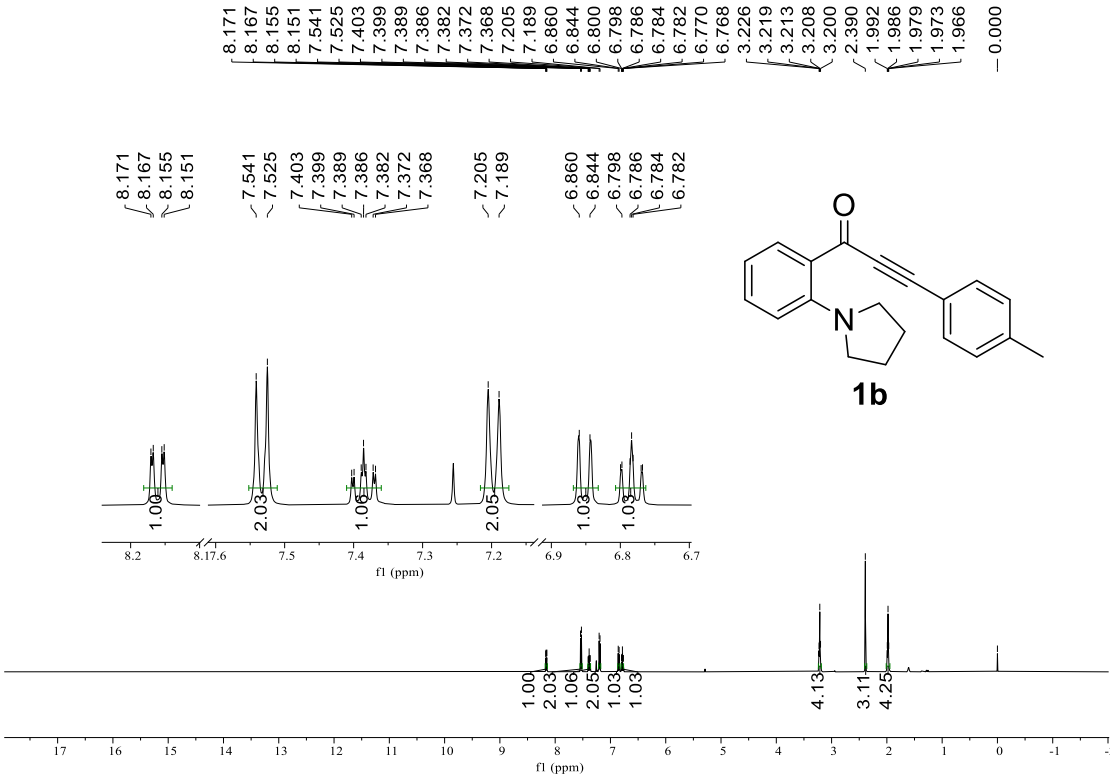

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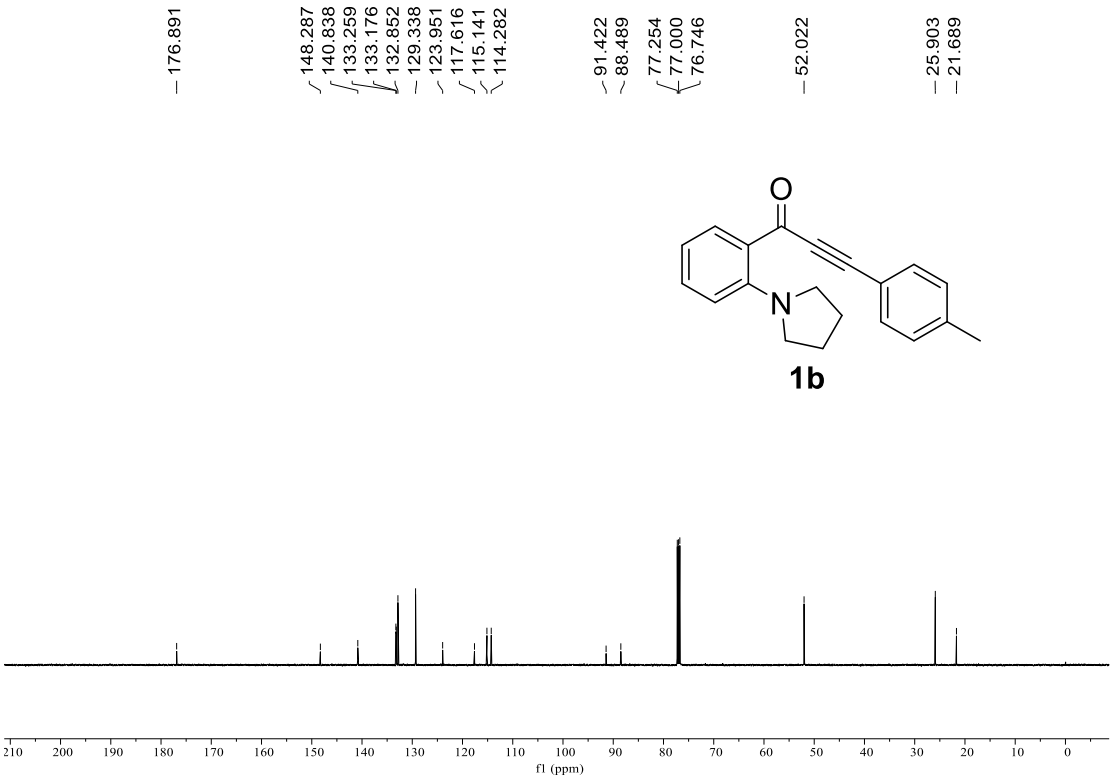
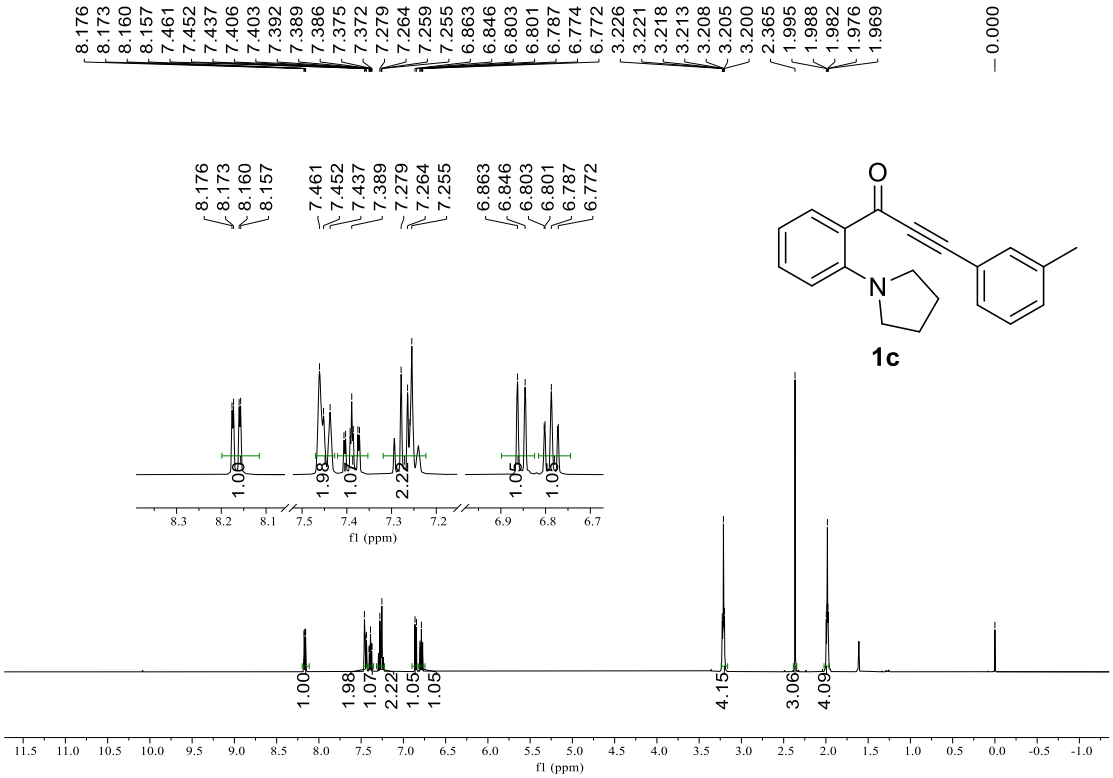
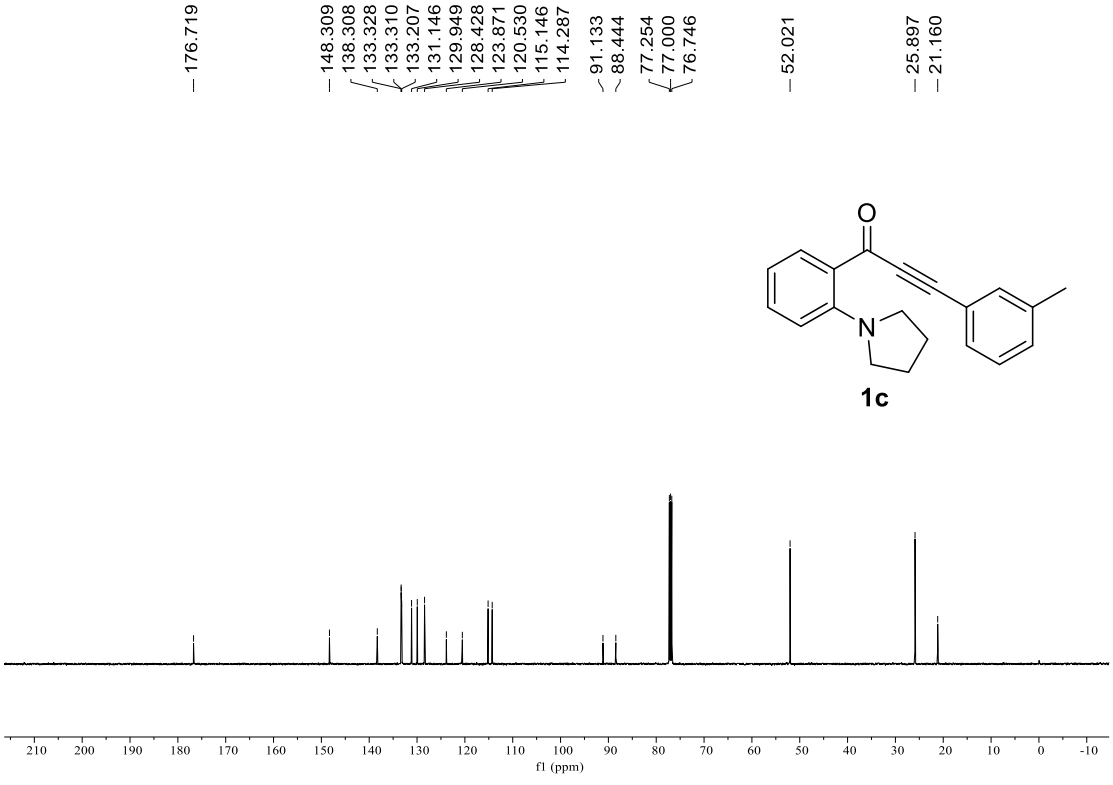


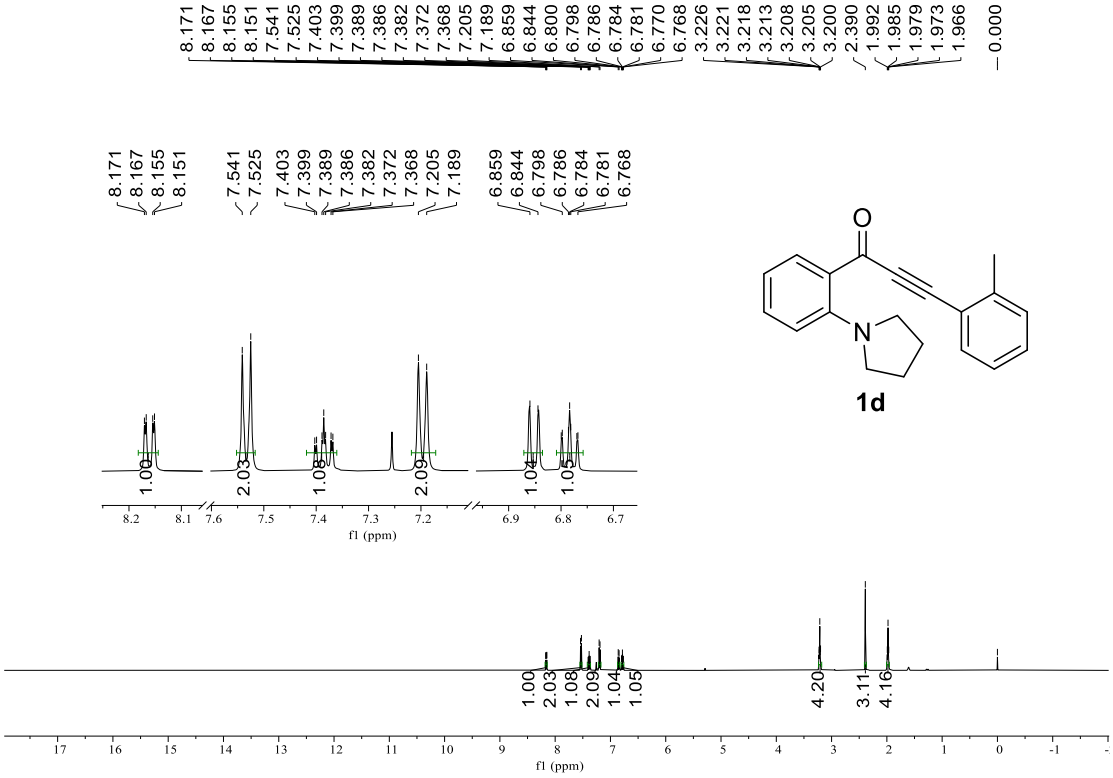
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

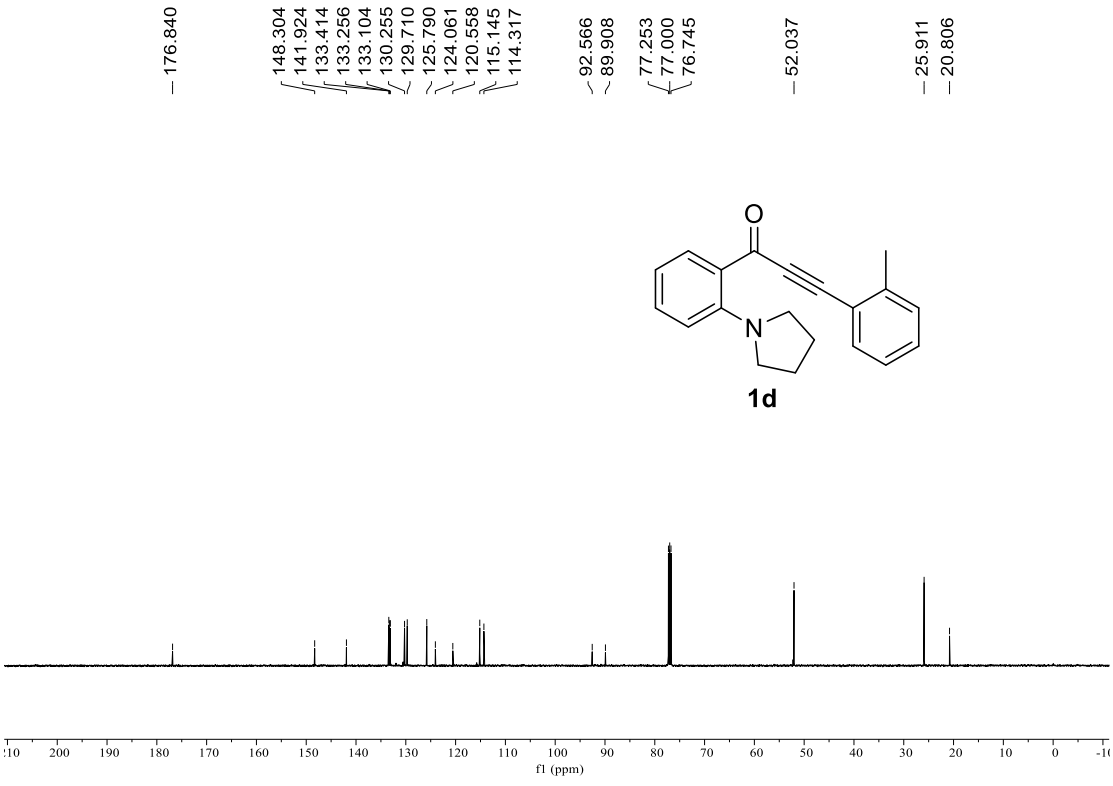


^{1}H NMR (500 MHz, $CDCl_3$)



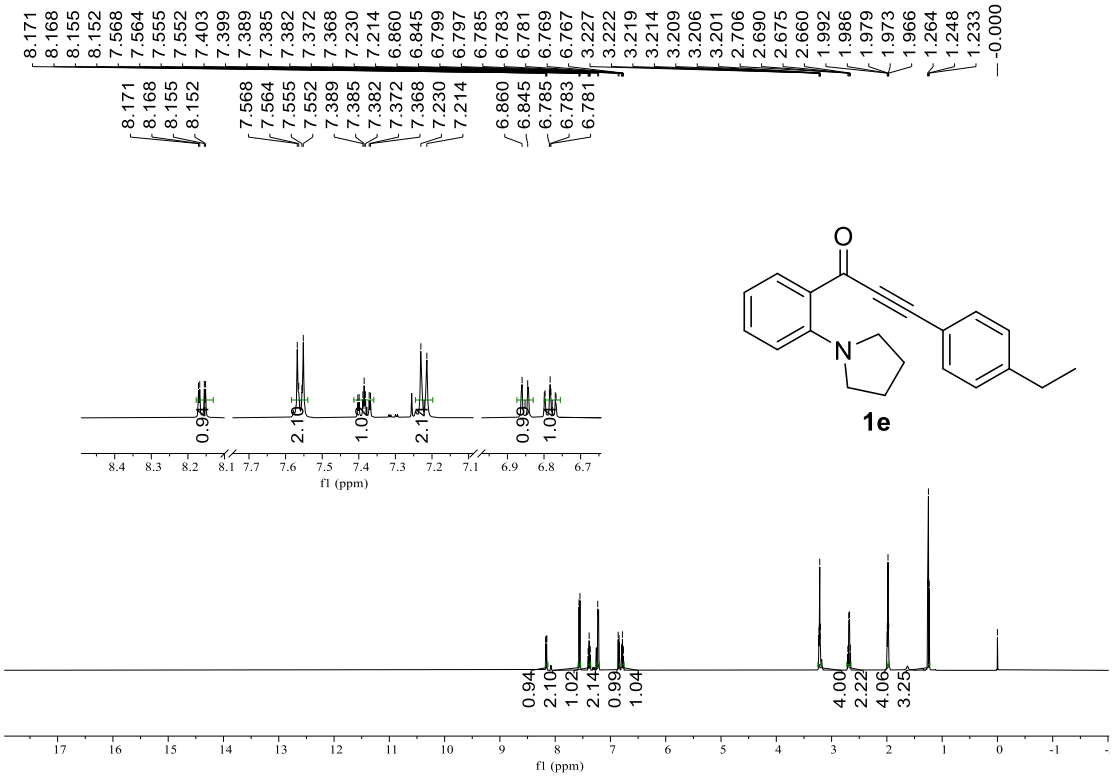
1d

^{13}C NMR (150 MHz, $CDCl_3$)



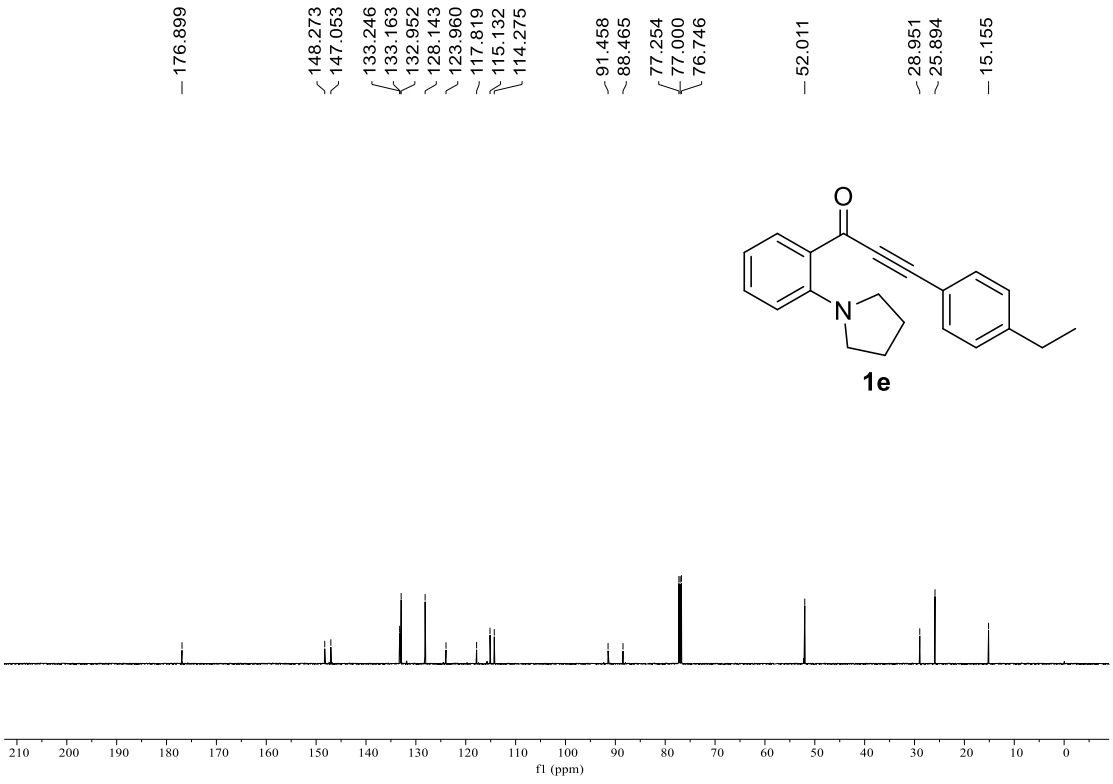
1d

^{1}H NMR (500 MHz, $CDCl_3$)



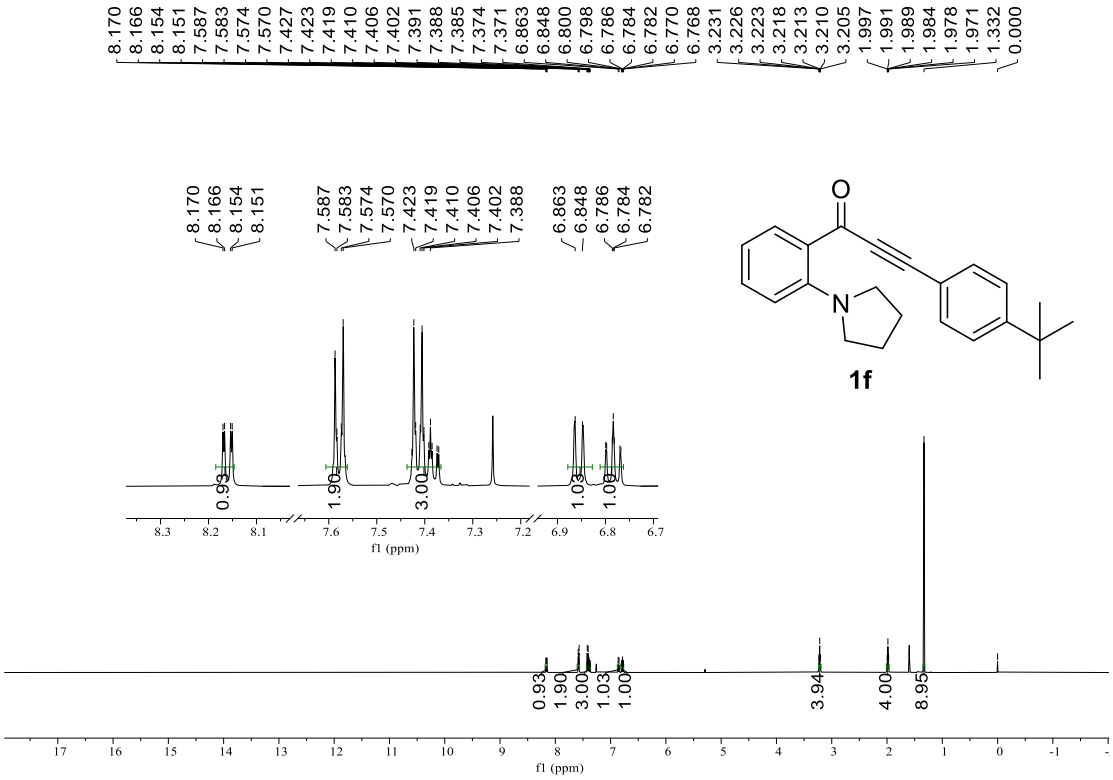
1e

^{13}C NMR (125 MHz, $CDCl_3$)



1e

^{1}H NMR (500 MHz, $CDCl_3$)



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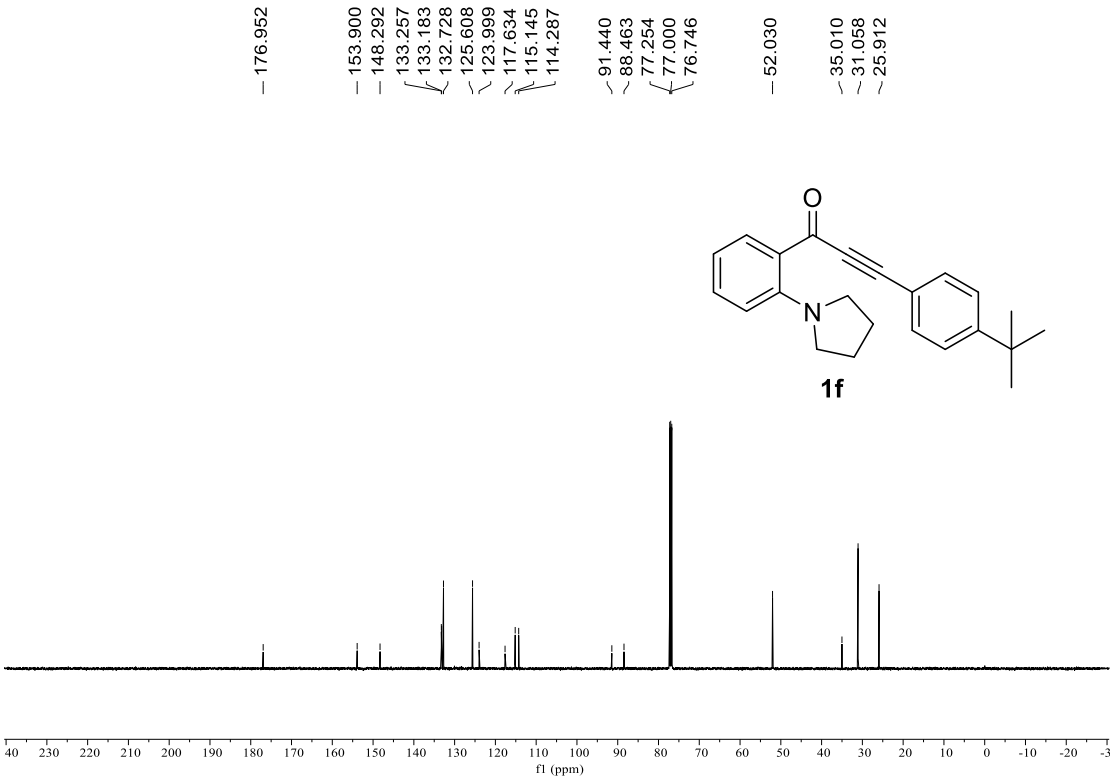

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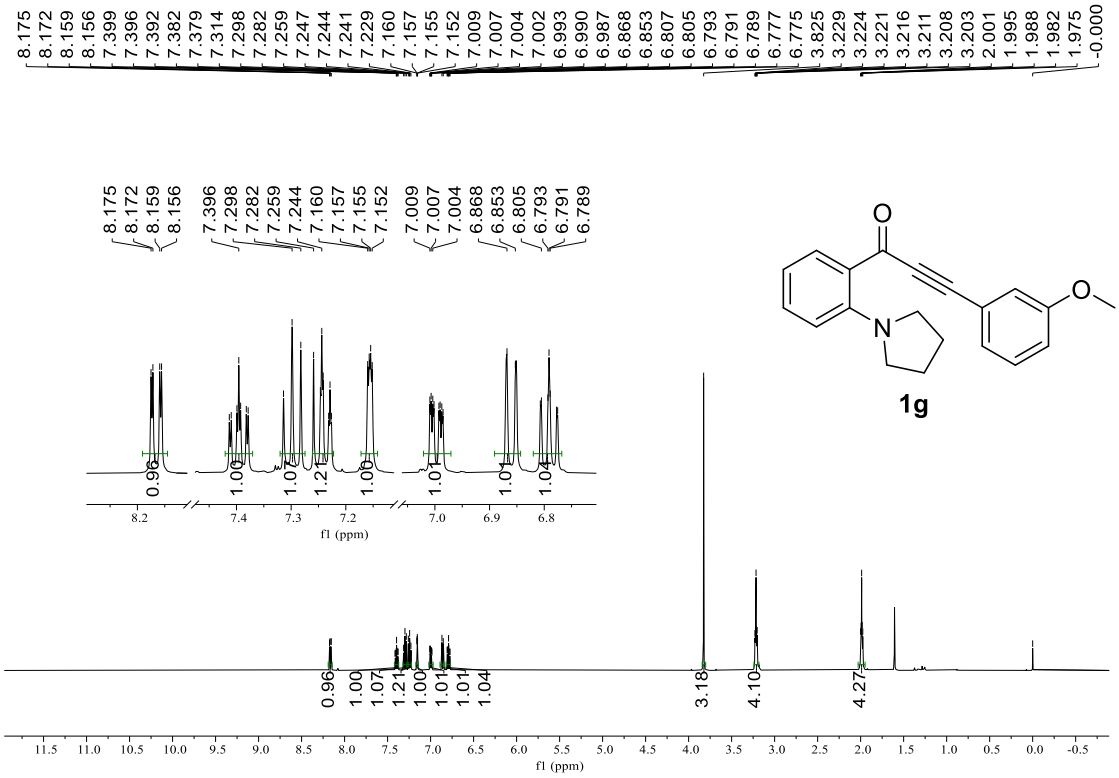

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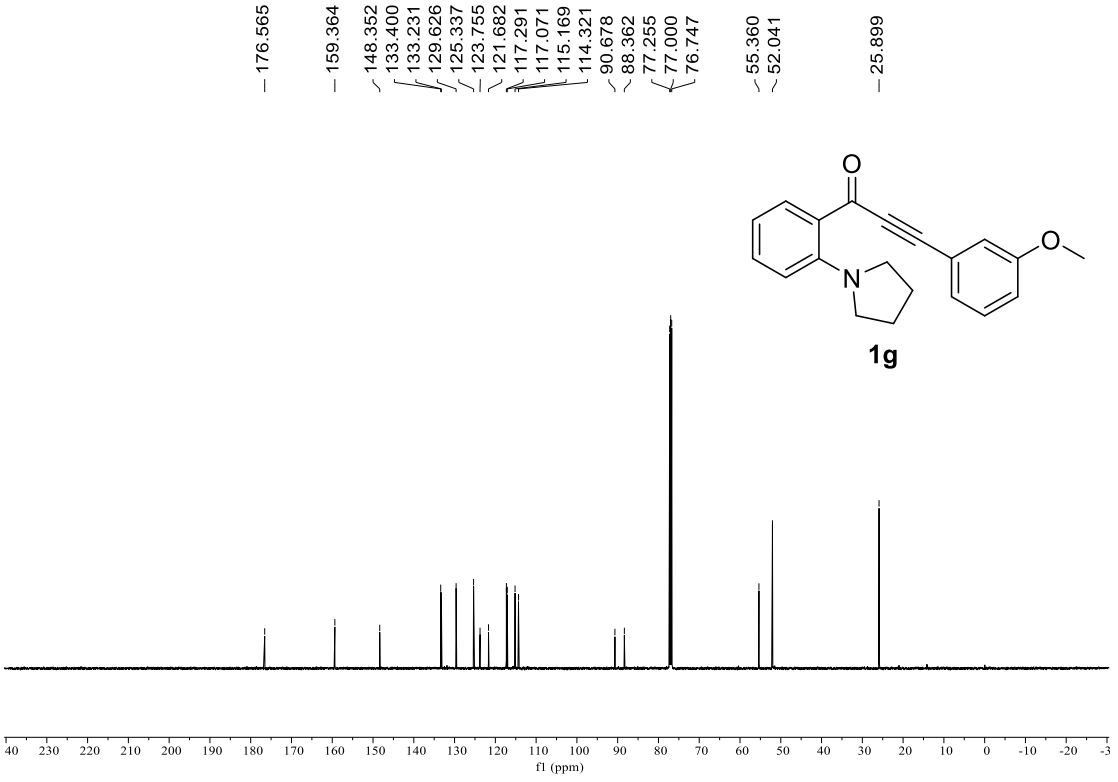

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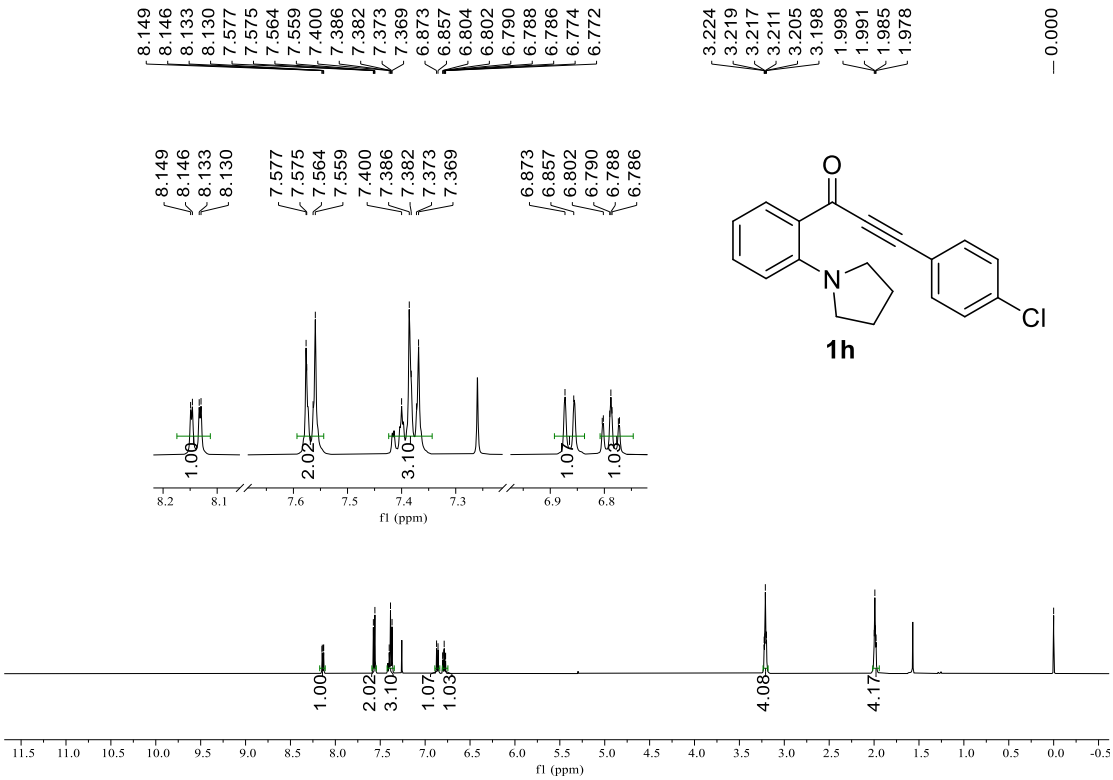

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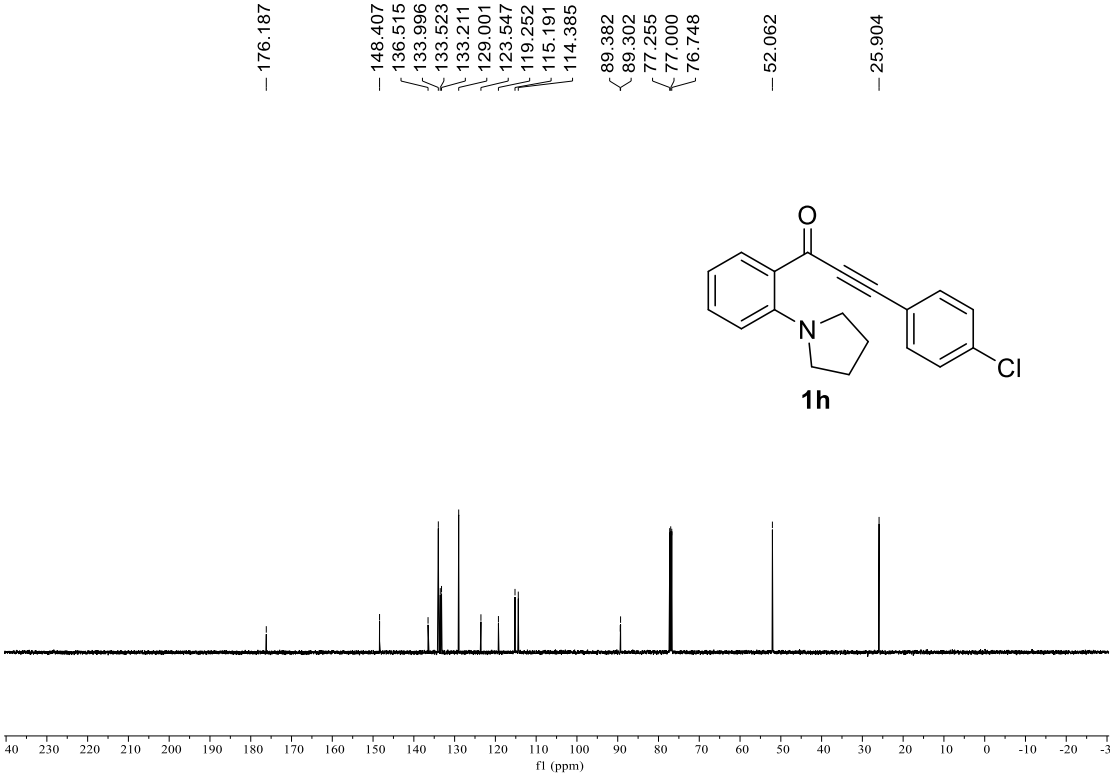

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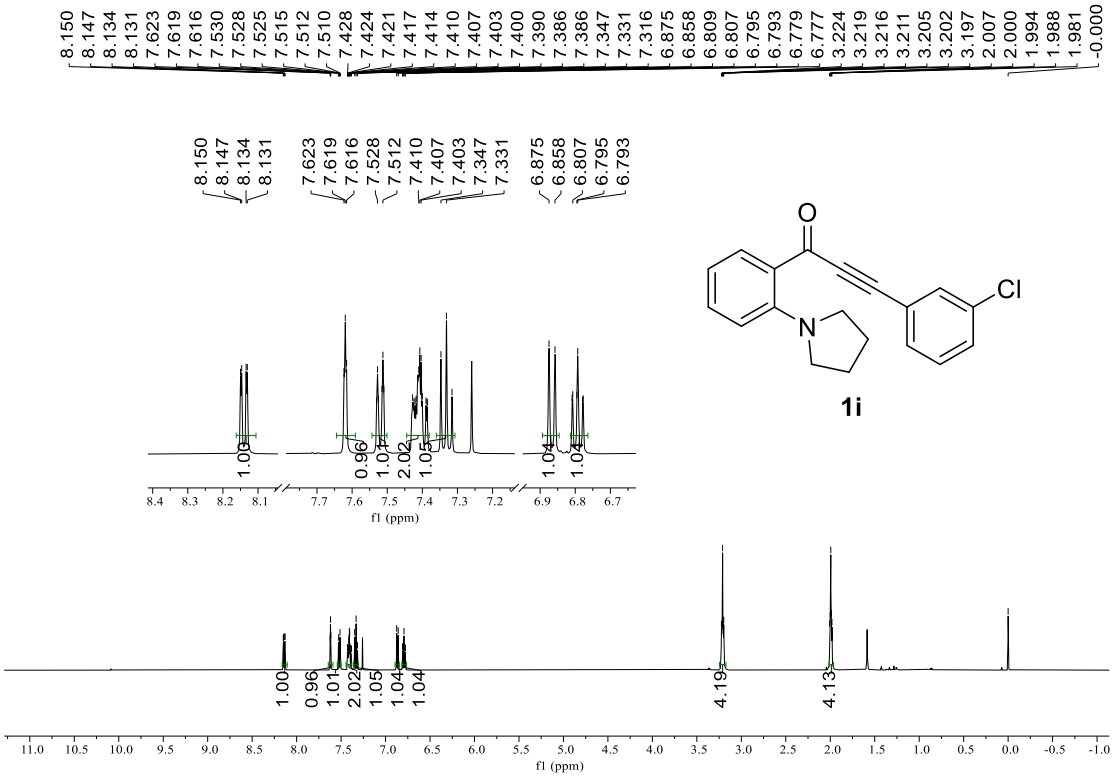

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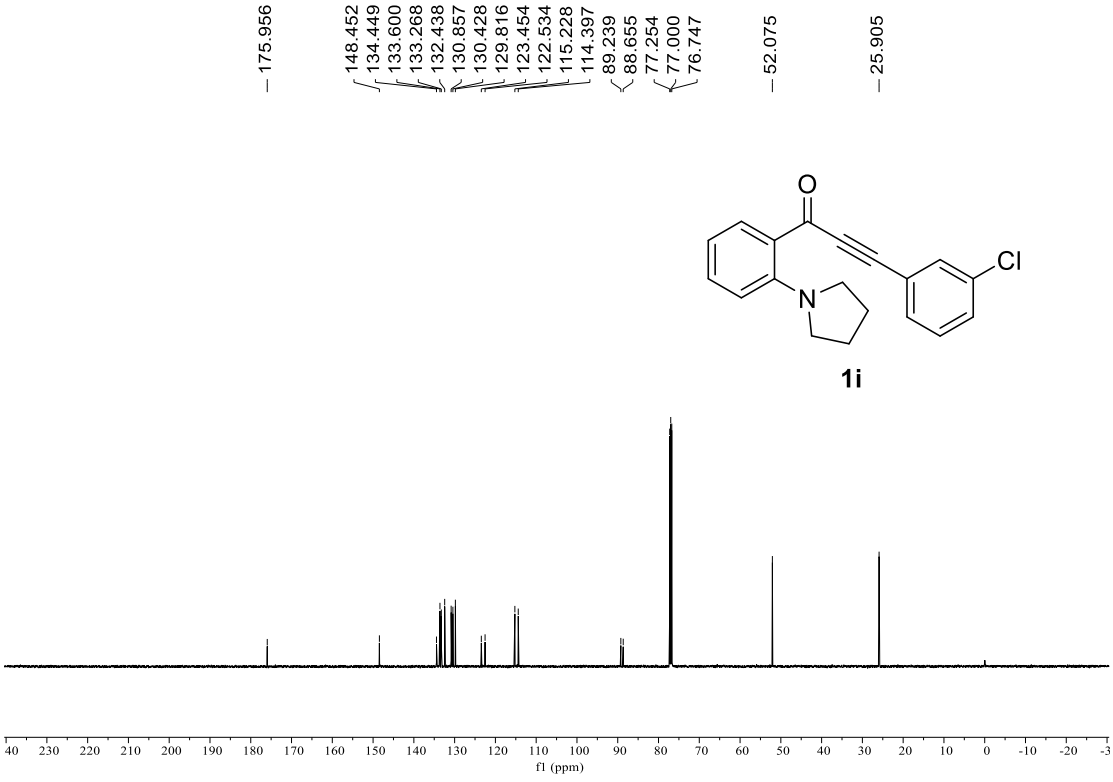

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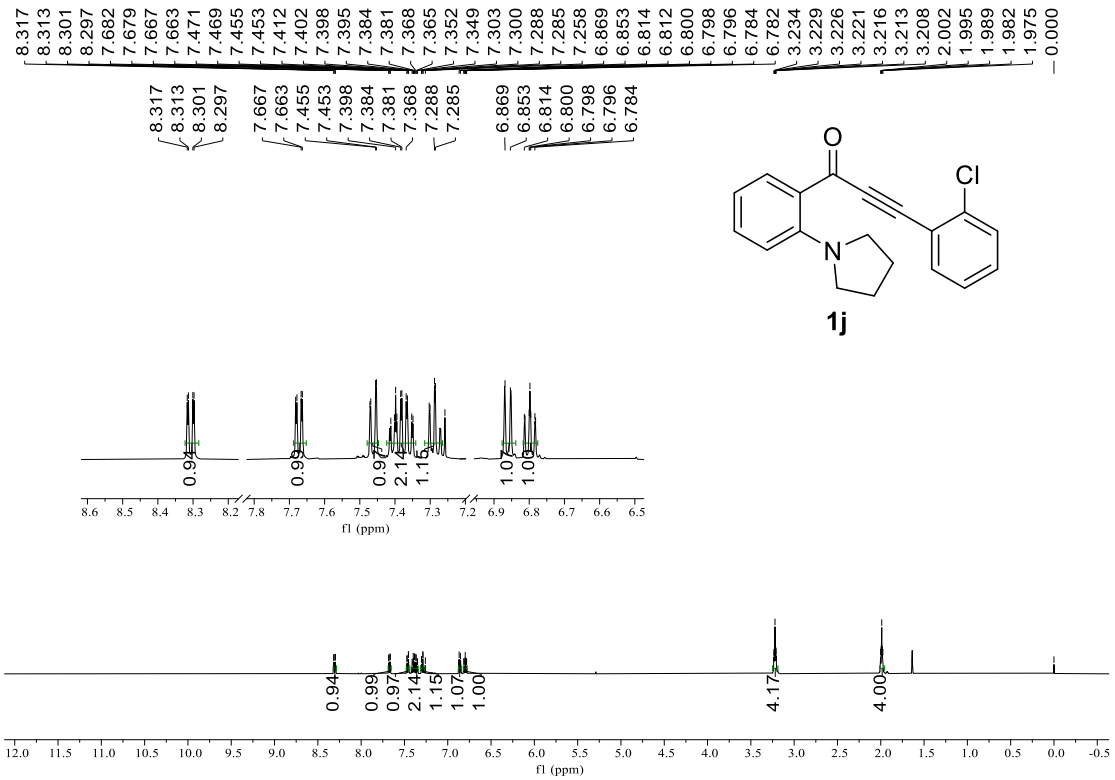

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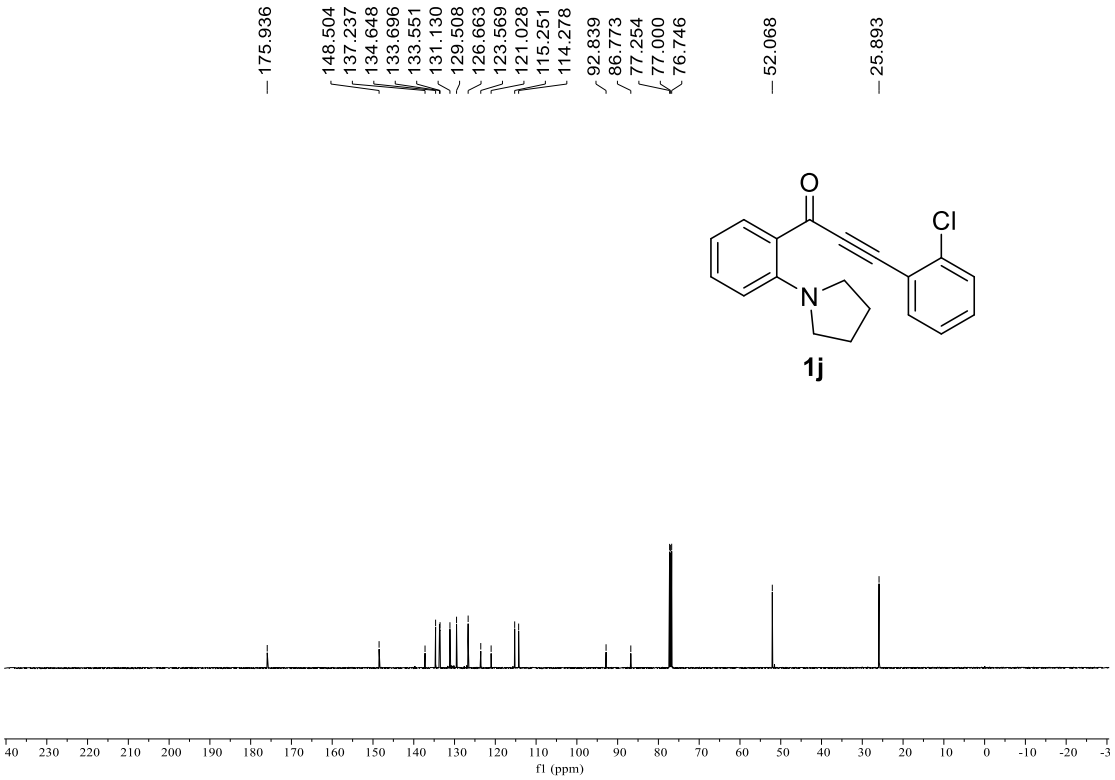

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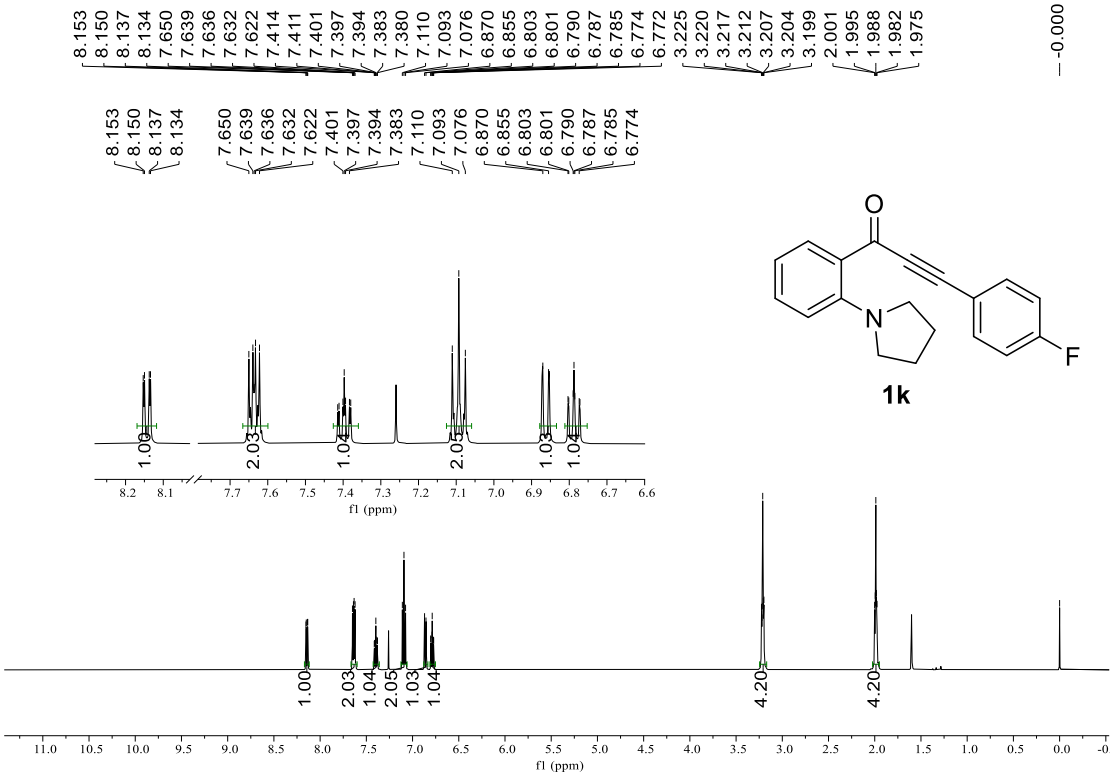

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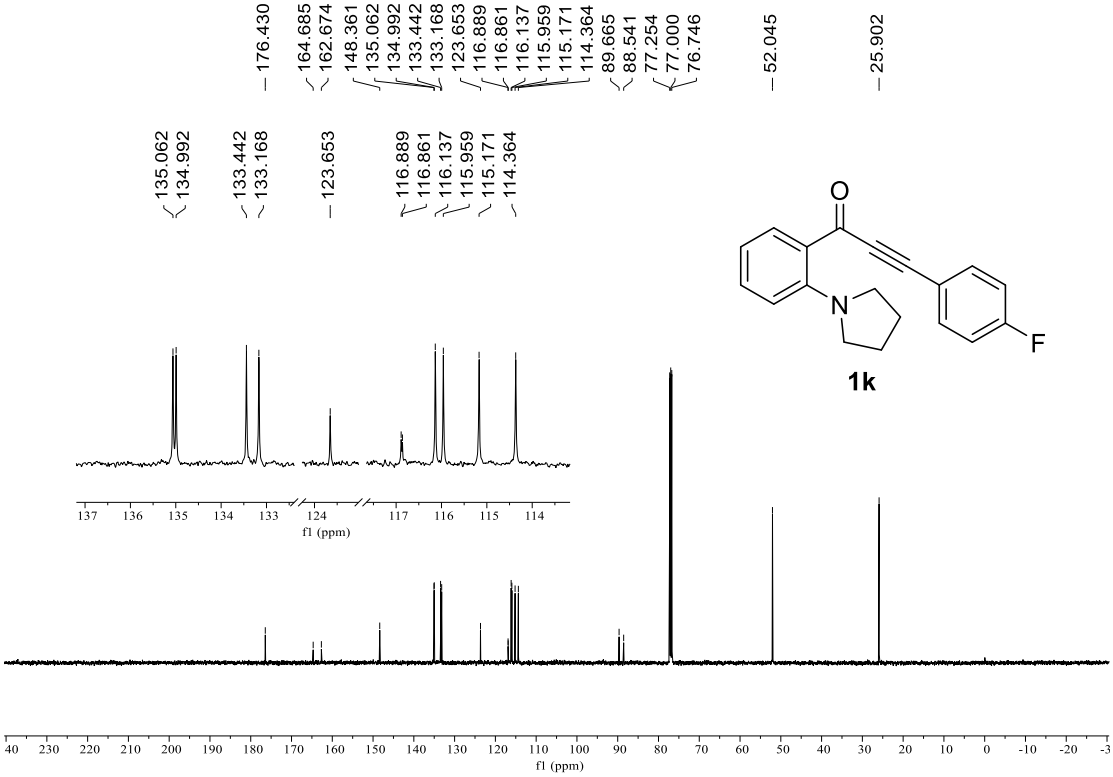

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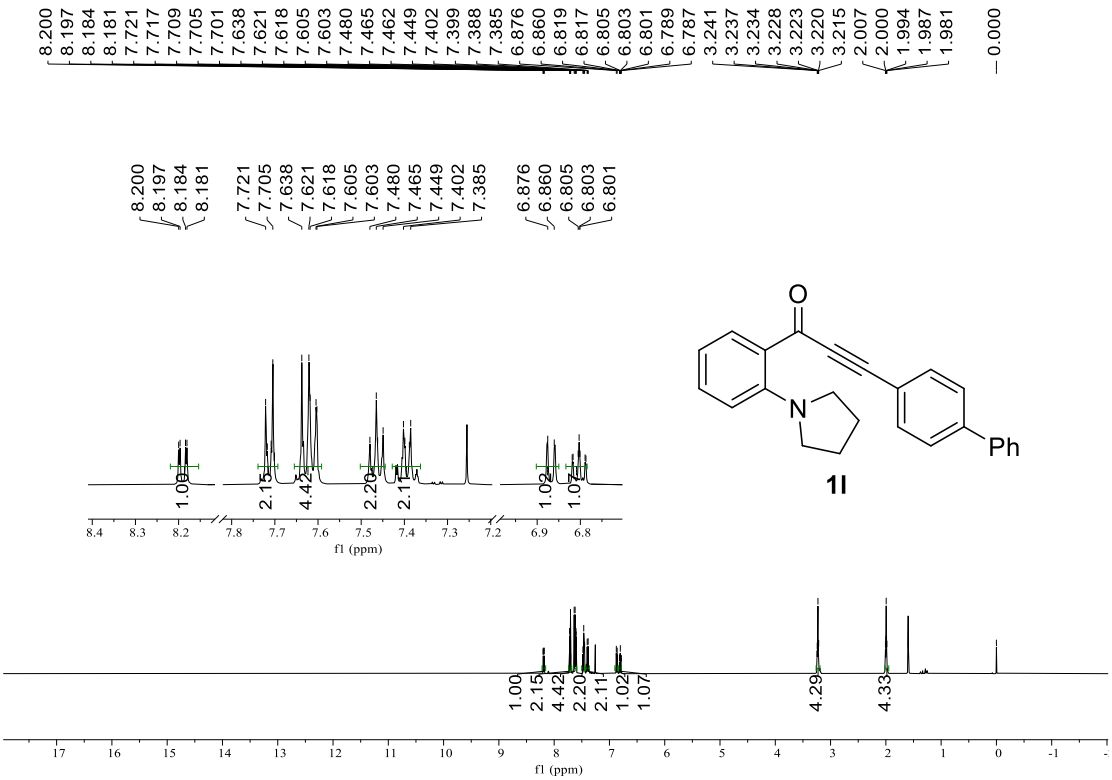

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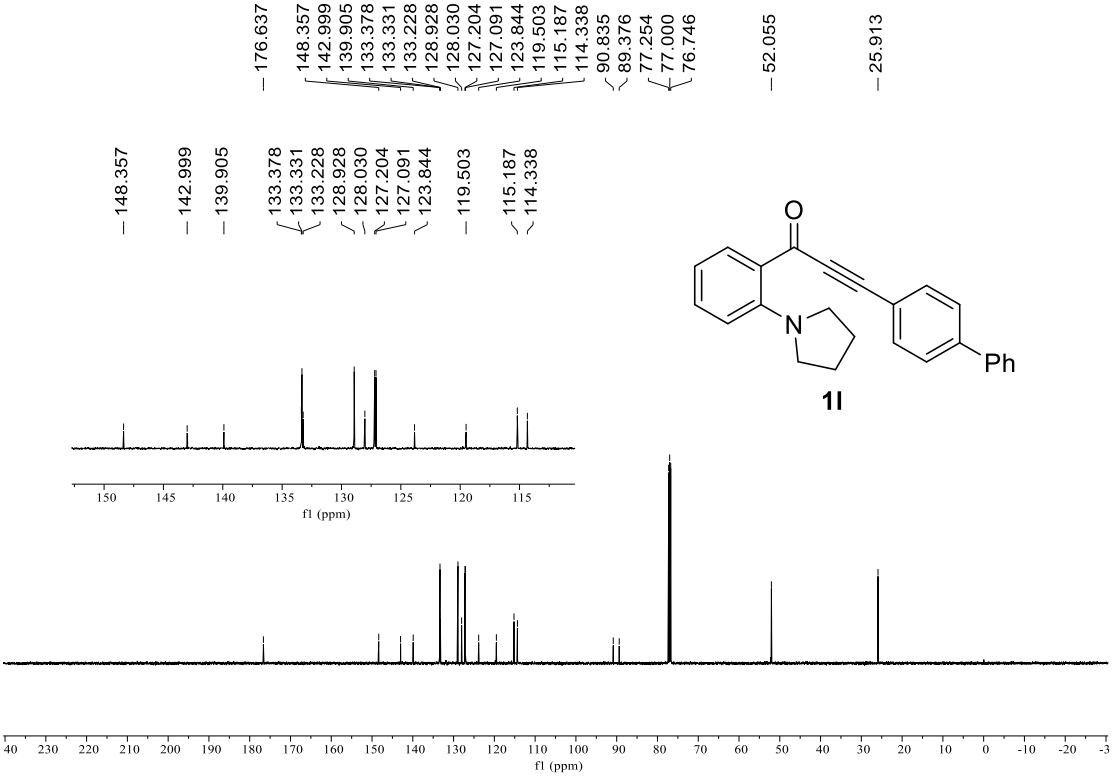

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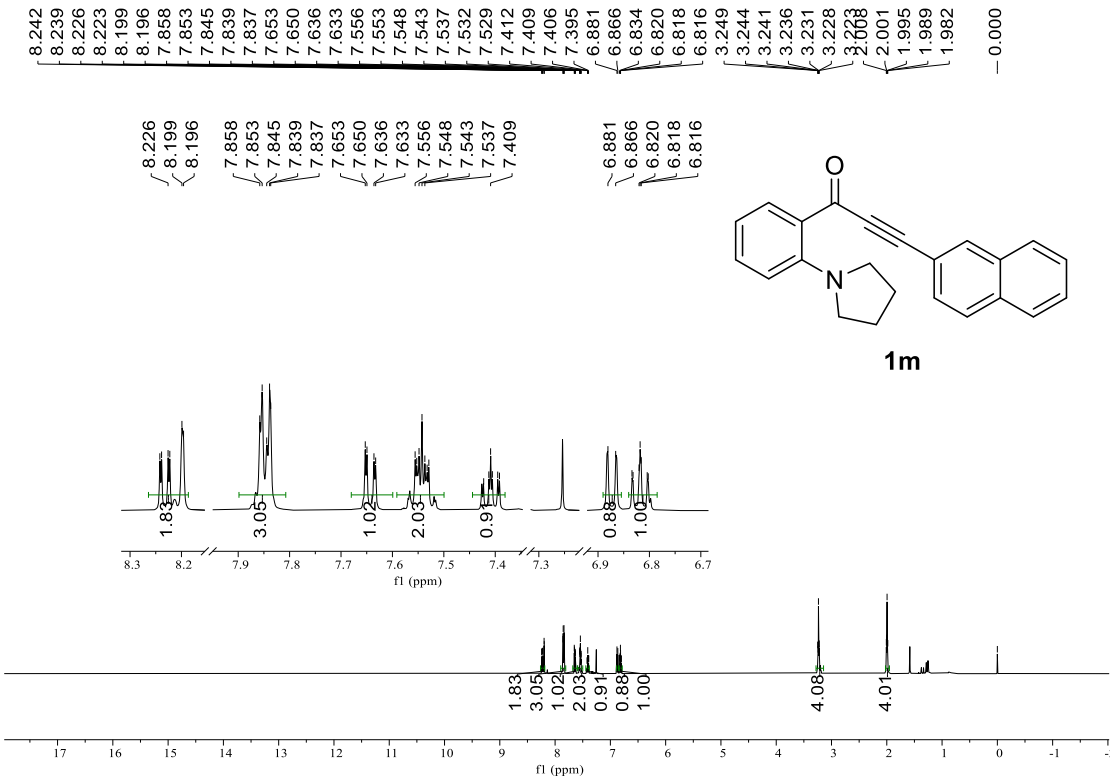

1m

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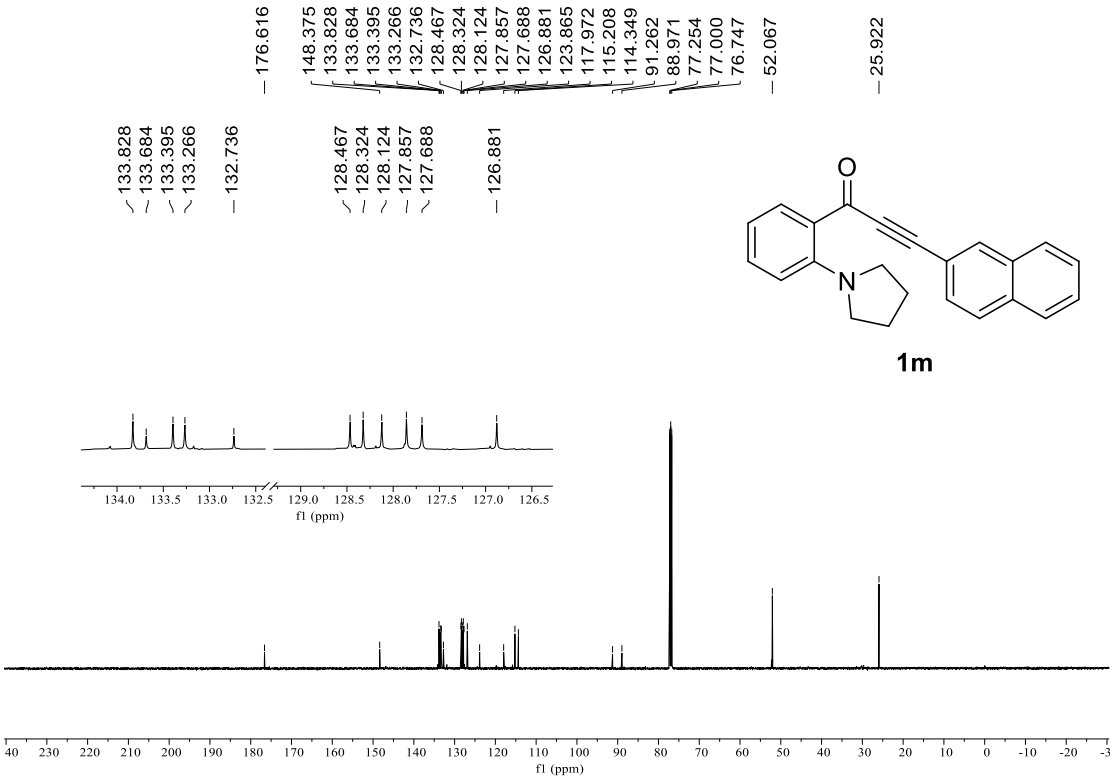

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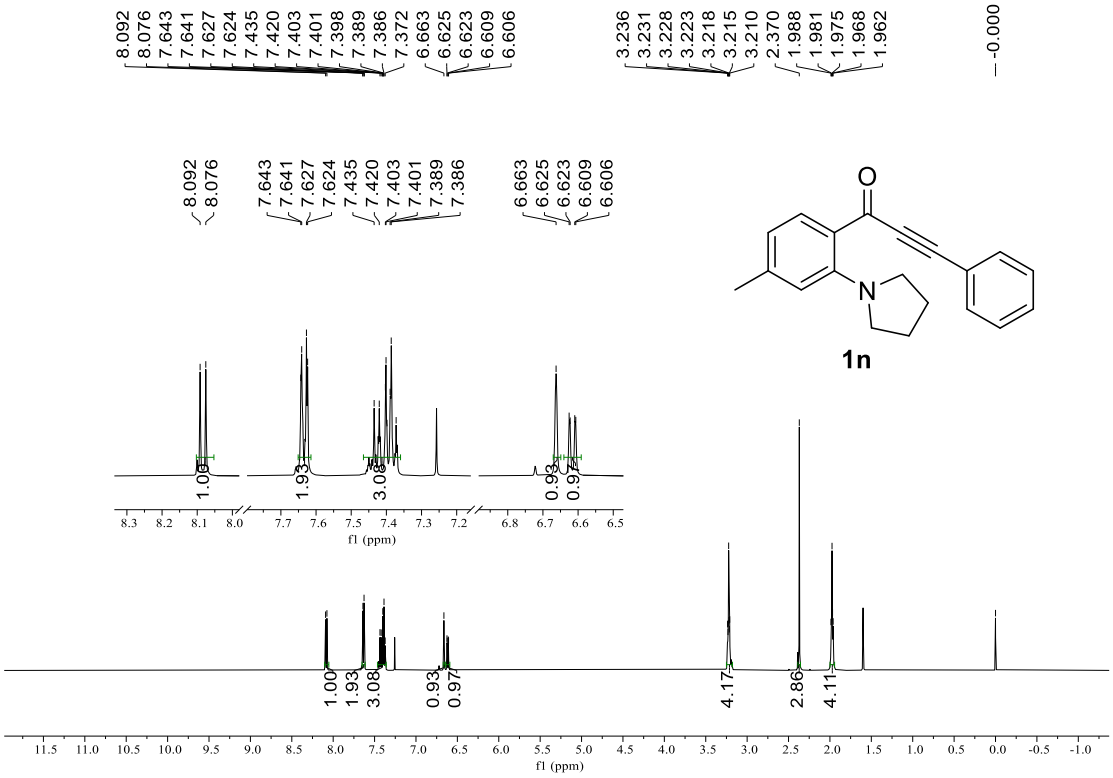

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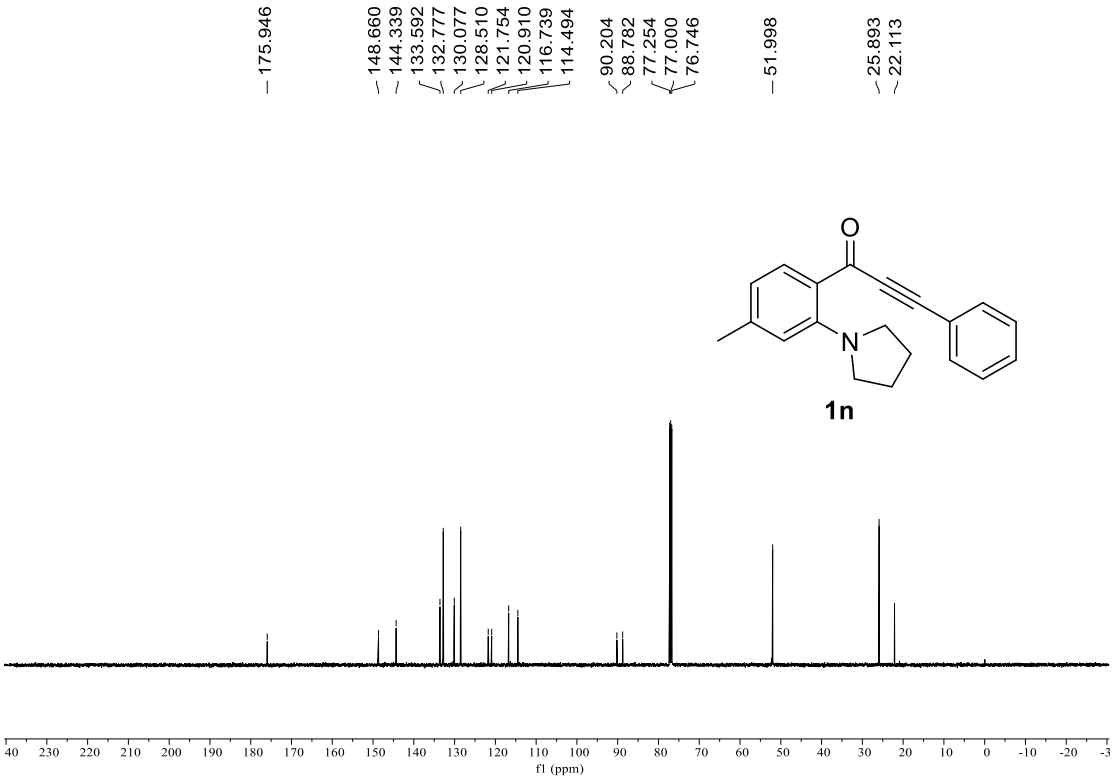

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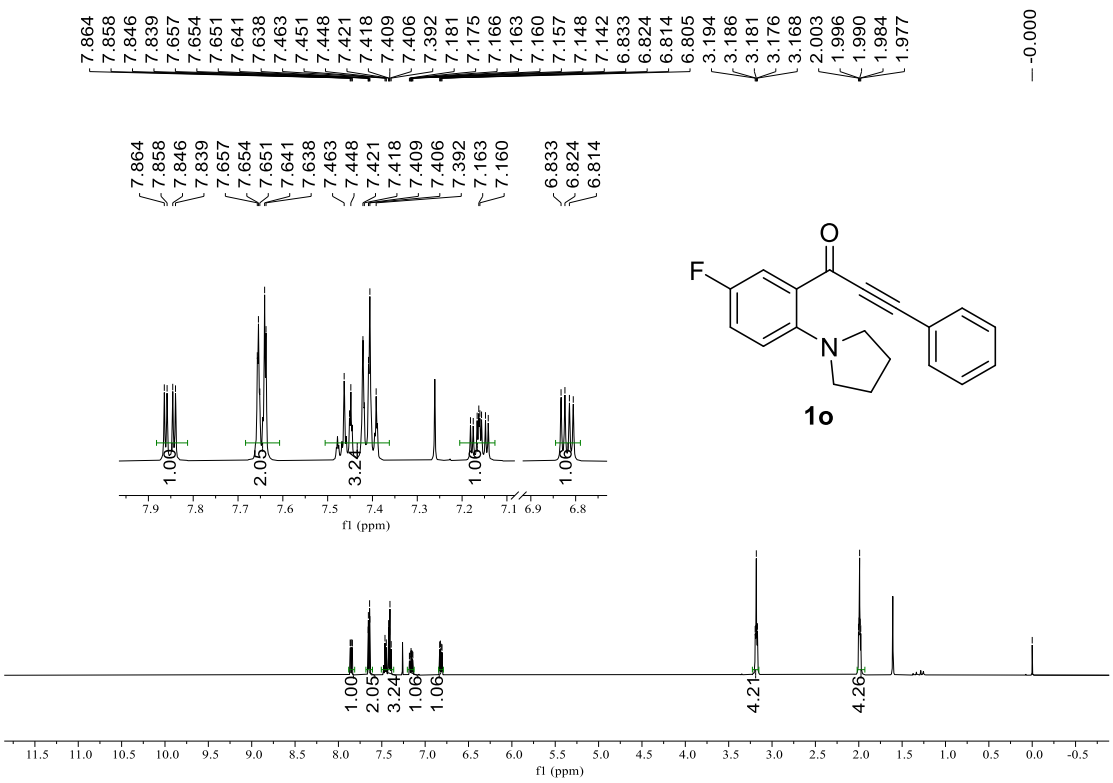

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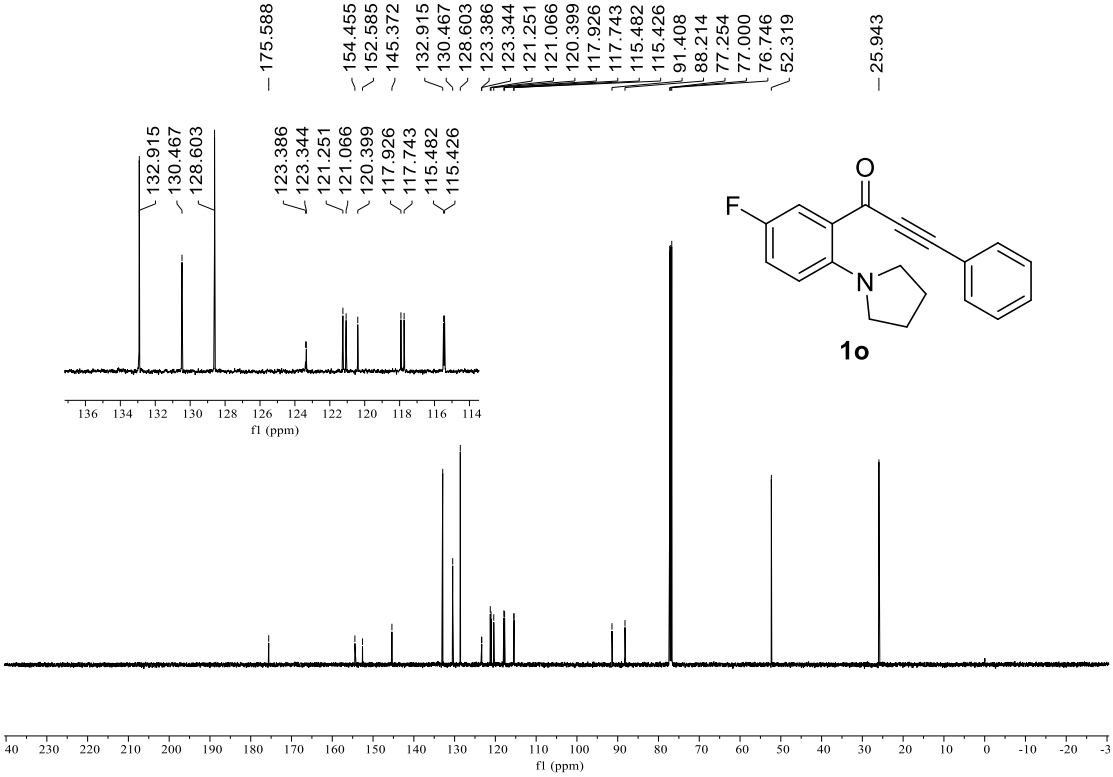

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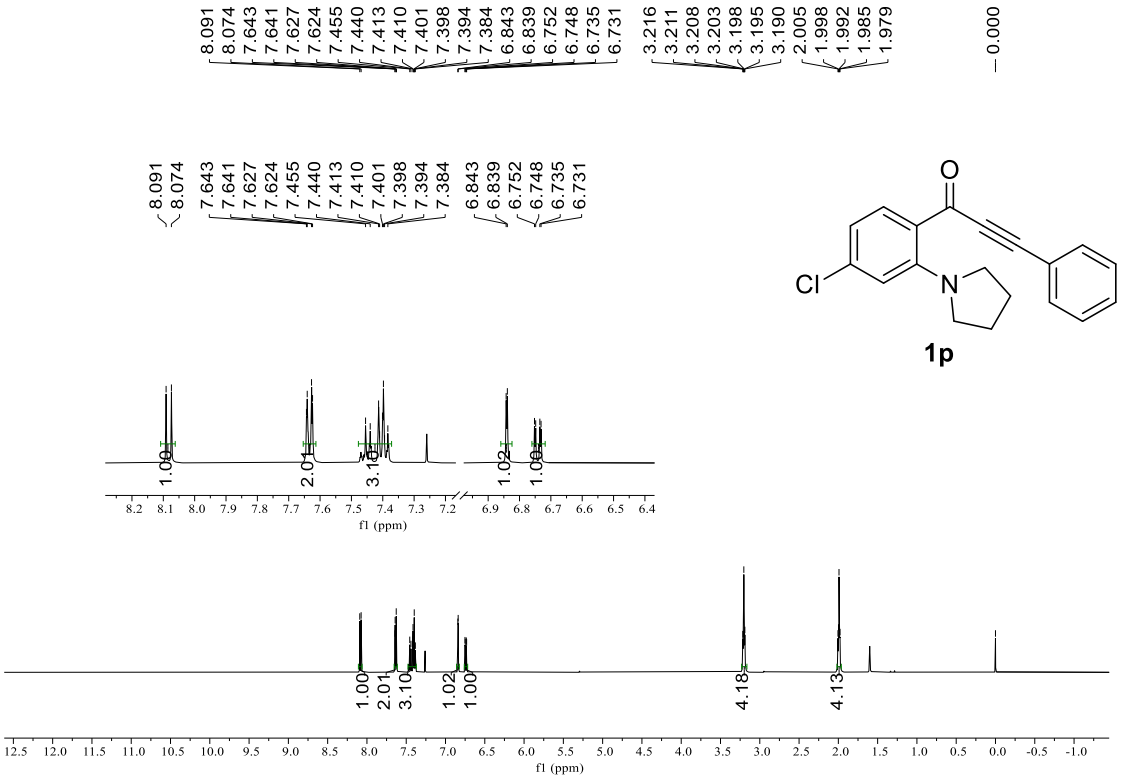

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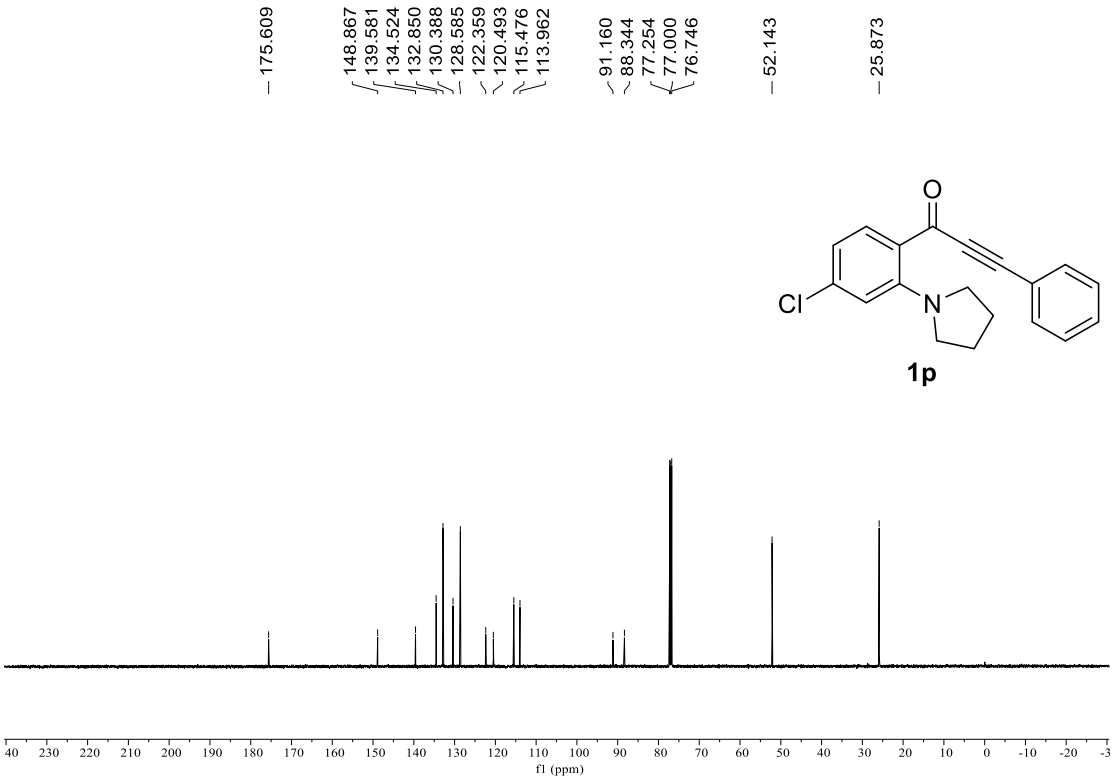
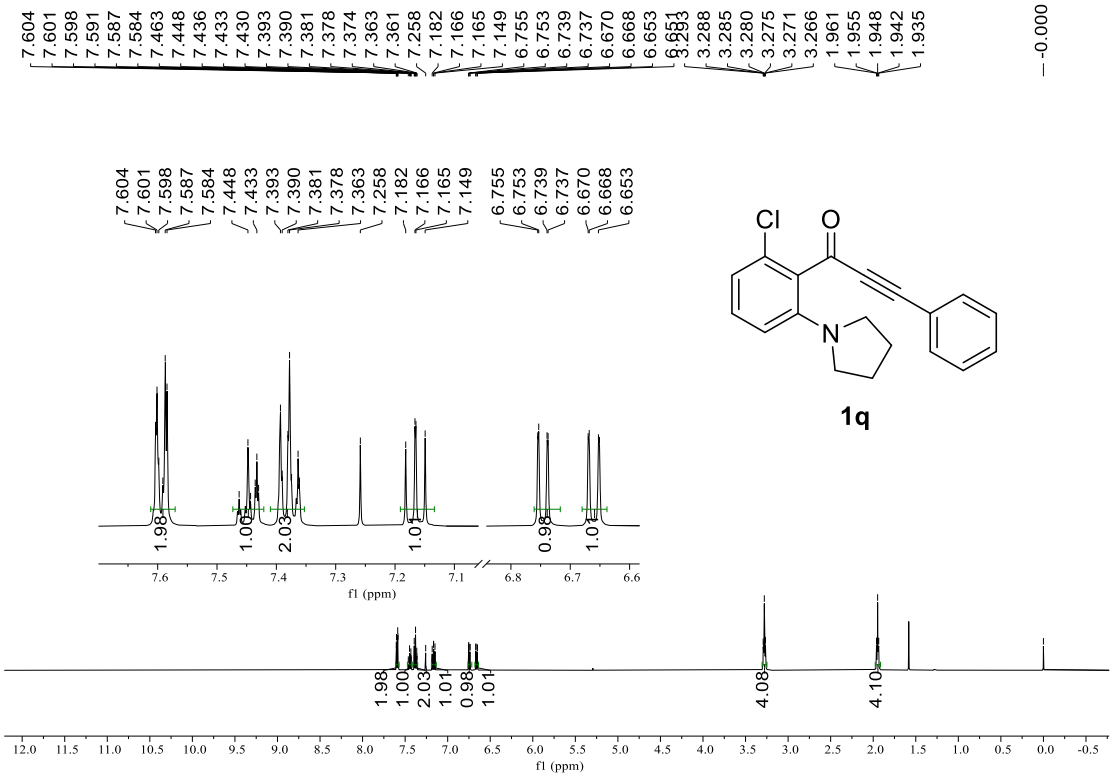
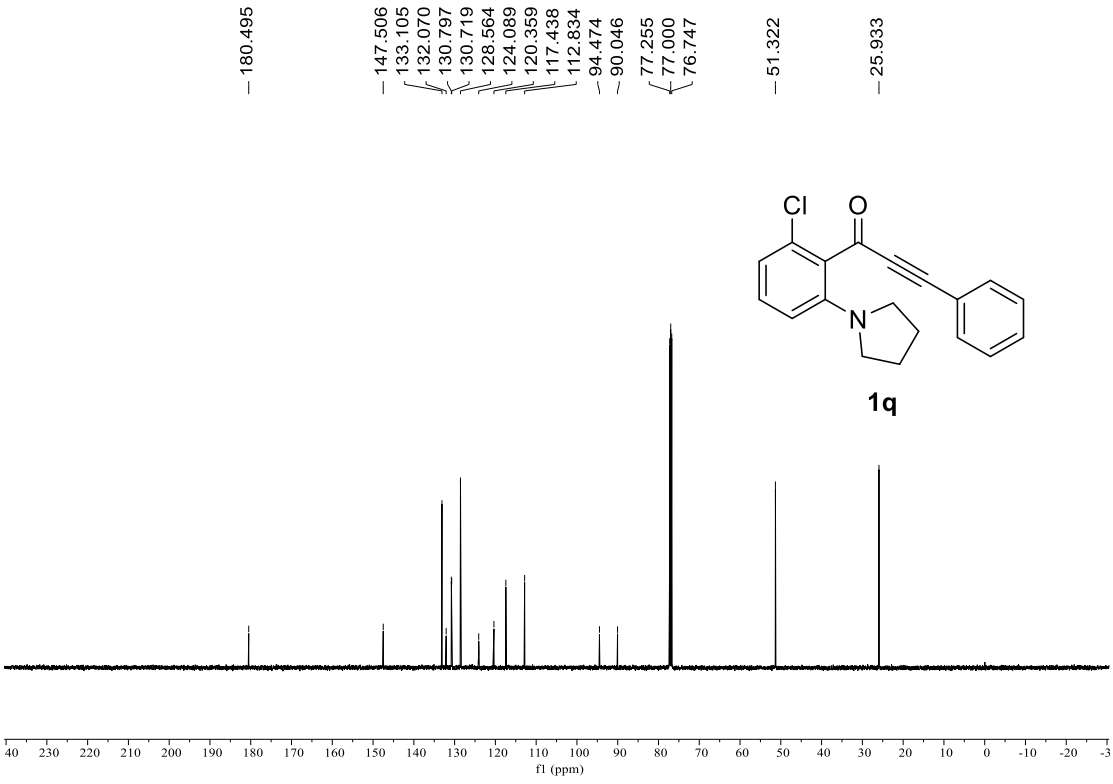


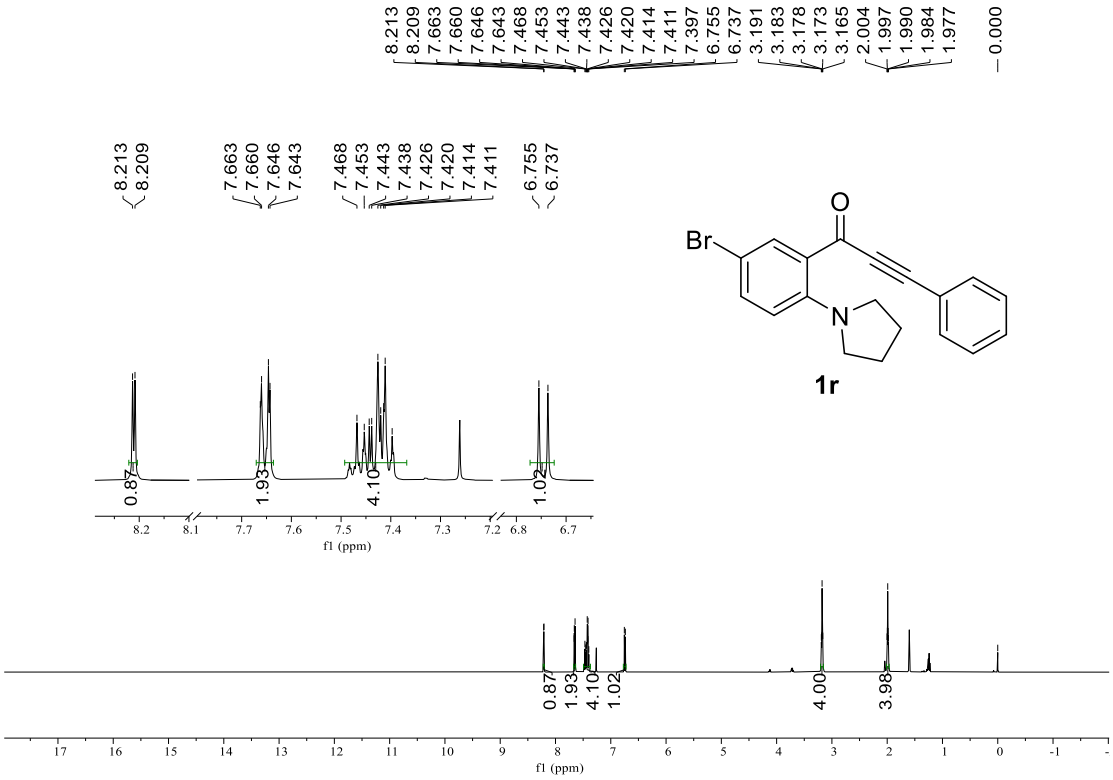
^{1}H NMR (500 MHz, $CDCl_3$)



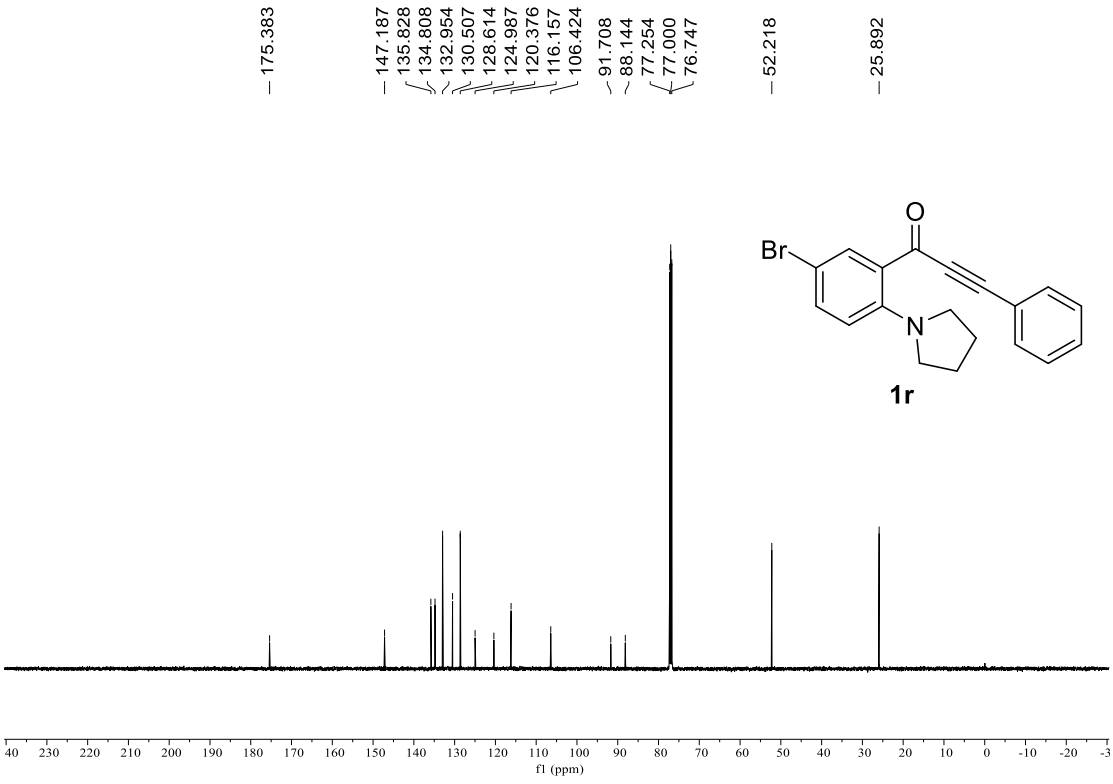
^{13}C NMR (125 MHz, $CDCl_3$)



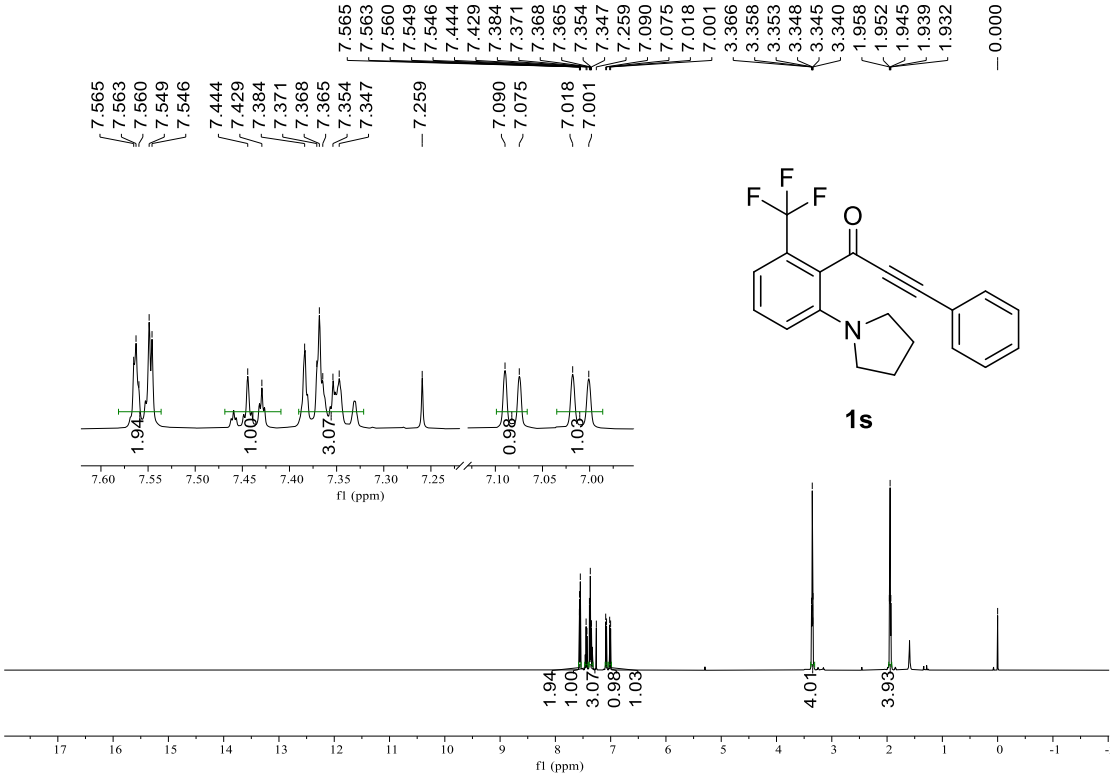
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

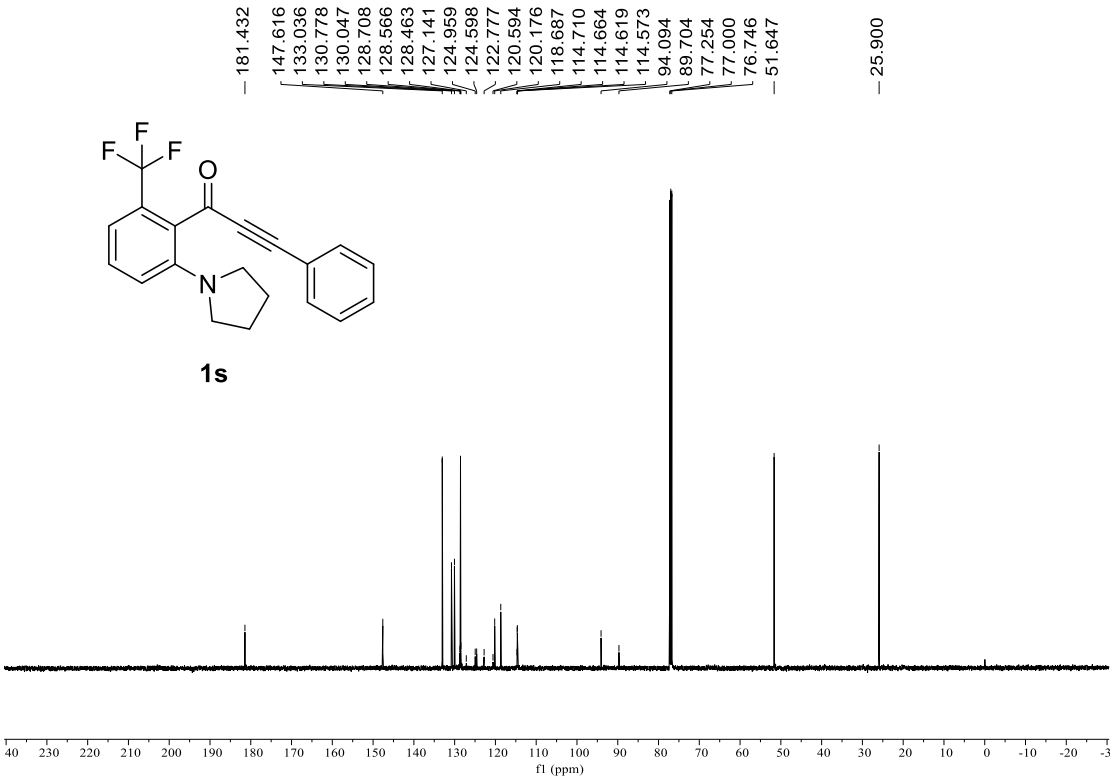


^{1}H NMR (500 MHz, $CDCl_3$)



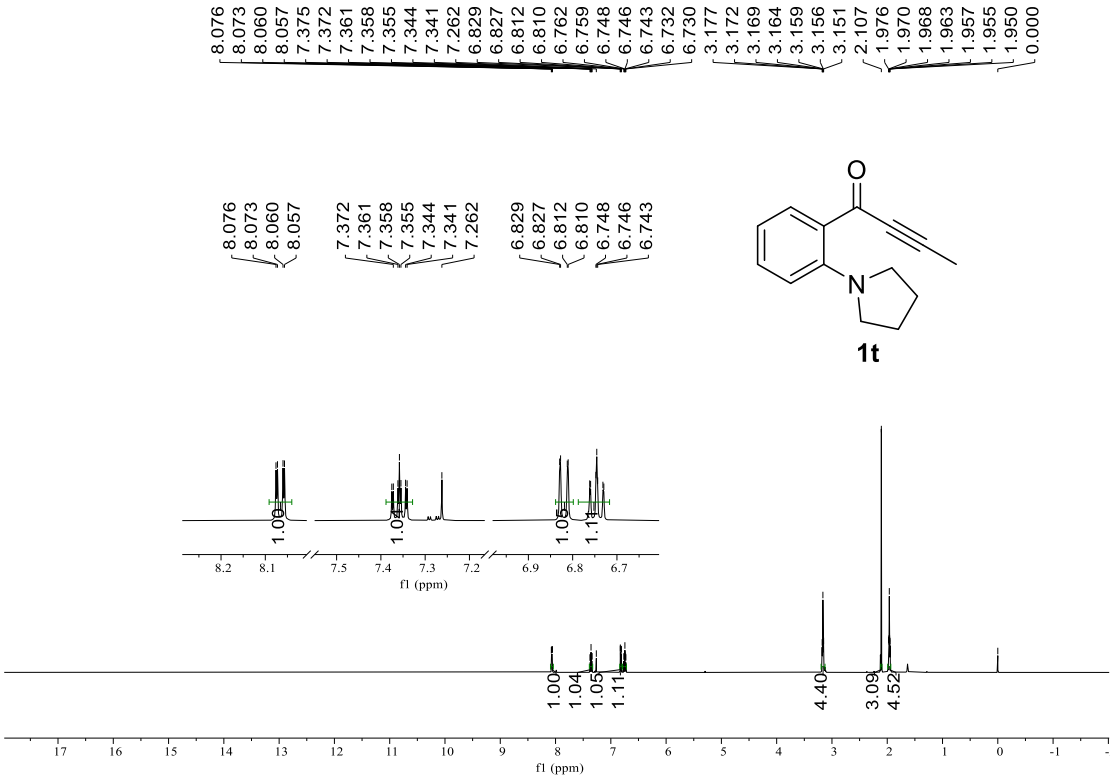
1s

^{13}C NMR (125 MHz, $CDCl_3$)

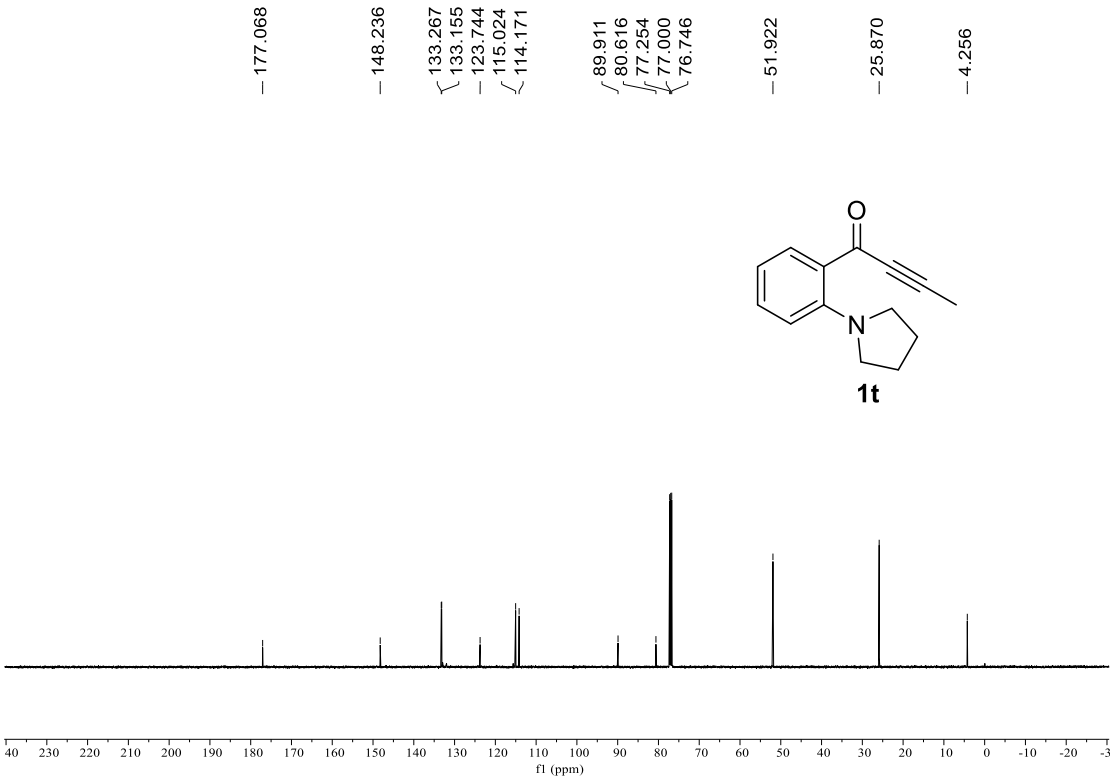


1s

^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)



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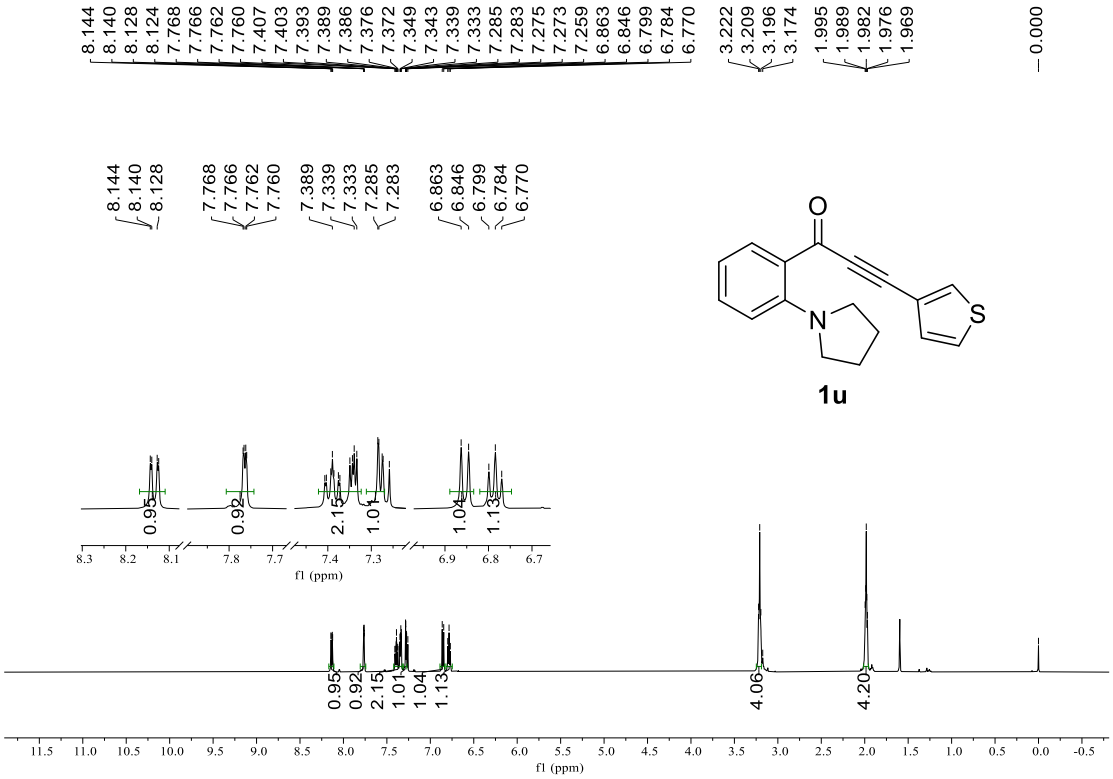

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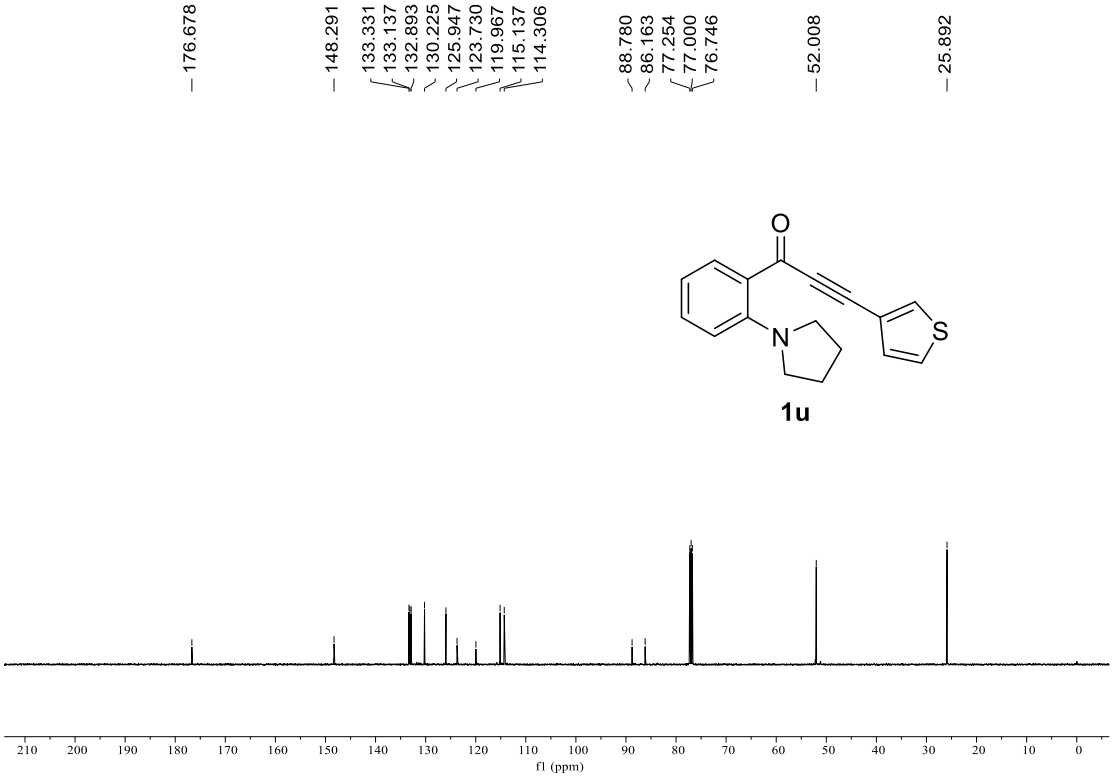

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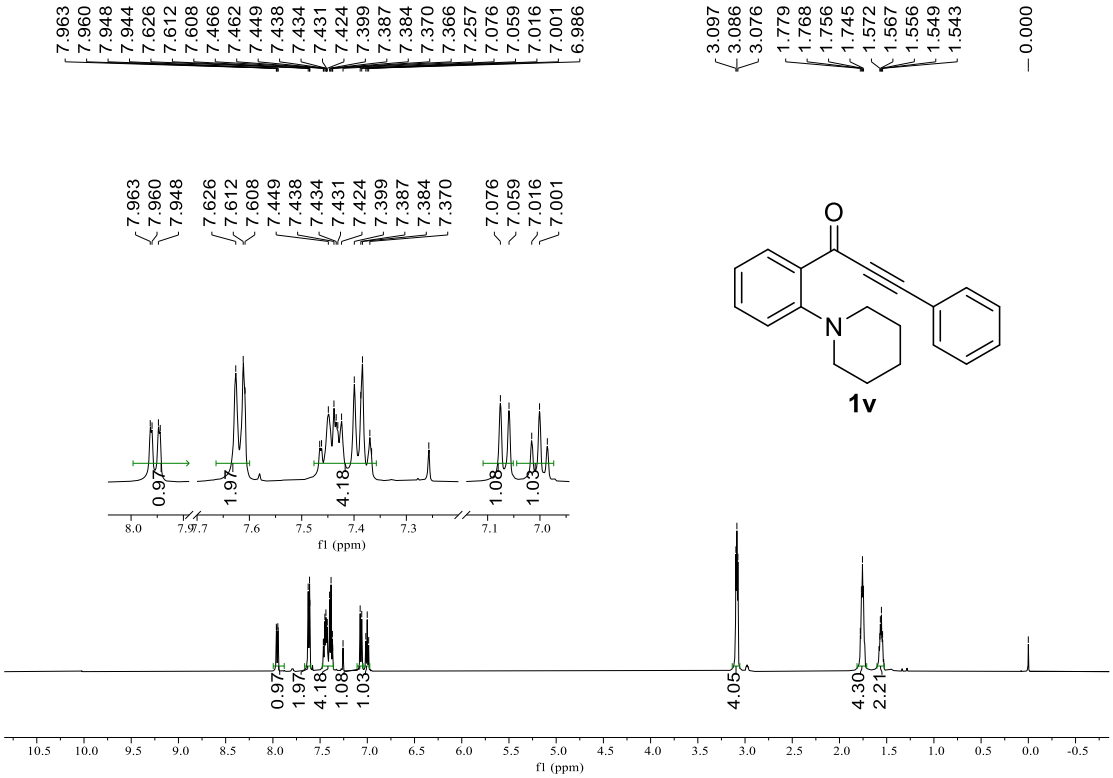

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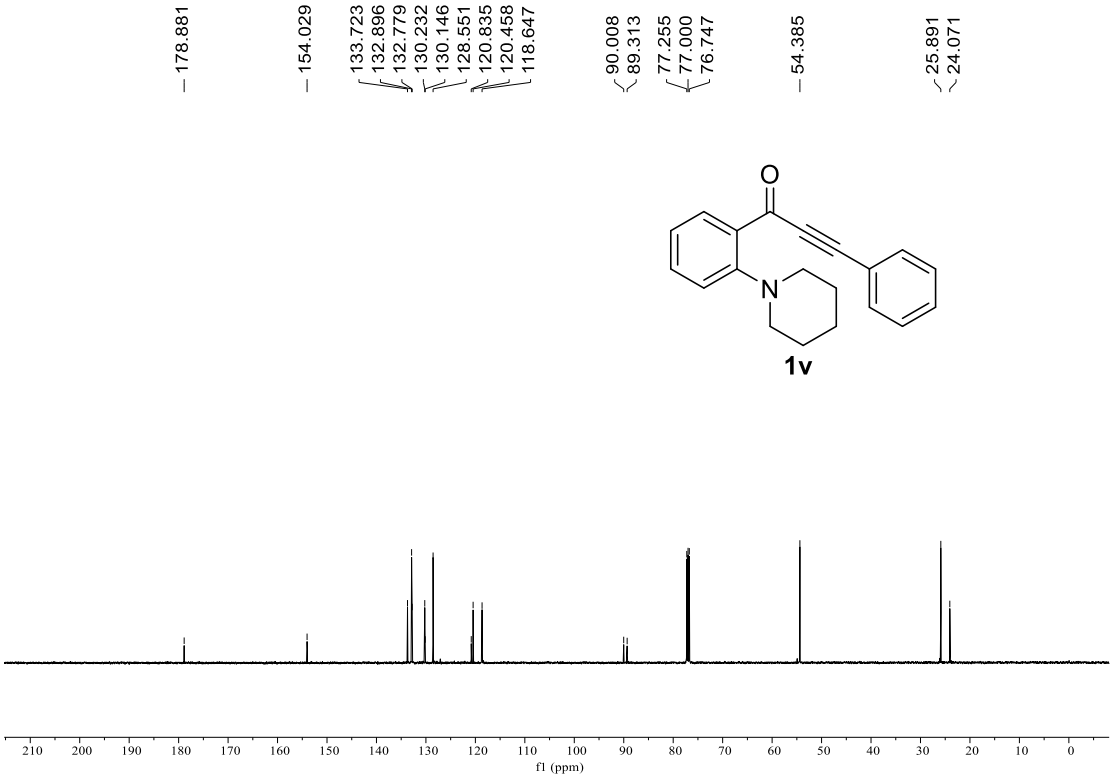
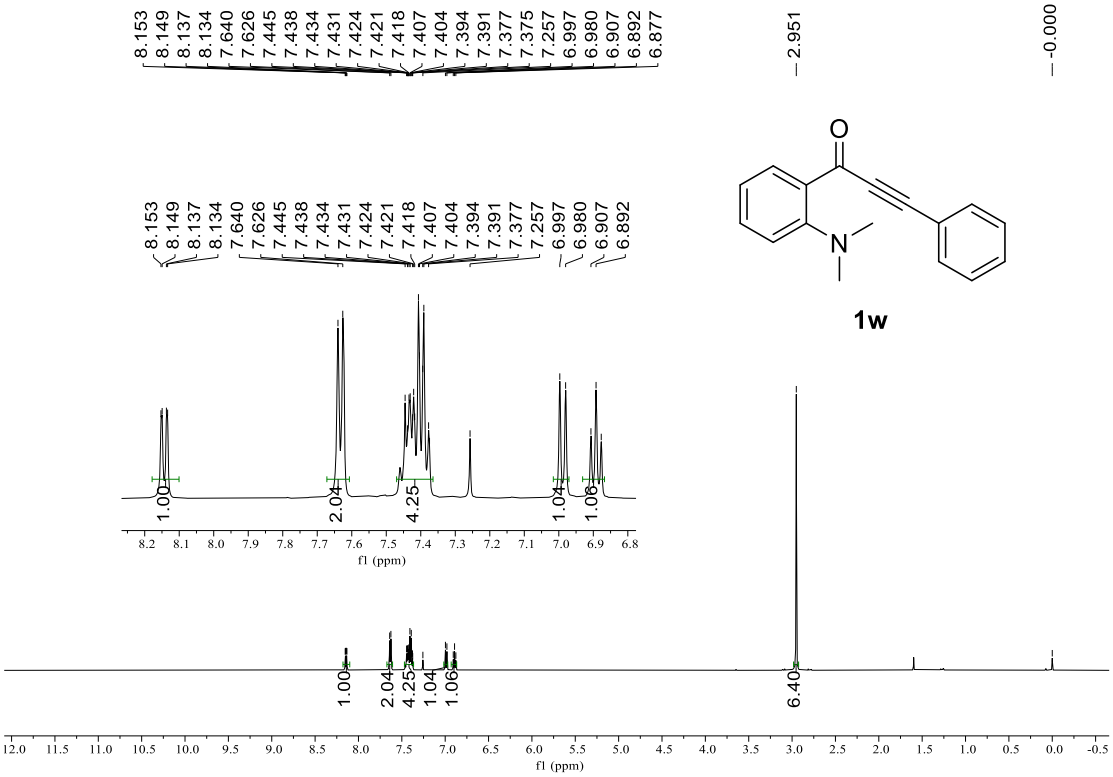
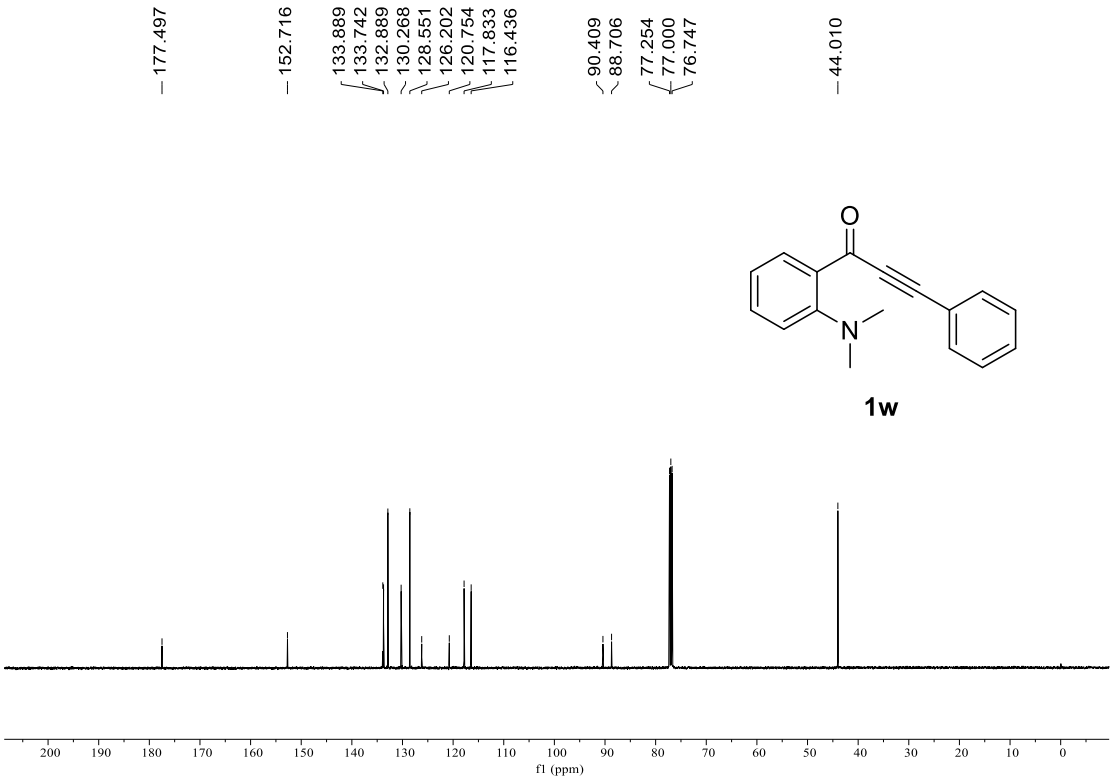


^{1}H NMR (500 MHz, $CDCl_3$)



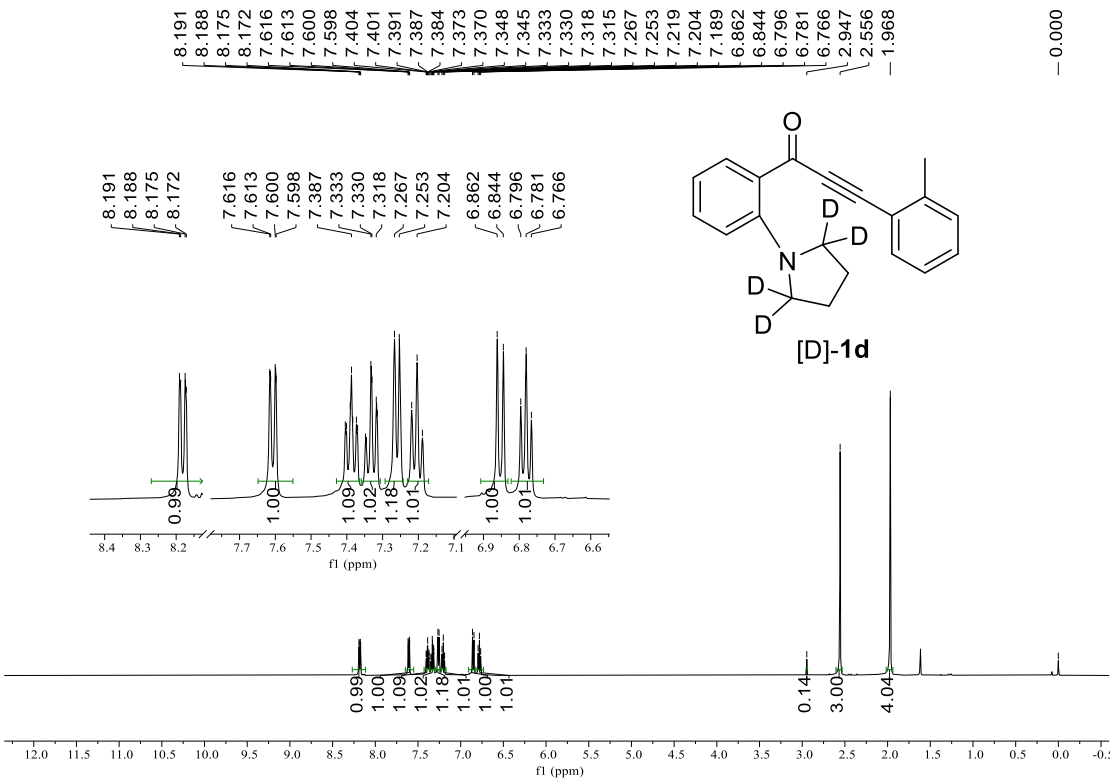
1w

^{13}C NMR (125 MHz, $CDCl_3$)

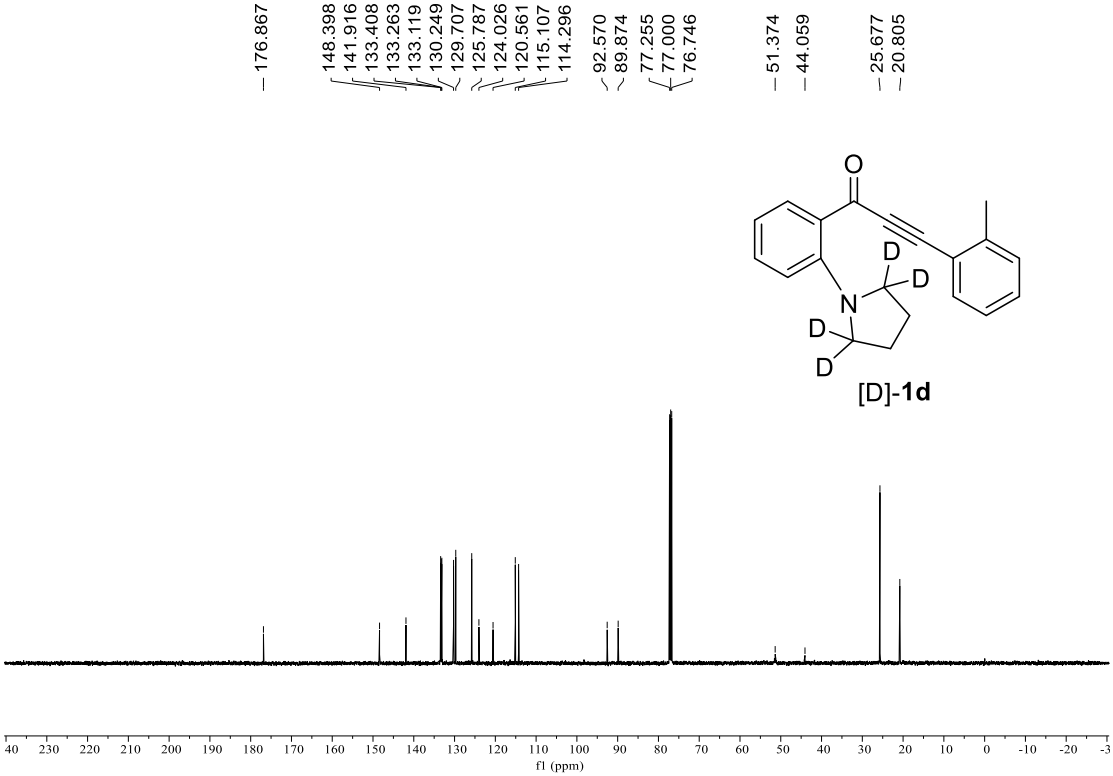


1w

^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)



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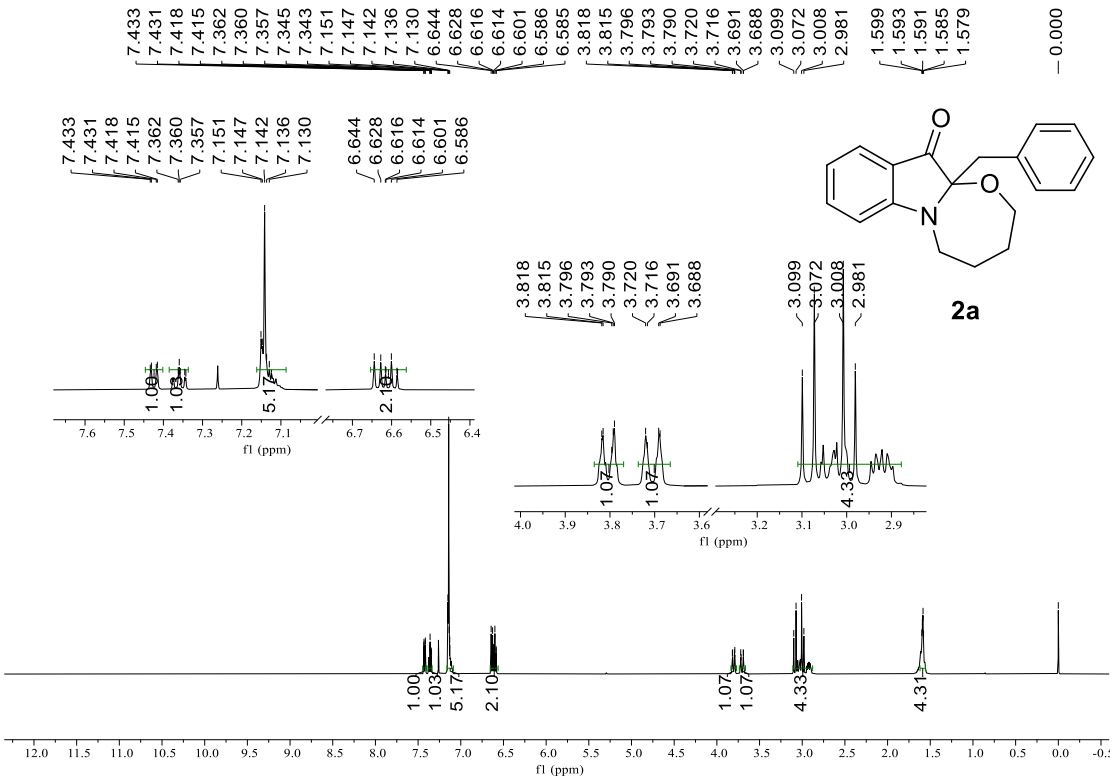
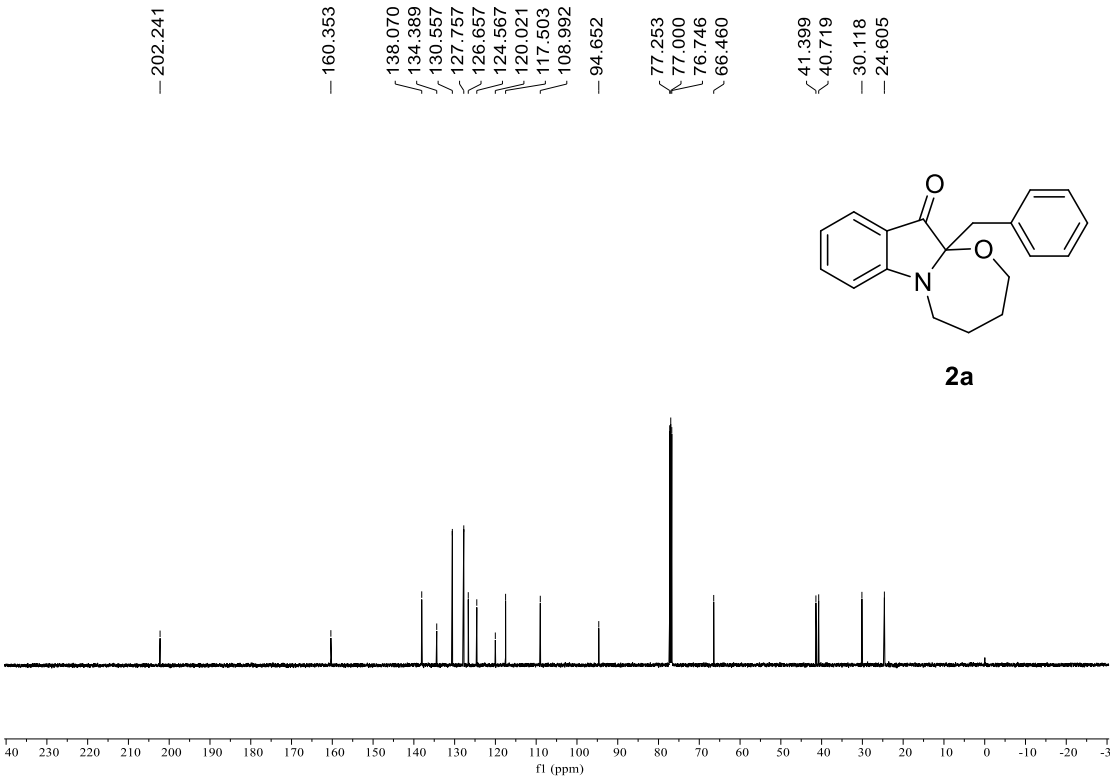
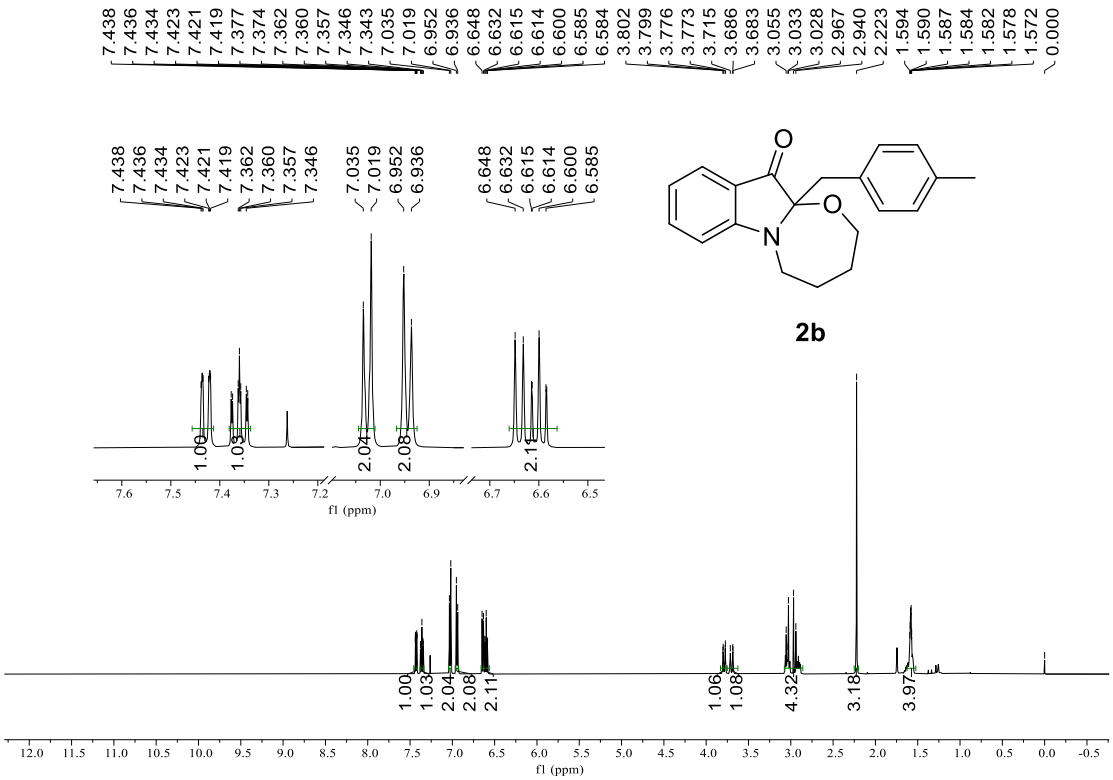


^{13}C NMR (125 MHz, $CDCl_3$)

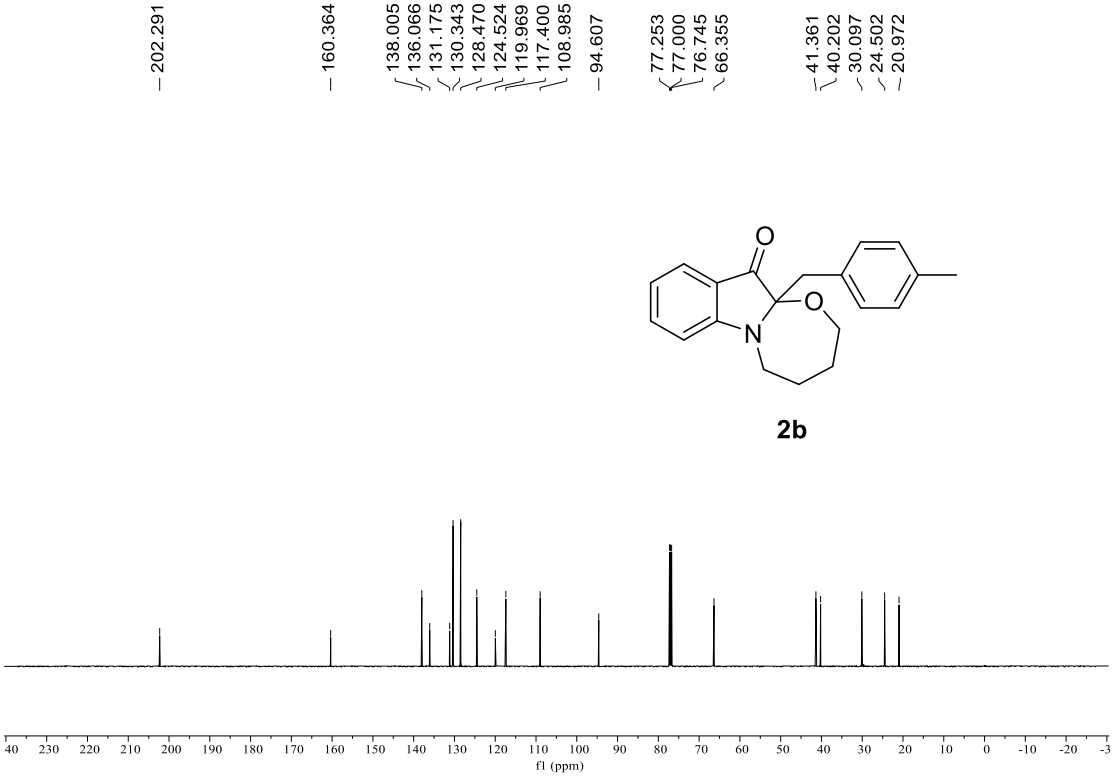


^{1}H NMR (500 MHz, $CDCl_3$)



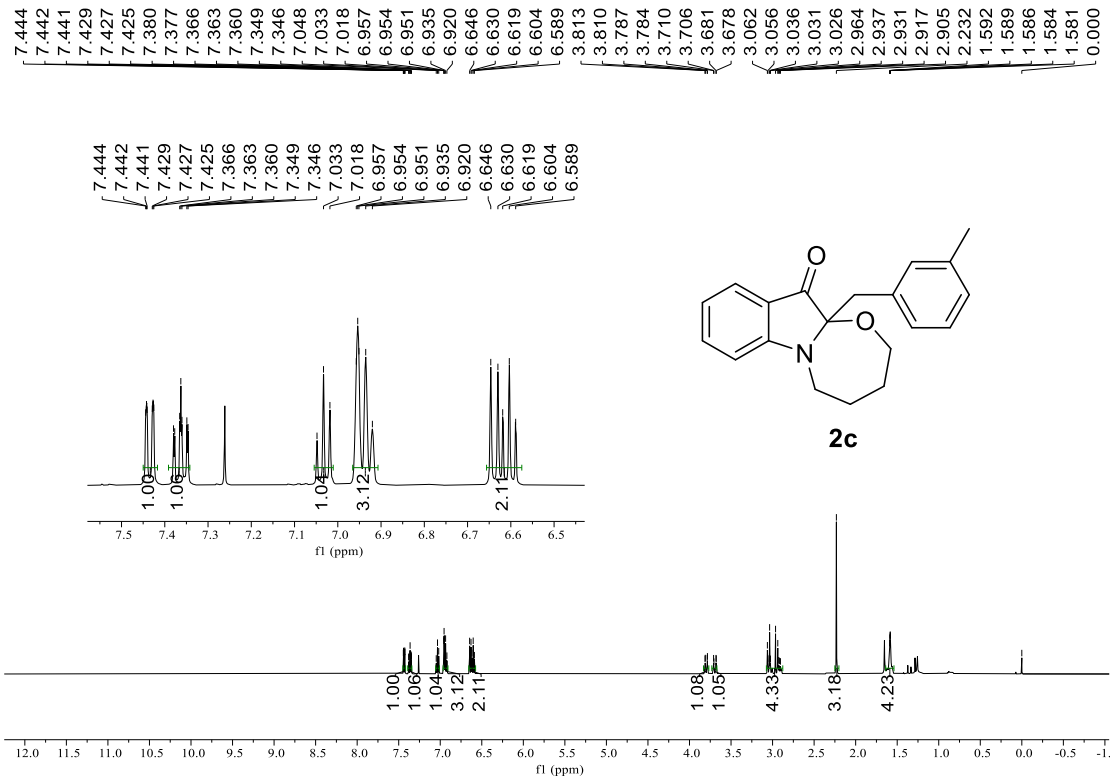
2b

^{13}C NMR (125 MHz, $CDCl_3$)

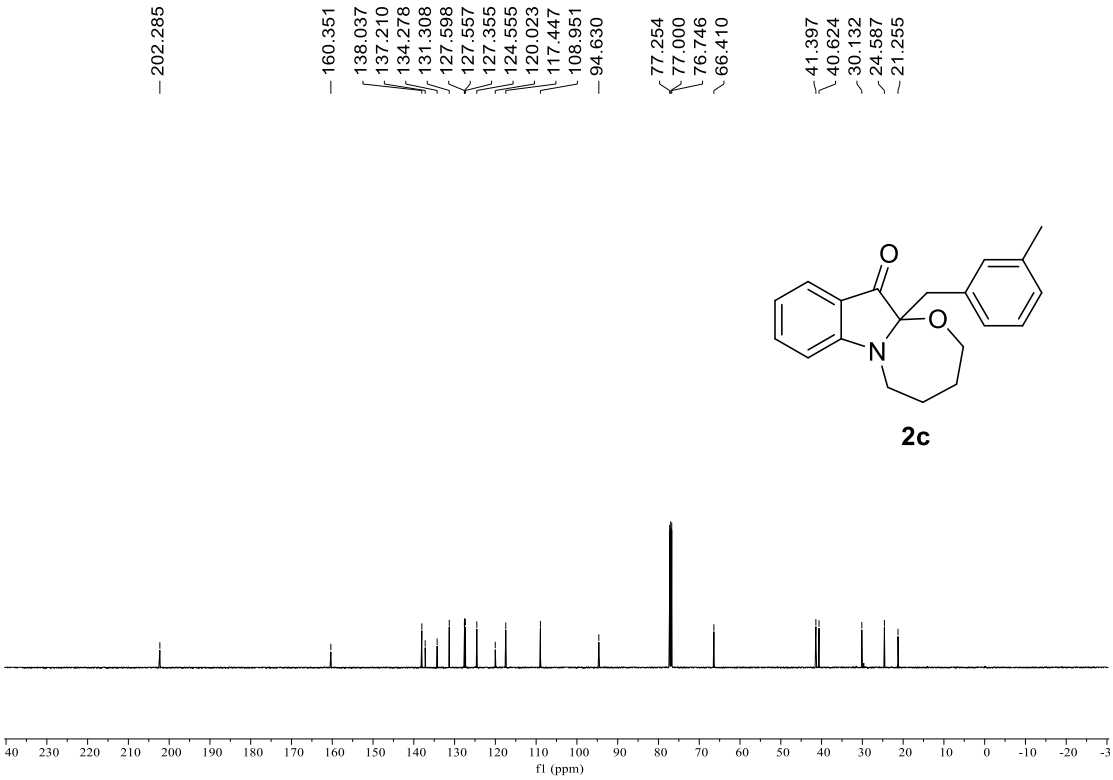


2b

^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)



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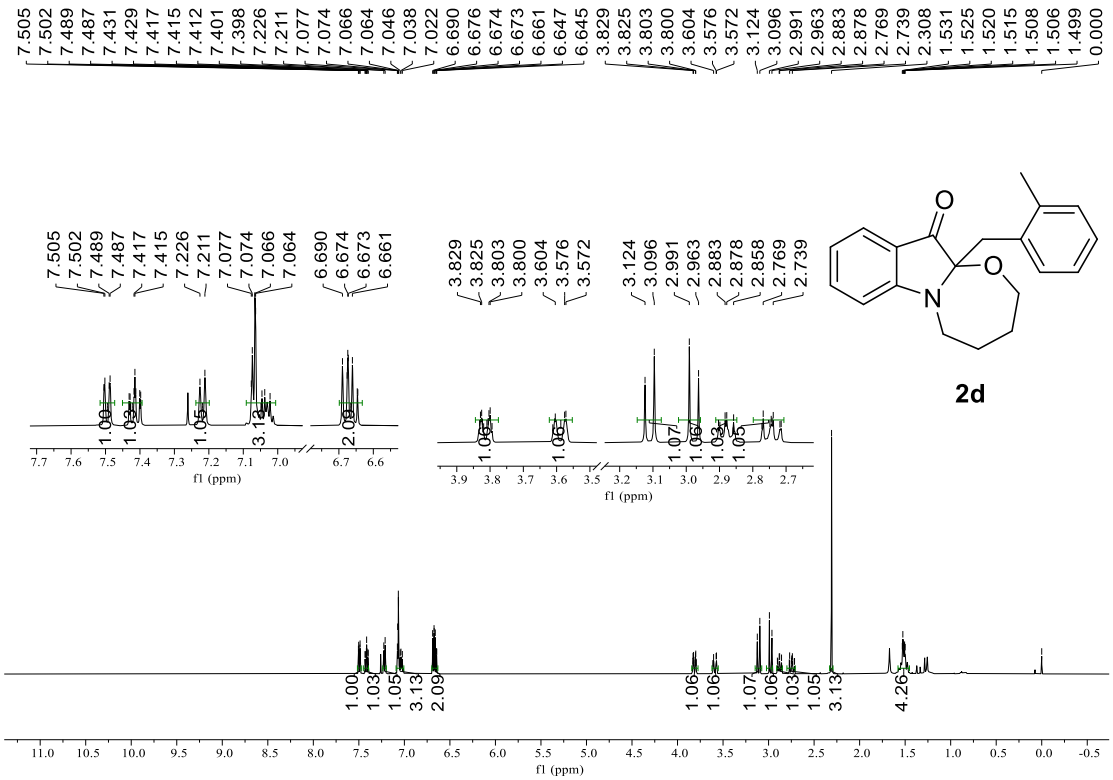
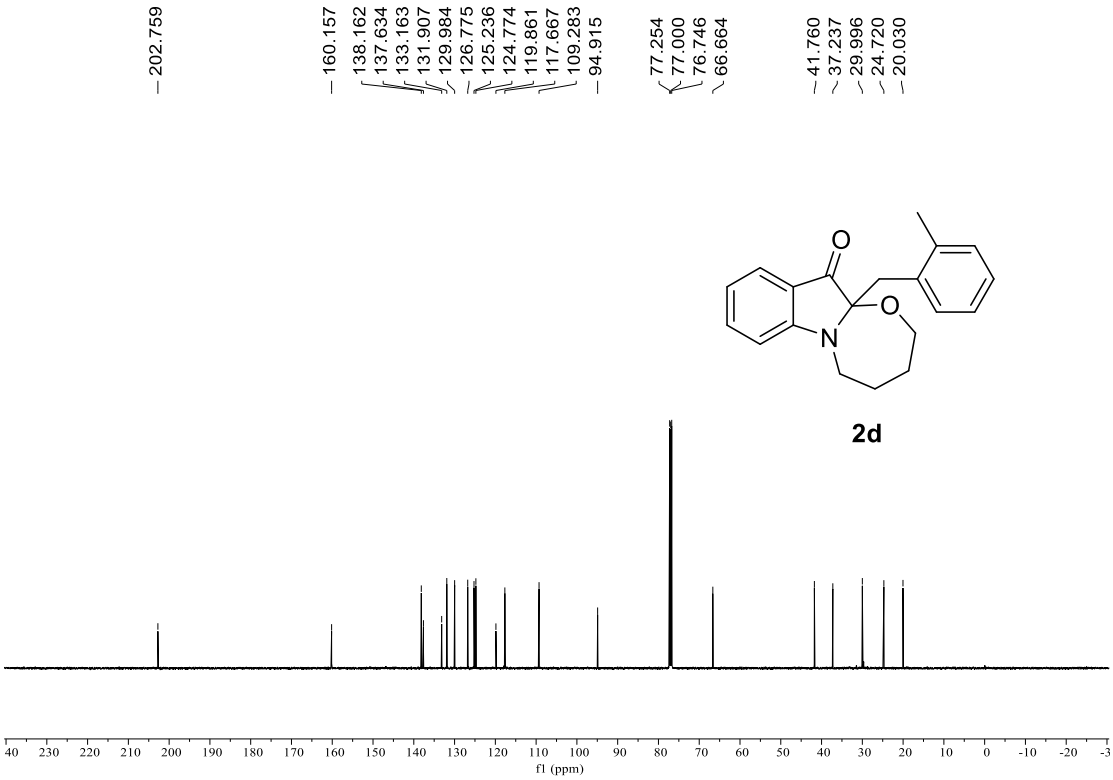


^{13}C NMR (125 MHz, $CDCl_3$)



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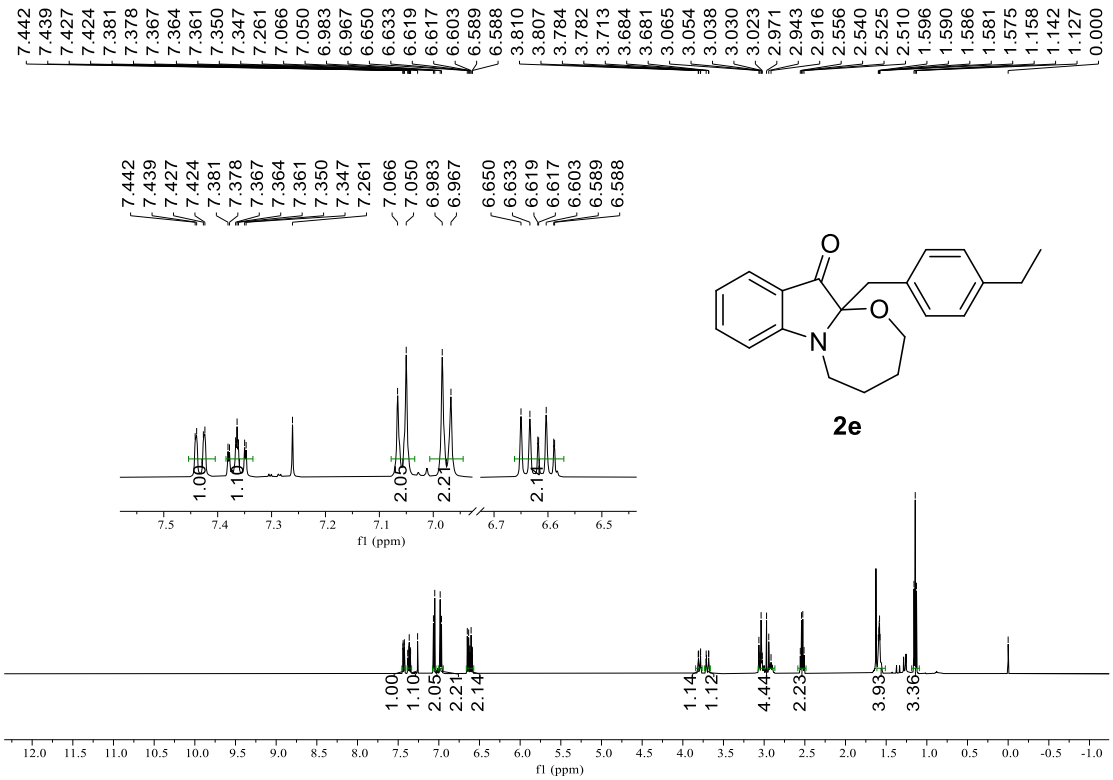
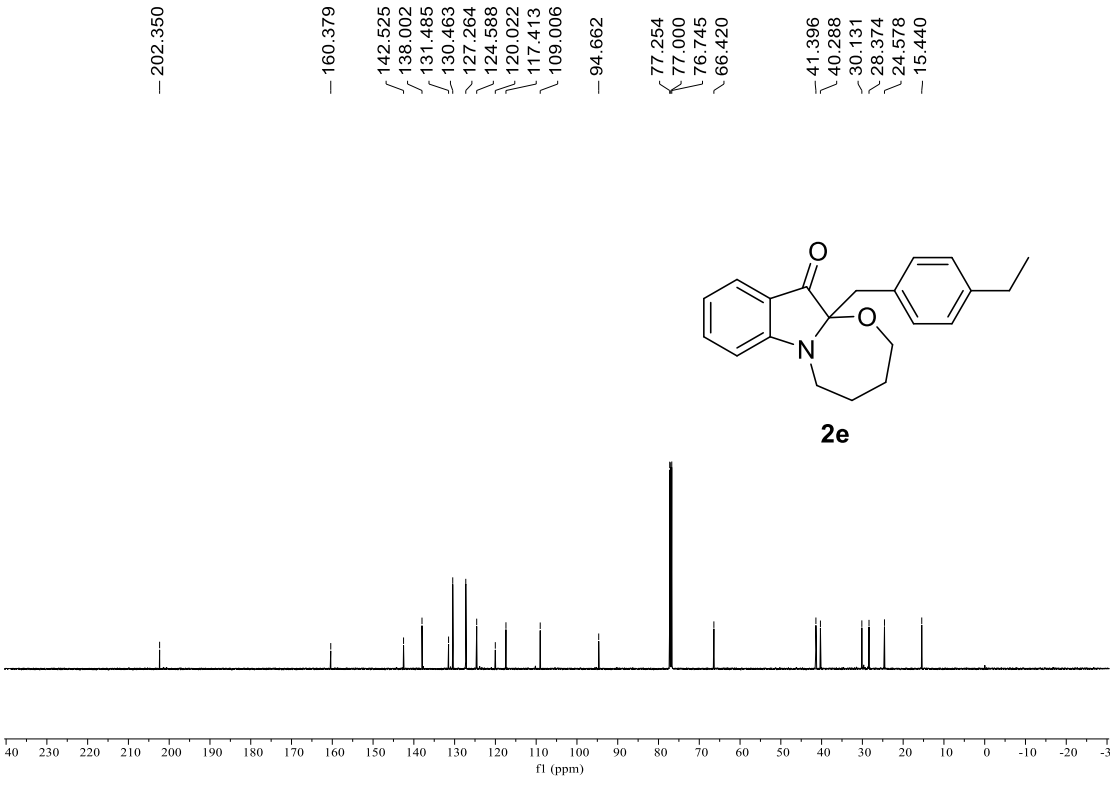
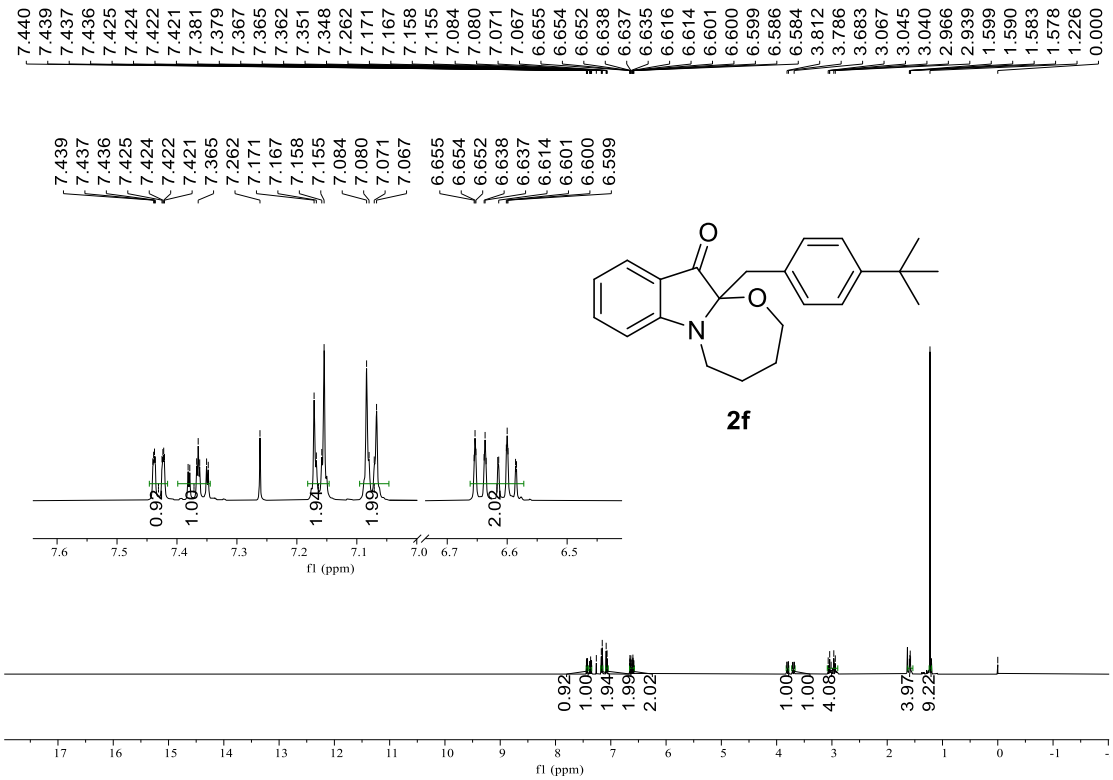


^{13}C NMR (125 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)



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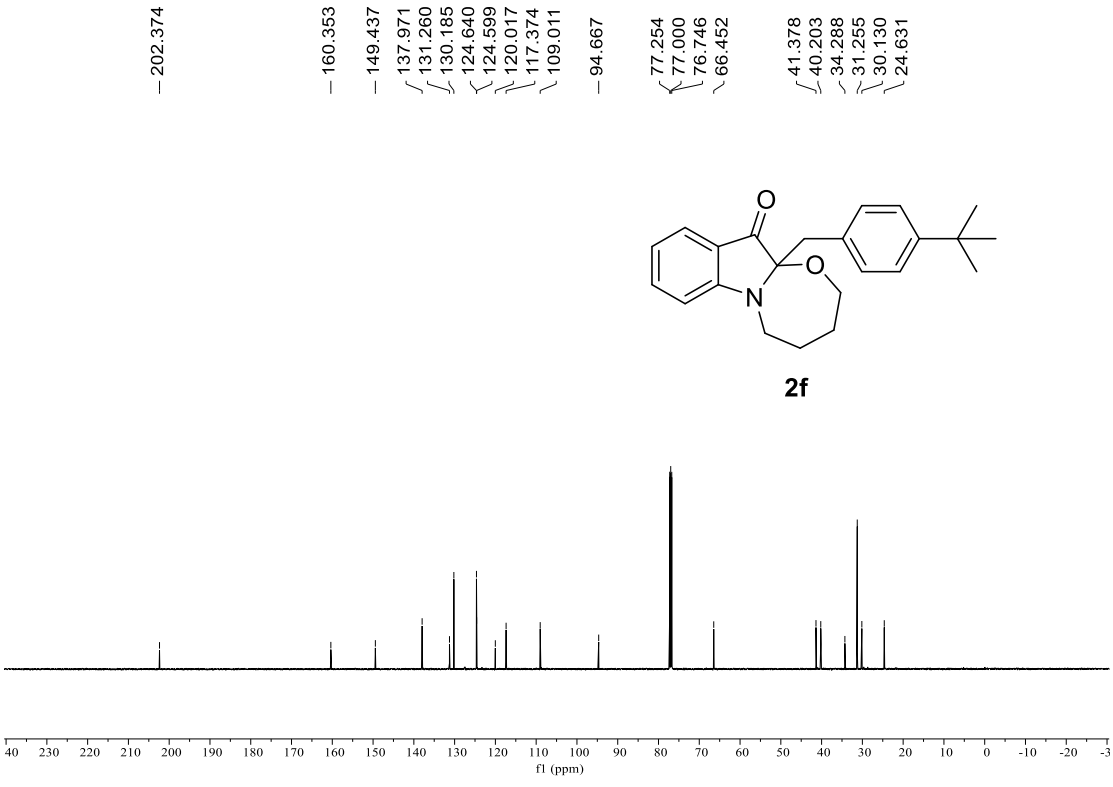
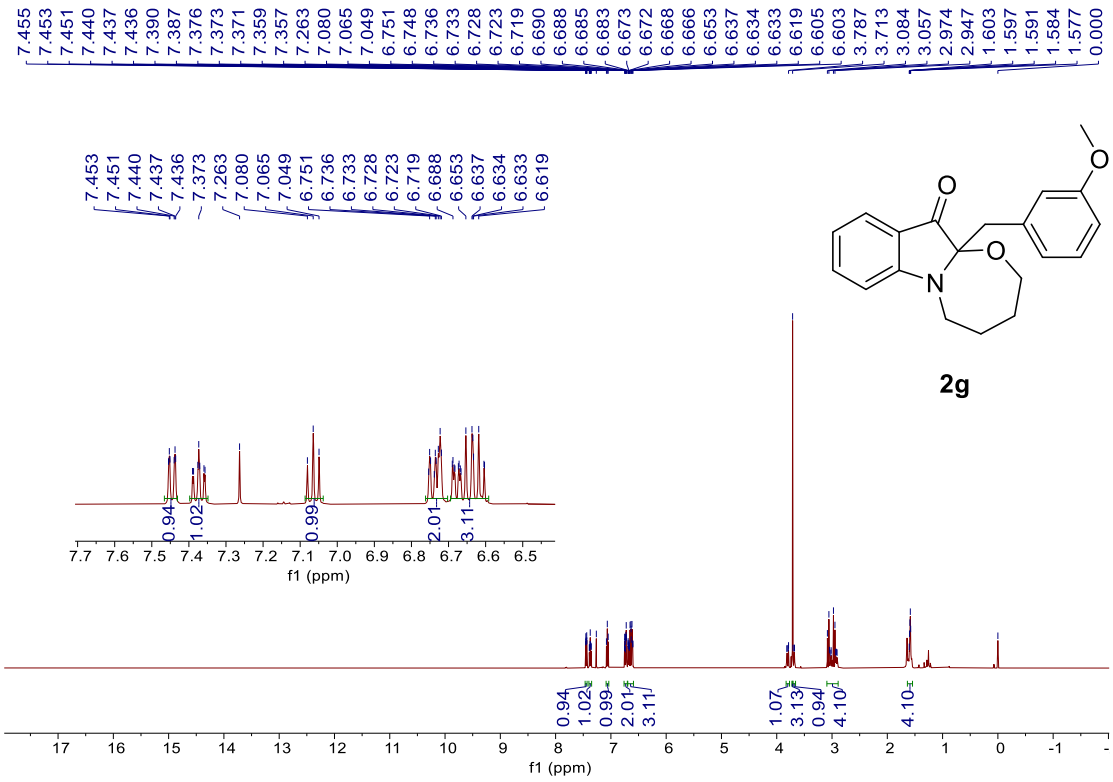
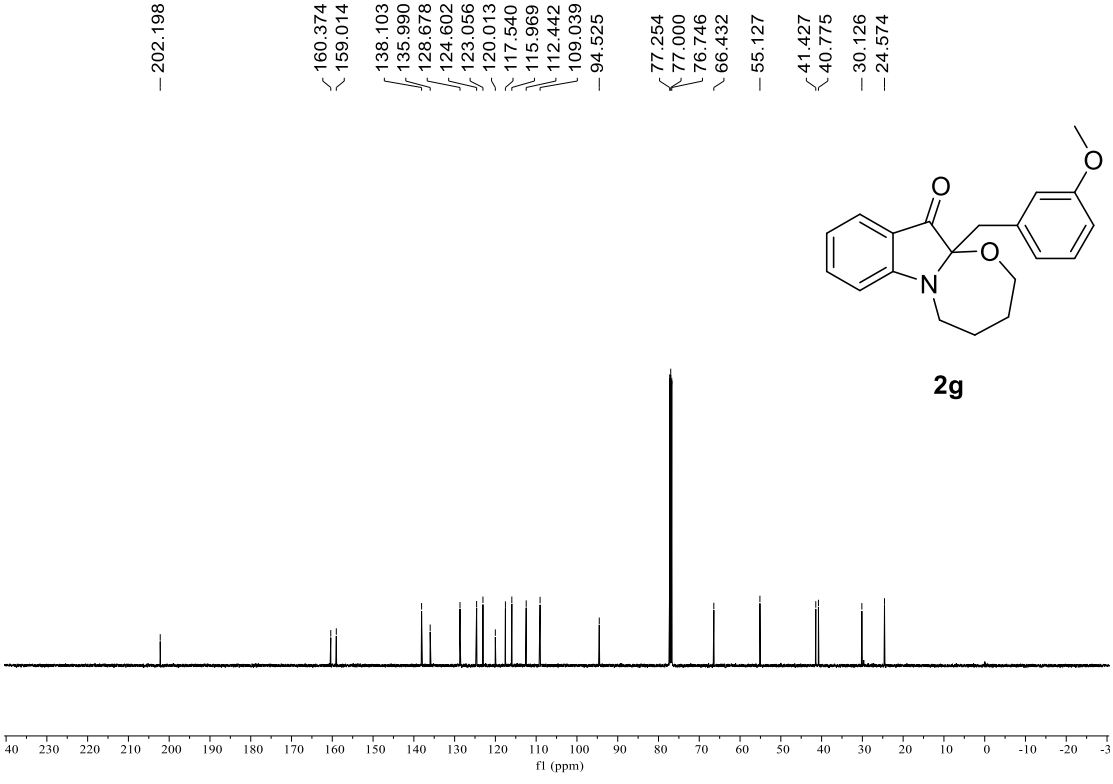


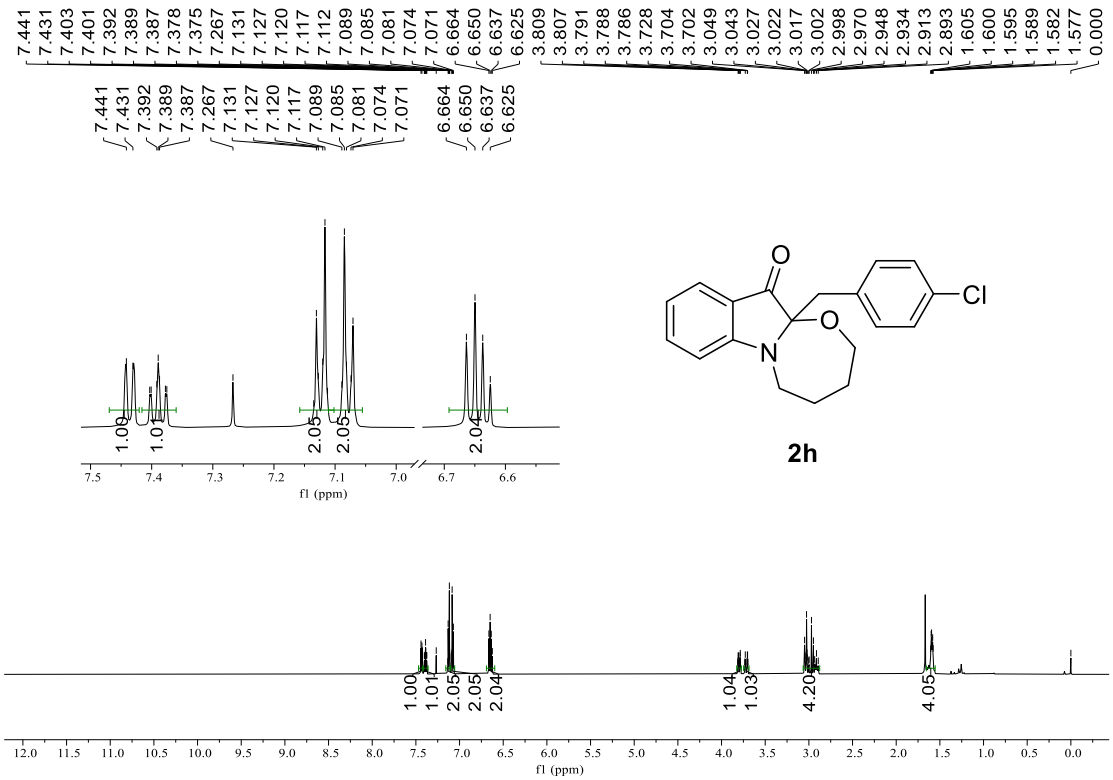
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

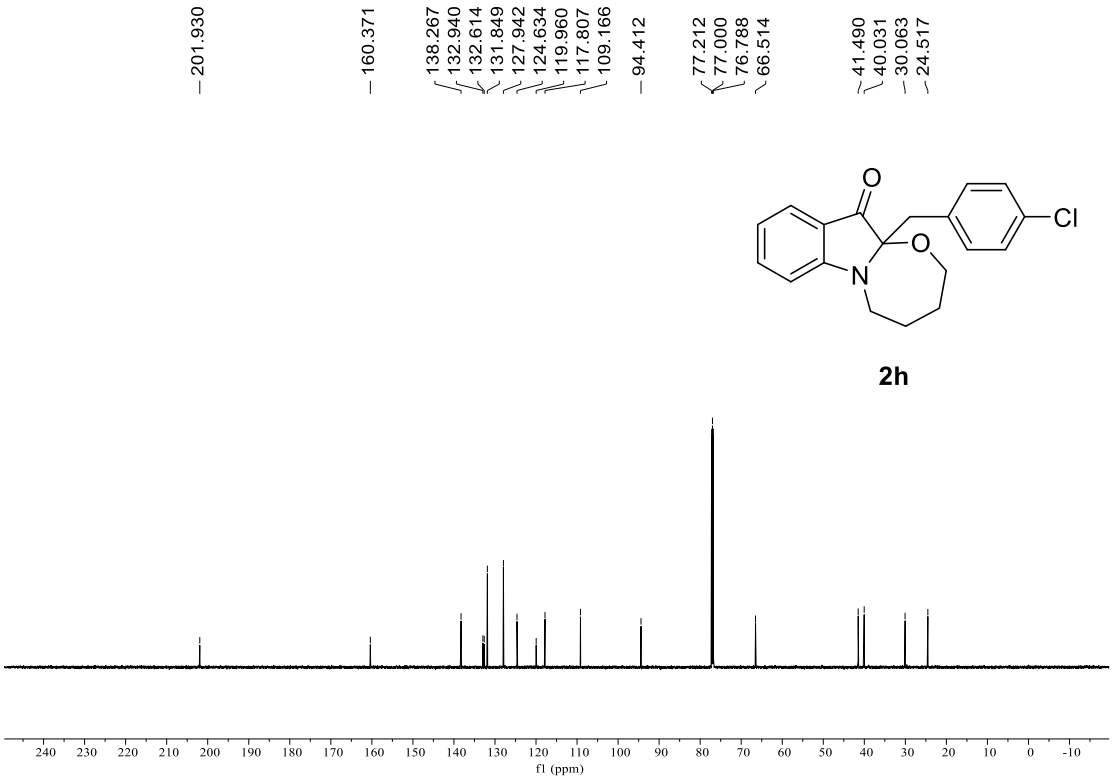


^{1}H NMR (600 MHz, $CDCl_3$)



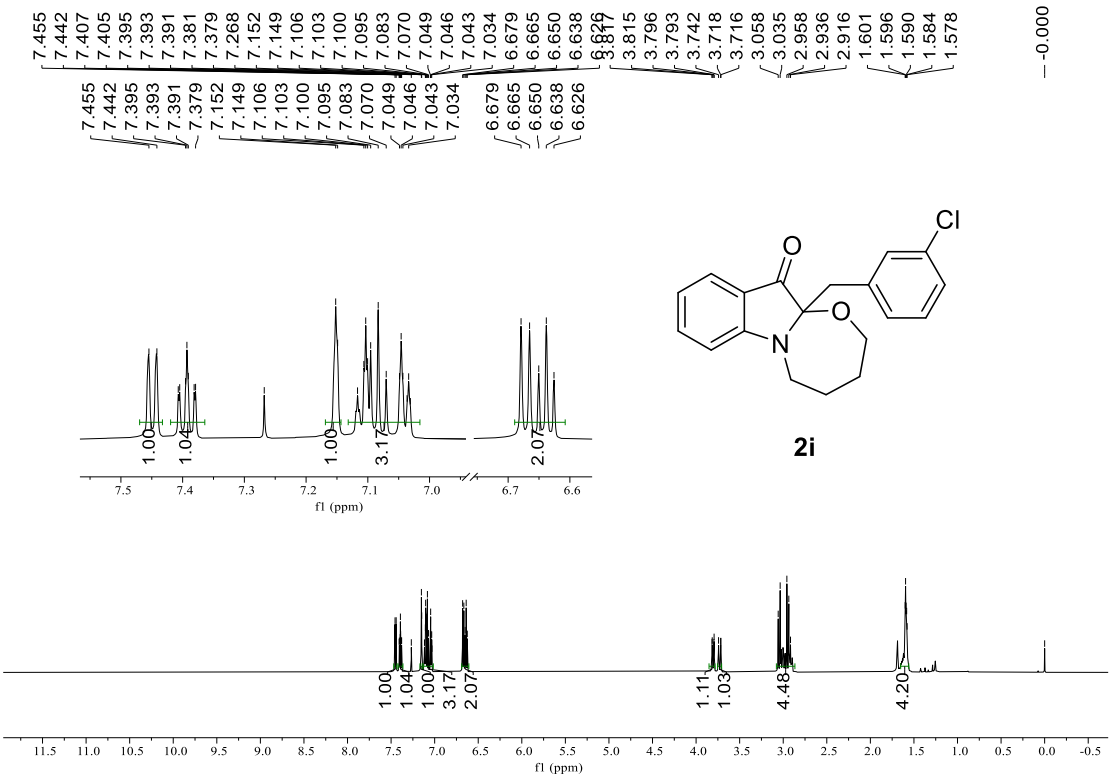
2h

^{13}C NMR (150 MHz, $CDCl_3$)

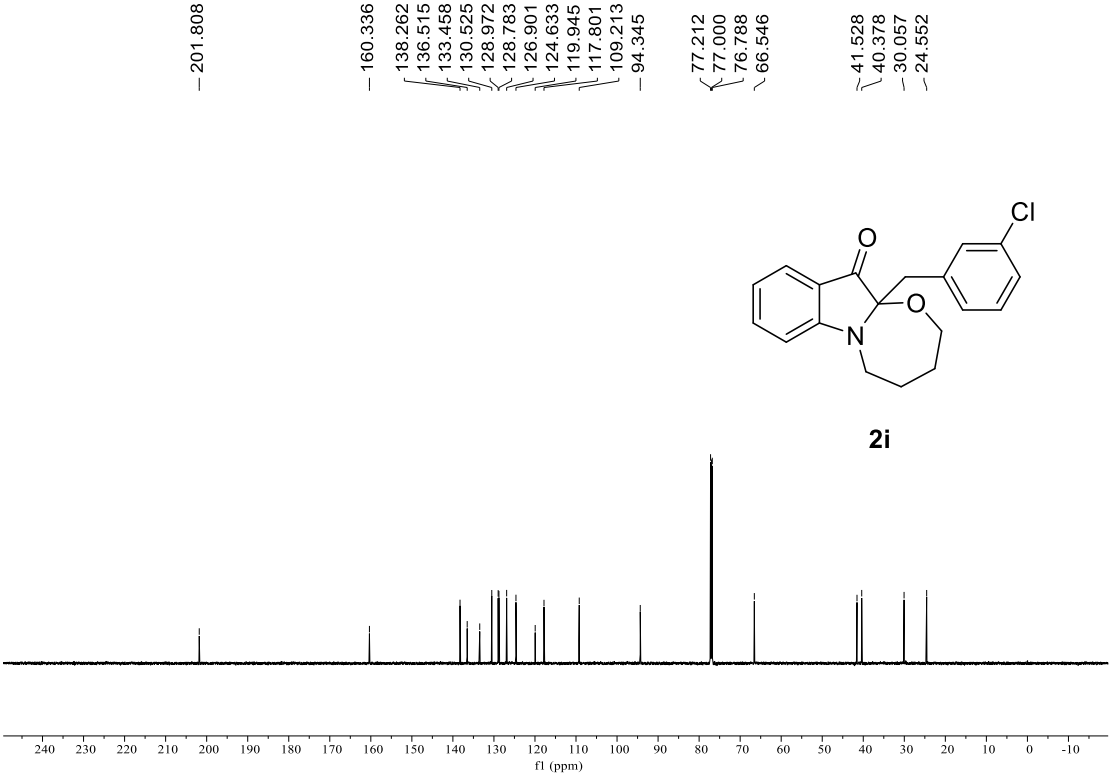


2h

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



^{13}C NMR (150 MHz, $CDCl_3$)



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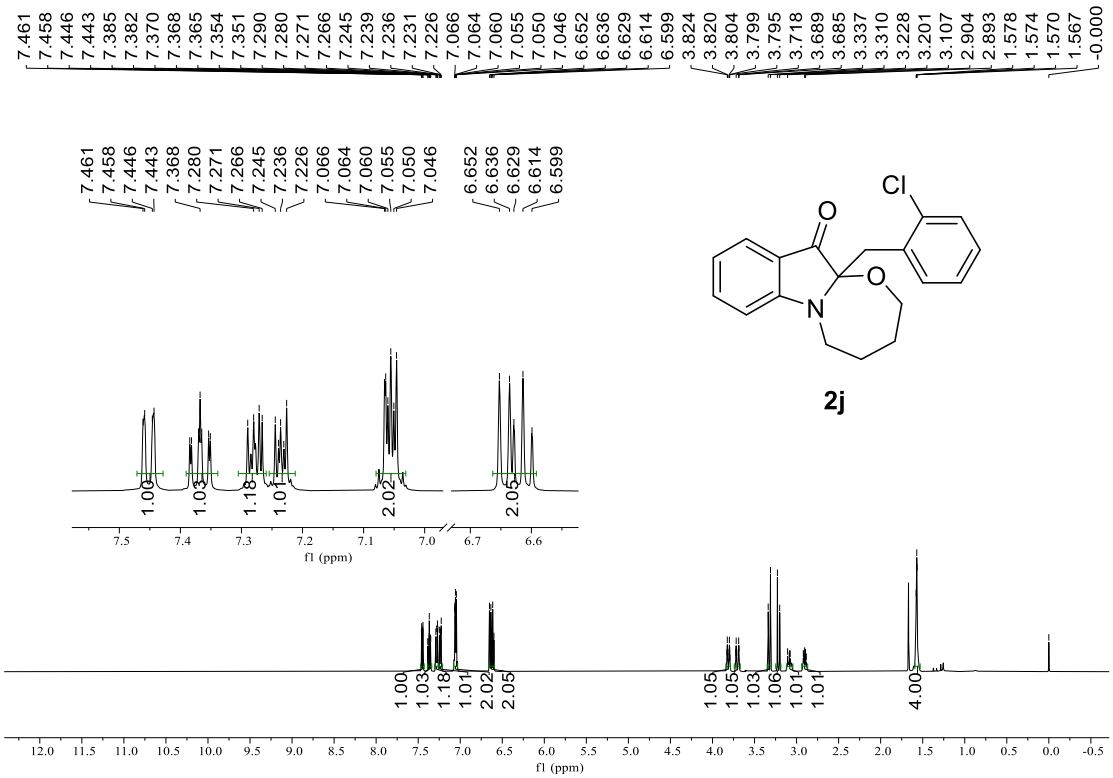
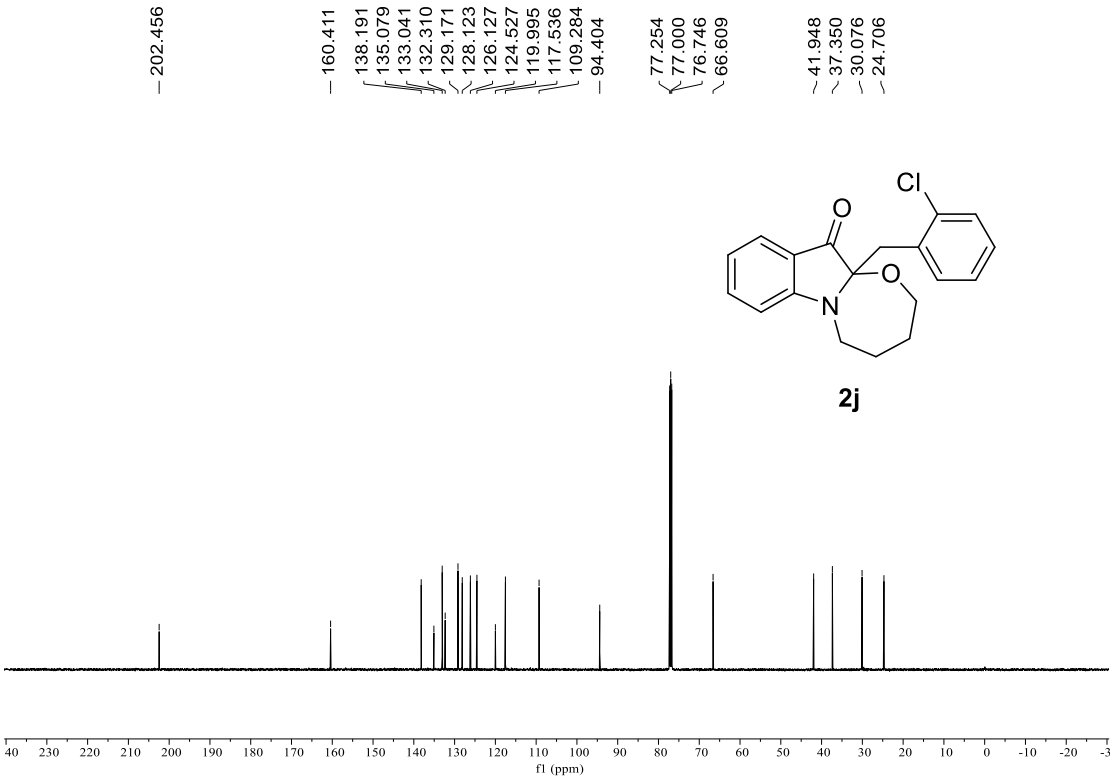
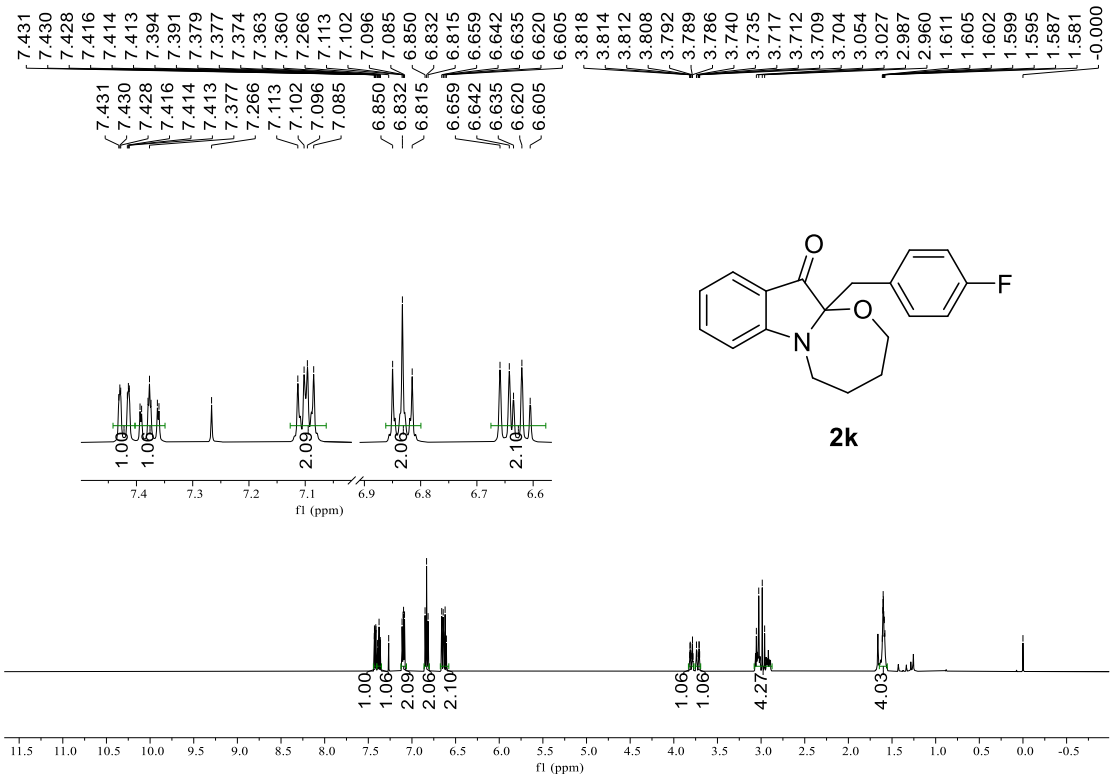


^{13}C NMR (125 MHz, $CDCl_3$)

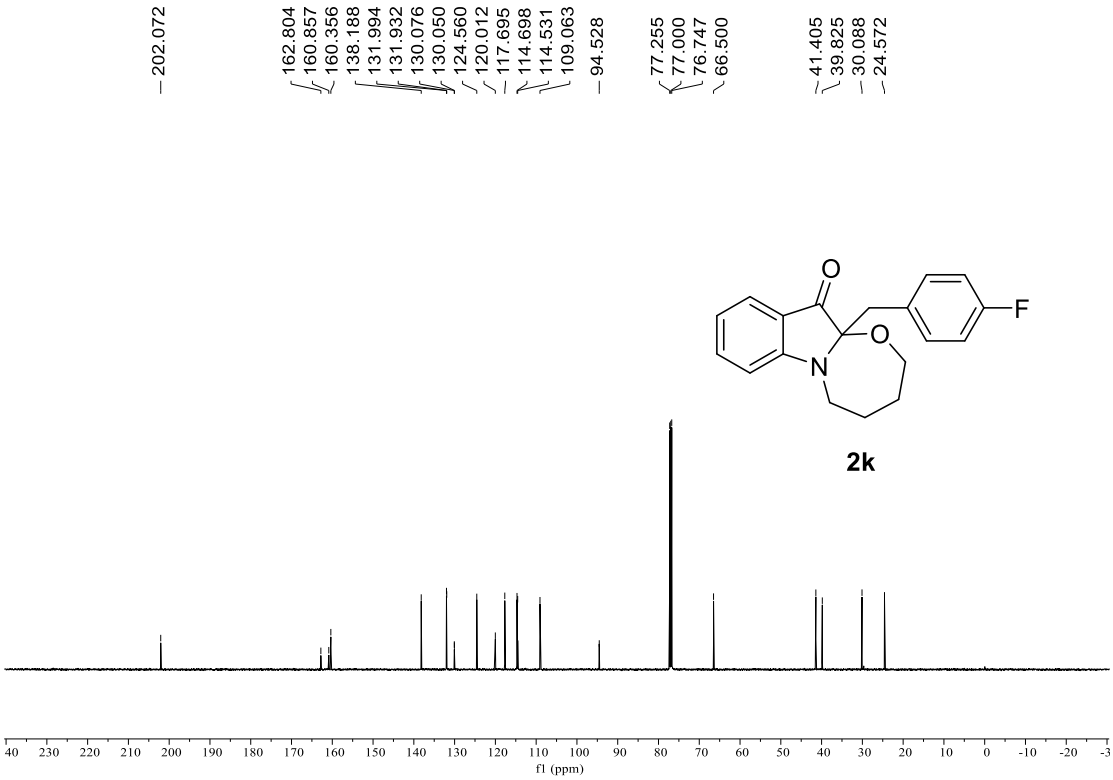


^{1}H NMR (500 MHz, $CDCl_3$)



2k

^{13}C NMR (125 MHz, $CDCl_3$)



2k

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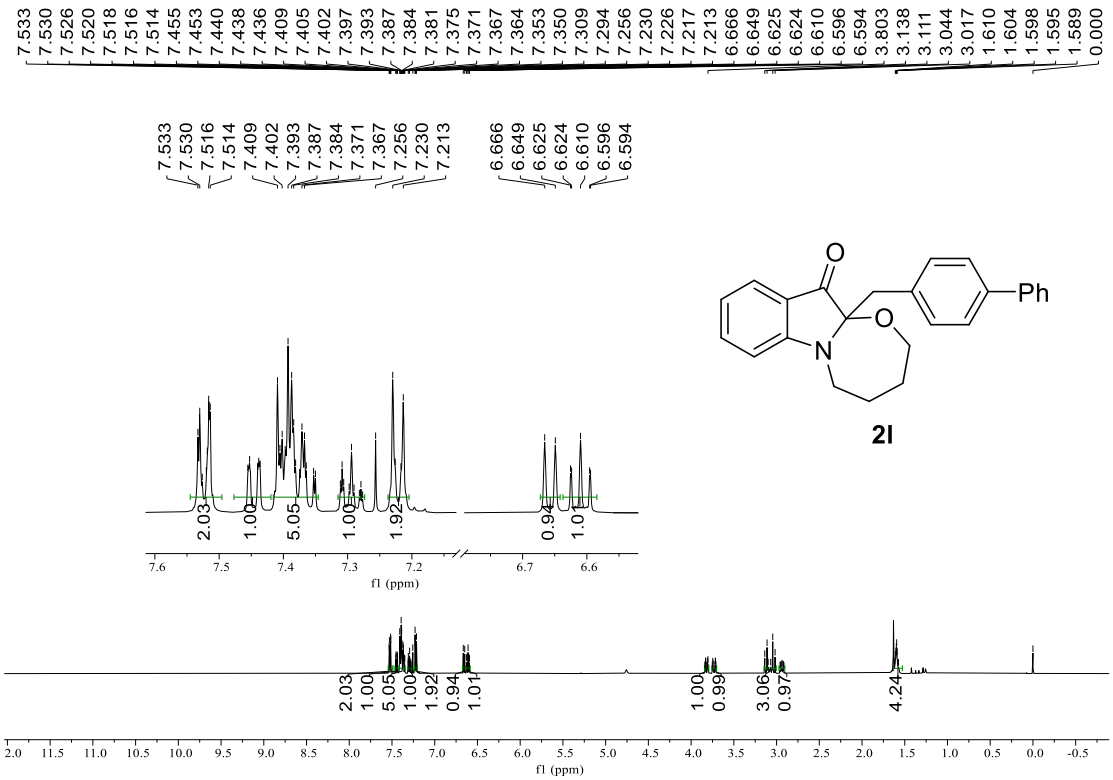

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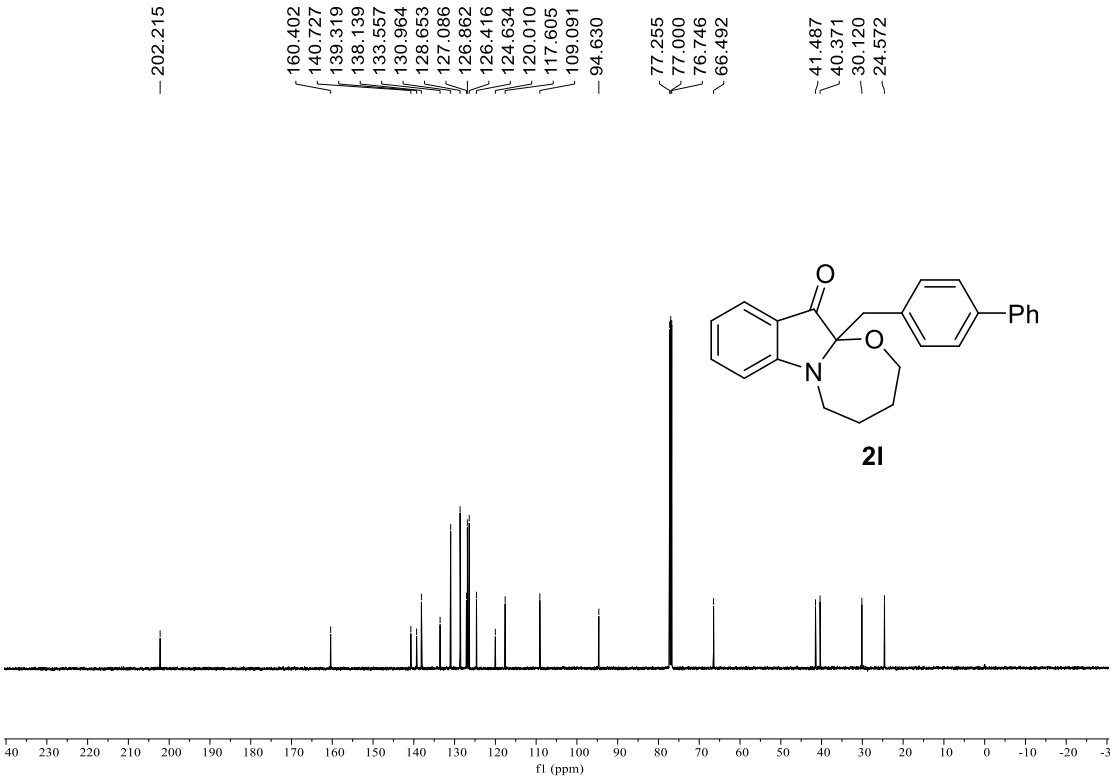

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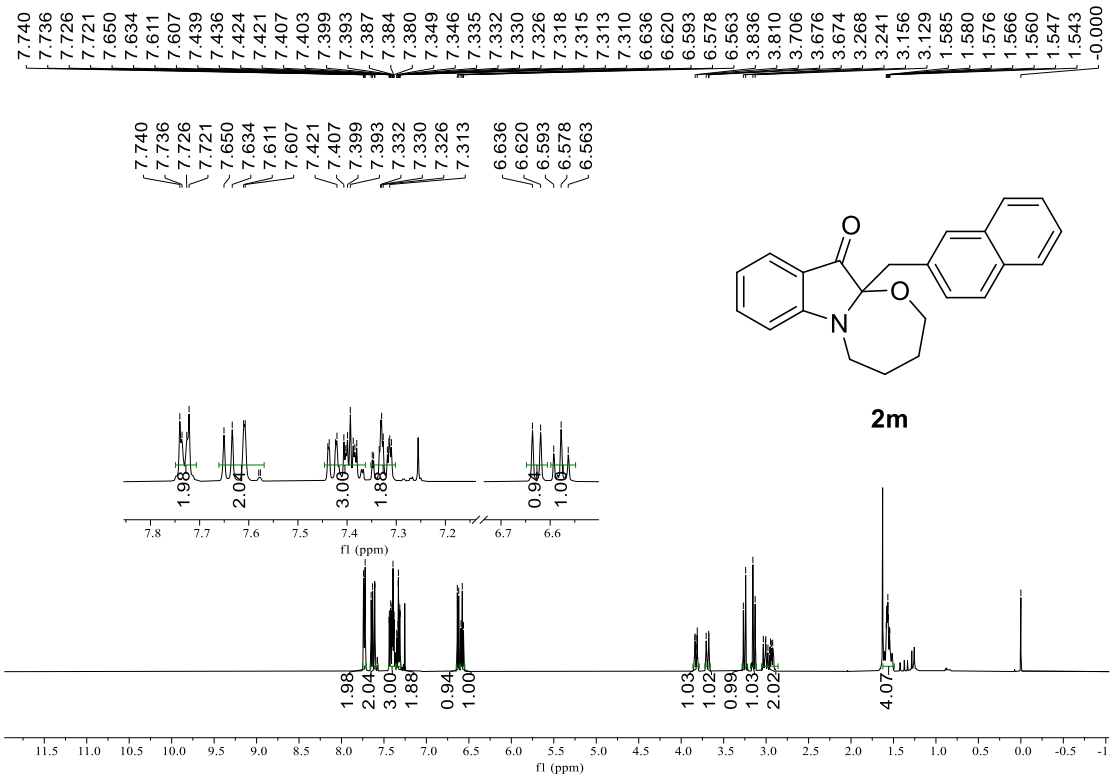

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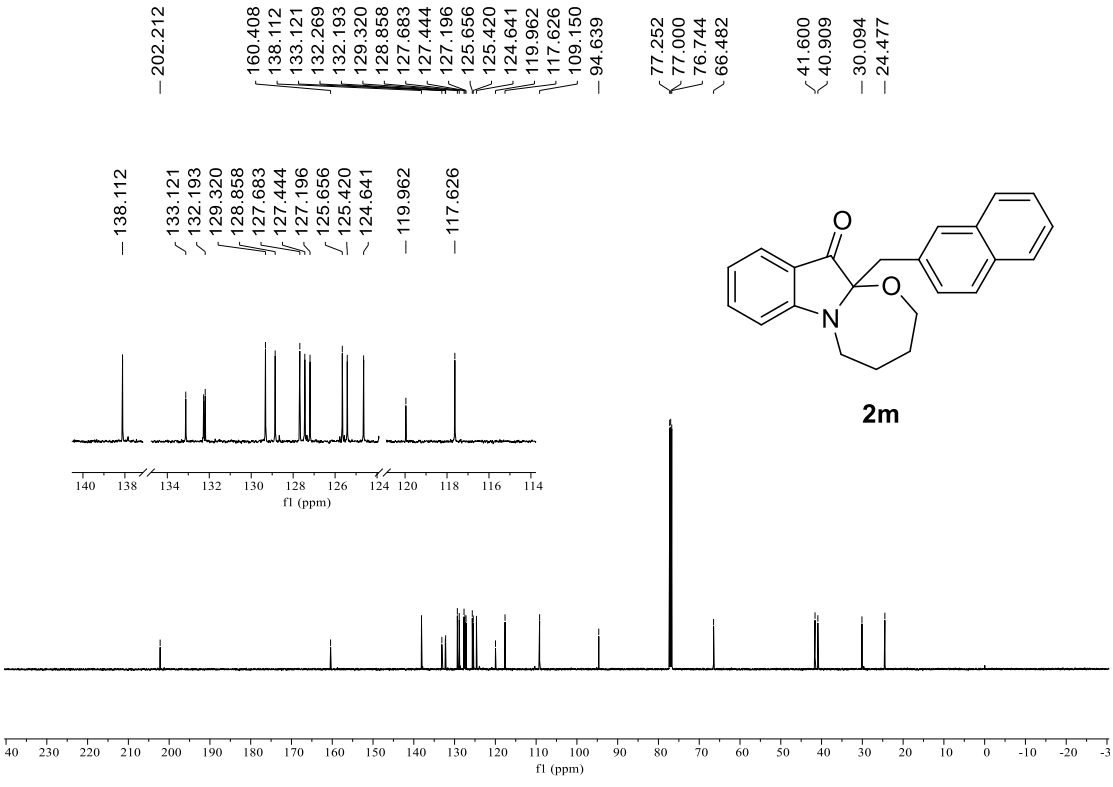
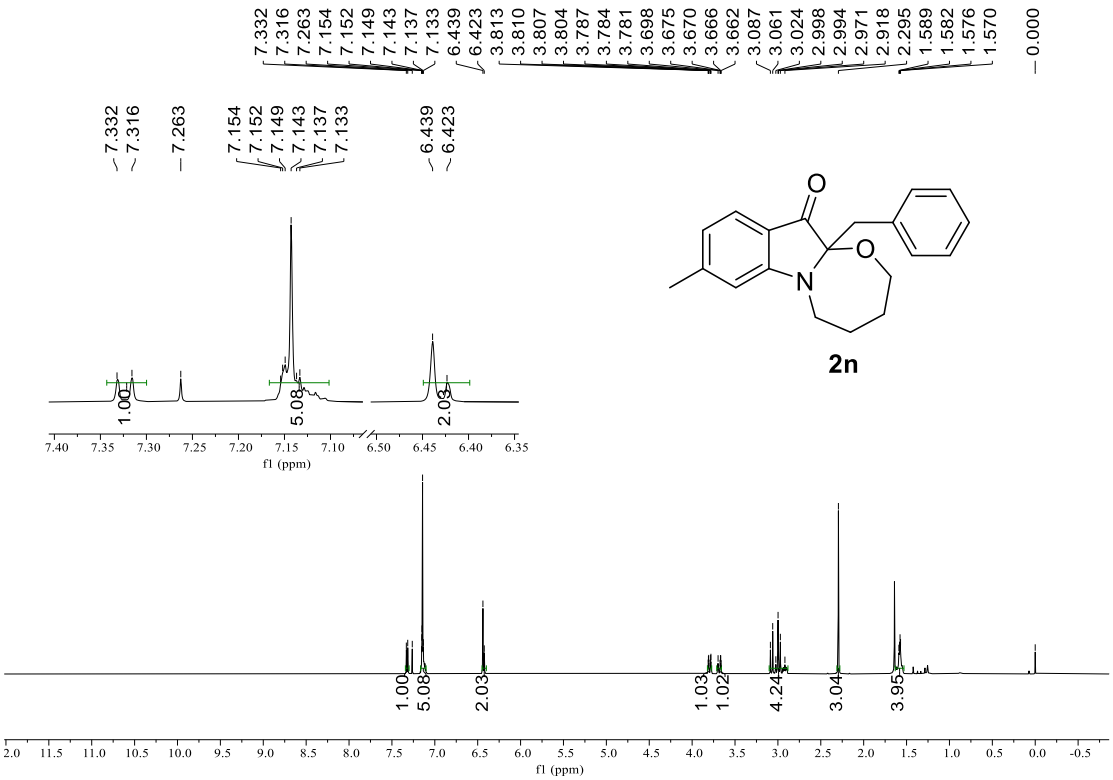
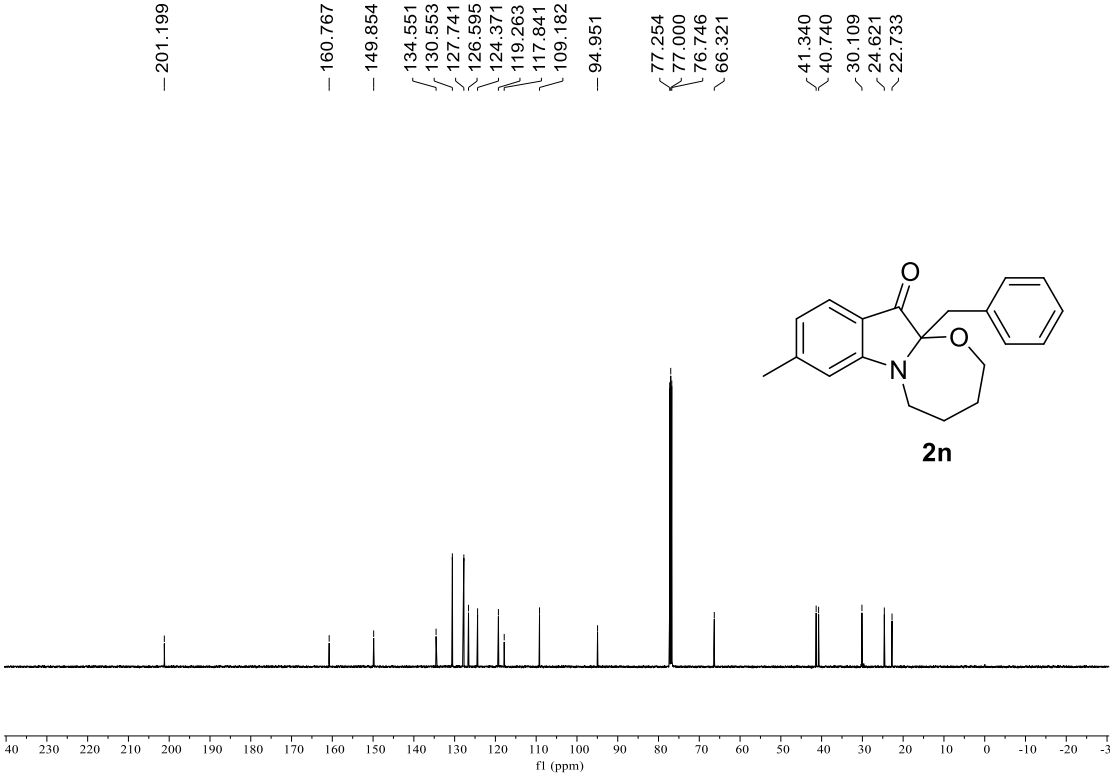


^{1}H NMR (500 MHz, $CDCl_3$)



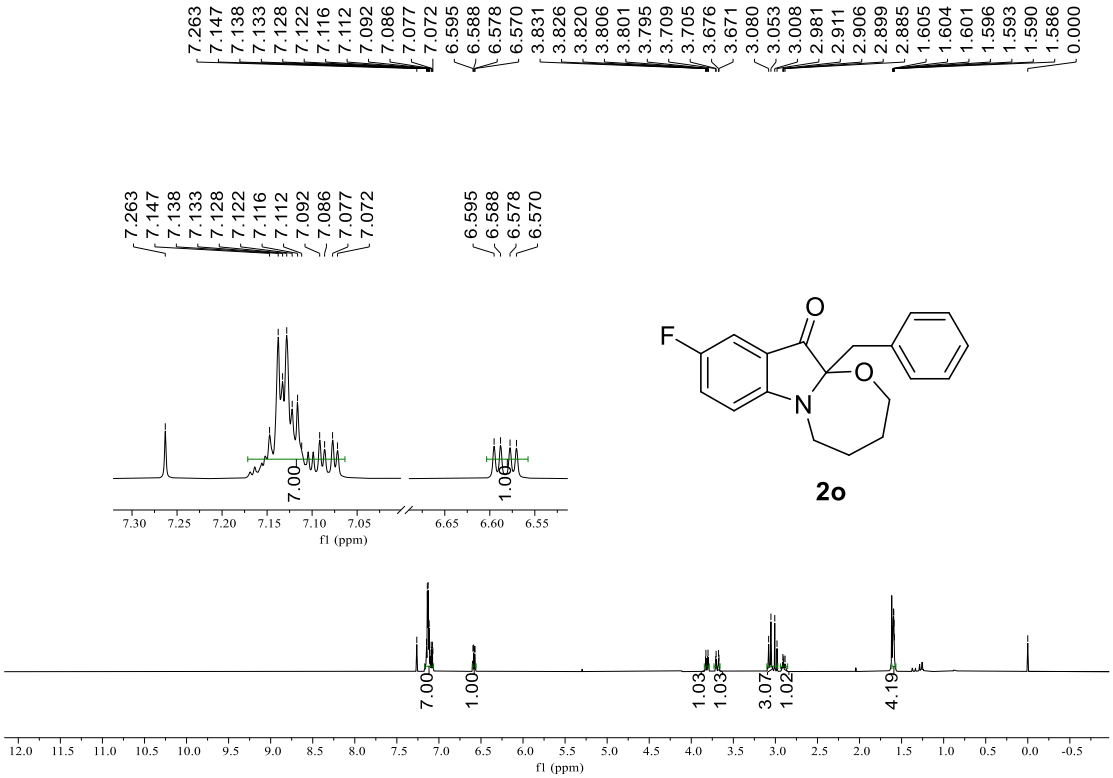
2n

^{13}C NMR (125 MHz, $CDCl_3$)

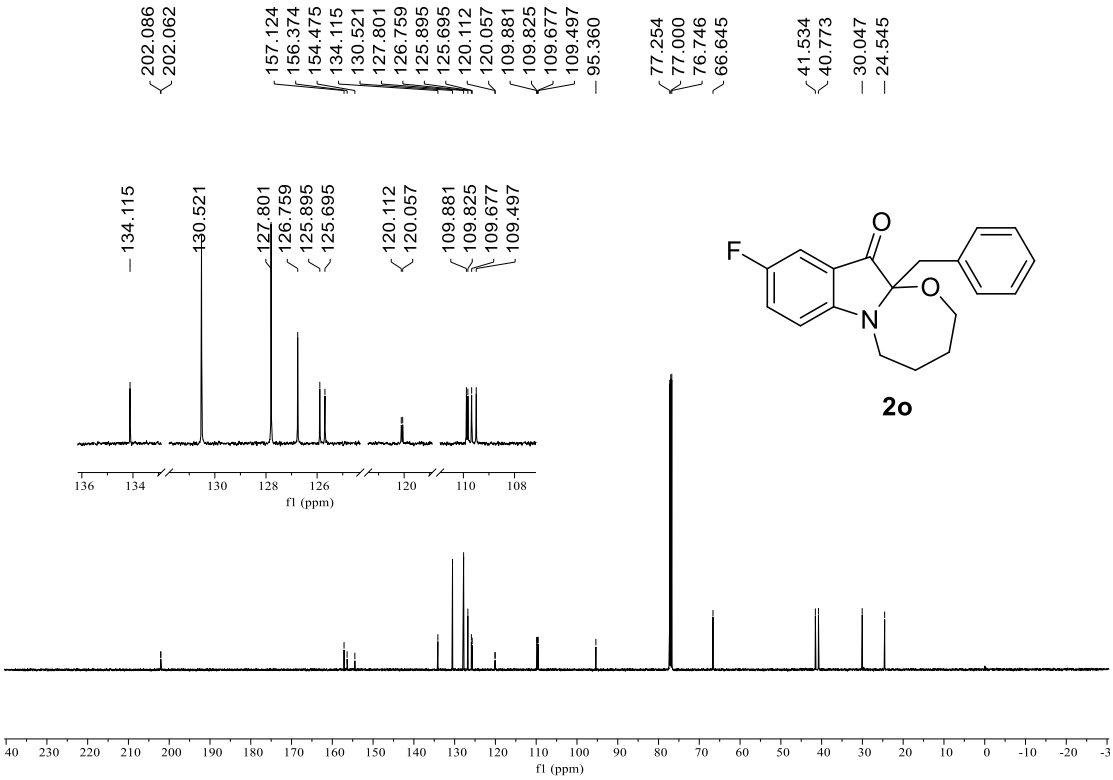


2n

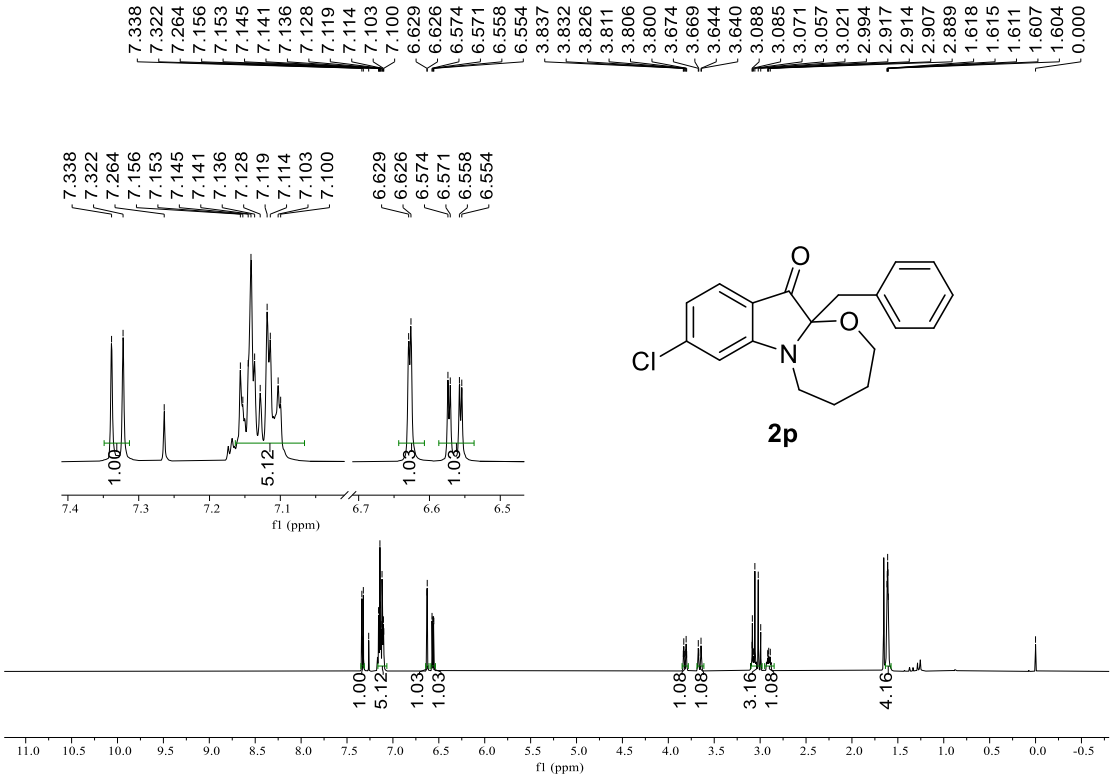
^{1}H NMR (500 MHz, $CDCl_3$)



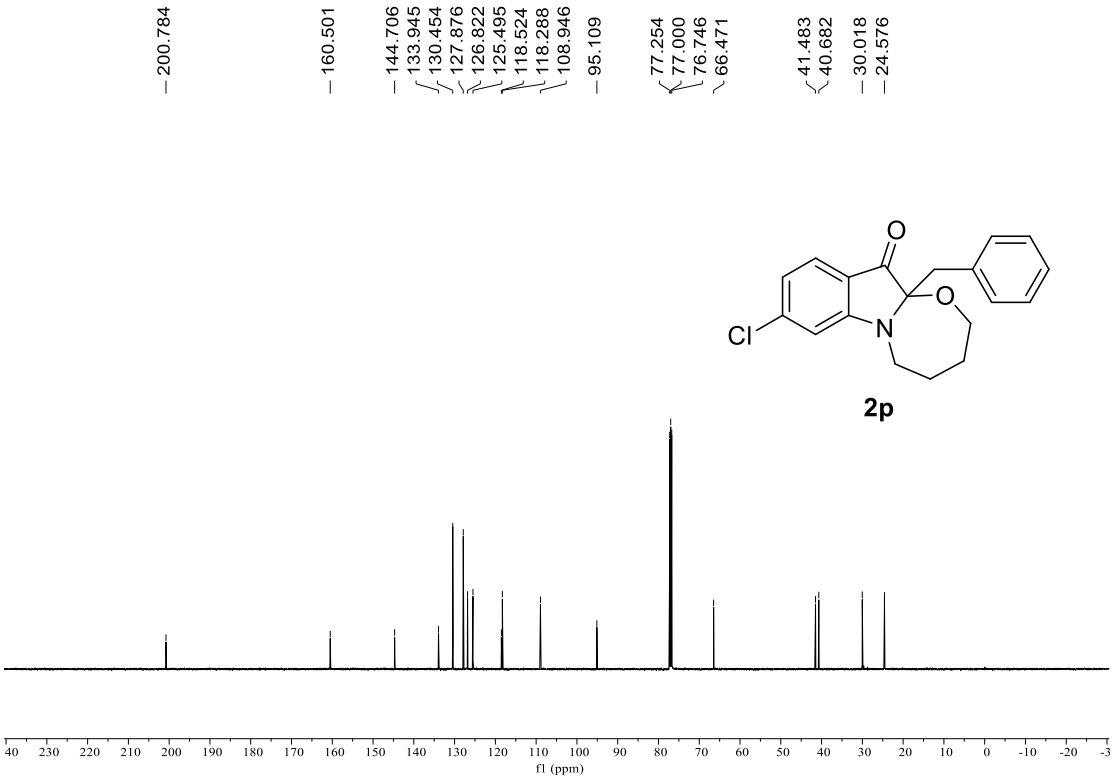
^{13}C NMR (125 MHz, $CDCl_3$)



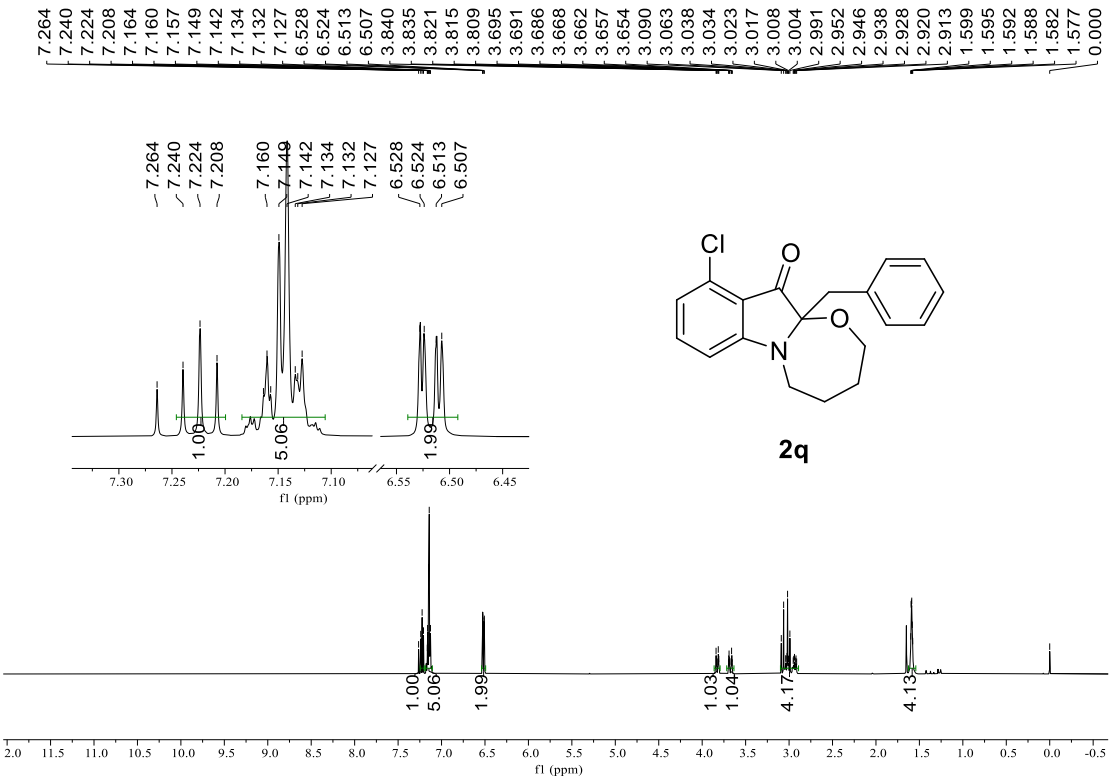
^{1}H NMR (500 MHz, $CDCl_3$)



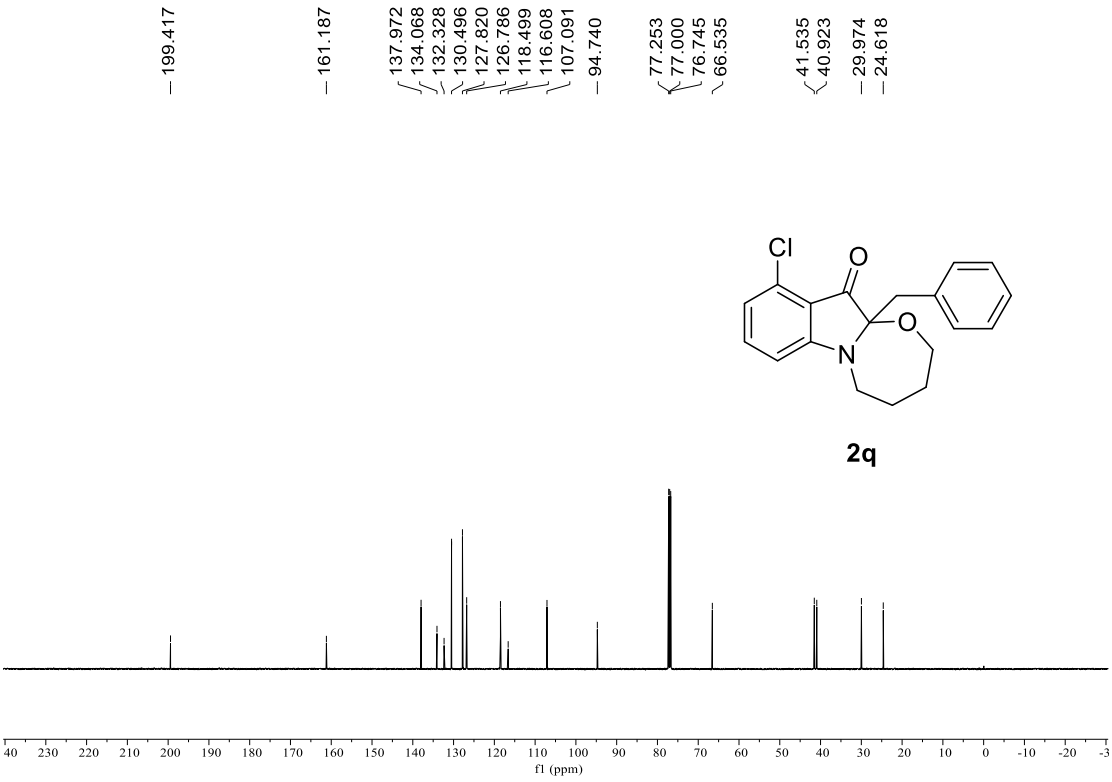
^{13}C NMR (125 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)



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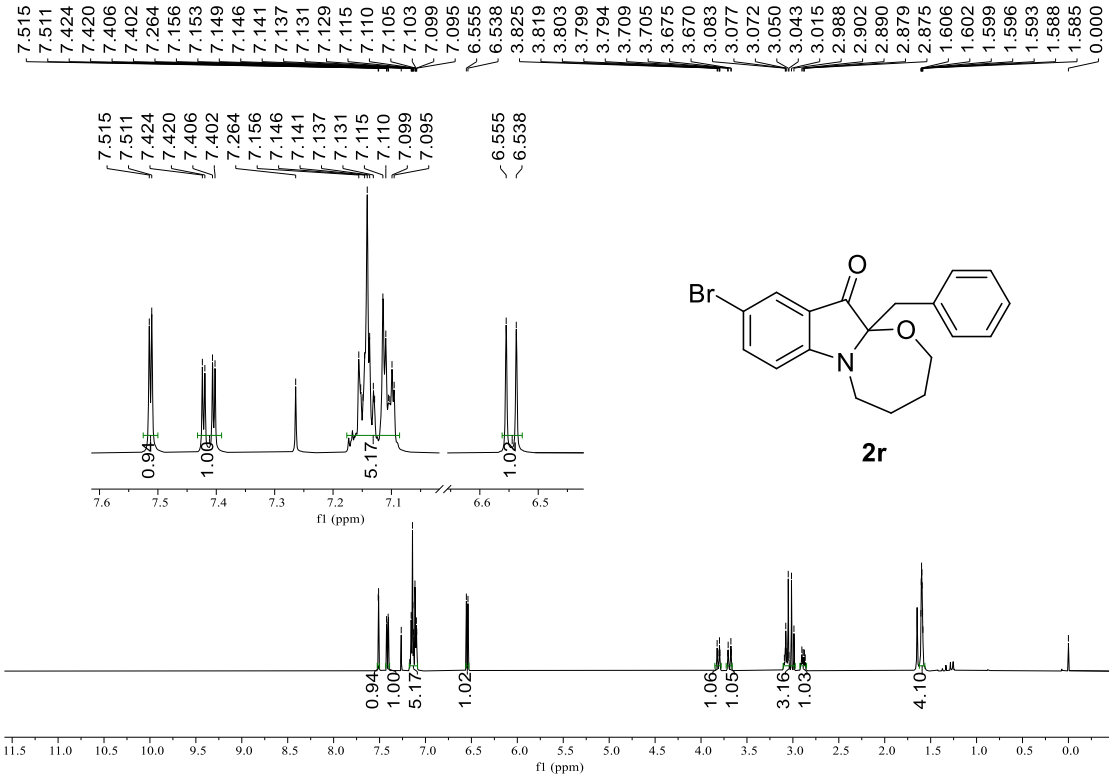

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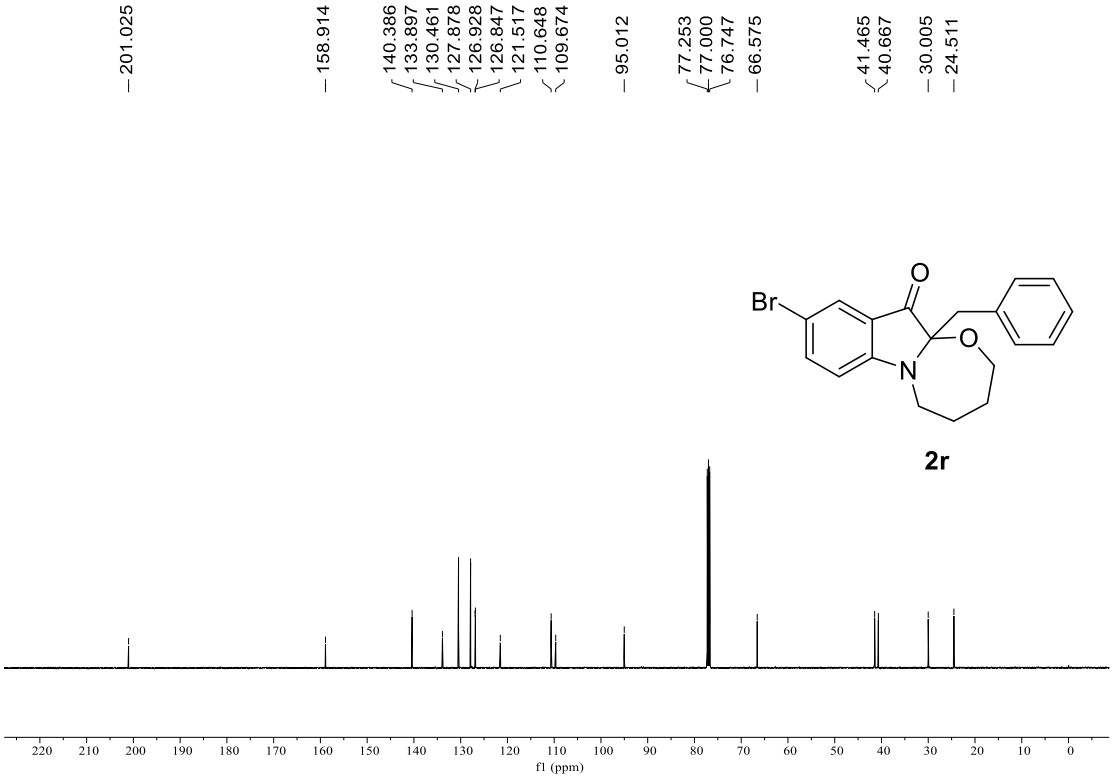

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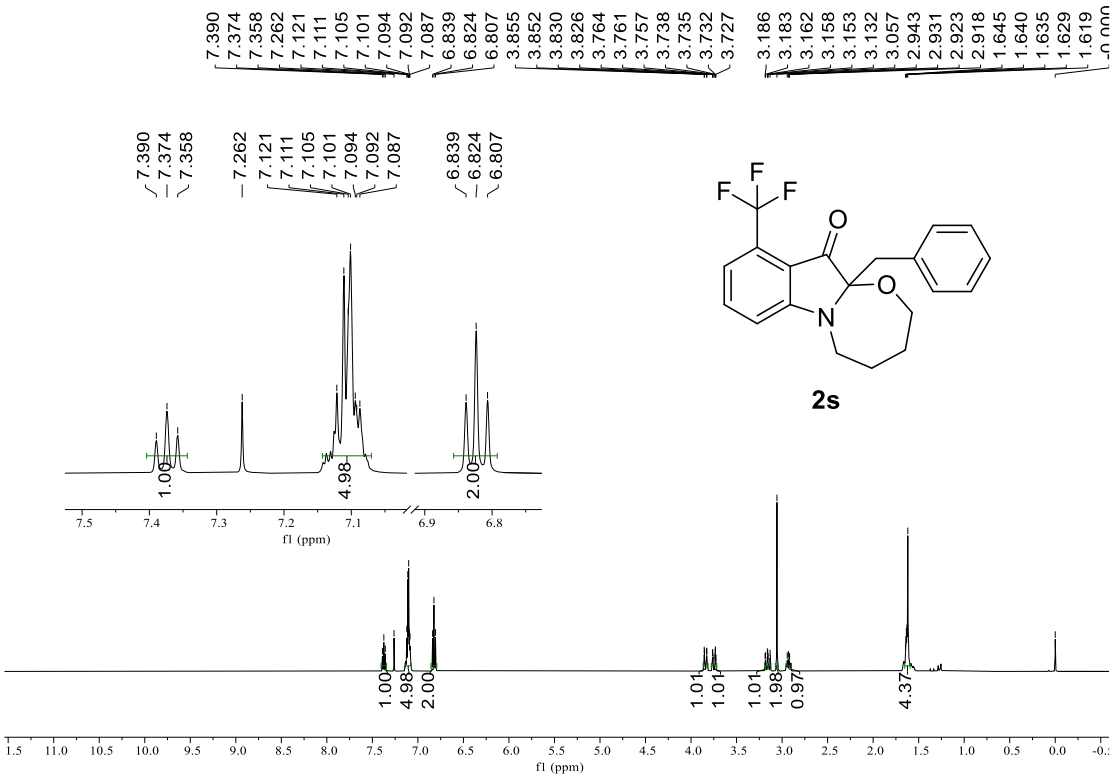
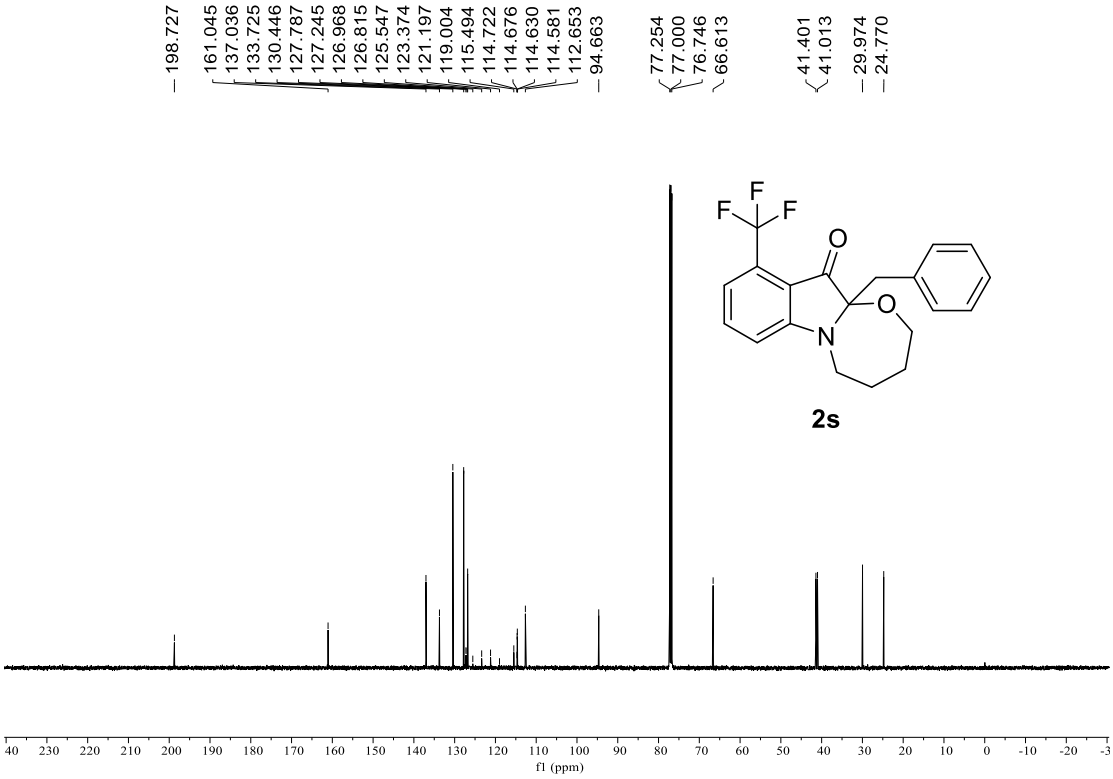
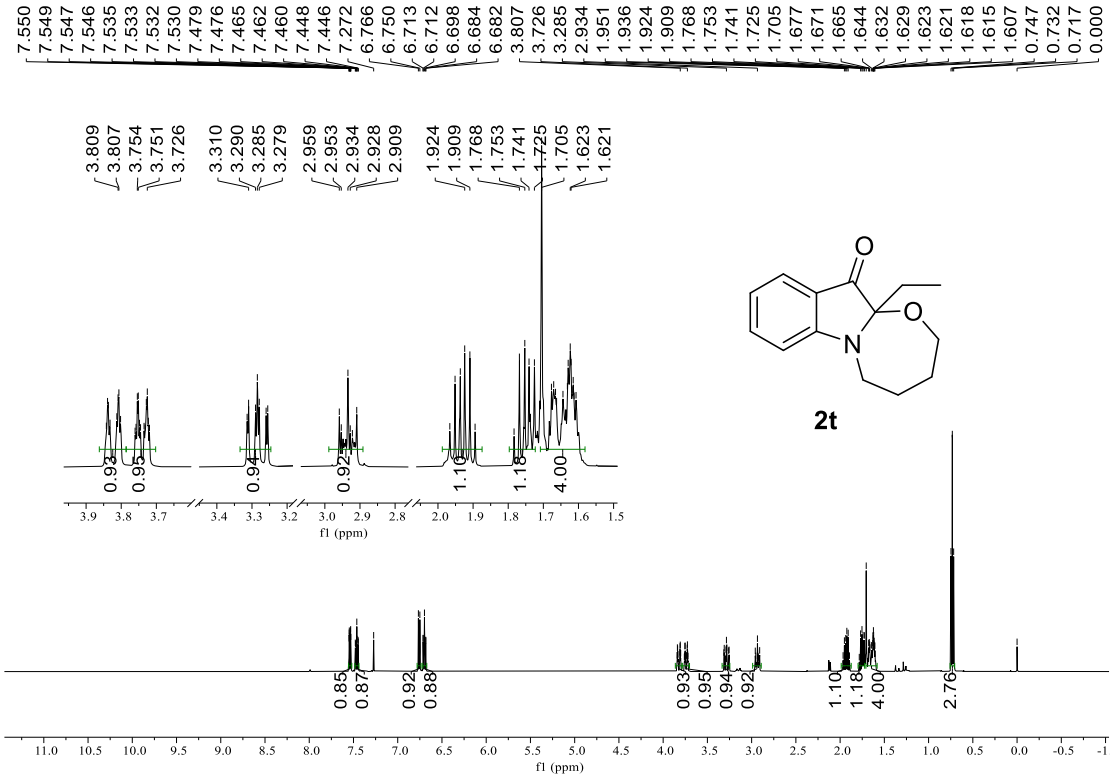


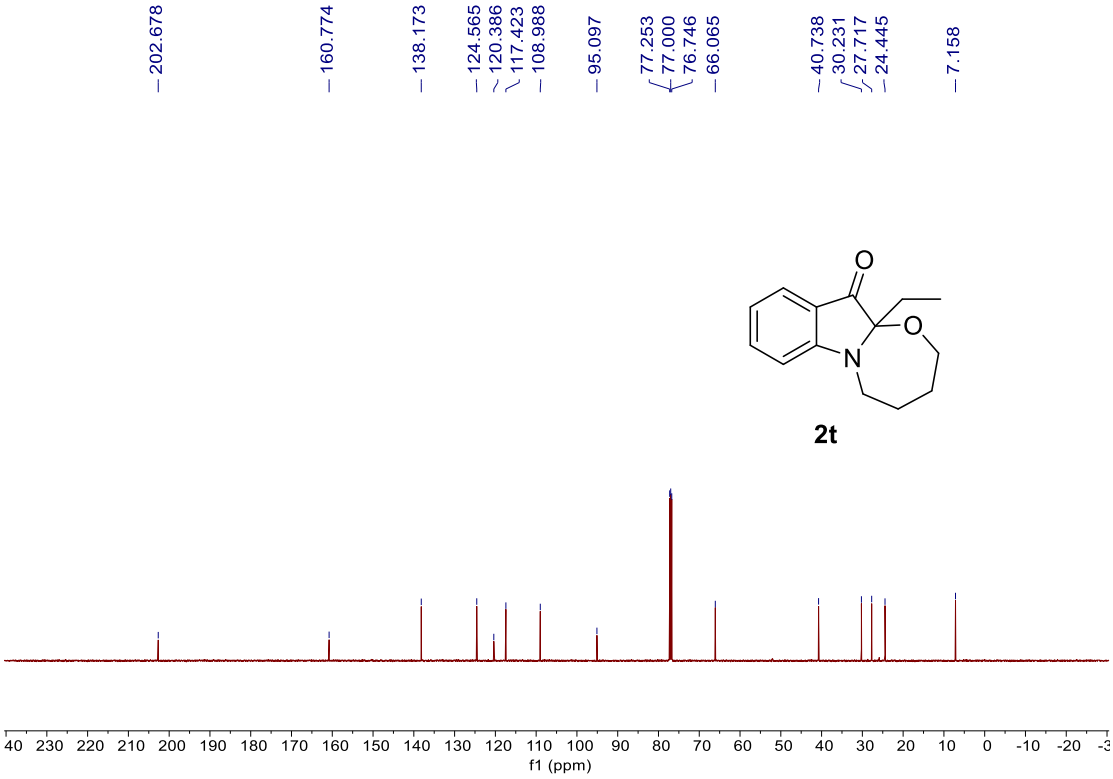
^{13}C NMR (125 MHz, $CDCl_3$)



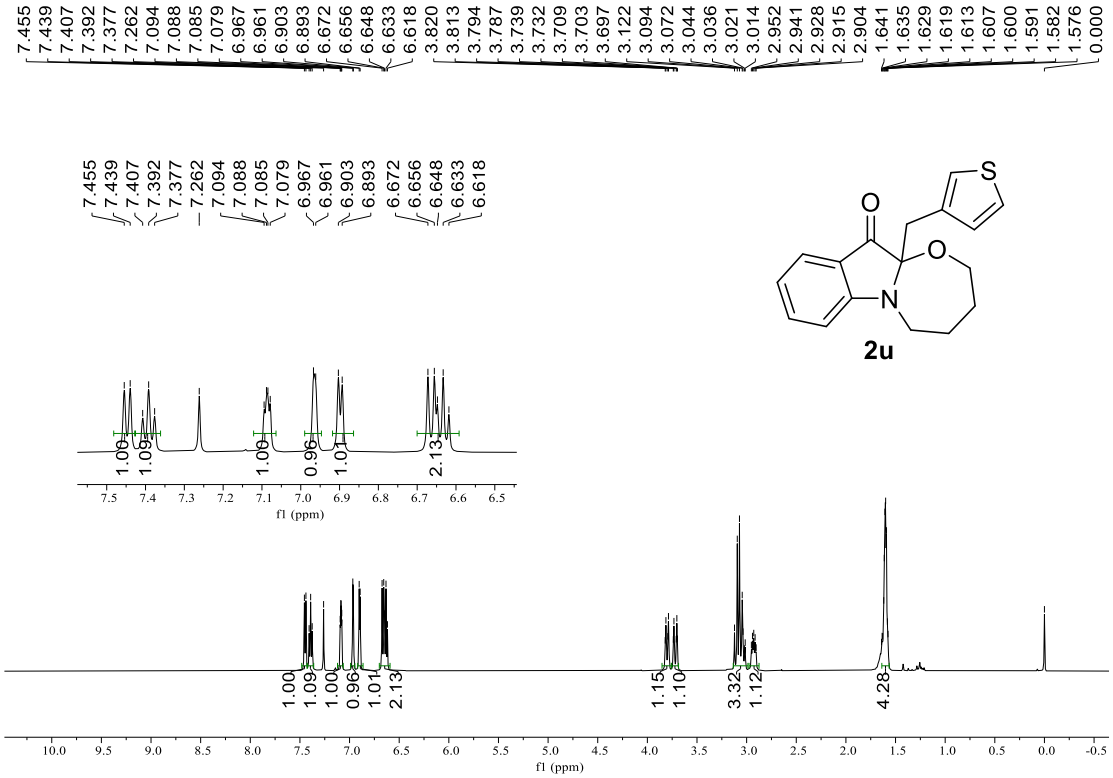
^{1}H NMR (500 MHz, $CDCl_3$)



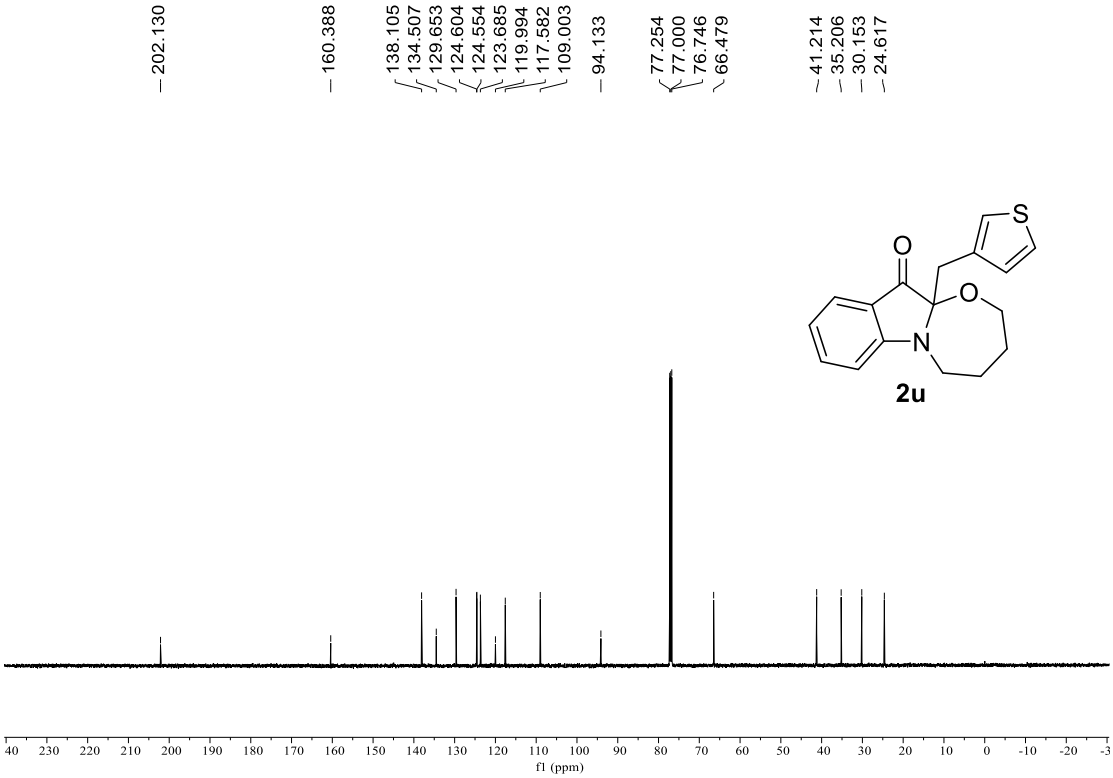
^{13}C NMR (125 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)



9. X-ray crystallography of compound 2a.

11a-benzyl-2,3,4,5-tetrahydro-[1,3]oxazepino[3,2-a]indol-11(11aH)-one **(2a, 2305869)**

(Ortep ellipsoids are depicted at the 50% level)

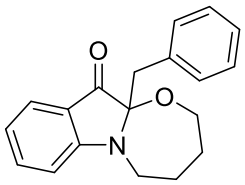
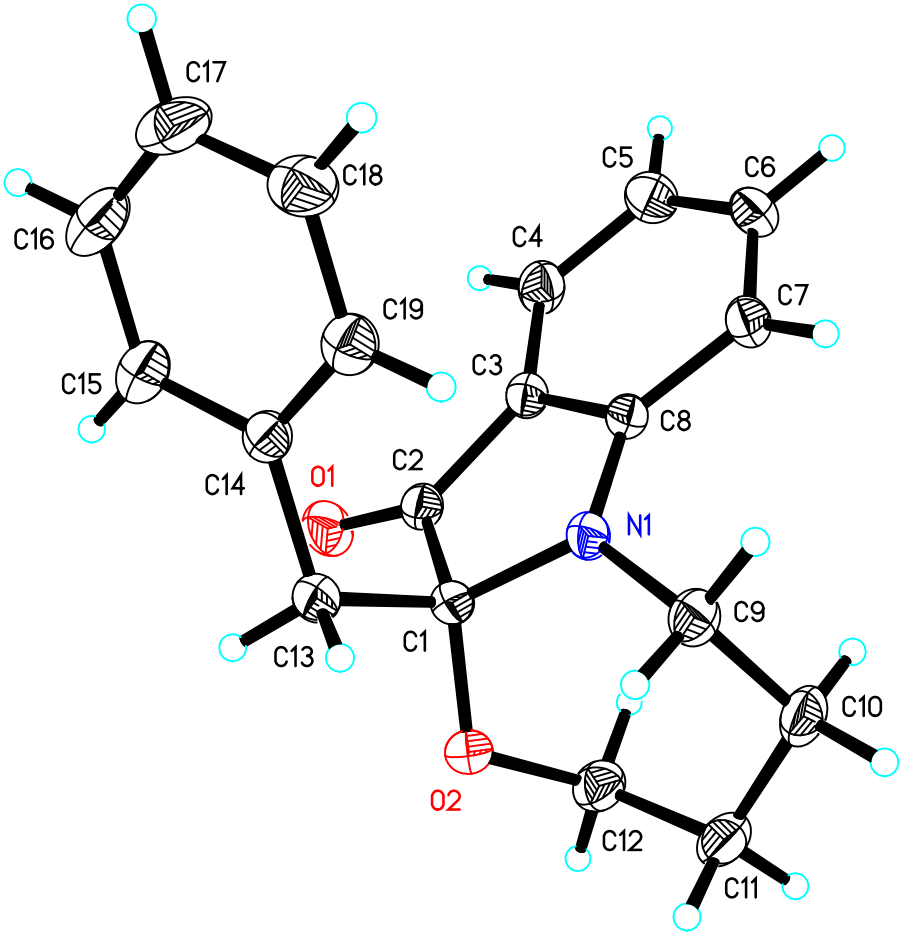
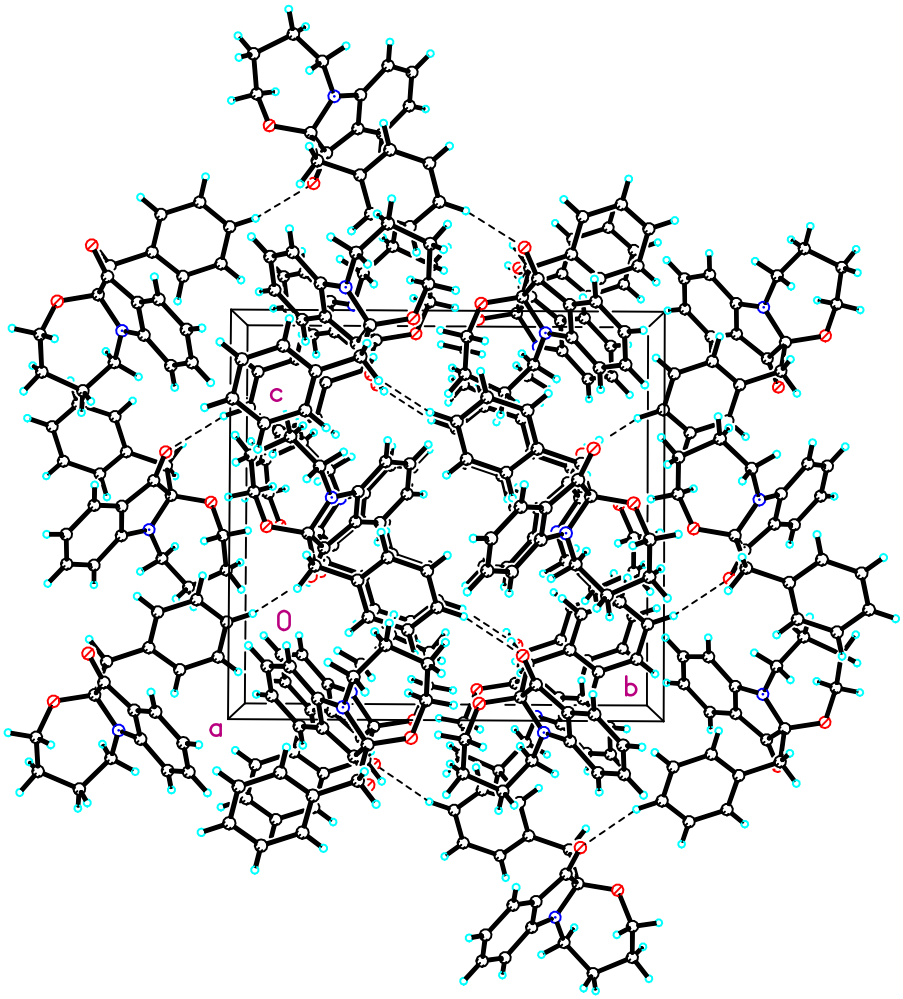


Table S1. Crystal data and structure refinement for 2a.

Identification code	**2a**
Empirical formula	$C_{19}H_{19}NO_2$
Formula weight	293.35
Temperature	213(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 21/n
Unit cell dimensions	a = 7.9979 (3) Å, α= 90°. b = 14.3194 (5) Å, β= 91.7040 (10)°. c = 13.4938 (4) Å, γ = 90°.
Volume	1544.70(9) $Å^3$
Z	4
Density (calculated)	1.261 Mg/m^3
Absorption coefficient	0.082 mm^{-1}
F(000)	624
Crystal size	0.160 x 0.130 x 0.100 mm^3
Theta range for data collection	2.918 to 25.998°.
Index ranges	-9<=h<=7, -17<=k<=17, -16<=l<=16
Reflections collected	14655
Independent reflections	3028 [R(int) = 0.0436]
Completeness to theta = 26.000°	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6535
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3028 / 0 / 200
Goodness-of-fit on F^2	1.061
Final R indices [I>2sigma(I)]	R1 = 0.0423, wR2 = 0.0867
R indices (all data)	R1 = 0.0594, wR2 = 0.0957
Extinction coefficient	0.029(4)
Largest diff. peak and hole	0.151 and -0.139 $e.Å^{-3}$


C17
C18
C16
C19
C15
C14
O1
C2
C3
C5
C6
C4
C7
C8
N1
C9
C1
C13
C10
O2
C12
C11


c
0
a
b