Supporting Information

Synthesis of [4.6] Spirocarbocycles: A Base-promoted Ring-Expansion and Subsequent I_2-mediated Regioselective Spirocyclization Protocol

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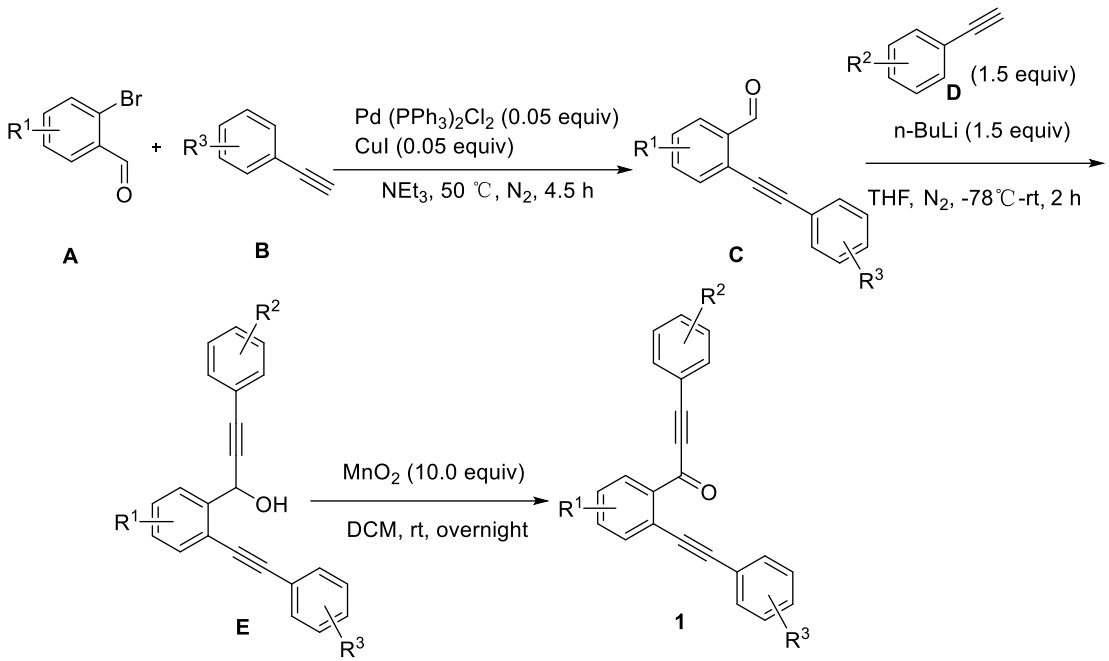
1. General methods

Unless noted, all commercial reagents were used without further purification. DMSO is dried in calcium hydride and 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 $CDCl_3$ (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) as internal reference. High-resolution mass spectra were recorded 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 in Bruker SMARTAPEX diffractiometers with molybdenum cathodes.

The crystal preparation and measurement methods of **3a** as follows: Place 60.0 mg of **3a** in a 50 ml round bottom flask, dissolve **3a** with 3 mL of dichloromethane, then add 30 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 1



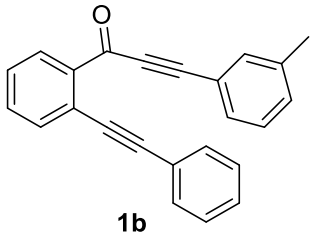
2-Bromobenzaldehyde derivatives **A** (3.0 mmol), $Pd(PPh_3)_2Cl_2$ (0.15 mmol, 0.05 equiv, 105.3 mg) and CuI (0.15 mmol, 0.05 equiv, 28.6 mg) were dissolved in dry Et_3N (9 mL) in a schlenk flask under a nitrogen atmosphere at 50 °C using an oil bath. The corresponding terminal alkyne **B** (3.75 mmol,1.25 equiv) was added and the reaction mixture was stirred for 4.5 h. After the completion of the reaction as monitored by TLC, the reaction mixture was quenched with a saturated solution of NH_4Cl and extracted with ethyl acetate (5 mL × 3). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Finally, the crude product was purified by column chromatography (silica gel, petroleum ether/EtOAc) to get pure 2-(arylethynyl)benzaldehyde derivatives **C**.

To a solution of alkyne **D** (1.5 equiv) in dry THF at -78 °C under a nitrogen, n-BuLi (2.5 M in hexanes, 1.5 equiv) was added slowly and stirred for 1 h at -78 °C and then a solution of 2-(arylethynyl)benzaldehyde **C** (2.0 mmol) in THF was added slowly. The resulting mixture was stirred for 1 h at room temperature. After completion of the reaction as indicated by TLC, the reaction mixture was quenched by aqueous sat. NH_4Cl solution and the organic layer was extracted with EtOAc (5 mL × 3) and dried over anhydrous Na_2SO_4. The organic layer was concentrated under reduced pressure. The obtained crude product was used directly in the next step.

MnO_2 (10.0 equiv) was added to a solution of the alcohol derivatives **E** in DCM and stirred at room temperature overnight. After completion of the reaction as monitored by TLC, the reaction mixture was filtered through Celite and concentrated under

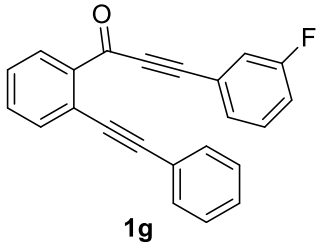
reduced pressure. The residue was purified by column chromatography to yield the corresponding 1,6-diyn-3-ones **1**.

The aryl-fused 1,6-diyn-3-ones **1a**,**1c, 1d**, **1e**, **1g**, **1h, 1i, 1l**, **1n, 1o**, **1p** and **1q** are reported in the literature, and the analytical data of the synthesized compounds are in good accordance with the literature data[1,2,3,4].



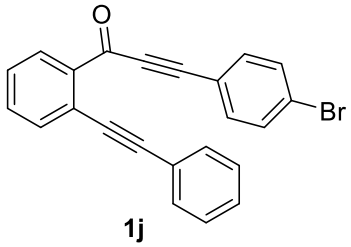
1b

1-(2-(phenylethynyl)phenyl)-3-(m-tolyl)prop-2-yn-1-one (**1b)**. Yellow oil, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 30:1); yield: 78%, 500.2 mg. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.19-8.18 (m, 1H), 7.68-7.67 (m, 1H), 7.57-7.54 (m, 3H), 7.49-7.46 (m, 1H), 7.43-7.41 (m, 2H), 7.324-7.318 (m, 3H), 7.25-7.24 (m, 2H), 2.29 (s, 3H). ^{13}C NMR (125 MHz, CD_2Cl_2) δ 177.2, 138.6, 138.3, 134.3, 133.5, 132.5, 131.8, 131.7, 131.6, 130.1, 128.7, 128.5, 128.4, 128.1, 123.1, 122.7, 119.8, 95.1, 93.4, 88.3, 87.7, 20.8. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{24}H_{16}NaO$ 343.1093, found 343.1094.



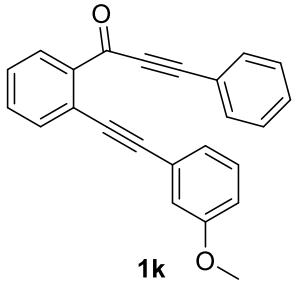
1g

3-(3-fluorophenyl)-1-(2-(phenylethynyl)phenyl)prop-2-yn-1-one (**1g)**. Yellow oil, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 30:1); yield: 75%, 489.1 mg. ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.29-8.27 (m, 1H), 7.77-7.72 (m, 2H), 7.66-7.65 (m, 1H), 7.64-7.61 (m, 1H), 7.58-7.57 (m, 1H), 7.55-7.53 (m, 2H), 7.53-7.50 (m, 1H), 7.45-7.39 (m, 4H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 175.8, 161.2 (d, J=244.1 Hz), 136.8, 133.8, 133.1, 131.5, 131.0, 130.7 (d, J=8.9 Hz), 128.9 (d, J=3.0 Hz), 128.7, 128.6, 128.2, 121.7, 121.1, 120.4 (d, J=7.9 Hz), 119.0 (d, J=23.6 Hz), 118.2 (d, J=21.2 Hz), 94.3, 90.6, 87.6, 87.2. ^{19}F NMR (471 MHz, $CDCl_3$) δ-111.82. HRMS (SI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{13}FNaO$ 347.0843, found 347.0847.



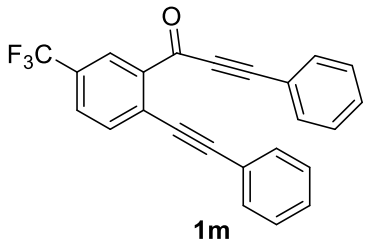
1j

3-(4-bromophenyl)-1-(2-(phenylethynyl)phenyl)prop-2-yn-1-one (**1j**). Yellow oil, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 30:1); yield: 82%, 629.9 mg. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.17-8.15 (m, 1H), 7.68-7.67 (m, 1H), 7.58-7.54 (m, 3H), 7.51-7.45 (m, 5H), 7.33-7.32 (m, 3H). ^{13}C NMR (125 MHz, CD_2Cl_2) δ 176.5, 137.6, 133.91, 133.90, 132.2, 131.5, 131.3, 131.1, 128.3, 128.0, 127.7, 125.0, 122.6, 122.4, 118.7, 94.8, 91.1, 88.2, 87.7. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{13}BrNaO$ 407.0042, found 407.0043.



1k

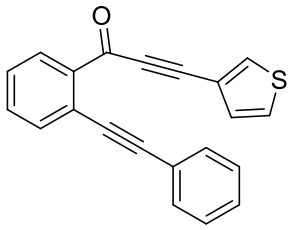
1-(2-((3-methoxyphenyl)ethynyl)phenyl)-3-phenylprop-2-yn-1-one (**1k**). Light yellow oil, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 30:1); yield: 58%, 393.3 mg. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.20-8.18 (m, 1H), 7.69-7.67 (m, 1H), 7.63-7.62 (m, 2H), 7.58-7.55 (m, 1H), 7.50-7.43 (m, 2H), 7.38-7.35 (m, 2H), 7.24-7.21 (m, 1H), 7.16-7.15 (m, 1H), 7.07 (s, 1H), 6.89-6.88 (m, 1H), 3.73 (s, 3H). ^{13}C NMR (125 MHz, CD_2Cl_2) δ 176.7, 159.0, 137.9, 133.9, 132.6, 132.1, 131.1, 130.4, 129.0, 128.21 127.7, 123.9, 123.6, 122.2, 119.6, 115.8, 115.0, 94.6, 92.5, 87.55, 87.49, 54.8. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{24}H_{16}NaO_2$ 359.1043, found 359.1049.



1m

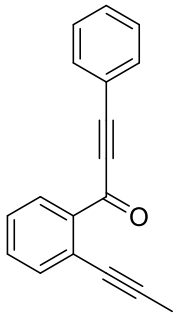
3-phenyl-1-(2-(phenylethynyl)-5-(trifluoromethyl)phenyl)prop-2-yn-1-one (**1m**). Brown oil, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 30:1); yield: 40%, 301.7 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.80-7.76 (m,

2H), 7.62-7.56 (m, 4H), 7.47-7.44 (m, 1H), 7.38-7.33 (m, 4H), 7.31-7.30 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.1, 138.6, 134.7, 133.2, 132.1, 131.1, 129.8 (q, J=33.3Hz), 129.2, 128.2 (q, J=3.5Hz), 128.6, 128.4, 128.2 (q, J=3.9Hz),126.6, 123.4 (q, J=270.8Hz), 122.4, 119.8, 98.4, 94.7, 87.7, 87.1. ^{19}F NMR (471 MHz, $CDCl_3$) δ-62.92. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{24}H_{13}F_3NaO$ 397.0811, found 397.0814.



1p

1-(2-(phenylethynyl)phenyl)-3-(thiophen-3-yl)prop-2-yn-1-one (**1p**). Brown oil, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 30:1); yield: 80%, 502.1 mg. ^{1}H NMR (500 MHz, DMSO-d_6) 8.27-8.20 (m, 2H), 7.73-7.68 (m, 3H), 7.62-7.59 (m, 1H), 7.54-7.53 (m, 2H), 7.39-7.37 (m, 4H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 177.0, 138.1, 136.5, 134.7, 133.7, 132.1, 131.9, 130.6, 129.6, 129.4, 129.2, 128.3, 122.8, 122.0, 118.6, 95.2, 89.5, 88.7, 88.2. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{12}NaOS$ 397.0811, found 397.0814.



1r

3-phenyl-1-(2-(prop-1-yn-1-yl)phenyl)prop-2-yn-1-one (**1r**). Brown oil, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 50:1); yield: 50%, 270.4 mg. ^{1}H NMR (600 MHz, $CDCl_3$) 8.10 (d, J=7.8 Hz, 1H), 7.65 (d, J=8.4 Hz, 2H), 7.54-7.53 (m, 1H), 7.49-7.45 (m, 2H), 7.41-7.39 (m, 3H), 2.07 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 177.8, 138.4, 134.5, 133.0, 132.3, 131.1, 130.6, 128.6, 127.3, 123.8, 120.3, 93.1, 92.8, 88.1, 78.2, 4.9. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{12}NaO$ 267.0780, found 267.0788.

3. Reference

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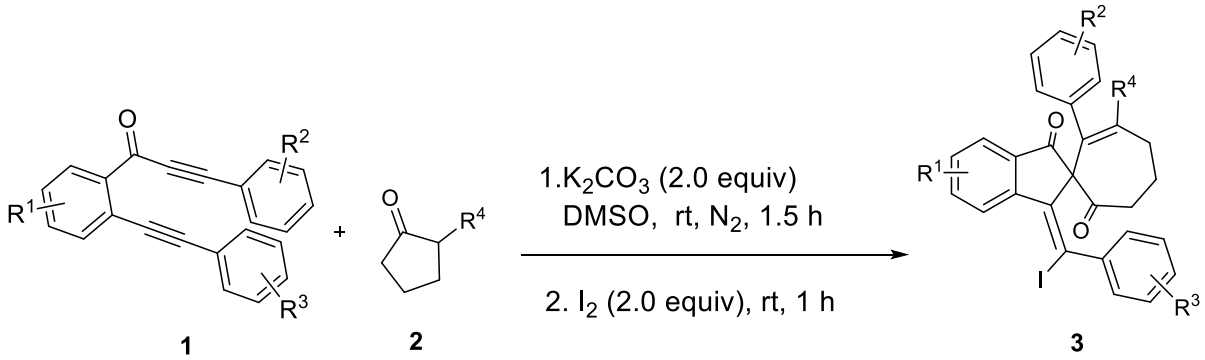
(2) M. Mandal, S. Sakthivel, and R. Balamurugan, Brønsted/Lewis Acid-Promoted Site-Selective Intramolecular Cycloisomerizations of Aryl-Fused 1,6-Diyn-3-ones for Diversity-Oriented Synthesis of Benzo-Fused Fluorenes and Fluorenones and Naphthyl Ketones. *J. Org. Chem.*, 2021, **86**, 333-351.

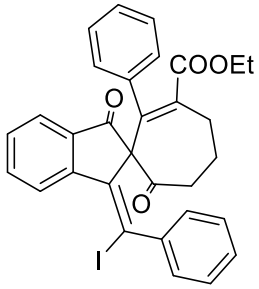
(3) T. Ponpandian, S. Muthusubramanian, S. Rajagopal, Sequential [3 + 2] Cycloaddition/Air Oxidation Reactions: Triazoloyl Ion Assisted Oxidative Cleavage of Alkynes. *Eur. J. Org. Chem.*, 2013, 3974-3977.

(4) F. Ye, M. Haddad, V. Michelet and V. Ratovelomanana-Vidal, Access toward fluorenone derivatives through solvent-free ruthenium trichloride mediated [2 + 2 + 2] cycloadditions, *Org. Lett.*, 2016, **18**, 5612–5615.

4. Synthesis of 3

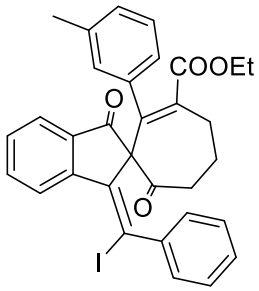


To a solution of corresponding aryl-fused 1,6-diyn-3-ones **1** (0.2 mmol, 61.2 mg) in DMSO (2.0 mL), β-diketones **2** (0.4 mmol, 2.0 equiv, 60 μL) and K_2CO_3 (0.4 mmol, 2.0 equiv, 55.3 mg) were added and stirred under N_2 at room temperature. After 1.5 h, I_2 (0.4 mmol, 2.0 equiv, 101.5 mg) was added and stirred for 1 h. After the completion of the reaction monitored by TLC, the reaction mixture was quenched with aqueous sat. $Na_2S_2O_3$ solution (2 mL). Then the filtrate was extracted with ethyl acetate (3 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 **3a-3v**.



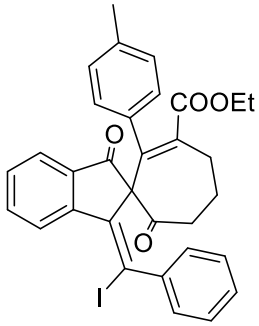
3a

Ethyl (E)-1'-(iodo(phenyl)methylene)-3',7-dioxo-2-phenyl-1',3'-dihydrospiro[cycloheptane-1,2'-inden]-2-ene-3-carboxylate **(3a)**. Light yellow solid, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: 91%, 107.5 mg, m.p. 206-208 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.33 (d, *J* = 8.5 Hz, 1H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.48-7.43 (m, 3H), 7.35-7.32 (m, 1H), 7.27-7.26 (m, 2H), 7.21-7.16 (m, 3H), 7.08-7.07 (m, 3H), 3.81 (q, *J* = 7.0 Hz, 2H), 3.72-3.66 (m, 1H), 2.23 (t, *J* = 7.5 Hz, 1H), 2.03-1.95 (m, 1H), 1.68-1.59 (m, 1H), 1.55-1.52 (m, 1H), 0.82 (t, *J* = 7.5 Hz, 3H), 0.48-0.41 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.6, 195.3, 169.9, 149.0, 146.2, 139.3, 139.2, 138.3, 138.2, 135.3, 134.6, 130.1, 129.0, 128.4, 128.3, 128.2, 127.7, 127.5, 124.9, 124.7, 97.9, 83.4, 60.3, 37.1, 26.2, 24.0, 13.5. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{31}H_{25}INaO_4$ 611.0690, found 611.0692.



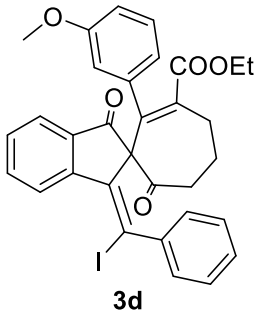
3b

Ethyl (E)-1'-(iodo(phenyl)methylene)-3',7-dioxo-2-(m-tolyl)-1',3'-dihydrospiro[cycloheptane-1,2'-inden]-2-ene-3-carboxylate **(3b)**. Light yellow solid, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: 85%, 102.3 mg, m.p. 150-152 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.32 (d, *J* = 8.0 Hz, 1H), 7.68 (t, *J* = 8.0 Hz, 1H), 7.49-7.42 (m, 3H), 7.36-7.33 (m, 1H), 7.27-7.26 (m, 2H), 7.19-7.16 (m, 1H), 7.02-6.94 (m, 3H), 6.88-6.86 (m, 1H), 3.81 (q, *J* = 10.0 Hz, 2H), 3.74-3.69 (m, 1H), 2.24-2.20 (m, 1H), 2.17 (s, 3H), 2.03-1.95 (m, 1H), 1.65-1.63 (m, 1H), 1.55-1.52 (m, 1H), 0.84 (t, *J* = 7.5 Hz, 3H), 0.49-0.42 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.8, 195.2, 170.0, 149.1, 146.2, 139.6, 139.3, 138.2, 137.9, 137.1, 135.4, 134.5, 130.0, 128.5, 128.3, 128.2, 127.6, 125.8, 124.9, 124.8, 97.9, 83.4, 60.3, 37.2, 26.2, 24.0, 21.2, 13.5. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{32}H_{27}INaO_4$ 625.0846, found 625.0853.



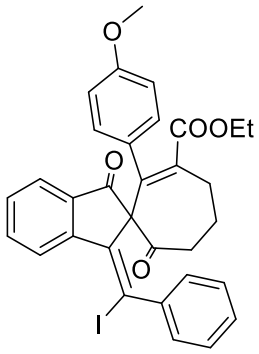
3c

Ethyl (E)-1'-(iodo(phenyl)methylene)-3',7-dioxo-2-(p-tolyl)-1',3'-dihydrospiro[cycloheptane-1,2'-inden]-2-ene-3-carboxylate **(3c)**. Light yellow solid, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: 84%, 101.5 mg, m.p. 120-122 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.33 (d, *J* = 8.5 Hz, 1H), 7.69 (t, *J* = 8.5 Hz, 1H), 7.50-7.48 (m, 1H), 7.43-7.42 (m, 2H), 7.37-7.34 (m, 1H), 7.28-7.26 (m, 2H), 7.18-7.15 (m, 1H), 7.09-7.08 (m, 2H), 6.90-6.88 (m, 2H), 3.82 (q, *J* = 10.0 Hz, 2H), 3.75-3.69 (m, 1H), 3.23-3.19 (m, 1H), 2.17 (s, 3H), 2.04-1.94 (m, 1H), 1.68-1.67 (m, 1H), 1.52-1.47 (m, 1H), 0.87 (t, *J* = 7.0 Hz, 3H), 0.48-0.41 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.8, 195.3, 170.0, 149.1, 146.2, 139.5, 139.3, 138.0, 137.2, 135.44, 135.40, 134.5, 130.0, 128.8, 128.5, 128.3, 128.2, 125.0, 124.8, 97.9, 83.6, 60.3, 37.0, 26.1, 24.2, 21.0, 13.6. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{32}H_{27}INaO_4$ 625.0846, found 625.0853.



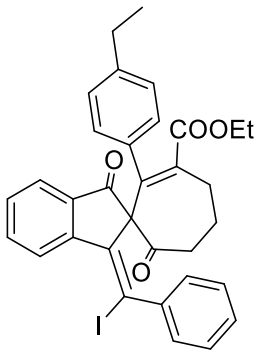
3d

Ethyl (E)-1'-(iodo(phenyl)methylene)-2-(3-methoxyphenyl)-3',7-dioxo-1',3'-dihydrospiro[cycloheptane-1,2'-inden]-2-ene-3-carboxylate **(3d)**. Light yellow oil, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: 93%, 115.0 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.34 (d, *J* = 8.5 Hz, 1H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.51-7.49 (m, 1H), 7.44-7.42 (m, 2H), 7.38-7.35 (m, 1H), 7.28-7.26 (m, 2H), 7.19-7.16 (m, 1H), 7.00-6.98 (m, 1H), 6.82-6.78 (m, 2H), 6.64-6.62 (m, 1H), 3.83 (q, *J* = 9.5 Hz, 2H), 3.78-3.71 (m, 1H), 3.64 (s, 3H), 2.24-2.20 (m, 1H), 2.04-1.95 (m, 1H), 1.67-1.65 (m, 1H), 1.53-1.49 (m, 1H),0.88 (t, *J* = 7.0 Hz, 3H), 0.47-0.40 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.6, 195.0, 169.9, 158.8, 149.0, 146.1, 139.64, 139.63, 138.9, 138.2, 135.4, 134.6, 130.2, 128.8, 128.3, 128.2, 124.9, 124.8, 121.8, 114.3, 113.3, 97.8, 83.4, 60.3, 55.3, 36.9, 26.1, 24.1, 13.6. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{32}H_{27}INaO_5$ 641.0795, found 641.0797.



3e

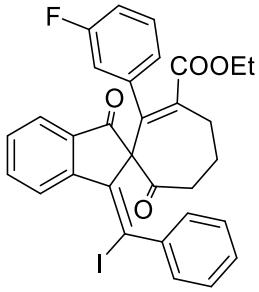
Ethyl (E)-1'-(iodo(phenyl)methylene)-2-(4-methoxyphenyl)-3',7-dioxo-1',3'-dihydrospiro[cycloheptane-1,2'-inden]-2-ene-3-carboxylate **(3e)**. Light yellow solid, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: 88%, 108.5 mg, m.p. 214-216 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.33 (d, *J* = 8.5 Hz, 1H), 7.70 (t, *J* = 5.5 Hz, 1H), 7.50-7.49 (m, 1H), 7.43-7.41 (m, 2H), 7.37-7.34 (m, 1H), 7.28-7.26 (m, 2H), 7.19-7.16 (m, 1H), 7.13-7.11 (m, 2H), 6.63-6.61 (m, 2H), 3.84 (q, *J* = 9.5 Hz, 2H), 3.77-3.72 (m, 1H), 3.66 (s, 3H), 2.23-2.19 (m, 1H), 2.02-1.93 (m, 1H), 1.65-1.61 (m, 1H), 1.53-1.49 (m, 1H), 0.90 (t, *J* = 7.0 Hz, 3H), 0.48-0.41 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.7, 195.4, 170.0, 158.8, 149.0, 146.2, 139.5, 138.7, 138.2, 135.4, 134.6, 130.7, 130.2, 130.1, 128.4, 128.3, 128.2, 124.9, 124.8, 113.1, 97.8, 83.5, 60.3, 55.0, 37.1, 26.2, 24.1, 13.7. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{32}H_{27}INaO_5$ 641.0795, found 641.0802.



3f

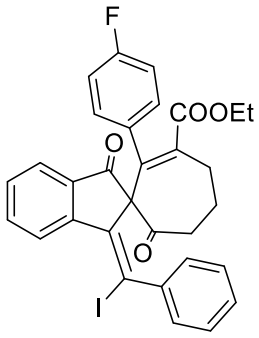
Ethyl (E)-2-(4-ethylphenyl)-1'-(iodo(phenyl)methylene)-3',7-dioxo-1',3'-dihydrospiro[cycloheptane-1,2'-inden]-2-ene-3-carboxylate **(3f)**. Light yellow solid, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: 85%, 105.0 mg, m.p. 146-148 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.32 (d, *J* = 8.0 Hz, 1H), 7.68 (t, *J* = 8.5 Hz, 1H), 7.49-7.47 (m, 1H), 7.43-7.42 (m, 2H), 7.36-7.33 (m, 1H), 7.26-7.25 (m, 2H), 7.18-7.15 (m, 1H), 7.12-7.10 (m, 2H), 6.92-6.80 (m, 2H), 3.81 (q, *J* = 9.5 Hz, 2H), 3.75-3.69 (m, 1H), 3.46 (q, *J* = 7.5 Hz, 2H), 3.23-3.19 (m, 1H), 3.01-2.95 (m, 1H), 2.65-2.63 (m, 1H), 2.54-2.49 (m, 1H), 1.08 (t, *J* = 7.5 Hz, 3H), 0.82 (t, *J*

= 7.0 Hz, 3H), 0.49-0.42 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.8, 195.3, 170.1, 149.1, 146.2, 143.5, 139.5, 139.3, 138.0, 135.7, 135.4, 134.5, 130.0, 128.9, 128.3, 128.2, 127.2, 125.0, 124.8, 97.8, 83.5, 60.2, 37.0, 28.3, 26.2, 24.1, 15.3 13.5. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{33}H_{29}INaO_4$ 639.1003, found 639.1007.



3g

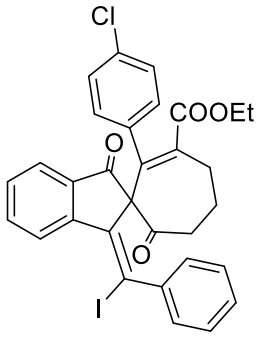
Ethyl (E)-2-(3-fluorophenyl)-1'-(iodo(phenyl)methylene)-3',7-dioxo-1',3'-dihydrospiro[cycloheptane-1,2'-inden]-2-ene-3-carboxylate **(3g)**. Light yellow solid, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: 88%, 106.3 mg, m.p. 162-164 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.34 (d, *J* = 8.0 Hz, 1H), 7.72 (t, *J* =7.0 Hz, 1H), 7.51-7.50 (m, 1H), 7.41-7.36 (m, 3H), 7.27-7.26 (m, 2H), 7.20-7.17 (m, 1H), 7.09-7.05 (m, 1H), 7.01-6.94 (m, 2H), 6.81-6.78 (m, 1H), 3.90-3.84 (m, 1H), 3.77 (q, *J* = 9.5 Hz, 2H), 2.26-2.21 (m, 1H), 2.03-1.95 (m, 1H), 1.68-1.63 (m, 1H), 1.55-1.51 (m, 1H), 0.89 (t, *J* = 7.0 Hz, 3H), 0.48-0.41 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.2, 195.1, 169.5, 162.0 (d, *J* = 245.0 Hz), 149.0, 146.1, 140.4 (d, *J* = 245.0 Hz), 139.2, 138.9, 137.9 (d, *J* = 1.9 Hz), 135.2, 134.8, 130.3, 129.3 (d, *J* = 8.3 Hz), 128.4, 128.3, 125.1, 125.0, 124.8, 116.2 (d, *J* = 22.9 Hz), 114.5 (d, *J* = 20.9 Hz), 98.1, 83.3, 60.5, 37.0, 26.2, 24.0, 13.6. ^{19}F NMR (471 MHz, $CDCl_3$) δ -113.07. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{31}H_{24}FINaO_4$ 629.0596, found 629.0603.



3h

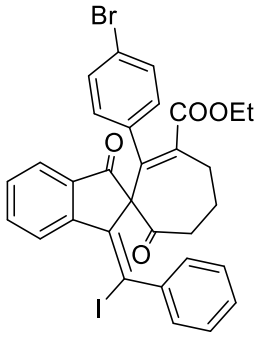
Ethyl (E)-2-(4-fluorophenyl)-1'-(iodo(phenyl)methylene)-3',7-dioxo-1',3'-dihydrospiro[cycloheptane-1,2'-inden]-2-ene-3-carboxylate **(3h)**. Light yellow solid, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: 85%, 102.8 mg, m.p. 223-225 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.35 (d, *J* = 8.0 Hz,

1H), 7.73 (t, *J* =7.0 Hz, 1H), 7.53-7.51 (m, 1H), 7.44-7.38 (m, 3H), 7.30-7.28 (m, 2H), 7.22-7.19 (m, 3H), 6.83-6.80 (m, 2H), 3.84 (q, *J* = 9.5 Hz, 2H), 3.80-3.73 (m, 1H), 2.28-2.24 (m, 1H), 2.02-1.97 (m, 1H), 1.65-1.63 (m, 1H), 1.58-1.54 (m, 1H), 0.92 (t, *J* = 7.0 Hz, 3H), 0.49-0.42 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.4, 195.3, 169.7, 163.0, 162.0 (d, *J* = 246.0 Hz), 149.0, 146.1, 139.2, 138.8, 138.0, 135.3, 134.8, 134.2 (d, *J* = 3.5 Hz), 130.93, 130.87, 130.3, 128.3 (d, *J* = 12.9 Hz), 125.0, 124.8, 114.7 (d, *J* = 21.0 Hz), 98.0, 83.4, 60.4, 37.1, 26.2, 23.9, 13.7. ^{19}F NMR (471 MHz, $CDCl_3$) δ -114.12. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{31}H_{24}FINaO_4$ 629.0596, found 629.0602.



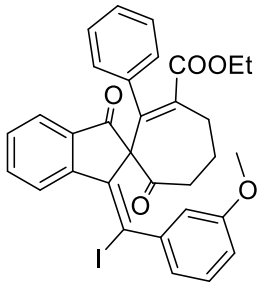
3i

Ethyl (E)-2-(4-chlorophenyl)-1'-(iodo(phenyl)methylene)-3',7-dioxo-1',3'-dihydrospiro[cycloheptane-1,2'-inden]-2-ene-3-carboxylate **(3i)**. Light yellow solid, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: 87%, 108.6 mg, m.p. 197-199 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.33 (d, *J* = 8.0 Hz, 1H), 7.72 (t, *J* =7.0 Hz, 1H), 7.51-7.49 (m, 1H), 7.40-7.37 (m, 3H), 7.27-7.26 (m, 2H), 7.20-7.15 (m, 3H), 7.09-7.08 (m, 2H), 3.90-3.83 (m, 1H), 3.76 (q, *J* = 9.5 Hz, 2H), 2.24-2.21 (m, 1H), 2.02-1.94 (m, 1H), 1.67-1.62 (m, 1H), 1.55-1.50 (m, 1H), 0.92 (t, *J* = 7.0 Hz, 3H), 0.47-0.40 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.2, 195.2, 169.5, 148.9, 146.1, 139.2, 138.9, 138.0, 136.8, 135.2, 134.8, 133.6, 130.4, 130.3, 128.4, 128.3, 128.0, 125.0, 124.9, 98.1, 83.4, 60.5 36.9, 26.1, 24.0, 13.6. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{31}H_{24}ClINaO_4$ 645.0300, found 645.0309.



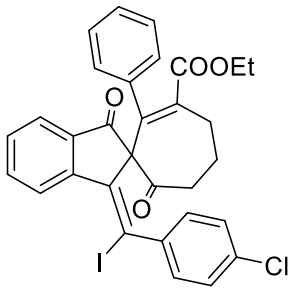
3j

Ethyl (E)-2-(4-bromophenyl)-1'-(iodo(phenyl)methylene)-3',7-dioxo-1',3'-dihydrospiro[cycloheptane-1,2'-inden]-2-ene-3-carboxylate **(3j)**. Light yellow solid, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: 84%, 111.8 mg, m.p. 189-191 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.33 (d, *J* = 8.5 Hz, 1H), 7.74-7.68 (m, 1H), 7.52-7.47 (m, 1H), 7.44-7.39 (m, 3H), 7.33-7.24 (m, 4H), 7.20-7.17 (m, 1H), 7.10-7.08 (m, 2H), 3.90-3.83 (m, 1H), 3.76 (q, *J* = 9.5 Hz, 2H), 2.24-2.21 (m, 1H), 2.01-1.93 (m, 1H), 1.67-1.64 (m, 1H), 1.54-1.49 (m, 1H), 0.90 (t, *J* = 7.0 Hz, 3H), 0.47-0.40 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.2, 195.2, 169.5, 149.0, 146.1, 139.2, 138.9, 138.1, 137.4, 135.2, 134.9, 131.0, 130.7, 130.3, 128.4, 128.3, 127.7, 125.1, 125.0, 121.9, 98.1, 83.4, 60.5, 36.9, 26.2, 24.0, 13.6. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{31}H_{24}BrINaO_4$ 688.9795, found 688.9801.



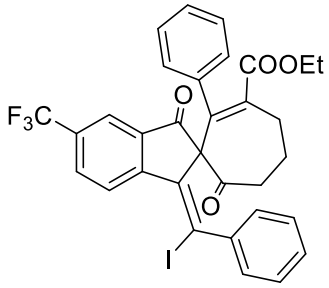
3k

Ethyl (E)-1'-(iodo(3-methoxyphenyl)methylene)-3',7-dioxo-2-phenyl-1',3'-dihydrospiro[cycloheptane-1,2'-inden]-2-ene-3-carboxylate **(3k)**. Light yellow solid, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: 92%, 114.0 mg, m.p. 126-128 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.31 (d, *J* = 8.4 Hz, 1H), 7.69 (t, *J* = 7.2 Hz, 1H), 7.48-7.47 (m, 1H), 7.36-7.33 (m, 1H), 7.19-7.18 (m, 3H), 7.09-7.06 (m, 3H), 7.03-7.02 (m, 1H), 6.95 (s, 1H), 6.75-6.74 (m, 1H), 3.82 (q, *J* = 9.6 Hz, 2H), 3.77 (s, 3H), 3.74-3.72 (m, 1H), 2.27-2.24 (m, 1H), 2.05-1.99 (m, 1H), 1.72-1.67 (m, 1H), 1.65-1.61 (m, 1H), 0.81 (t, *J* = 7.2 Hz, 3H), 0.69-0.64 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 203.8, 195.3, 169.9, 159.0, 149.1, 147.3 139.4, 138.4, 138.0, 135.4, 134.6, 130.1, 129.1, 127.7, 127.5, 125.0, 124.8, 114.8, 97.6, 83.5, 60.3, 54.4, 37.3, 26.3, 24.2, 13.5. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{32}H_{27}INaO_5$ 641.0795, found 641.0803.



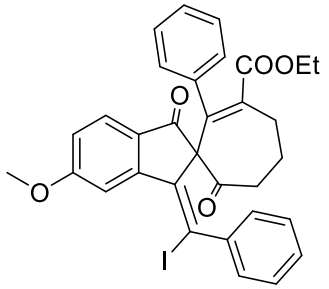
3l

Ethyl (E)-1'-((4-chlorophenyl)iodomethylene)-3',7-dioxo-2-phenyl-1',3'-dihydrospiro[cycloheptane-1,2'-inden]-2-ene-3-carboxylate **(3l)**. Light yellow oil, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: 82%, 101.7 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.30 (d, *J* = 8.5 Hz, 1H), 7.69 (t, *J* = 7.0 Hz, 1H), 7.48-7.46 (m, 1H), 7.39-7.33 (m, 3H), 7.27-7.25 (m, 2H), 7.19-7.17 (m, 2H), 7.09-7.07 (m, 3H), 3.85 (q, *J* = 9.5 Hz, 2H), 3.76-3.69 (m, 1H), 2.27-2.23 (m, 1H), 2.09-2.00 (m, 1H), 1.72-1.63 (m, 2H), 0.84 (t, *J* = 7.5 Hz, 3H), 0.56-0.49 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.5, 194.9, 169.7, 148.7, 144.5, 140.0, 139.2, 138.14, 138.07, 135.3, 134.6, 134.2, 130.3, 130.1, 128.9, 128.3, 127.8, 127.6, 124.9, 124.8, 95.9, 83.4, 60.4, 36.9, 26.2, 24.1, 13.5. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{31}H_{24}ClINaO_4$ 645.0300, found 645.0306.



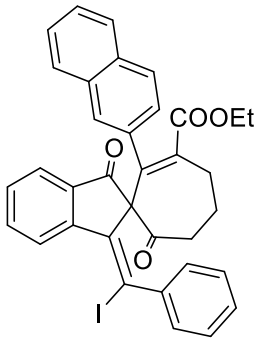
3m

Ethyl (E)-2-(3-fluorophenyl)-1'-(iodo(phenyl)methylene)-3',7-dioxo-1',3'-dihydrospiro[cycloheptane-1,2'-inden]-2-ene-3-carboxylate **(3m)**. Light yellow solid, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: 97%, 126.0 mg, m.p. 190-192 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.48 (d, *J* = 8.5 Hz, 1H), 7.91 (d, *J* = 8.5 Hz, 1H), 7.73 (s, 1H), 7.43-7.42 (m, 2H), 7.29-7.26 (m, 2H), 7.22-7.19 (m, 3H), 7.11-7.10 (m, 3H), 3.82 (q, *J* = 9.5 Hz, 2H), 3.75-3.67 (m, 1H), 2.25-2.21 (m, 1H), 2.04-1.96 (m, 1H), 1.64-1.63 (m, 1H), 1.57-1.54 (m, 1H), 0.83 (t, *J* = 7.0 Hz, 3H), 0.50-0.43 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.0, 194.5, 169.7, 151.6, 145.8, 138.8, 138.6, 138.5, 138.1, 135.5, 132.2 (q, 33.6 Hz), 130.9 (q, 3.6 Hz), 129.0, 128.6, 128.3, 127.9, 127.8, 125.6, 123.1 (q, 270.0 Hz), 121.8 (q, 4.1 Hz), 101.2, 83.8, 60.4, 37.0 26.2, 23.9, 13.5. ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.03. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{32}H_{24}F_3INaO_4$ 679.0564, found 679.0565.



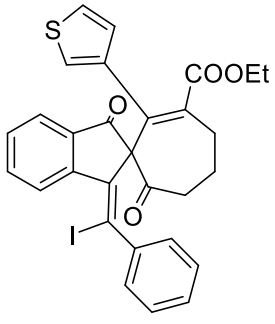
3n

Ethyl (E)-3'-(iodo(phenyl)methylene)-5'-methoxy-1',7-dioxo-2-phenyl-1',3'-dihydrospiro[cycloheptane-1,2'-inden]-2-ene-3-carboxylate **(3n)**. Light yellow solid, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: 84%, 104.2 mg, m.p. 178-180 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.81 (d, *J* = 2.5 Hz, 1H),7.44-7.40 (m, 3H), 7.28-7.26 (m, 2H), 7.22-7.16 (m, 3H), 7.12-7.08 (m, 3H), 6.91-6.89 (m, 1H), 3.94 (s, 3H), 3.83 (q, *J* = 9.5 Hz, 2H), 3.72-3.66 (m, 1H), 2.25-2.21 (m, 1H), 2.02-1.94 (m, 1H), 1.65-1.62 (m, 1H), 1.53-1.48 (m, 1H), 0.83 (t, *J* = 7.0 Hz, 3H), 0.45-0.38 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.2, 193.0, 169.9, 164.9, 151.3, 146.2, 139.4, 139.1, 138.4, 138.1, 129.0, 128.8, 128.3, 128.2, 127.7, 127.5, 126.4, 118.5, 108.1, 98.2, 83.6, 60.3, 55.9 37.1, 26.1, 24.1, 13.5. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{32}H_{27}INaO_5$ 641.0795, found 641.0798.



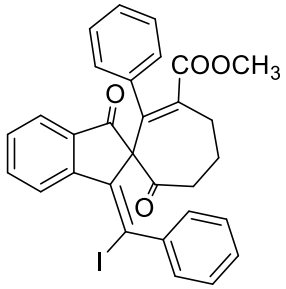
3o

Ethyl (E)-1'-(iodo(phenyl)methylene)-2-(naphthalen-2-yl)-3',7-dioxo-1',3'-dihydrospiro[cycloheptane-1,2'-inden]-2-ene-3-carboxylate **(3o)**. Light yellow oil, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: 93%, 119.1 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.31 (d, *J* = 8.5 Hz, 1H), 7.70-7.26 (m, 4H), 7.59-7.57 (m, 1H), 7.50-7.48 (m, 2H), 7.38-7.36 (m, 4H), 7.26-7.24 (m, 3H), 7.21-7.18 (m, 1H), 3.87 (q, *J* = 10.0 Hz, 1H), 3.79-3.72 (m, 1H), 3.63-3.56 (m, 1H), 2.28-2.24 (m, 1H), 2.08-2.00 (m, 1H), 1.71-1.67 (m, 1H), 1.59-1.55 (m, 1H), 0.65 (t, *J* = 7.0 Hz, 3H), 0.55-0.48 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.7, 195.2, 169.9, 149.1, 146.2, 139.7, 139.2, 138.8, 136.0, 135.3, 134.6, 132.7, 132.4, 130.1, 128.4, 128.3, 128.2, 127.30, 127.27, 127.1, 126.0, 125.9, 125.0, 124.9, 98.0, 83.7, 60.3, 37.0, 26.3, 24.2, 13.4. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{35}H_{27}INaO_4$ 661.0846, found 661.0857.



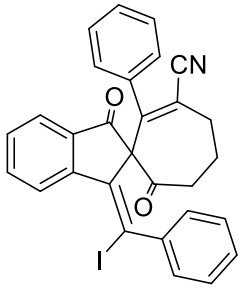
3p

Ethyl (E)-1'-(iodo(phenyl)methylene)-3',7-dioxo-2-(thiophen-3-yl)-1',3'-dihydrospiro[cycloheptane-1,2'-inden]-2-ene-3-carboxylate **(3p)**. Light yellow solid, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: 77%, 91.5 mg, m.p. 218-220 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.31 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 1H),7.55-7.54 (m, 1H), 7.41-7.38 (m, 3H), 7.28-7.26 (m, 2H), 7.19-7.17 (m, 1H), 7.04 (s, 1H), 6.91 (s, 1H), 3.93-3.88 (m, 1H), 3.77 (q, *J* = 10.0 Hz, 2H), 2.21-2.18 (m, 1H), 2.00-1.93 (m, 1H), 1.63-1.55 (m, 2H), 0.96 (t, *J* = 7.2 Hz, 3H), 0.57-0.51 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 203.5, 195.3, 169.9, 149.1, 145.9, 139.7, 138.3, 138.0, 135.4, 134.6, 134.4, 130.2, 128.7, 128.4, 128.3, 125.0, 124.8, 124.6, 123.7, 97.8, 83.4, 60.5, 37.1, 26.5, 23.6, 13.7. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{29}H_{23}INaO_4S$ 617.0254, found 617.0264.



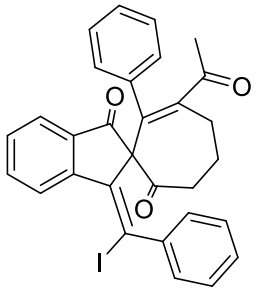
3q

Methyl (E)-1'-(iodo(phenyl)methylene)-3',7-dioxo-2-phenyl-1',3'-dihydrospiro[cycloheptane-1,2'-inden]-2-ene-3-carboxylate **(3q)**. Light yellow solid, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: 87%, 99.5 mg, m.p. 197-199 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.33 (d, *J* = 8.5 Hz, 1H), 7.68 (t, *J* = 10.0 Hz, 1H), 7.47-7.42 (m, 3H), 7.35-7.32 (m, 1H), 7.27-7.26 (m, 2H), 7.20-7.19 (m, 3H), 7.10-7.06 (m, 3H), 3.81 (q, *J* = 9.5 Hz, 1H), 3.30 (s, 3H), 2.25-2.21 (m, 1H), 2.03-1.94 (m, 1H), 1.65-1.63 (m, 1H), 1.54-1.50 (m, 1H), 0.48-0.41 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.5, 195.2, 170.2, 149.0, 146.1, 139.6, 139.3, 138.2, 138.0, 135.3, 134.6, 130.1, 128.8, 128.3, 128.2, 127.8, 127.6, 124.9, 124.7, 98.0 83.3, 51.3, 37.1, 26.1, 24.0. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{30}H_{23}INaO_4$ 597.0533, found 597.0541.



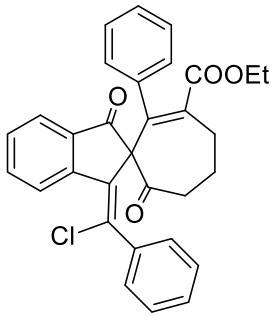
3r

(E)-1'-(iodo(phenyl)methylene)-3',7-dioxo-2-phenyl-1',3'-dihydrospiro[cycloheptane-1,2'-inden]-2-ene-3-carbonitrile **(3r)**. Light yellow solid, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: 84%, 91.2 mg, m.p. 251-253 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.32 (d, *J* = 8.5 Hz, 1H), 7.72 (t, *J* = 7.5 Hz, 1H), 7.51-7.49 (m, 1H), 7.40-7.34 (m, 7H), 7.26-7.25 (m, 1H), 7.22-7.21 (m, 3H), 3.69 (q, *J* = 10.0 Hz, 1H), 2.28-2.24 (m, 1H), 1.95-1.92 (m, 1H), 1.66-1.64 (m, 2H), 0.69-0.62 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.0, 194.1, 153.6, 148.9, 145.9, 138.6, 136.8, 135.0, 134.9, 130.4, 129.2, 128.84, 128.82, 128.6, 128.5, 125.2, 125.0, 119.0, 118.6, 98.1, 83.4, 36.6, 27.4, 23.0. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{29}H_{20}INNaO_2$ 564.0431, found 564.0440.



3s

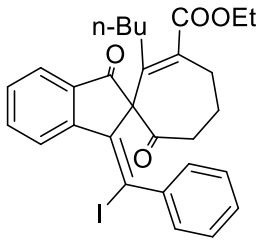
(E)-3-acetyl-1'-(iodo(phenyl)methylene)-2-phenylspiro[cycloheptane-1,2'-inden]-2-ene-3',7(1'H)-dione **(3s)**. Light yellow solid, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: 84%, 94.2 mg, m.p. 200-202 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.34 (d, *J* = 8.0 Hz, 1H), 7.70 (t, *J* = 8.5 Hz, 1H), 7.49-7.44 (m, 3H), 7.37-7.34 (m, 1H), 7.32-7.28 (m, 2H), 7.22-7.20 (m, 3H), 7.13-7.12 (m, 3H), 3.82 (q, *J* = 10.0 Hz, 1H), 2.25-2.21 (m, 1H), 2.02-1.98 (m, 1H), 1.76-1.70 (m, 1H), 1.61 (s, 3H), 1.41-1.38 (m, 1H), 0.49-0.42 (m, 1H).^{13}C NMR (125 MHz, $CDCl_3$) δ 206.3, 203.9, 195.3, 149.1, 146.6, 146.3, 139.7, 137.6, 136.6, 135.3, 134.6, 130.2, 129.6, 128.5, 128.3, 128.2, 125.1, 124.8, 97.5, 83.8, 36.9, 29.9, 26.1, 24.8. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{30}H_{23}INaO_3$ 581.0584, found 581.0580.



3t

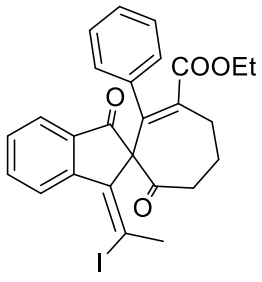
Ethyl (E)-1'-(chloro(phenyl)methylene)-3',7-dioxo-2-phenyl-1',3'-dihydrospiro[cycloheptane-1,2'-inden]-2-ene-3-carboxylate **(3t)**. Light yellow oil, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield:

81%, 80.1 mg. ^{1}H NMR (500 MHz, $CDCl_3$) 7.56-7.51 (m, 3H), 7.36-7.33 (m, 6H), 7.19-7.12 (m, 5H), 3.83 (q, J = 7.0 Hz, 2H), 3.27-3.22 (m, 1H), 3.10-3.05 (m, 1H), 2.75-2.70 (m, 1H), 2.55-2.50 (m, 1H), 2.27-2.19 (m, 2H), 0.79 (q, J = 7.0 Hz, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 201.5, 195.5, 169.1, 141.7, 138.4, 137.3, 136.2, 133.5, 131.8, 130.5, 129.8, 128.5, 128.4, 128.2, 128.0, 127.7, 126.4, 122.9, 122.0, 93.4, 87.0, 84.6, 60.8, 36.7, 27.1, 24.7, 13.4. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{31}H_{25}ClNaO_4$ 519.1334, found 519.1342.



3u

Ethyl (E)-2-butyl-1'-(iodo(phenyl)methylene)-3',7-dioxo-1',3'-dihydrospiro[cycloheptane-1,2'-inden]-2-ene-3-carboxylate **(3u)**. Light yellow oil, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: 83%, 94.3 mg. ^{1}H NMR (600 MHz, $CDCl_3$) 9.36 (d, J = 8.4 Hz, 1H), 7.83-7.80 (m, 2H), 7.56-7.53 (m, 1H), 7.27-7.23 (m, 4H), 7.17-7.14 (m, 1H), 4.20-4.11 (m, 2H), 3.57-3.52 (m, 1H), 2.42-3.37 (m, 1H), 2.10-2.07 (m, 1H), 1.86-1.80 (m, 1H), 1.67-1.64 (m, 1H), 1.56-1.52 (m, 1H), 1.42-1.38 (m, 1H), 1.34-1.26 (m, 4H), 1.12-1.05 (m, 2H), 0.71 (q, J = 7.2 Hz, 3H), 0.57-0.51(m, 1H).^{13}C NMR (150 MHz, $CDCl_3$) δ 204.5, 196.3, 169.5, 149.7, 146.0, 141.4, 139.6, 135.8, 134.9, 134.2, 130.3, 128.2, 128.1, 125.4, 124.9, 97.6, 85.4, 60.4, 36.7, 32.6, 32.5, 26.5, 23.6, 23.4, 14.1, 13.5. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{29}H_{29}INaO_4$ 591.1003, found 591.1013.

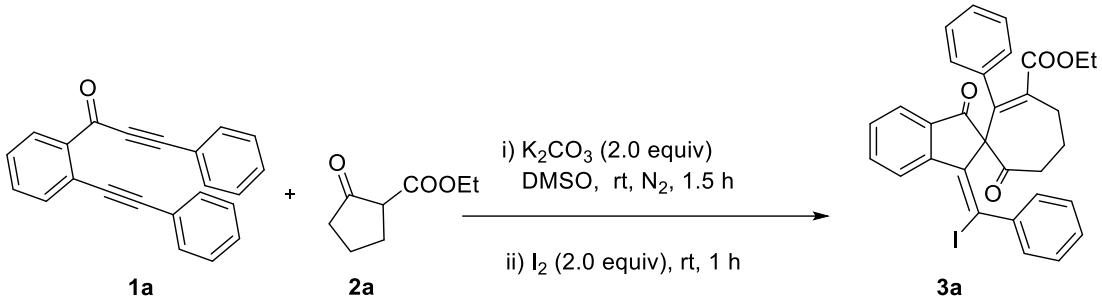


3v

Ethyl (E)-1'-(1-iodoethylidene)-3',7-dioxo-2-phenyl-1',3'-dihydrospiro[cycloheptane-1,2'-inden]-2-ene-3-carboxylate **(3v)**. Light yellow oil, purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: 74%, 77.6 mg. ^{1}H NMR (600 MHz, $CDCl_3$) 8.98 (d, J = 7.8 Hz, 1H), 7.62-7.61 (m, 1H),

7.58-7.55 (m, 1H), 7.34-7.31 (m, 1H), 7.03-6.99 (m, 3H), 6.92-6.91 (m, 2H), 3.75 (q, *J* = 7.2 Hz, 2H), 3.71-3.66 (m, 1H), 2.94 (s, 3H), 2.81-2.77 (m, 1H), 2.69-2.65 (m, 1H), 2.61-2.55 (m, 1H), 2.53-2.47 (m, 1H), 2.15-2.10 (m, 1H), 0.75 (q, *J* = 7.2 Hz, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ 202.6, 196.4, 170.1, 149.4, 138.5, 138.3, 138.2, 137.7, 135.6, 134.6, 129.3, 129.2, 127.5, 127.2, 124.5, 124.2, 97.5, 82.9, 60.7, 39.5, 36.9, 29.6, 22.9, 13.4. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{26}H_{23}INaO_4$ 549.0533, found 549.0536.

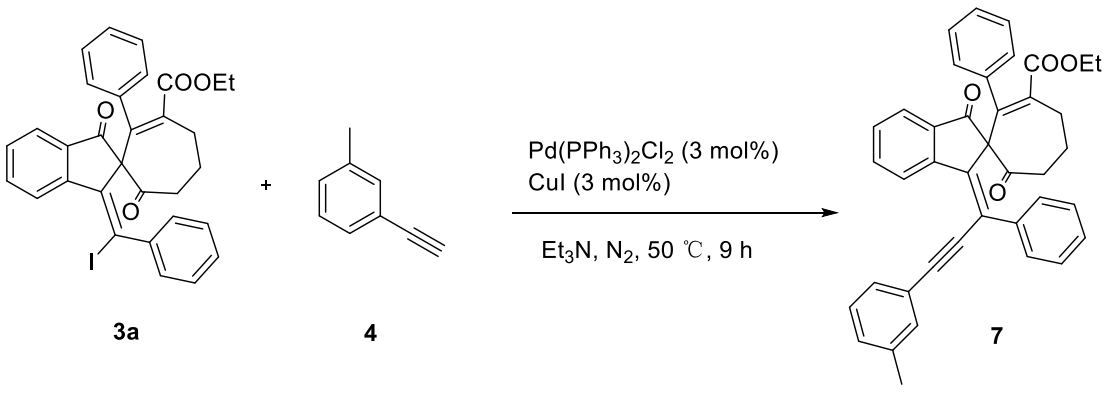
5. 1.0 mmol scale reaction for the preparation of 3a



1a **2a** **3a**

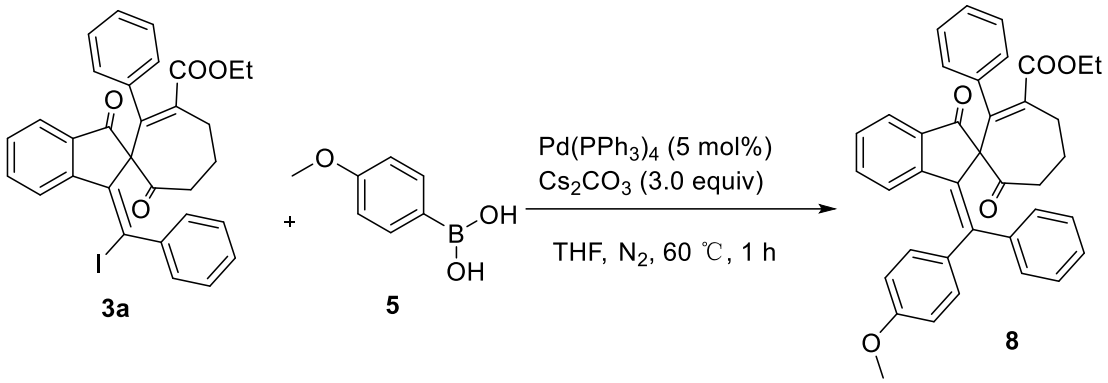
In a schlenk tube, aryl-fused 1,6-diyn-3-one **1a** (1.0 mmol, 306.4 mg), ethyl 2-oxocyclohexanecarboxylate **2a** (2.0 mmol, 2.0 equiv, 300 μL), K_2CO_3 (2.0 mmol, 2.0 equiv, 276.4 mg) and DMSO (10.0 mL) were stirred under N_2 at room temperature. After 1.5 h, I_2 (2.0 mmol, 2.0 equiv, 507.6 mg) was added and stirred for 1 h. After the completion of the reaction monitored by TLC, the reaction mixture was quenched with aqueous sat. $Na_2S_2O_3$ solution (5 mL). Then the filtrate was extracted with ethyl acetate (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 **3a** (Light yellow solid, 529.8 mg, 90%).

6. Synthetic transformation of compound 3a



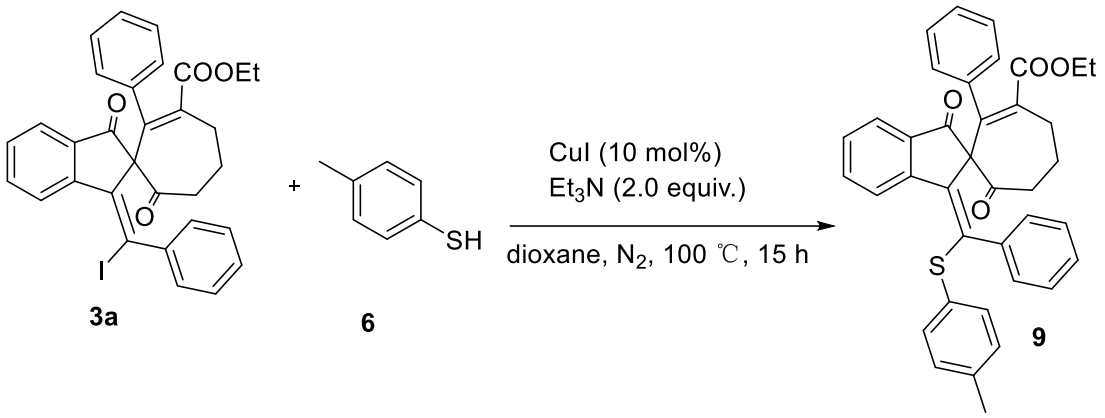
3a **4** **7**

In a schlenk tube, **3a** (0.2 mmol, 117.8 mg), $Pd(PPh_3)_2Cl_2$ (0.006 mmol, 3 mol%, 4.5 mg), CuI (0.006 mmol, 3 mol%, 1.7 mg) and NEt_3 (2 mL) were added under N_2 at room temperature. Then 1-ethynyl-3-methylbenzene **4** (0.3 mmol, 0.15 equiv, 39 μL) was added dropwise and the mixture was stirred at 50 ℃ in an oil bath for 9 h. After the completion of the reaction monitored by TLC, the reaction mixture was quenched with aqueous sat. NH_4Cl solution (2 mL). Then the filtrate was extracted with ethyl acetate (3 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 as the eluent to afford **7** (Yellow oil, 97.7 mg, 85%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.18 (d, *J* = 6.5 Hz, 1H), δ 7.65 (d, *J* = 7.0 Hz, 1H), 7.54-7.53 (m, 2H), 7.47-7.45 (m, 1H), 7.32-7.25 (m, 7H), 7.24-7.22 (m, 2H), 7.18-7.17 (m, 1H), 7.07-7.06 (m, 3H), 3.87 (q, *J* = 10.0 Hz, 2H). 3.74-3.67 (m, 1H), 2.35 (s, 3H), 2.29-2.26 (m, 1H), 2.07-1.99 (m, 1H), 1.74-1.69 (m, 1H), 1.56-1.52 (m, 1H), 0.83 (q, *J* = 7.5 Hz, 3H), 0.54-0.47 (m, 1H).^{13}C NMR (125 MHz,$CDCl_3$) δ 204.0, 196.2, 170.0, 149.7, 139.8, 139.7, 138.7, 138.4, 138.2, 137.7, 135.5, 132.0, 129.8, 129.6, 129.5, 128.9, 128.6, 128.4, 127.9, 127.6, 127.4, 125.2, 124.4, 124.1, 122.8, 101.1, 91.5, 81.3, 60.3, 37.2, 25.9, 24.5, 21.2, 13.5. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{40}H_{32}NaO_4$ 599.2193, found 599.2198.



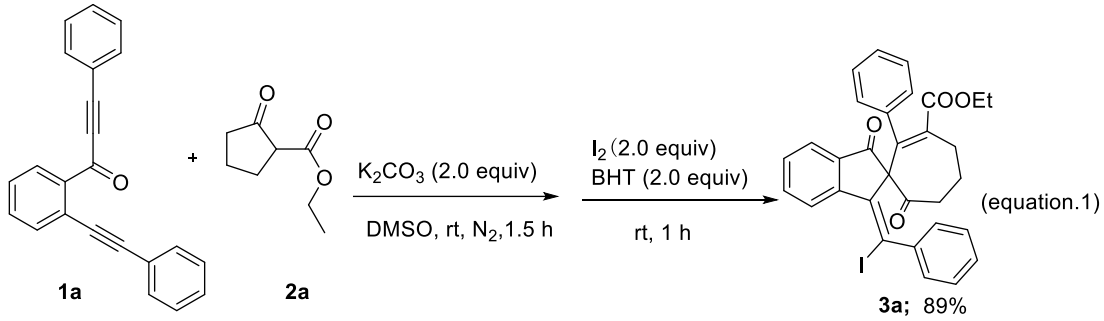
In a schlenk tube, **3a** (0.2 mmol, 117.8 mg), (4-methoxyphenyl)boronic acid **5** (0.4 mmol, 2.0 equiv, 60.8 mg), $Pd(PPh_3)_4$ (0.01 mmol, 5 mol%, 11.6 mg),Cs_2CO_3 (0.6 mmol, 3.0 equiv, 195.5 mg) and THF (2 mL) were added under N_2 and stirred at 60 ℃ in an oil bath for 1 h. After the completion of the reaction monitored by TLC, the reaction mixture was quenched with aqueous sat. NH_4Cl solution (2 mL). Then the filtrate was extracted with ethyl acetate (3 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 **8** (Yellow oil, 97.8 mg, 86%).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43-7.33 (m, 6H), 7.29-7.24 (m, 3H), 7.20-7.06 (m, 6H), 6.94-6.89 (m, 2H),

6.69-6.67 (m, 1H), 3.91 (q, *J* = 11.5 Hz, 1H), 3.83 (s, 3H), 3.75-3.67 (m, 2H), 2.30-2.26 (m, 1H), 2.06-1.99 (m, 1H), 1.78-1.70 (m, 1H), 1.62-1.57 (m, 1H), 0.82 (q, *J* = 7.5 Hz, 3H), 0.71-0.64 (m, 1H).^{13}C NMR (125 MHz, $CDCl_3$) δ 204.9, 197.3, 170.1, 159.4, 151.2, 145.0, 142.0, 140.2, 138.8, 137.4, 135.9, 134.60 134.5, 132.8, 130.4, 129.3, 129.2, 128.3, 128.1, 127.5, 127.4, 125.9, 124.3, 114.7, 114.6, 82.2, 60.2, 55.2, 37.3, 25.8, 24.5, 13.5. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{38}H_{32}NaO_5$ 591.2142, found 519.2149.

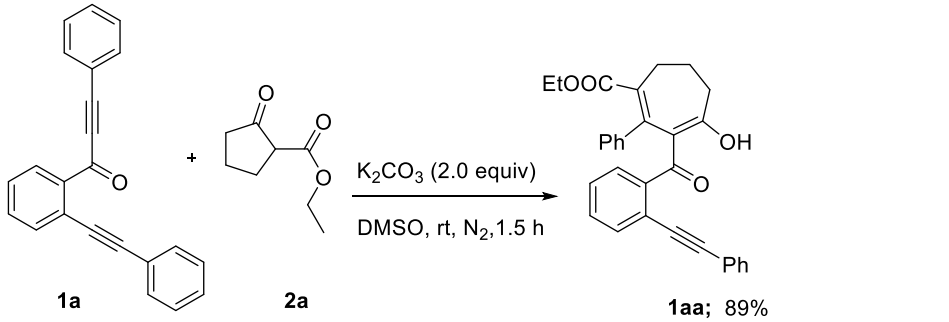


In a schlenk tube, **3a** (0.2 mmol, 117.8 mg), 4-methylbenzenethiol **6** (0.24 mmol, 1.2 equiv, 30.2 mg), CuI (0.02 mmol, 10 mol%, 4.3 mg), NEt_3 (0.4 mmol, 2.0 equiv, 60 μL) and dioxane (2 mL) were added under N_2 and stirred at 100 ℃ in an oil bath for 15 h. After the completion of the reaction monitored by TLC, the reaction mixture was quenched with aqueous sat. NH_4Cl solution (2 mL). Then the filtrate was extracted with ethyl acetate (3 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 = 20:1 as the eluent to afford **9** (Yellow oil, 68.1 mg, 58%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.11 (d, *J* = 8.0 Hz, 1H), 7.63 (t, *J* = 8.5 Hz, 1H), 7.47-7.46 (m, 1H), 7.26-7.21 (m, 4H), 7.15-7.05 (m, 8H), 6.972-6.966 (m, 3H), 3.89-3.85 (m, 1H), 3.82-3.78 (m, 1H), 3.72-3.65 (m, 1H), 2.24 (s, 3H), 2.22-2.20 (m, 1H), 2.00-1.92 (m, 1H), 1.62-1.61 (m, 1H), 1.46-1.42 (m, 1H), 0.82 (q, *J* = 7.0 Hz, 3H), 0.40-0.33 (m, 1H).^{13}C NMR (125 MHz,$CDCl_3$) δ 204.6, 196.9, 170.0, 150.0, 142.3, 139.9, 138.6, 137.4, 137.1, 135.4, 135.3, 134.5, 131.4, 130.8, 129.2, 129.1, 128.4, 127.7, 127.6, 127.5, 127.43, 127.35, 127.24, 127.23, 124.6, 82.7, 60.2, 37.2, 25.8, 24.2, 21.1, 13.5. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{38}H_{32}NaO_4S$ 607.1914, found 607.1920.

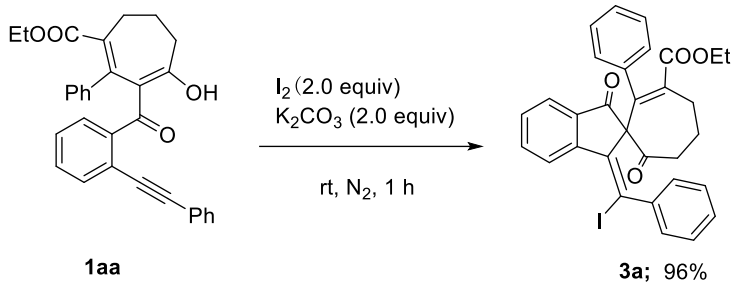
7. Mechanistic study



(equation.1)



(equation.2)



(equation.3)

In a schlenk tube, aryl-fused 1,6-diyn-3-one **1a** (0.2 mmol, 61.2 mg), ethyl 2-oxocyclohexanecarboxylate **2a** (0.4 mmol, 2.0 equiv, 60 μL), K_2CO_3 (0.4 mmol, 2.0 equiv, 55.3 mg) and DMSO (2.0 mL) were stirred under N_2 at room temperature. After 1.5 h, I_2 (0.4 mmol, 2.0 equiv, 101.5 mg) and butylated hydroxytoluene (BHT) (0.4 mmol, 2.0 equiv, 88.1 mg) were added and stirred for 1 h. After the completion of the reaction monitored by TLC, the reaction mixture was quenched with aqueous sat. $Na_2S_2O_3$ solution (2 mL). Then the filtrate was extracted with ethyl acetate (3 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 **3a** (Light yellow solid, 104.9 mg, 89%) (equation.1).

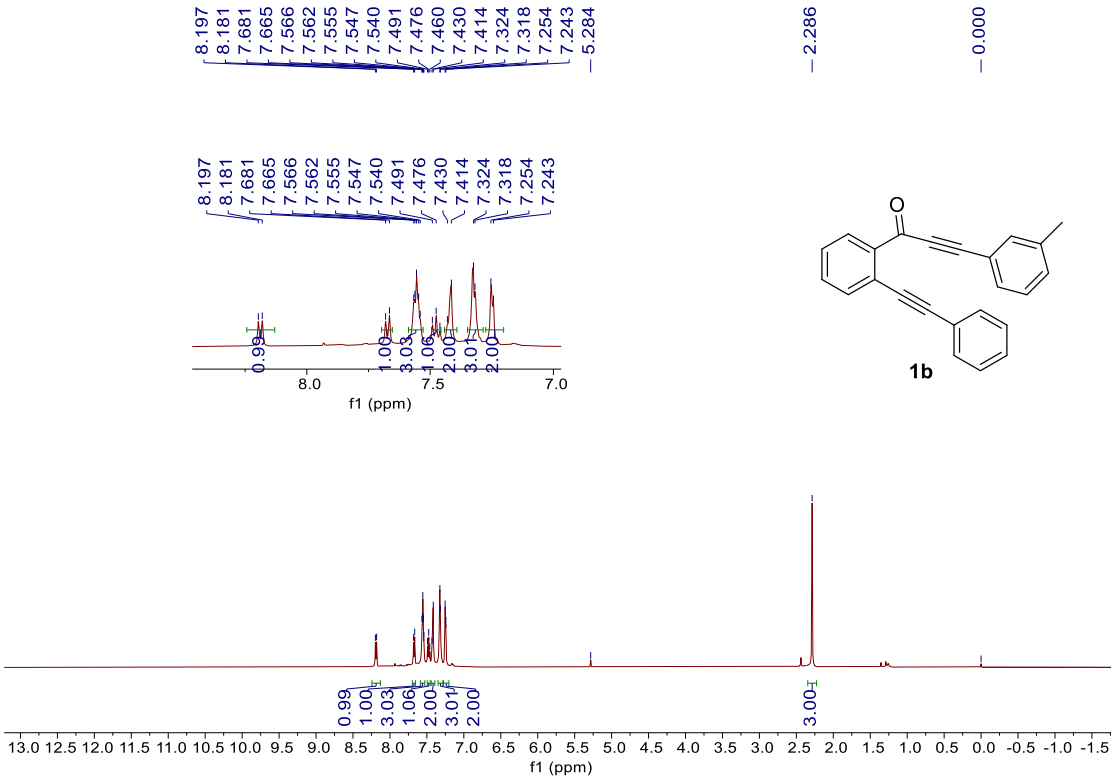
In a schlenk tube, aryl-fused 1,6-diyn-3-one **1a** (0.5 mmol, 154.1 mg), ethyl 2-oxocyclohexanecarboxylate **2a** (1.0 mmol, 2.0 equiv, 150 μL), K_2CO_3 (1.0 mmol, 2.0 equiv, 138.2 mg) and DMSO (5.0 mL) were stirred under N_2 at room temperature for 1.5 h. After the completion of the reaction monitored by TLC, the reaction mixture was

quenched with H_2O (2 mL). Then the filtrate was extracted with ethyl acetate (3 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 **1aa** (Light yellow oil, 206.2 mg, 89%) (equation.2). **1aa**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 17.1 (s, 1H), 7.52-7.50 (m, 2H), 7.36-7.35 (m, 3H), 7.21-7.19 (m, 1H), 7.11-7.08 (m, 1H), 6.99-6.88 (m, 4H), 6.78-6.72 (m, 3H), 3.86 (d, *J* = 7.0 Hz, 2H), 2.84-2.49 (m, 4H), 2.27-2.23 (m, 2H), 0.80 (t, *J* = 7.0 Hz, 3H).^{13}C NMR (125 MHz,$CDCl_3$) δ 197.2, 190.7, 170.1, 144.1, 140.7, 139.1, 132.1, 131.6, 131.5, 129.0, 128.4, 128.3, 128.1, 127.4, 127.1, 127.0, 126.9, 123.1, 120.6, 114.7, 93.1, 87.0, 60.4, 35.6, 31.1, 28.9, 13.4. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{31}H_{26}NaO_4$ 485.1723, found 485.1723.

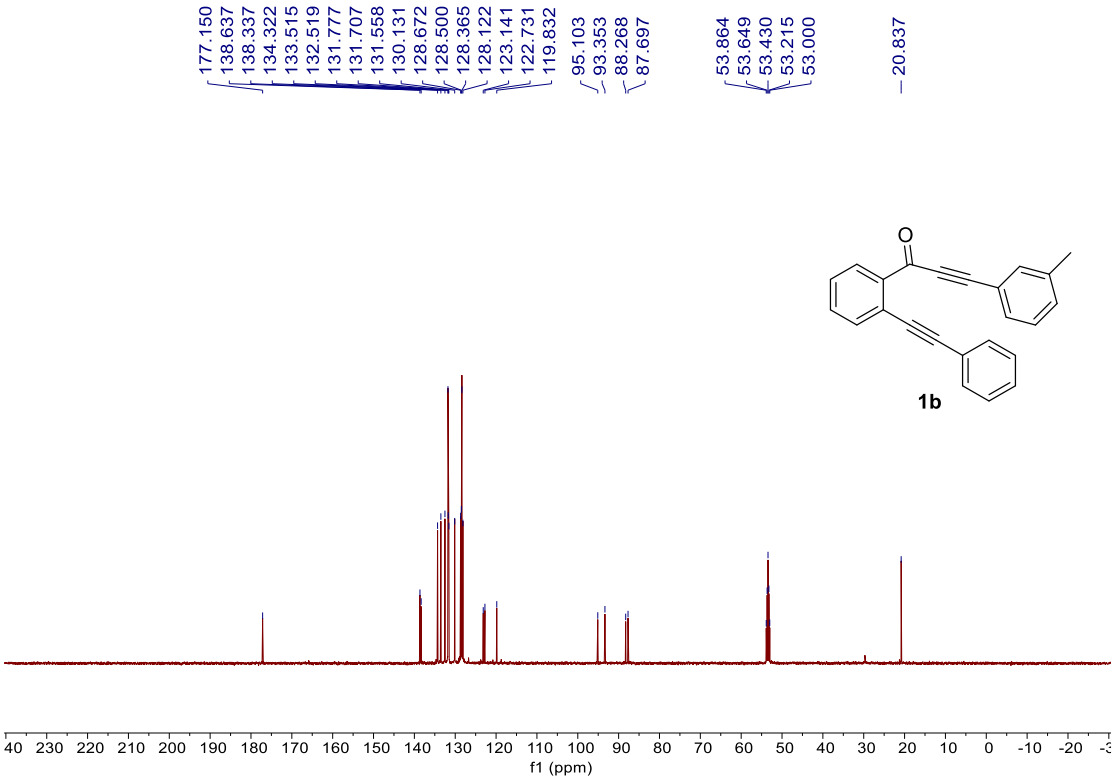
In a schlenk tube, **1aa** (0.2 mmol, 92.4 mg), K_2CO_3 (0.4 mmol, 2.0 equiv, 55.3 mg), I_2 (0.4 mmol, 2.0 equiv, 101.5 mg) and DMSO (2.0 mL) were stirred under N_2 at room temperature for 1.0 h, After the completion of the reaction monitored by TLC, the reaction mixture was quenched with aqueous sat. $Na_2S_2O_3$ solution (2 mL). Then the filtrate was extracted with ethyl acetate (3 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 **3a** (Light yellow solid, 112.8 mg, 96%) (equation.3).

8. NMR Copies of all the Synthesized New Starting Materials

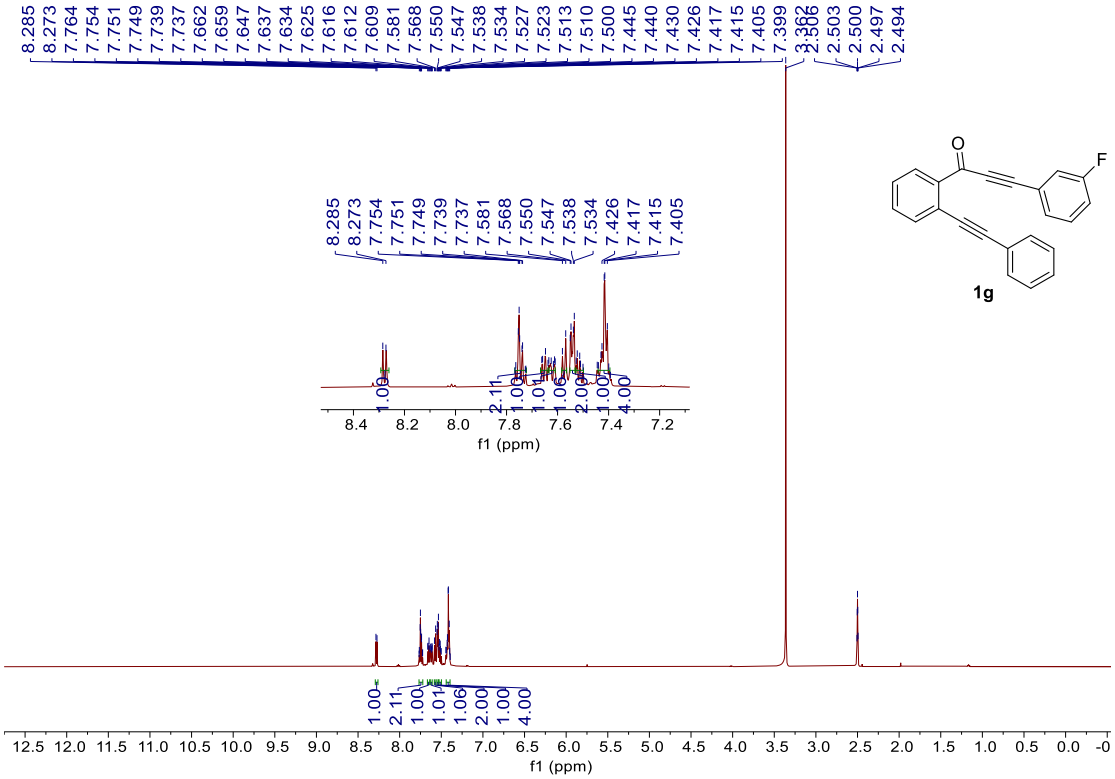
^{1}H NMR (500 MHz, CD_2Cl_2)



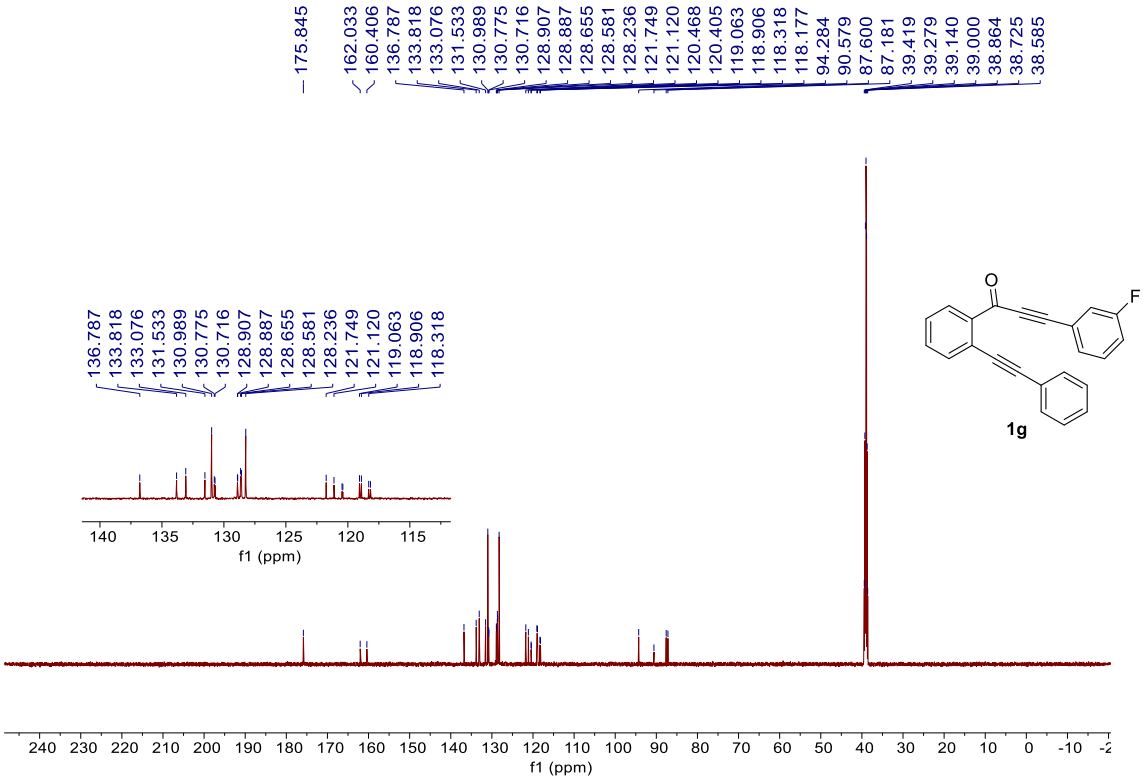
^{13}C NMR (125 MHz, CD_2Cl_2)



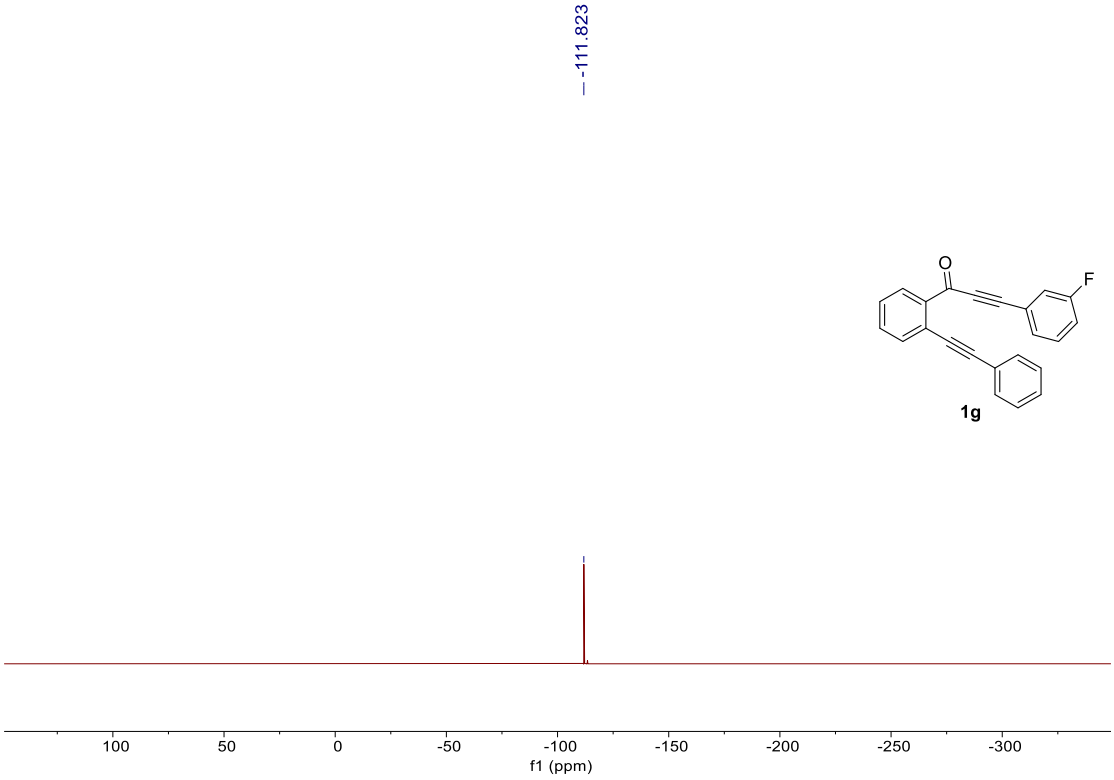
^{1}H NMR (600 MHz, DMSO-d_6)



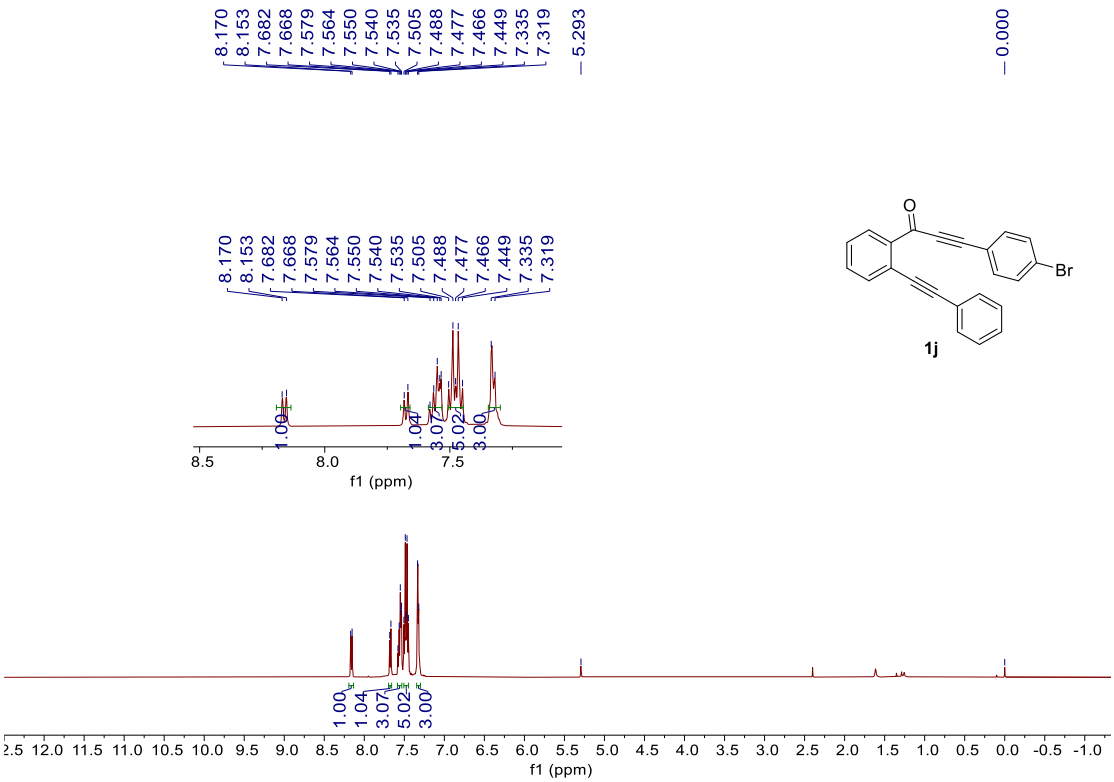
^{13}C NMR (150 MHz, DMSO-d_6)



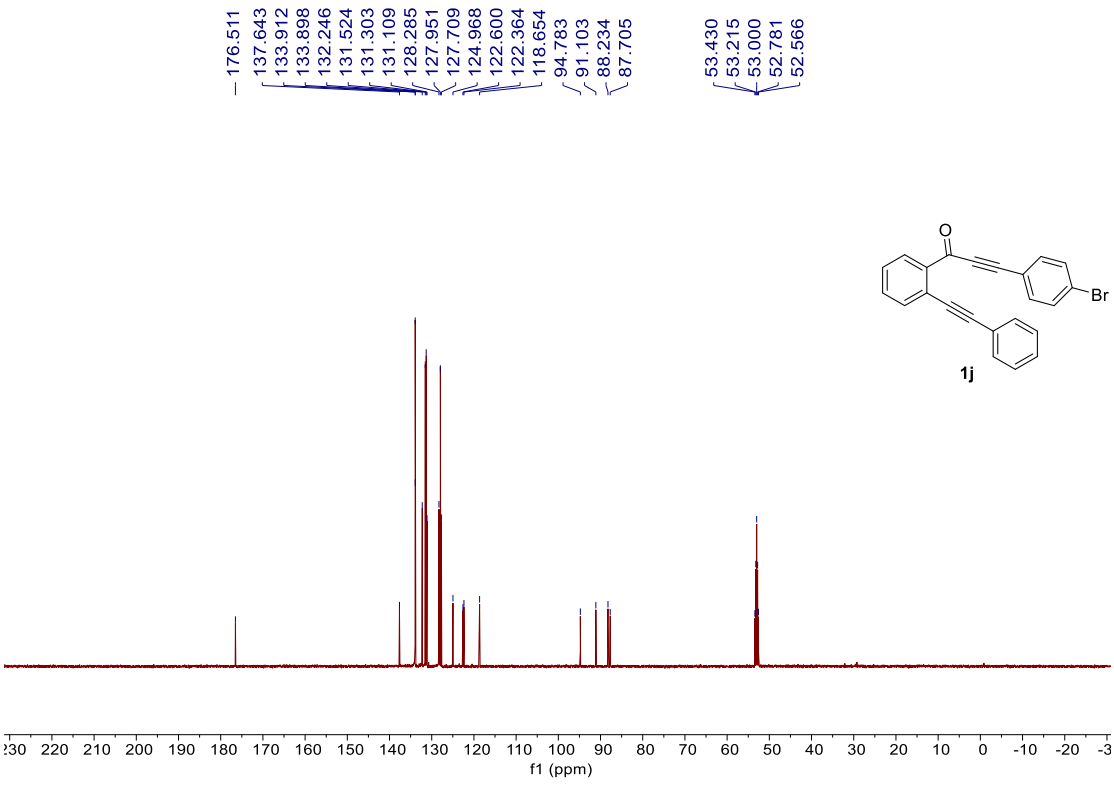
^{19}F NMR (471 MHz, $CDCl_3$)



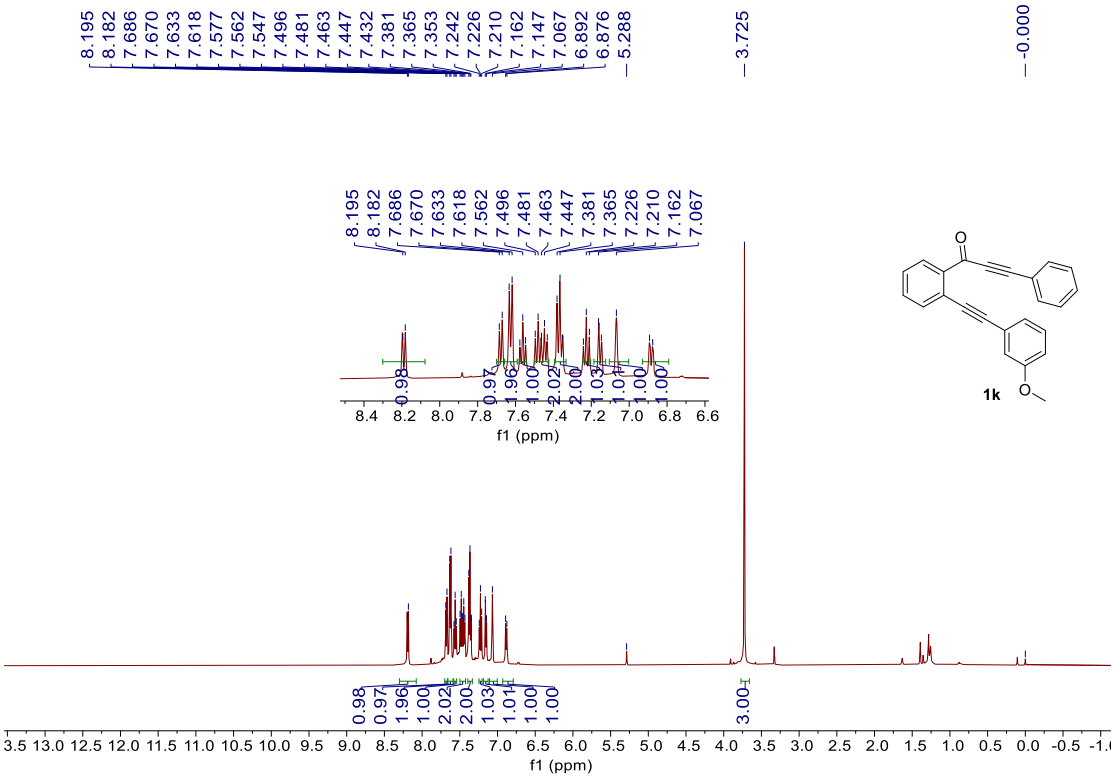
^{1}H NMR (500 MHz, CD_2Cl_2)



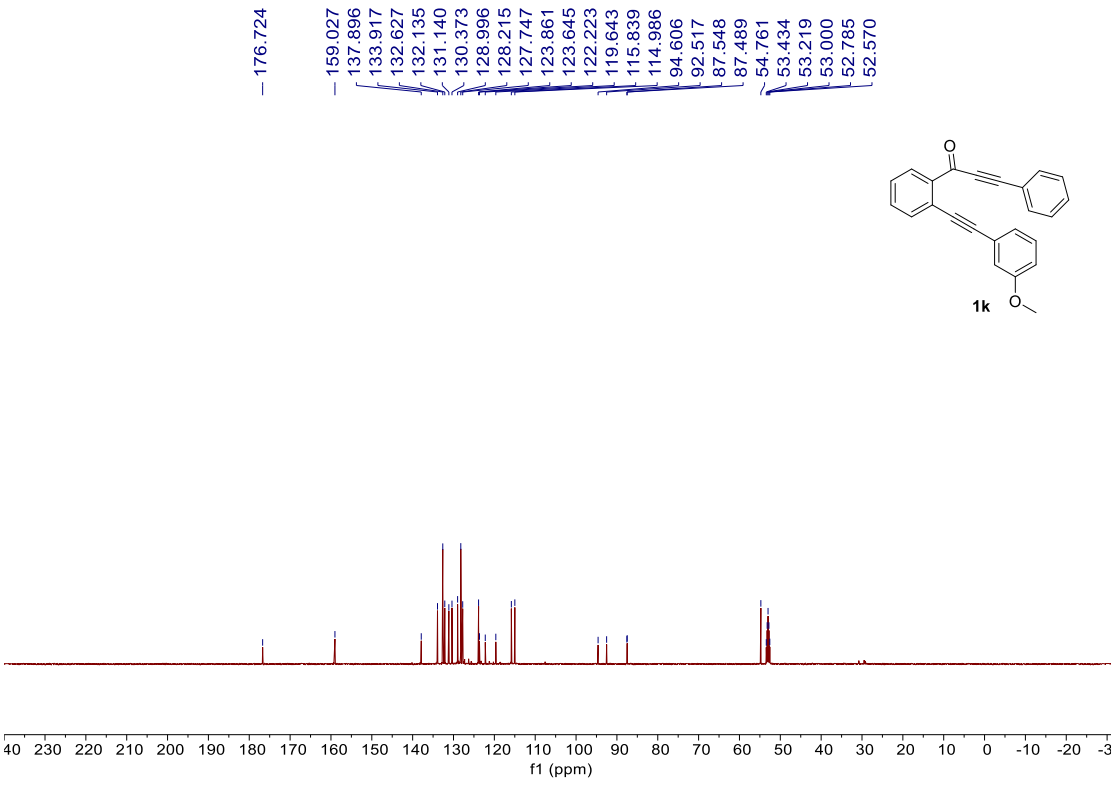
^{13}C NMR (125 MHz, CD_2Cl_2)



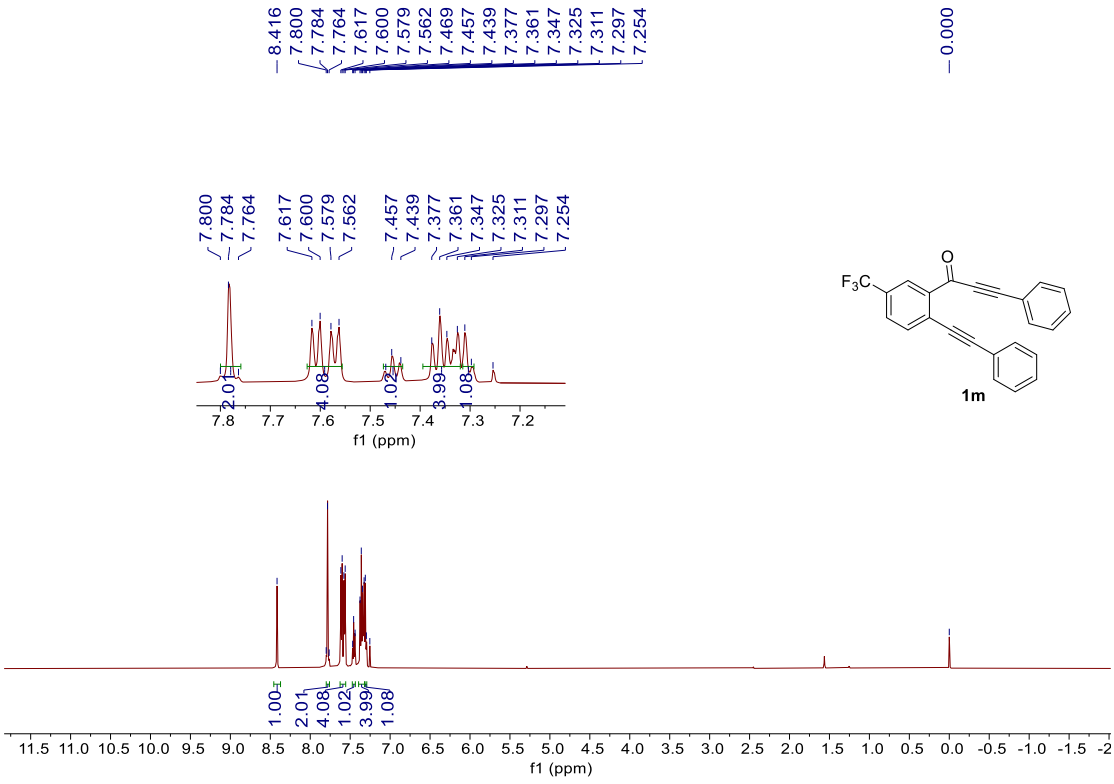
^{1}H NMR (500 MHz, CD_2Cl_2)



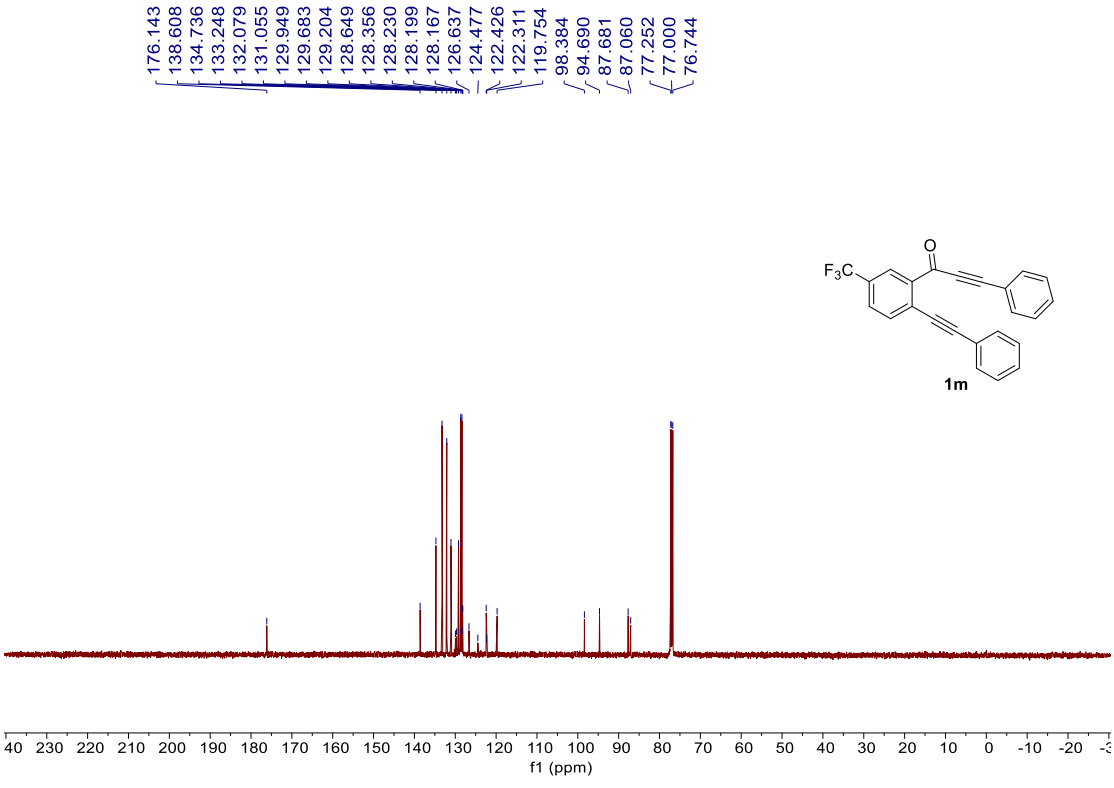
^{13}C NMR (125 MHz, CD_2Cl_2)



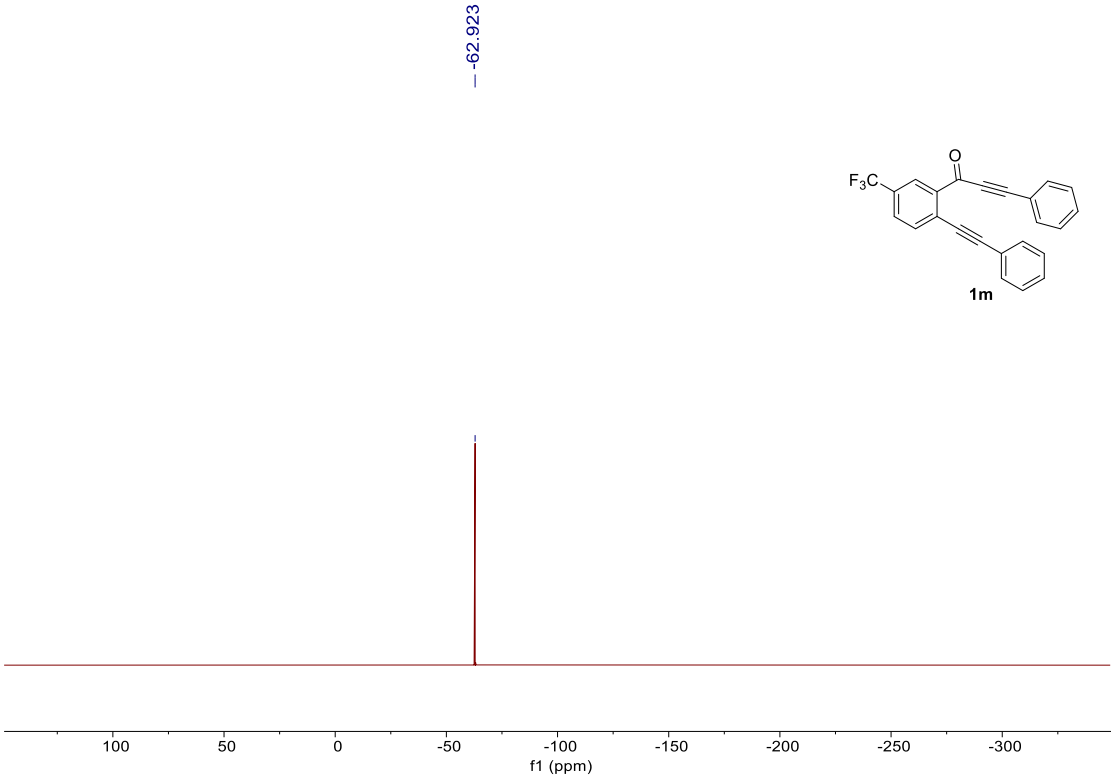
^{1}H NMR (500 MHz, $CDCl_3$)



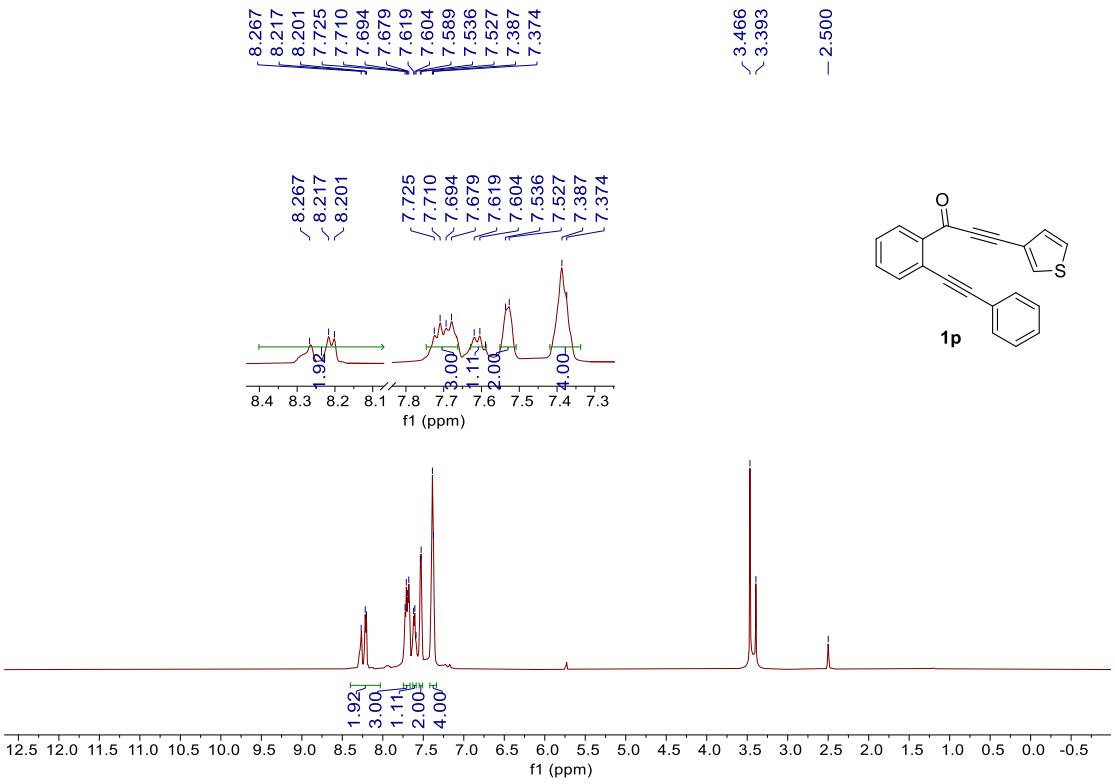
^{13}C NMR (125 MHz, $CDCl_3$)



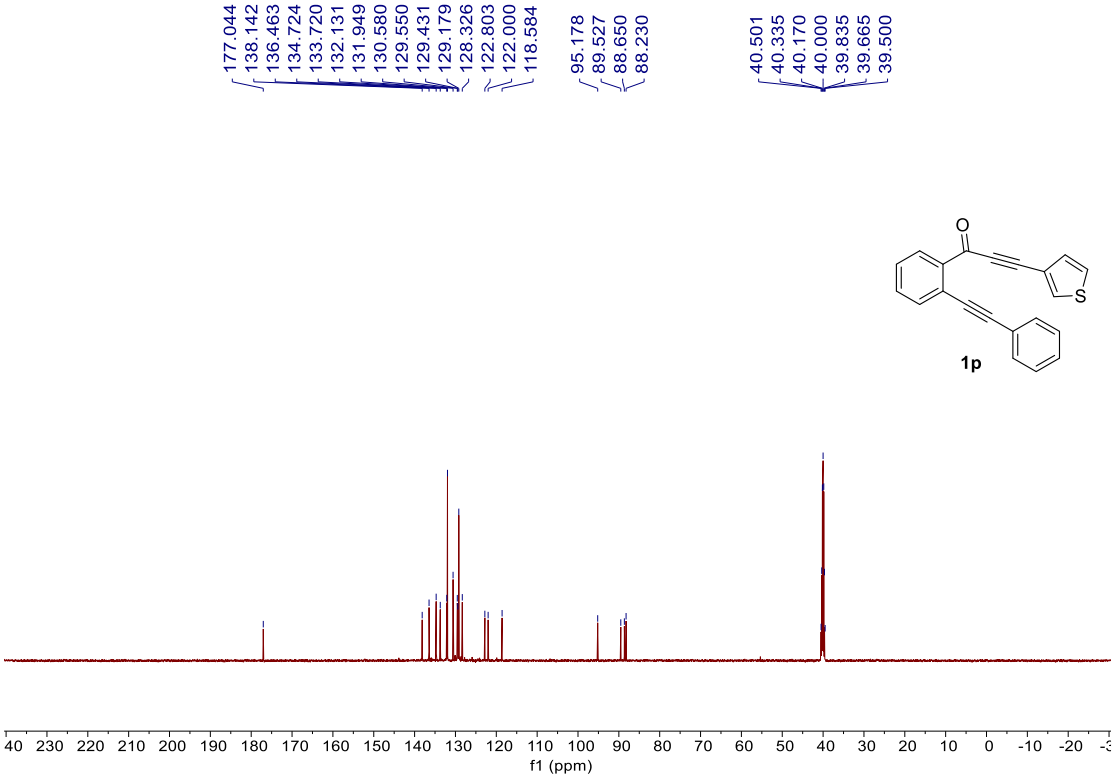
^{19}F NMR (471 MHz, $CDCl_3$)



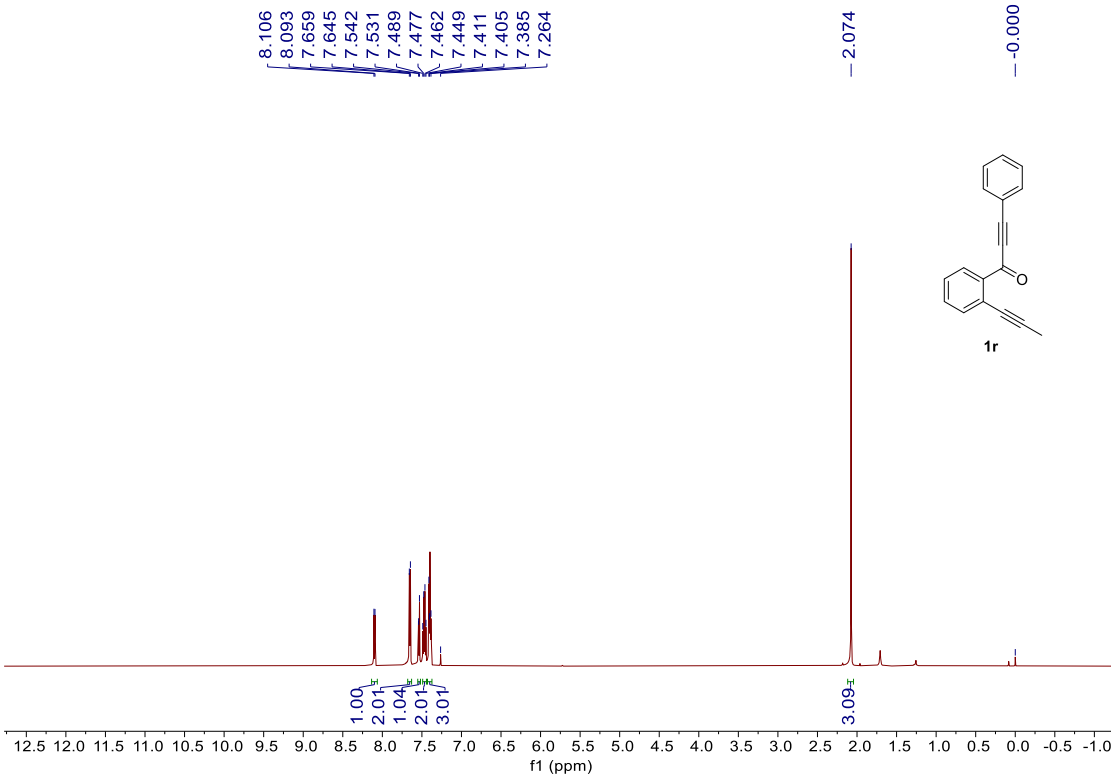
^{1}H NMR (500 MHz, DMSO-d_6)



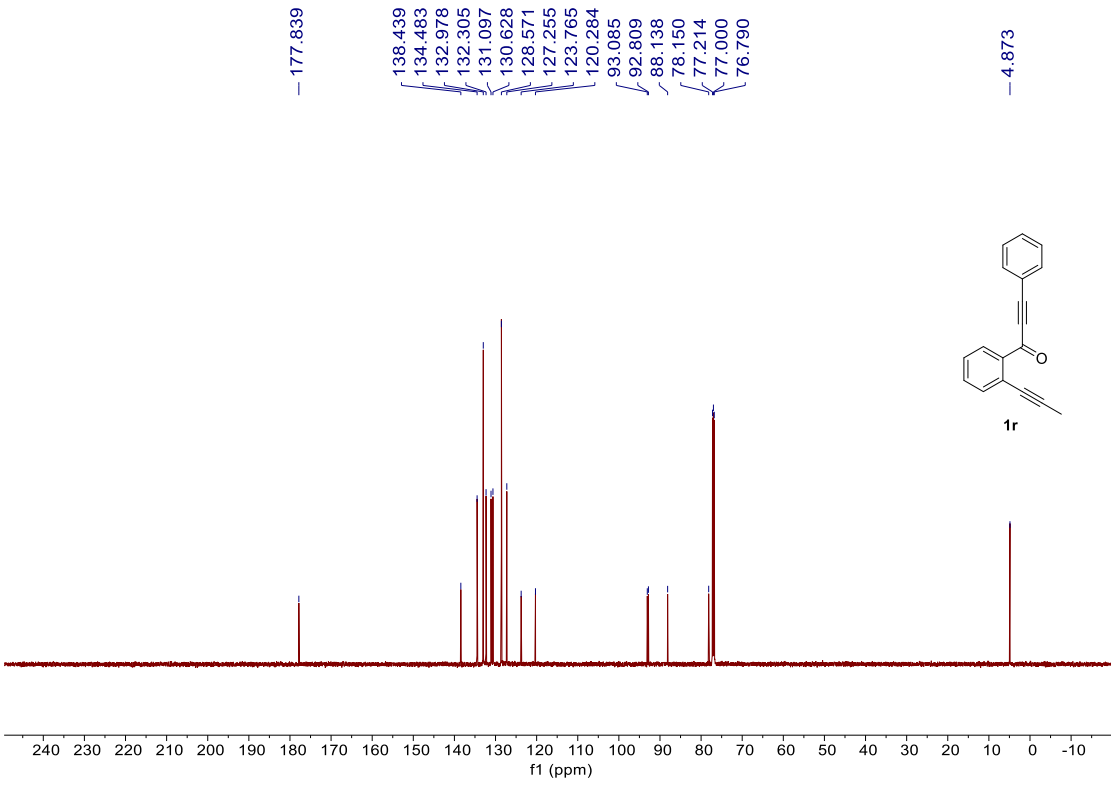
^{13}C NMR (125 MHz, DMSO-d_6)



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

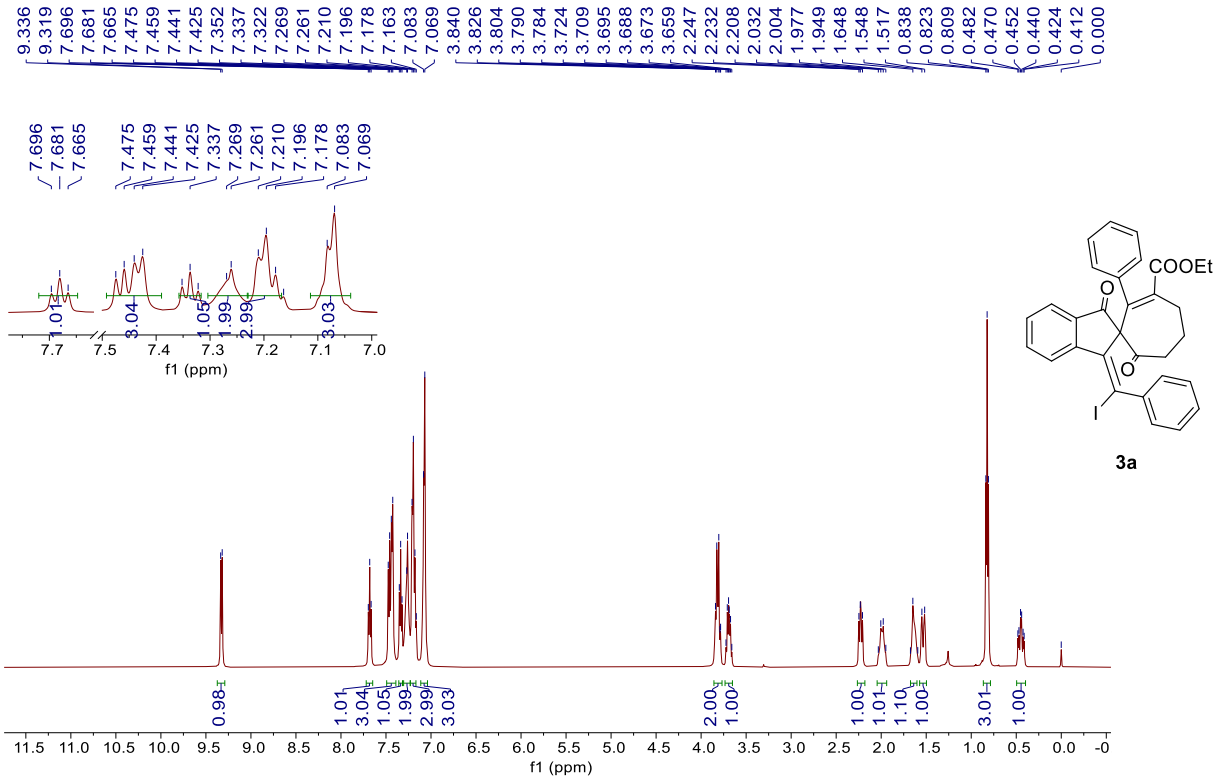


^{13}C NMR (600 MHz, $CDCl_3$)

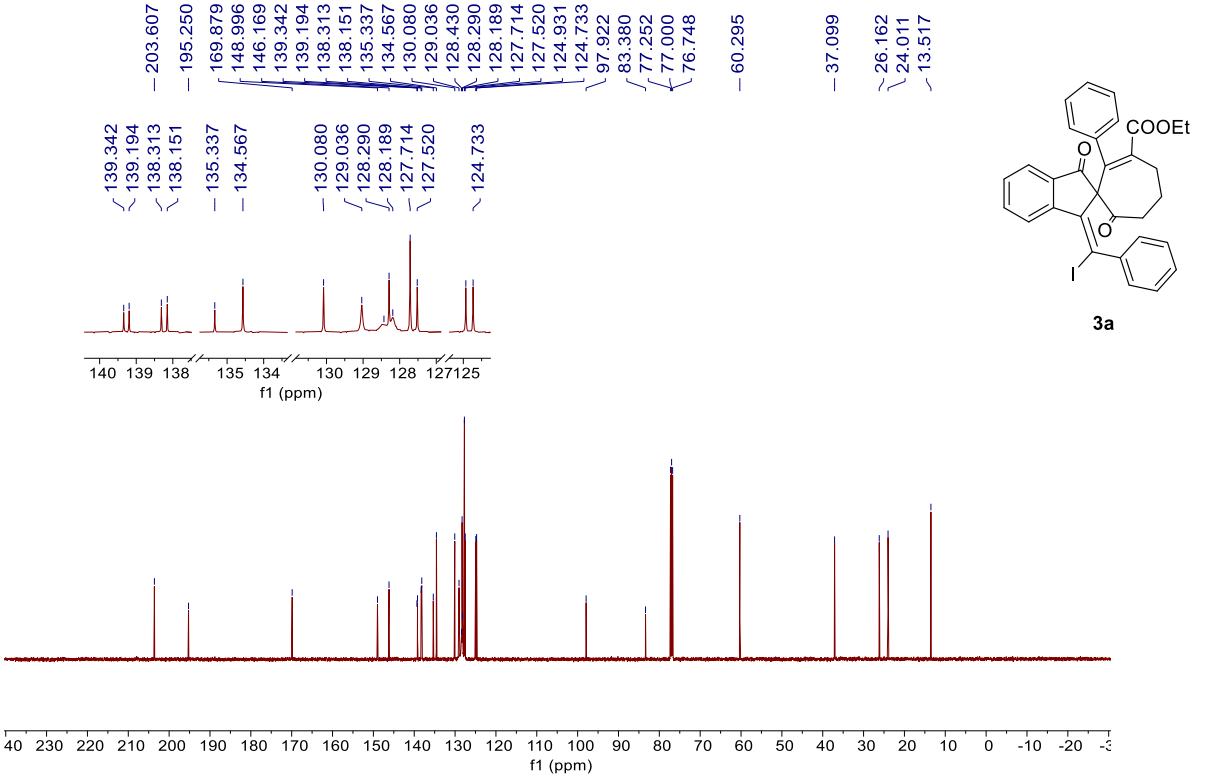


9. Copies of spectra of products

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



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



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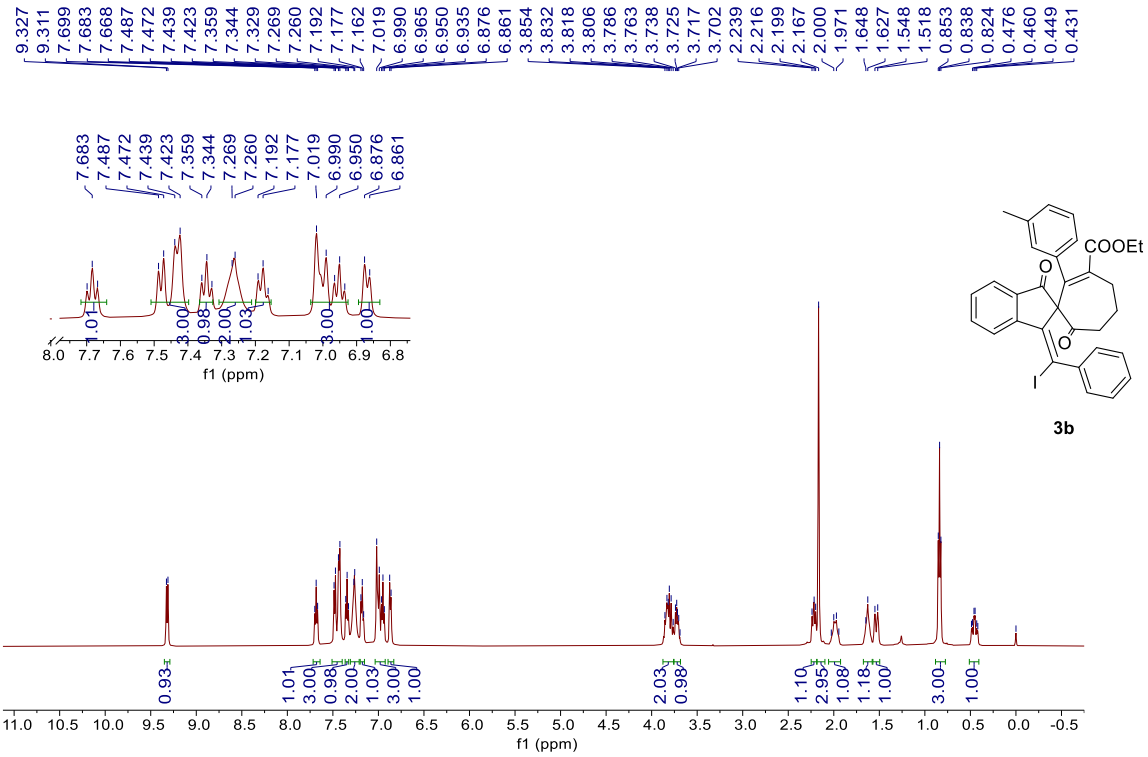

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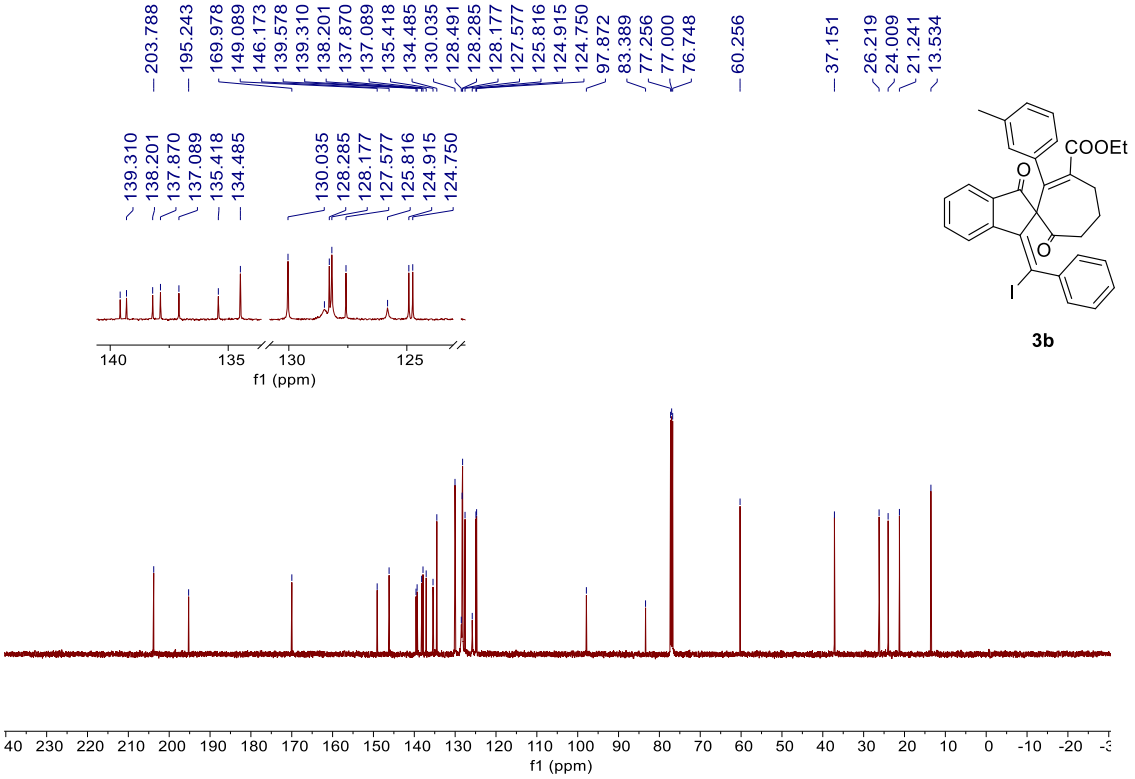

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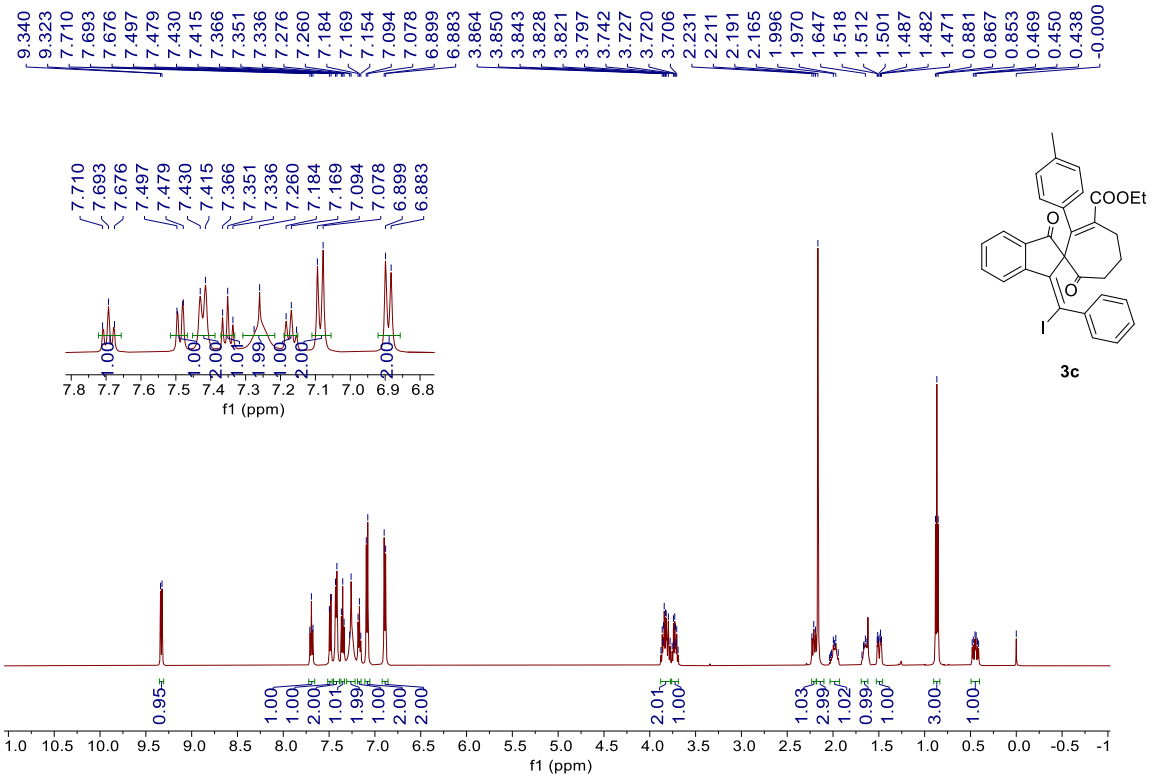
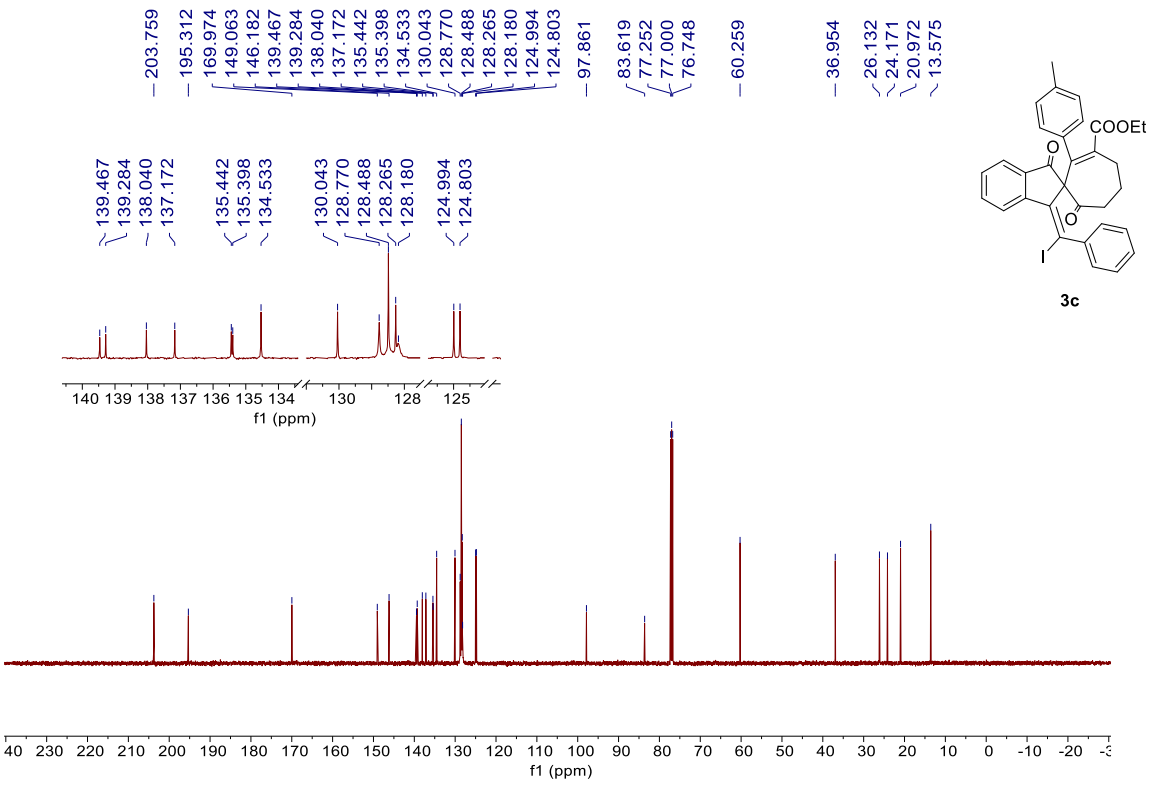


^{13}C NMR (125 MHz, $CDCl_3$)



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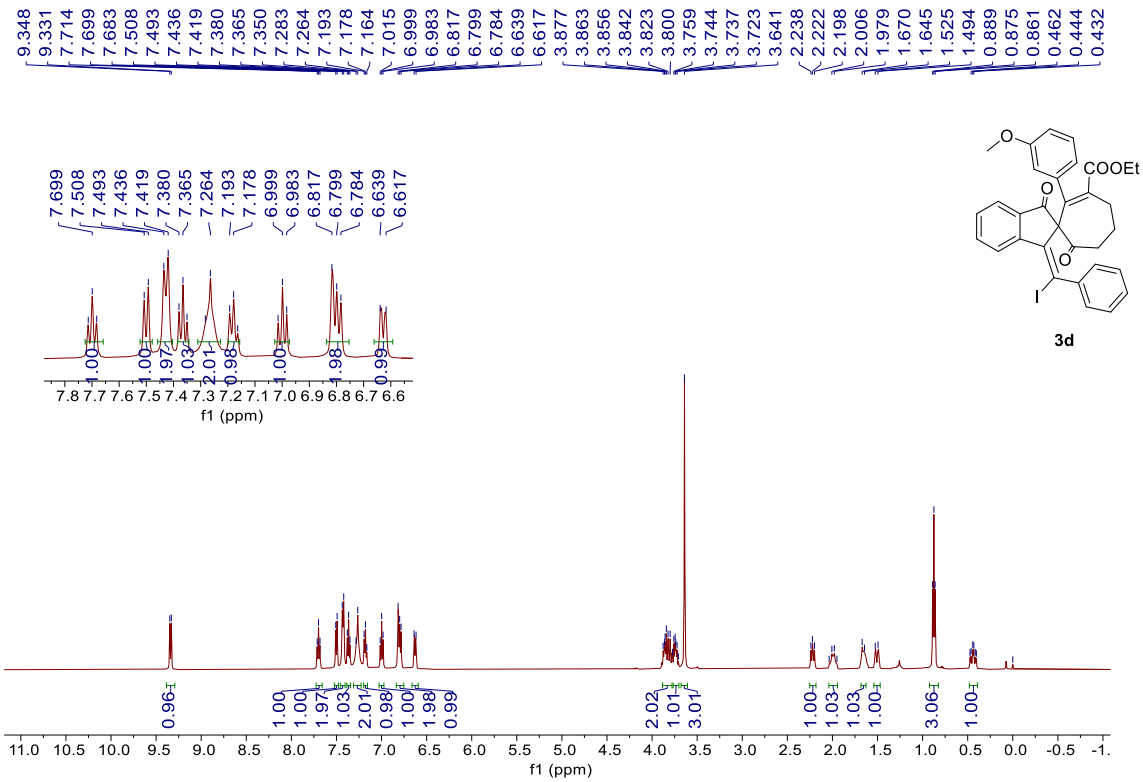
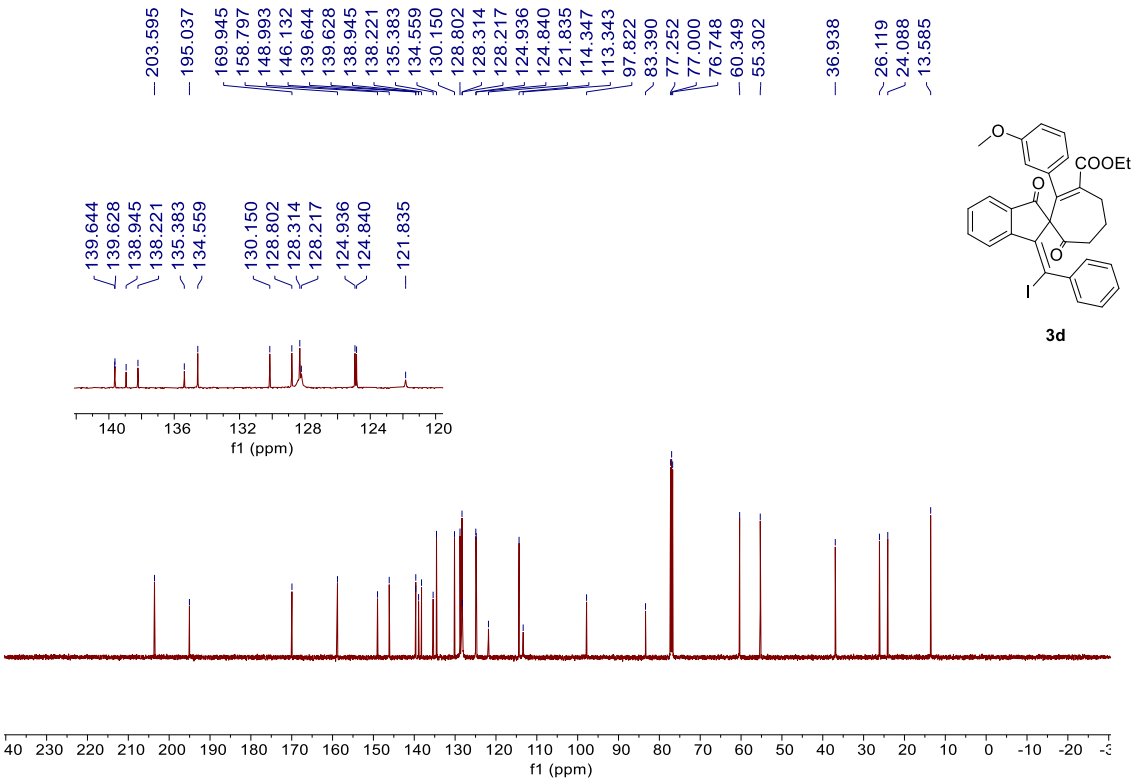


^{13}C NMR (125 MHz, $CDCl_3$)



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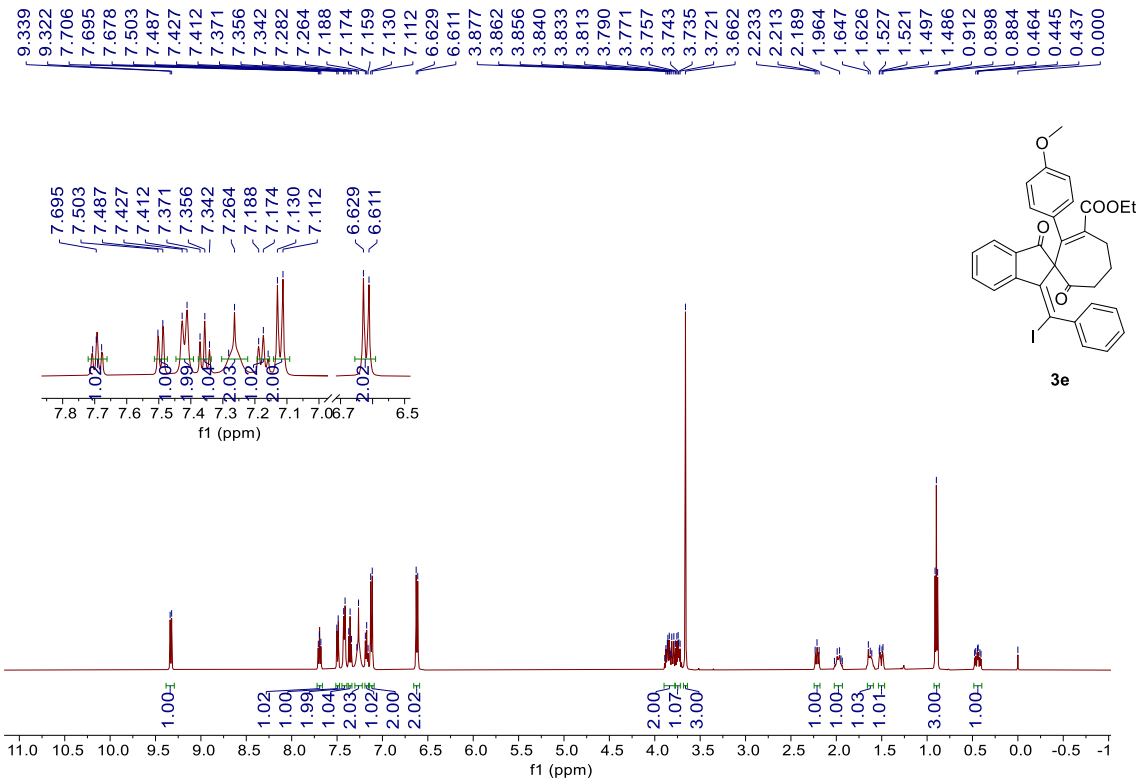

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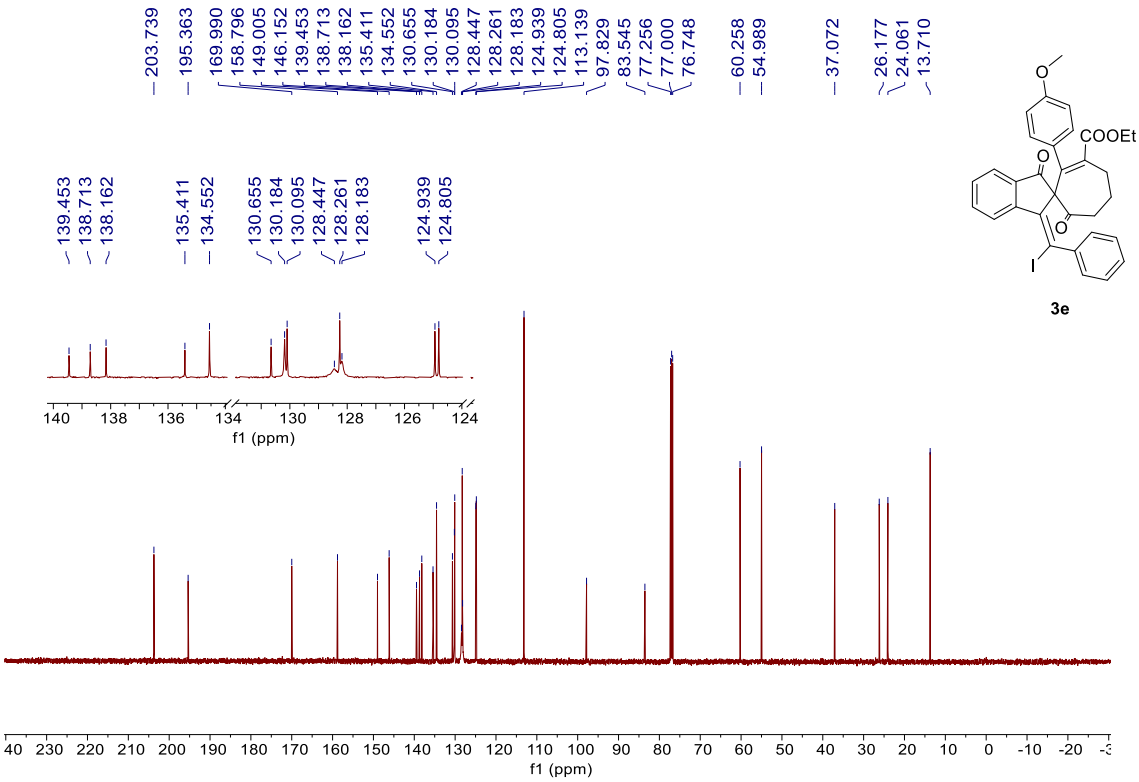

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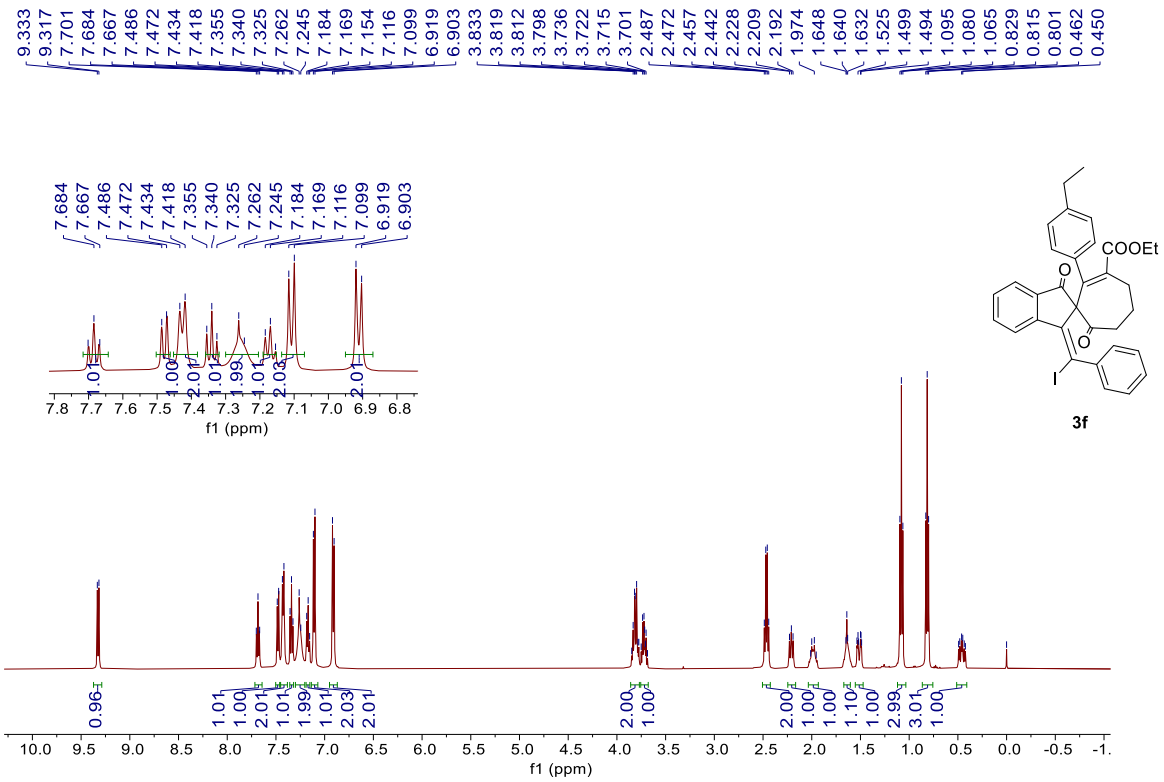
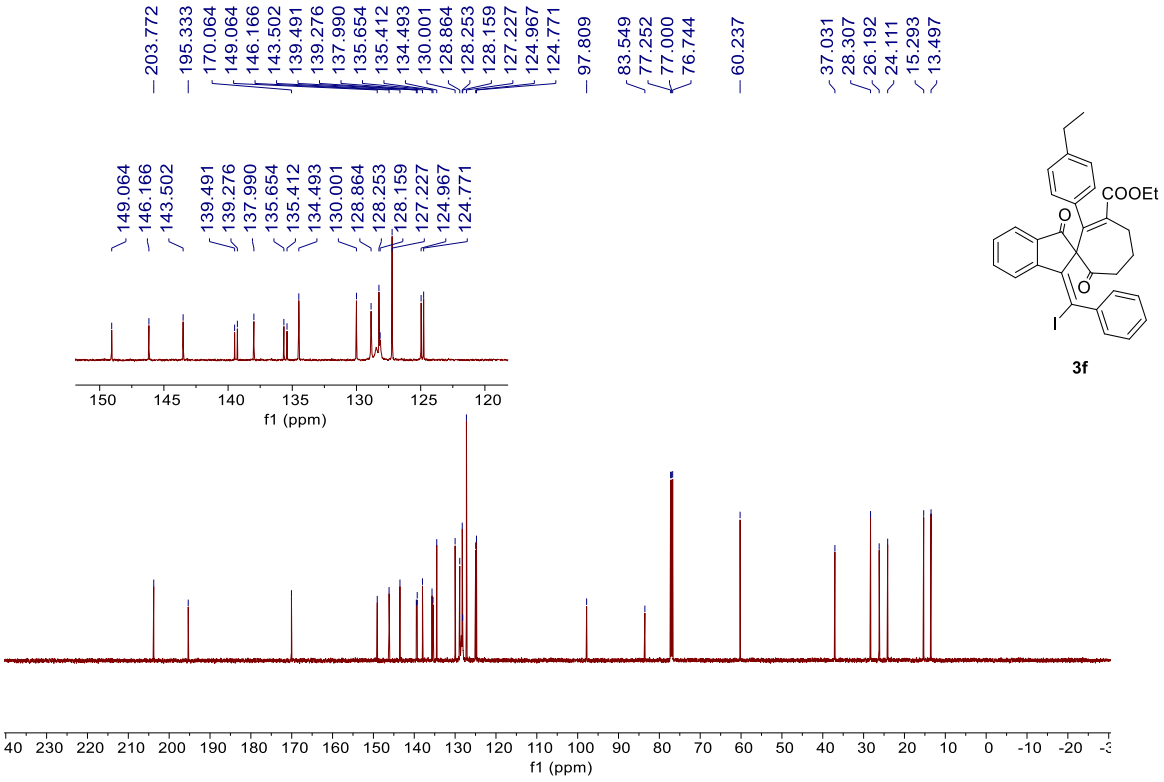
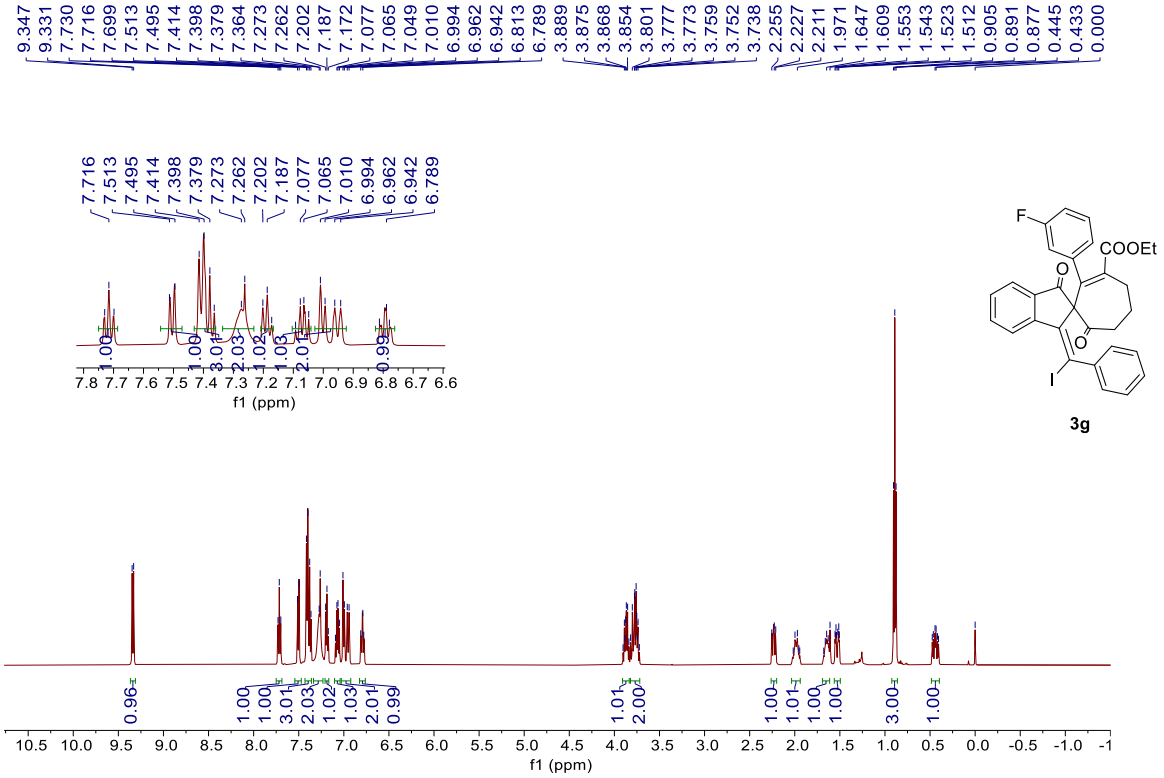


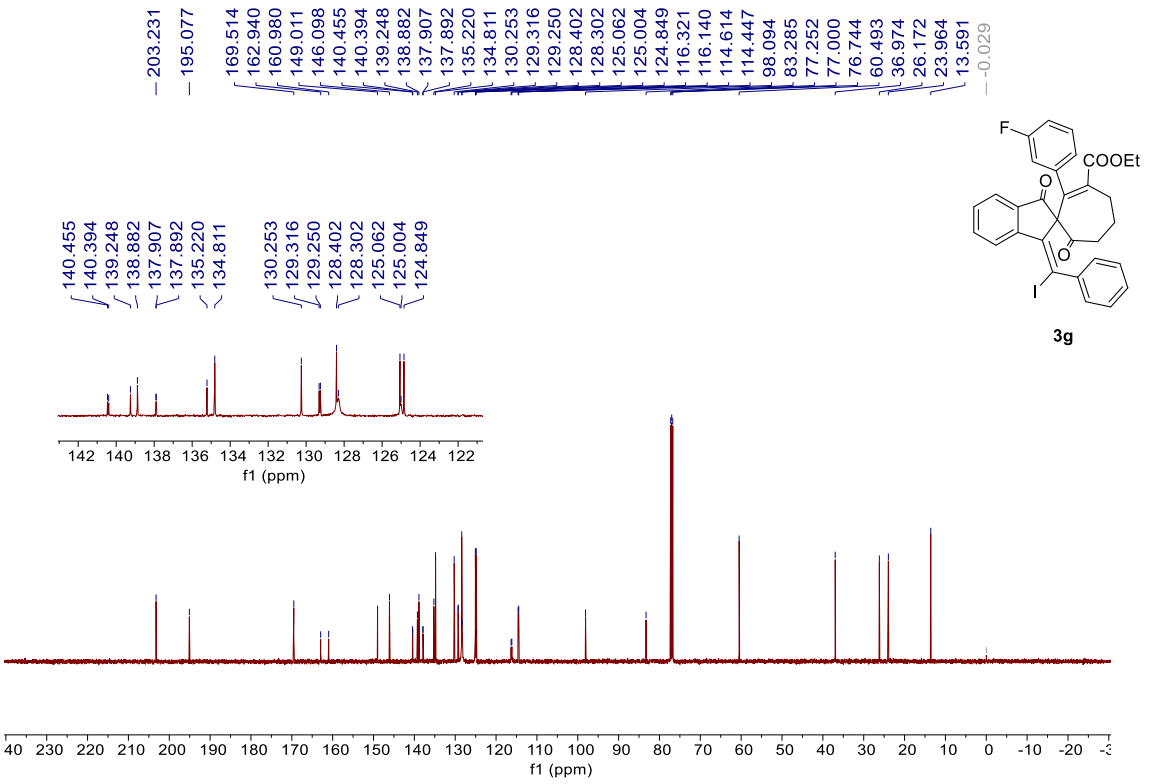
^{13}C NMR (125 MHz, $CDCl_3$)



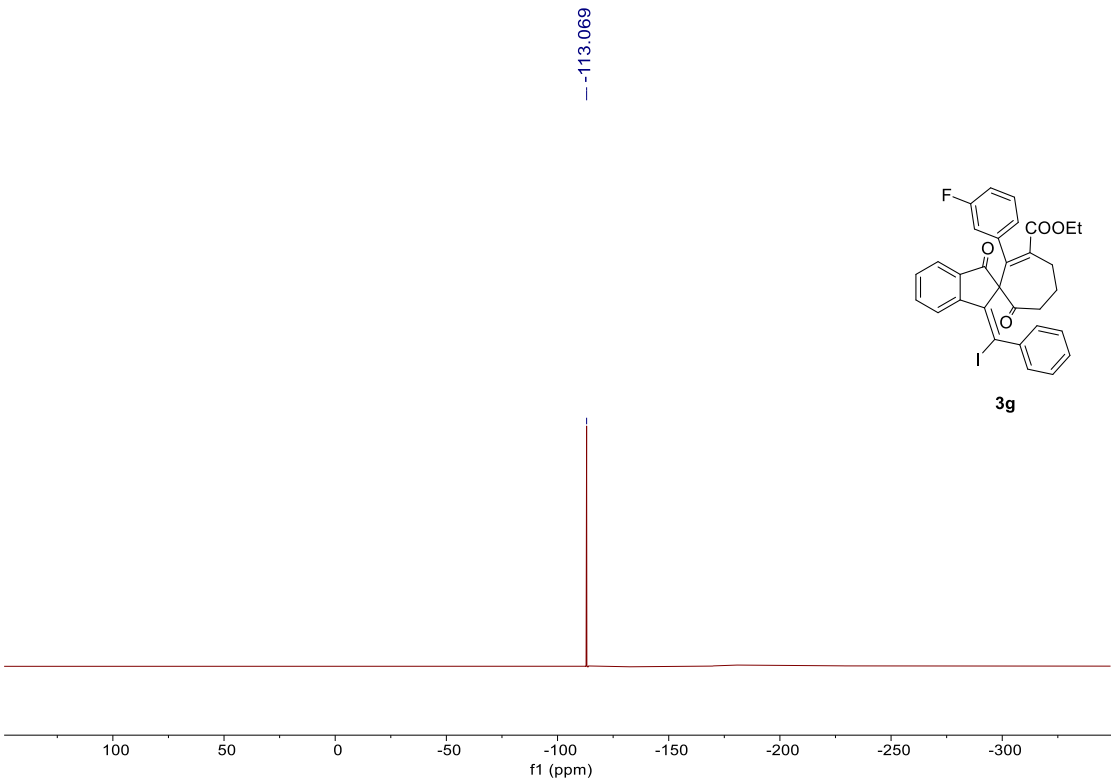
^{1}H NMR (500 MHz, $CDCl_3$)



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



^{19}F NMR (471 MHz, $CDCl_3$)



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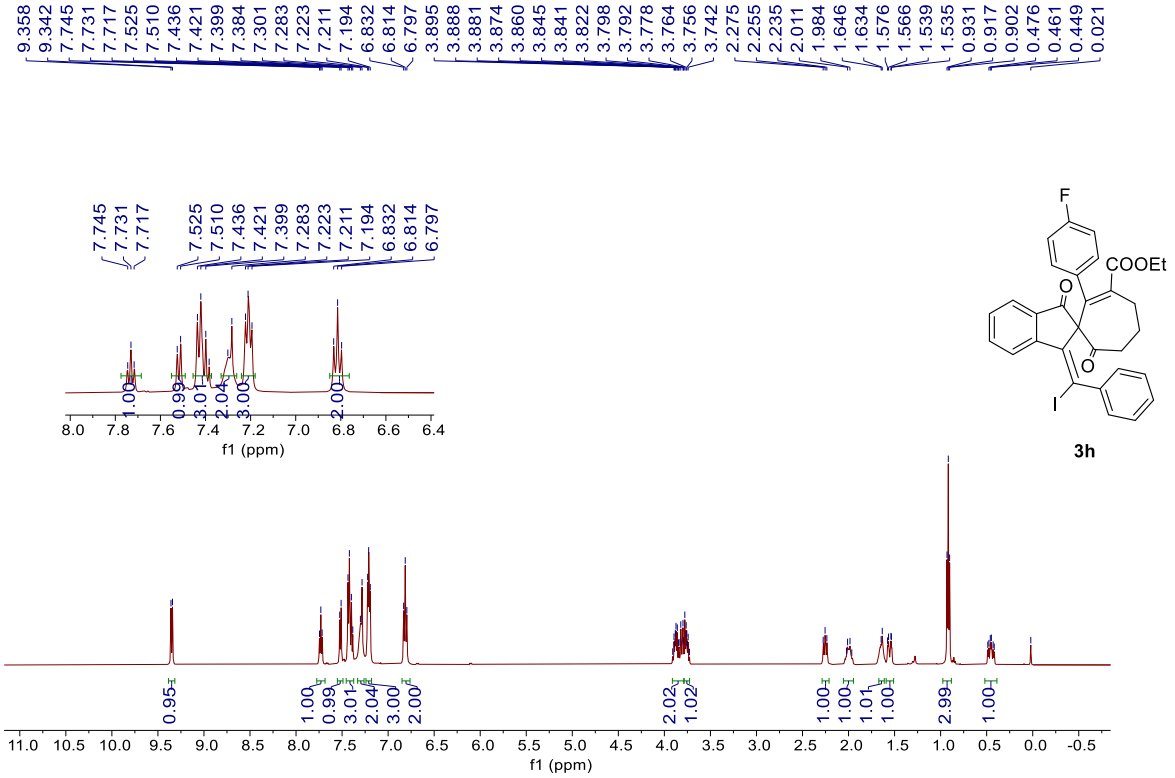

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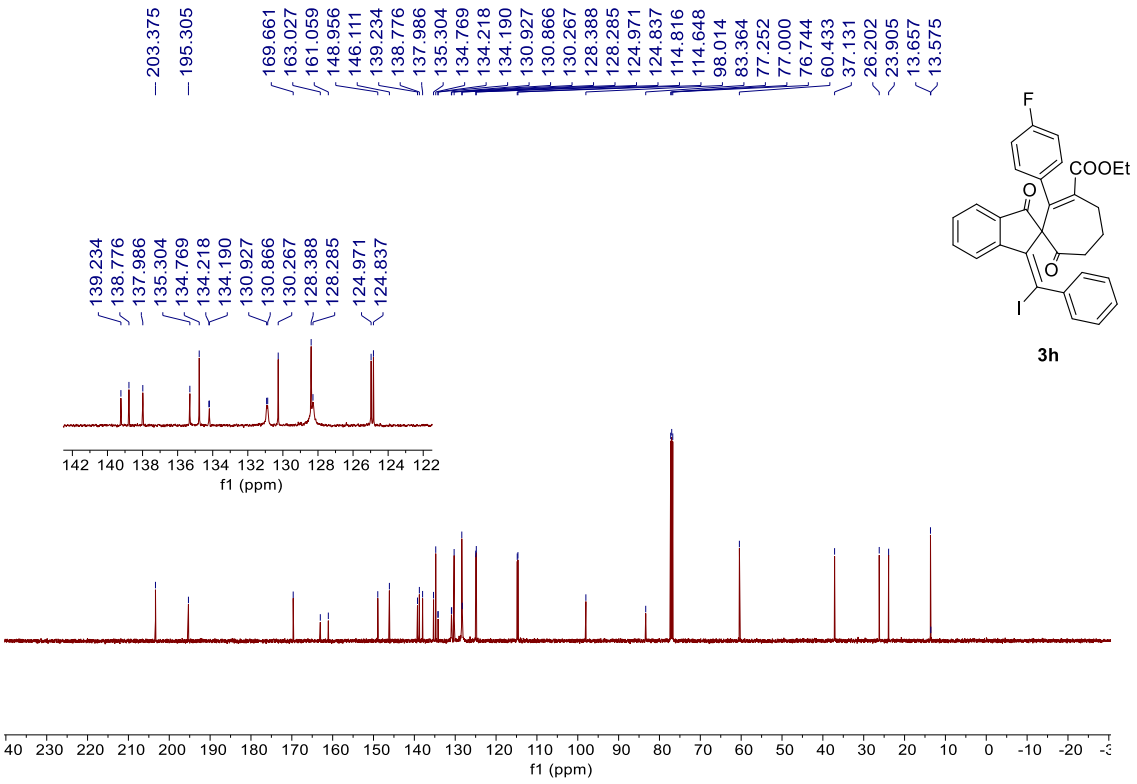

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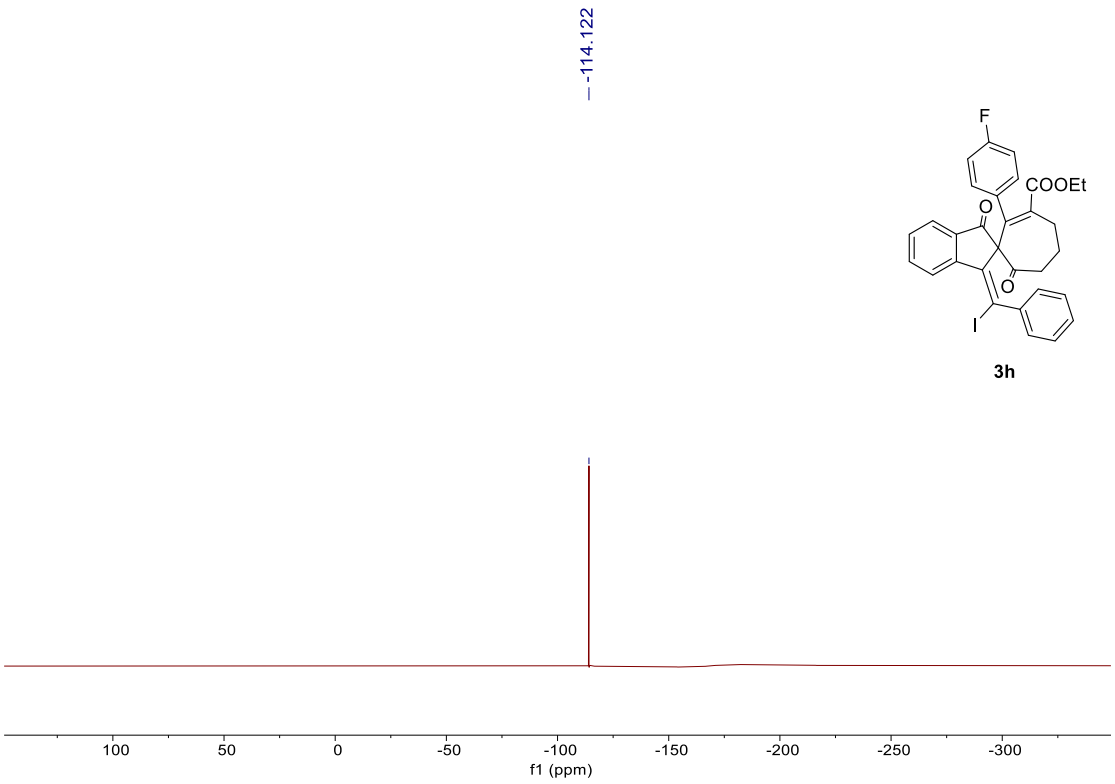

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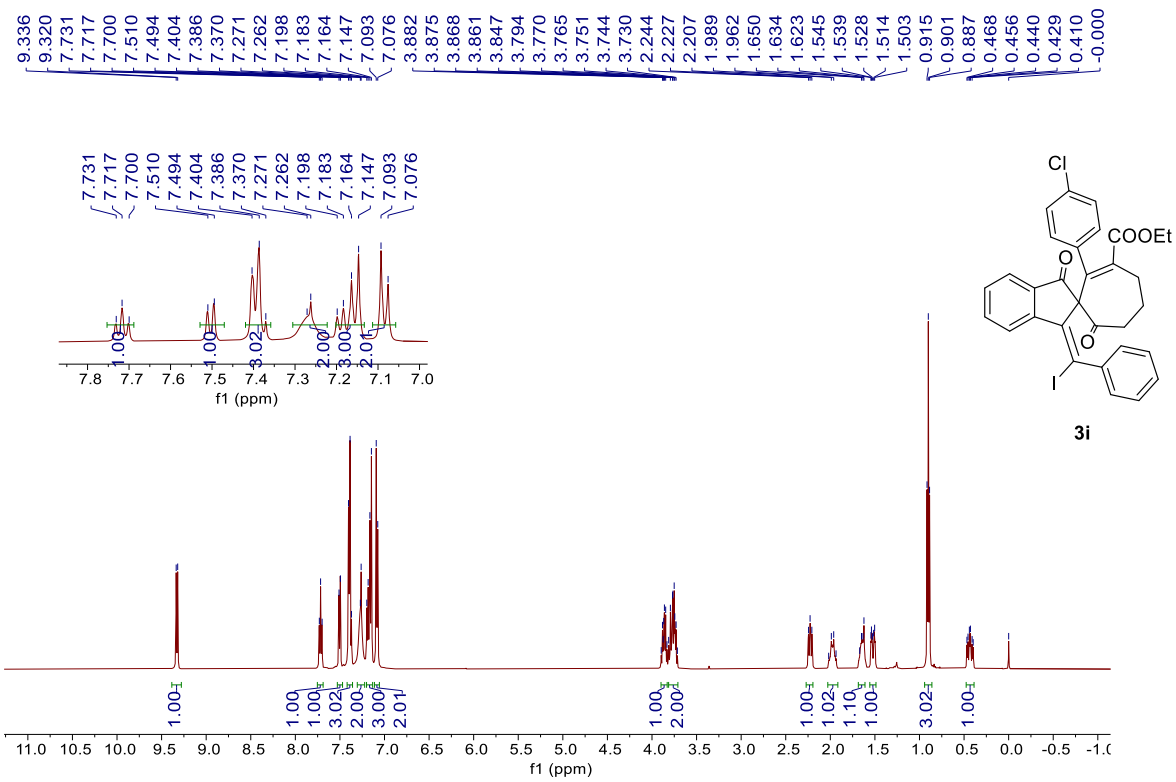

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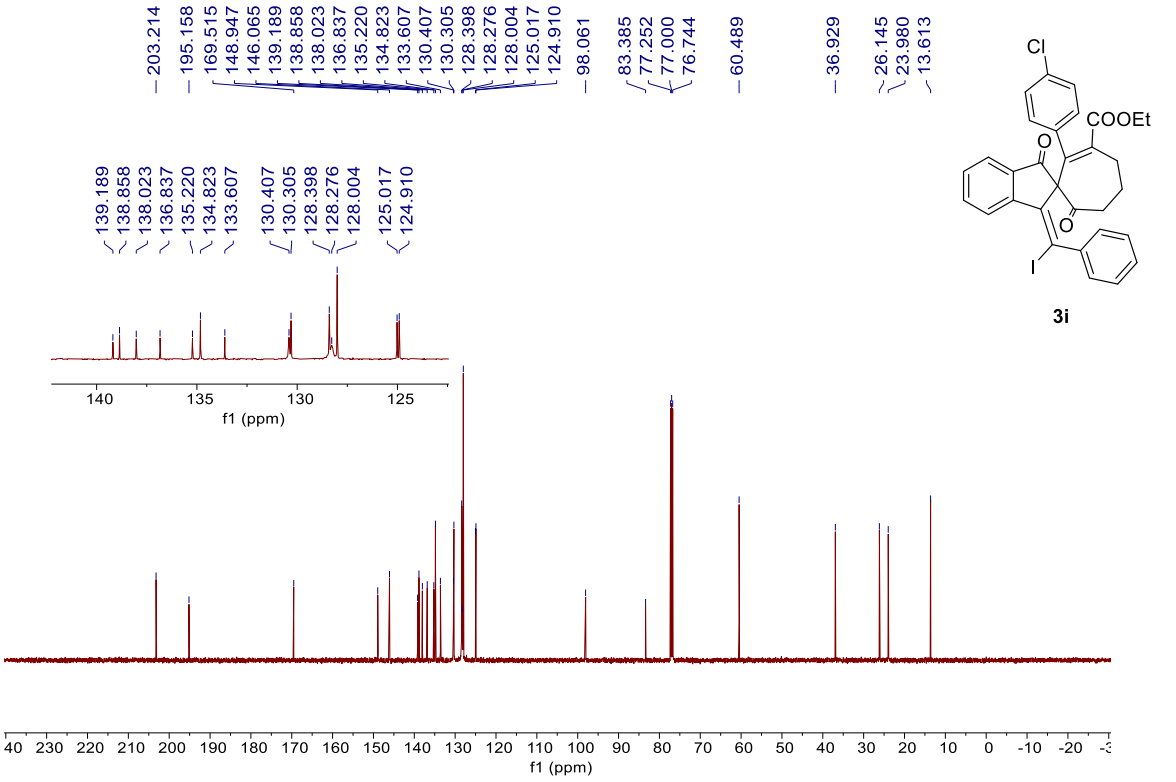

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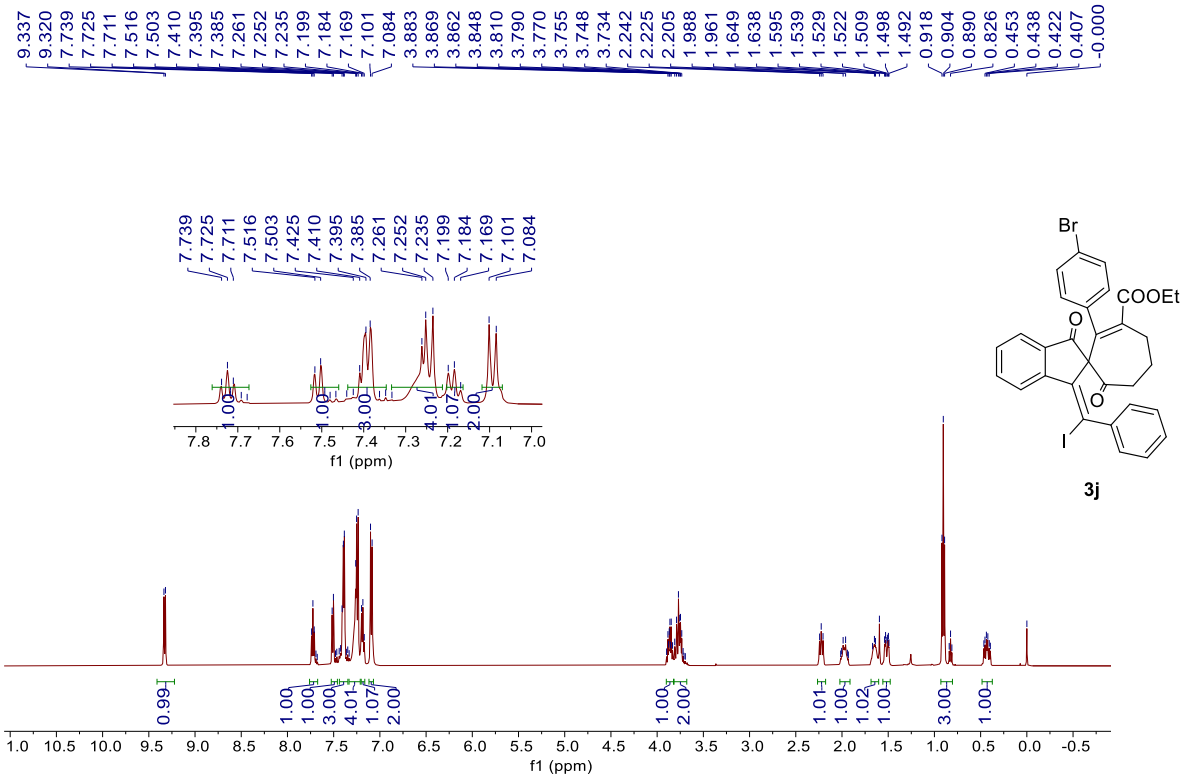
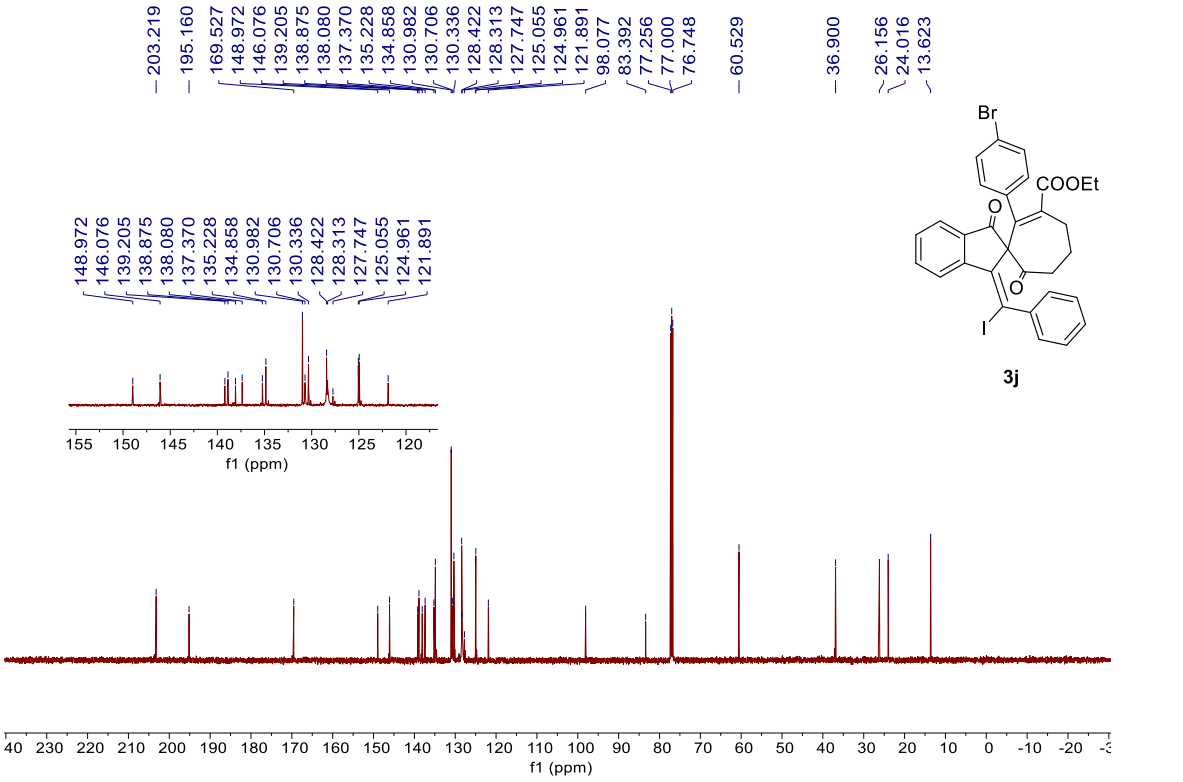
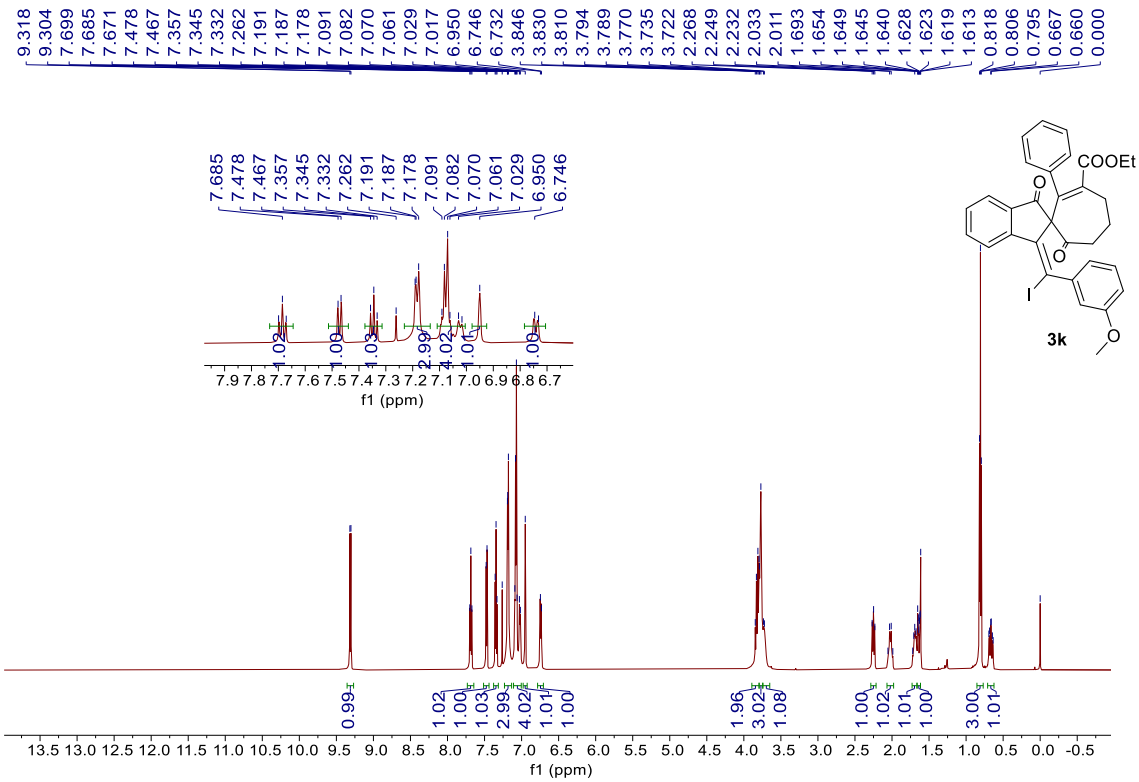


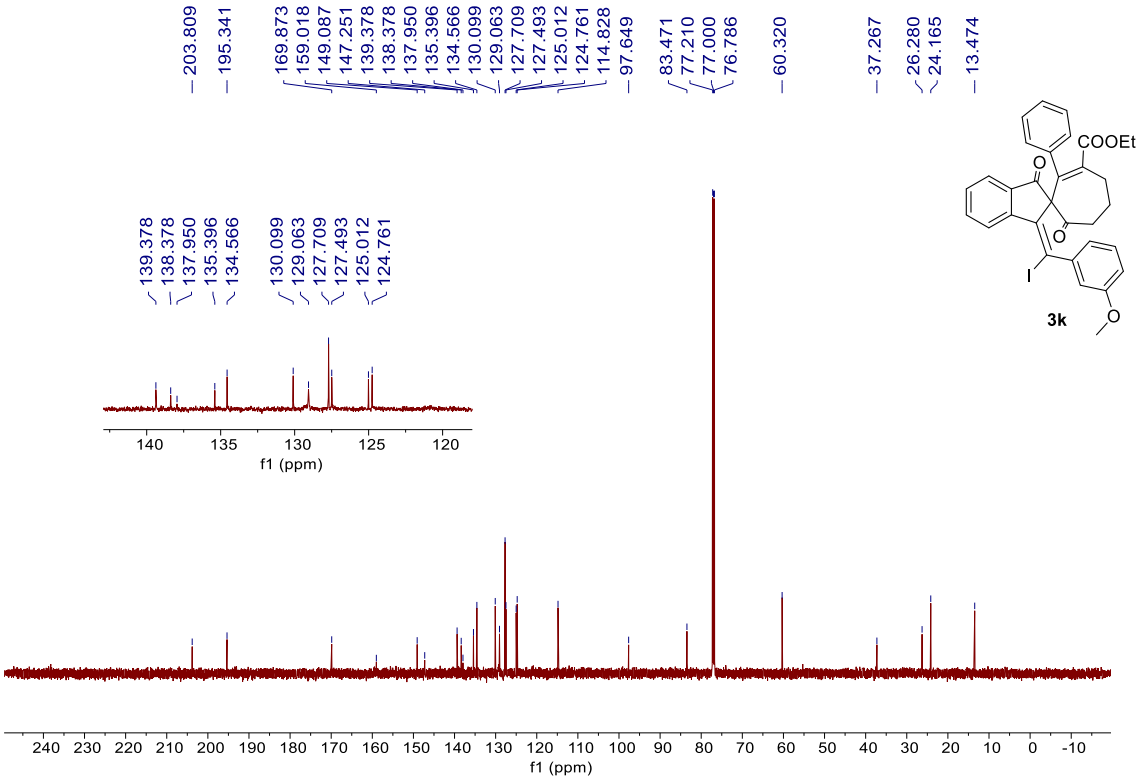
^{13}C NMR (125 MHz, $CDCl_3$)



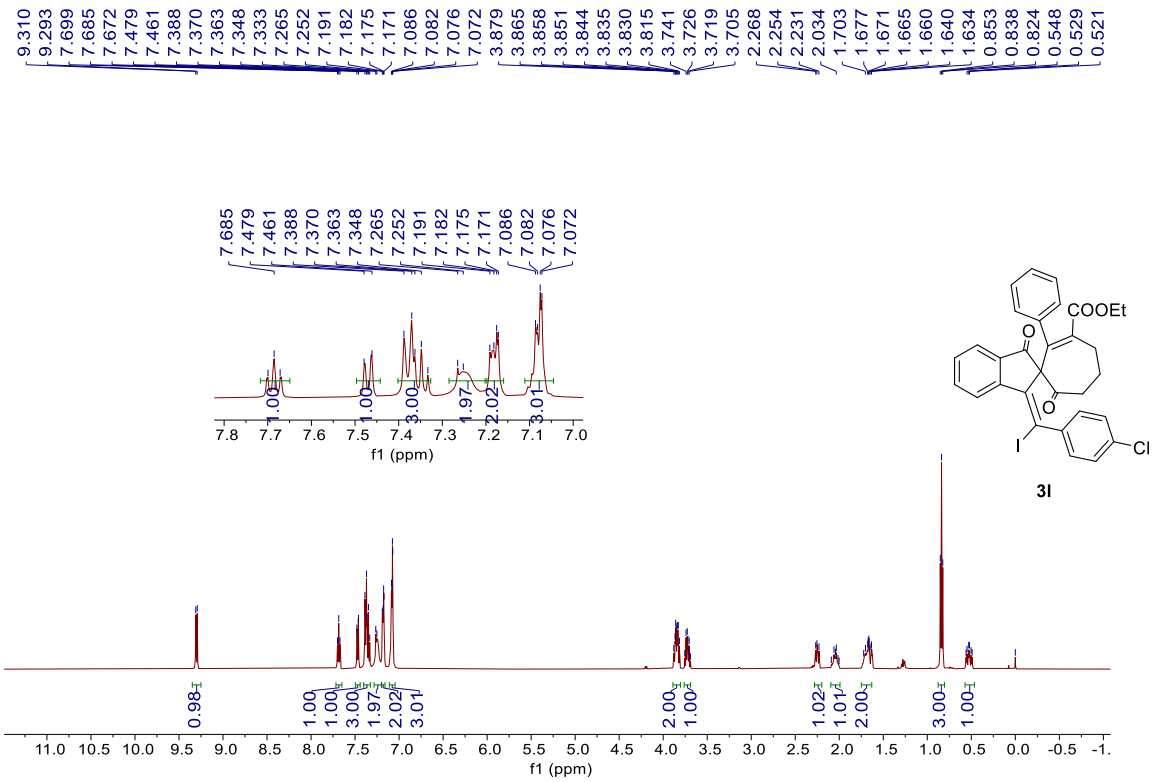
^{1}H NMR (600 MHz, $CDCl_3$)



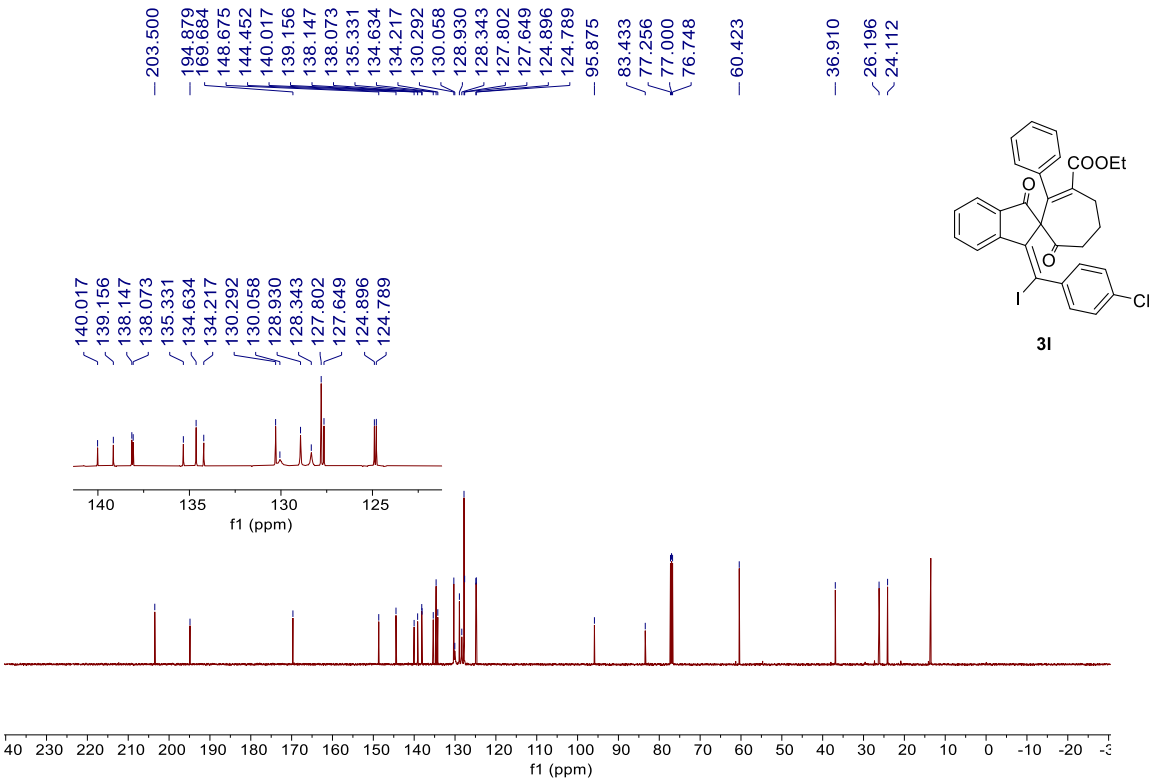
^{13}C NMR (150 MHz, $CDCl_3$)



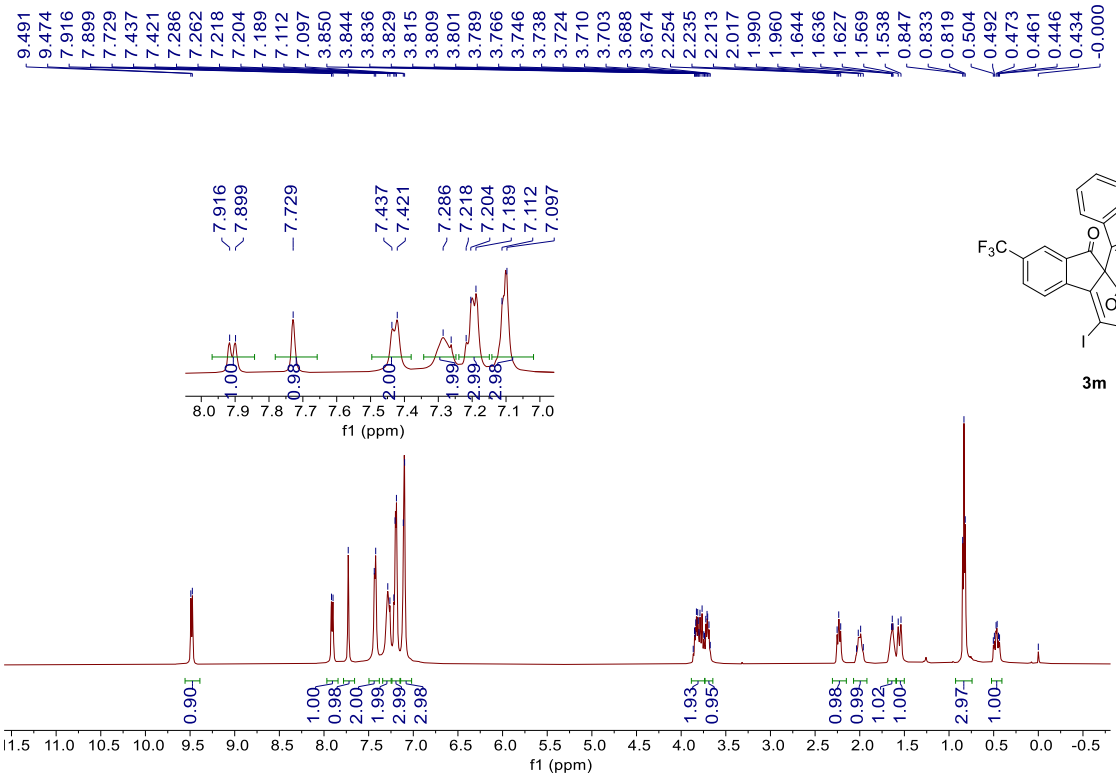
^{1}H NMR (500 MHz, $CDCl_3$)



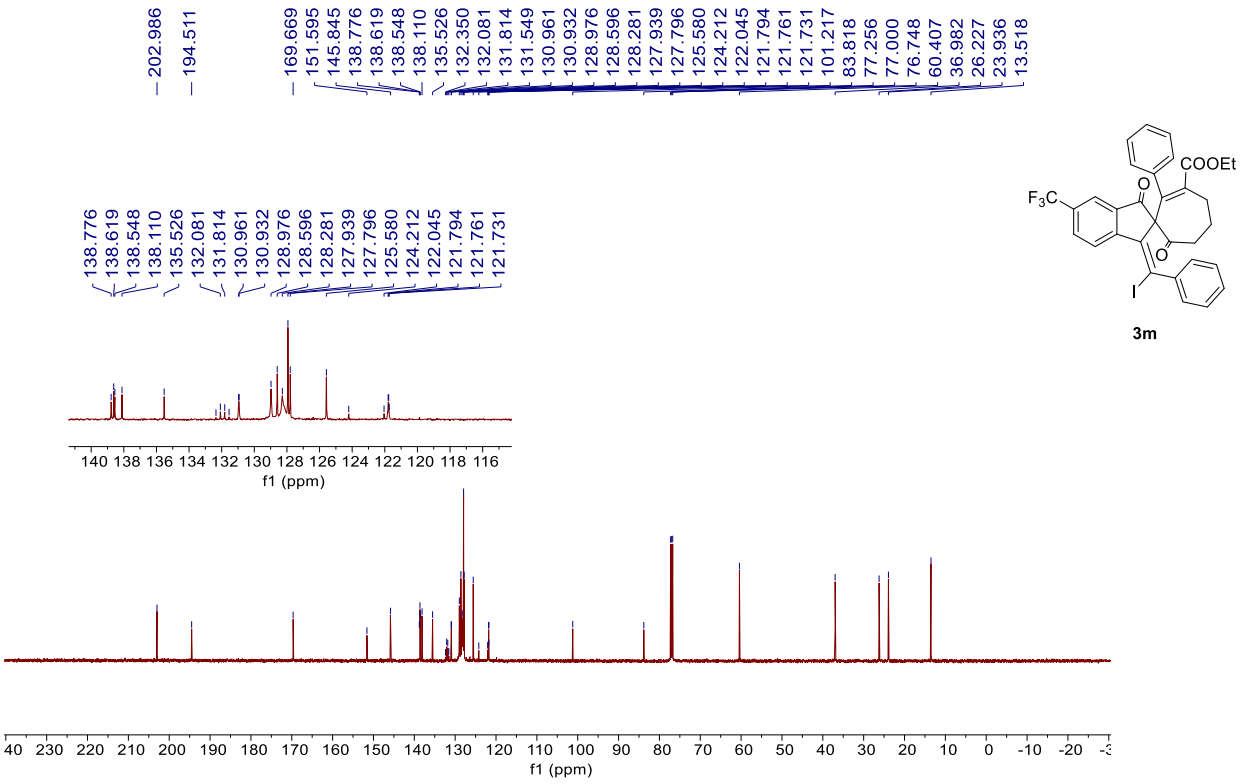
^{13}C NMR (125 MHz, $CDCl_3$)



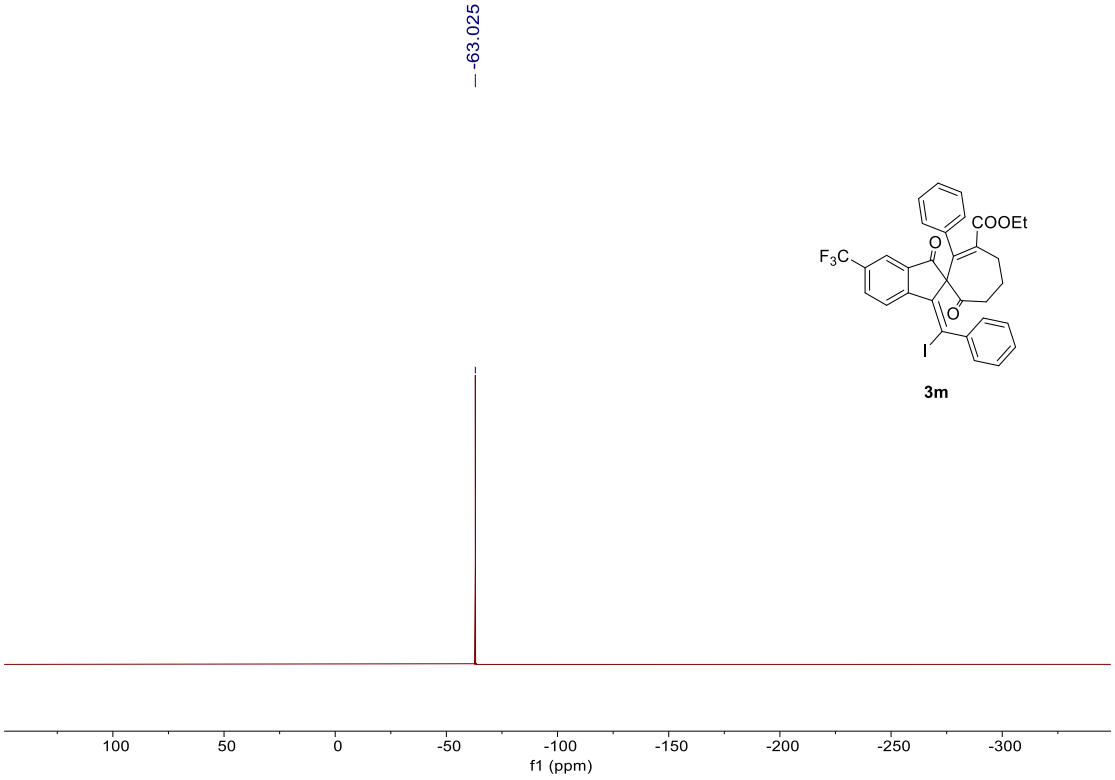
^{1}H NMR (500 MHz, $CDCl_3$)



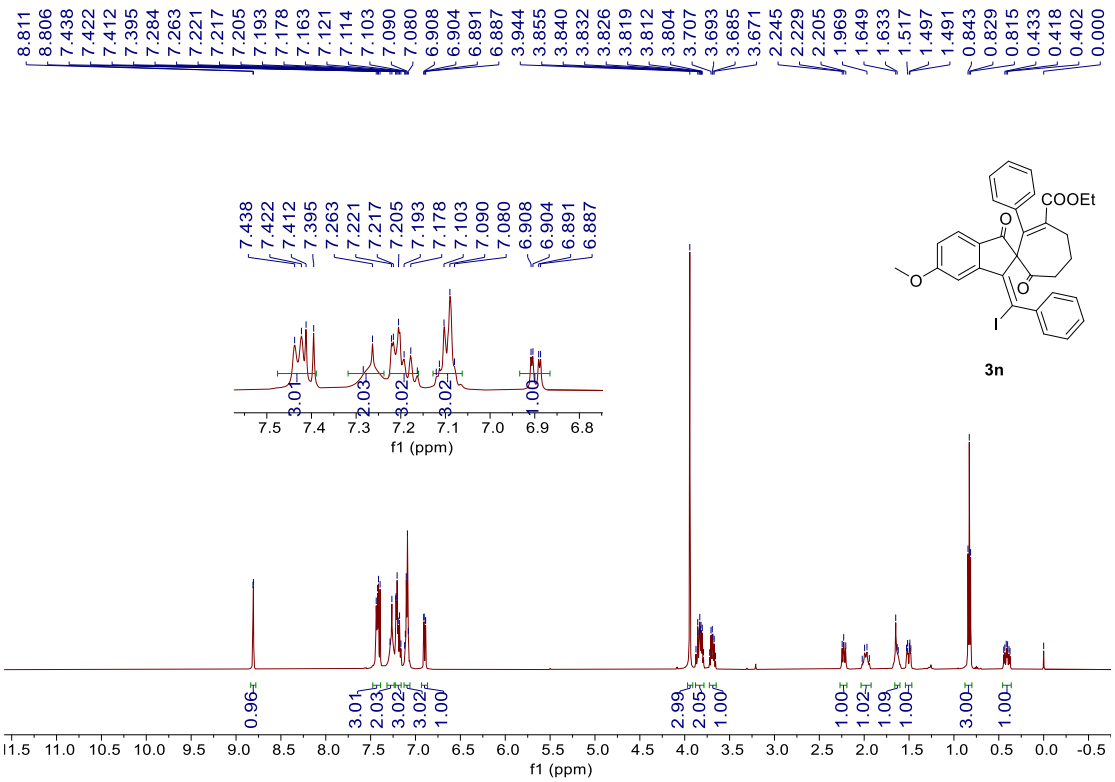
^{13}C NMR (125 MHz, $CDCl_3$)



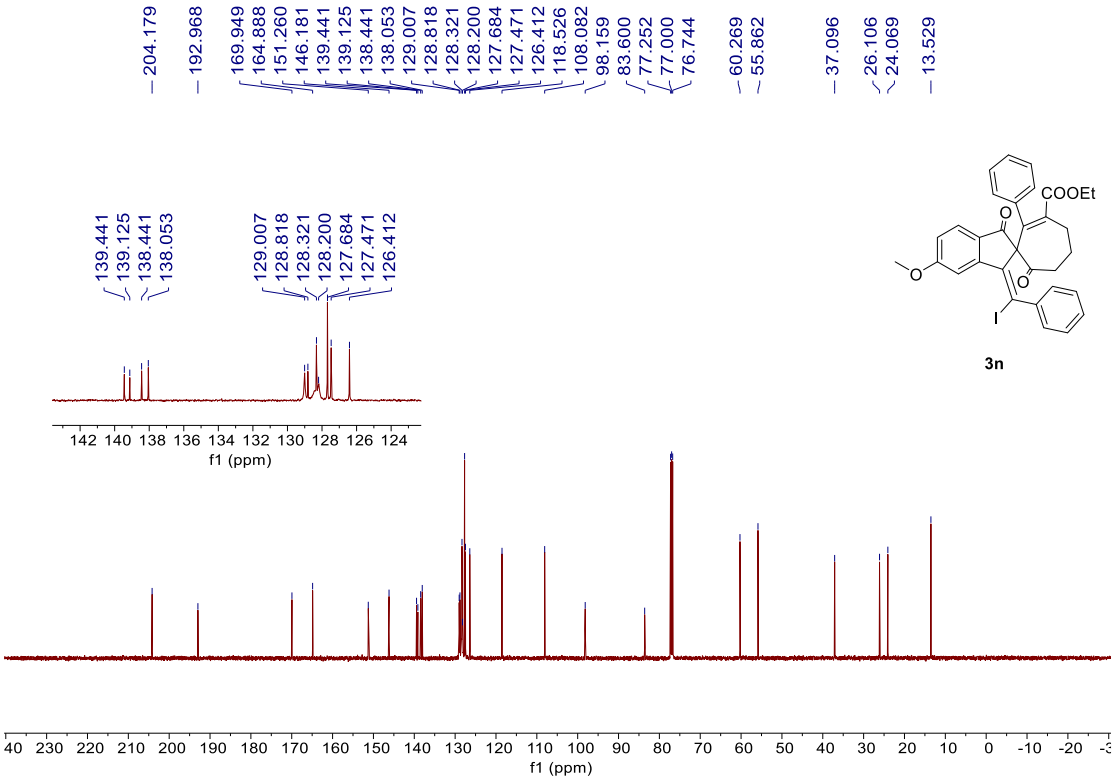
^{19}F NMR (471 MHz, $CDCl_3$)



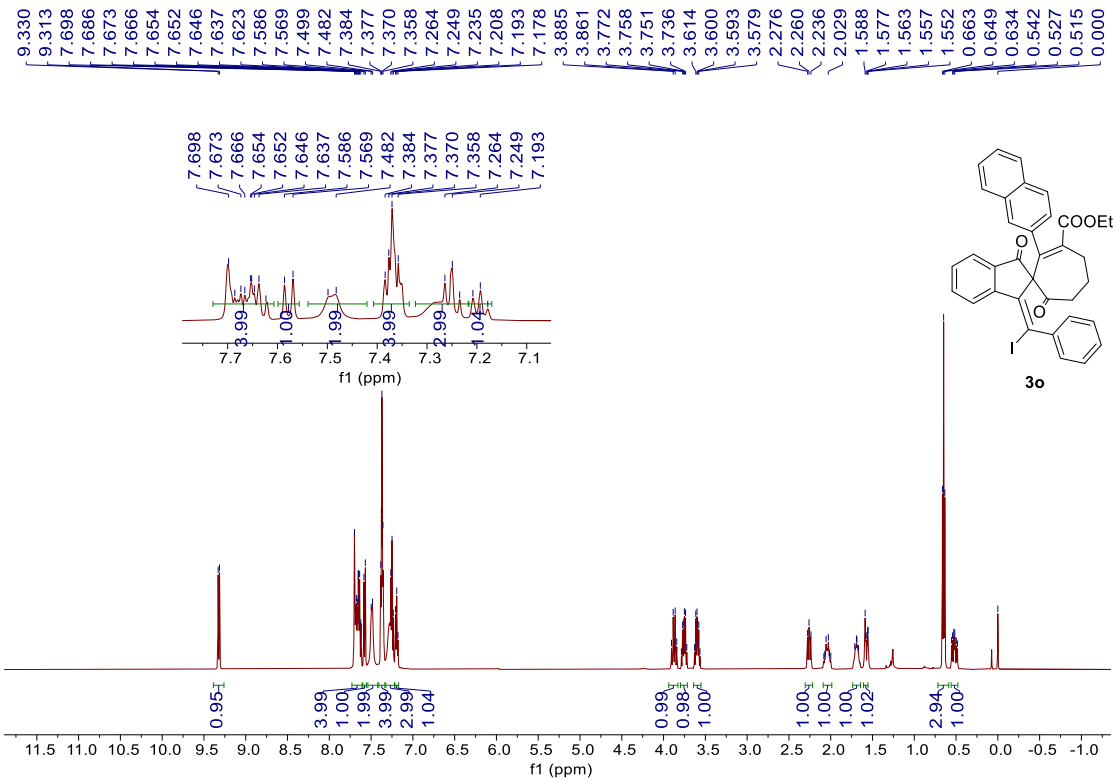
^{1}H NMR (500 MHz, $CDCl_3$)



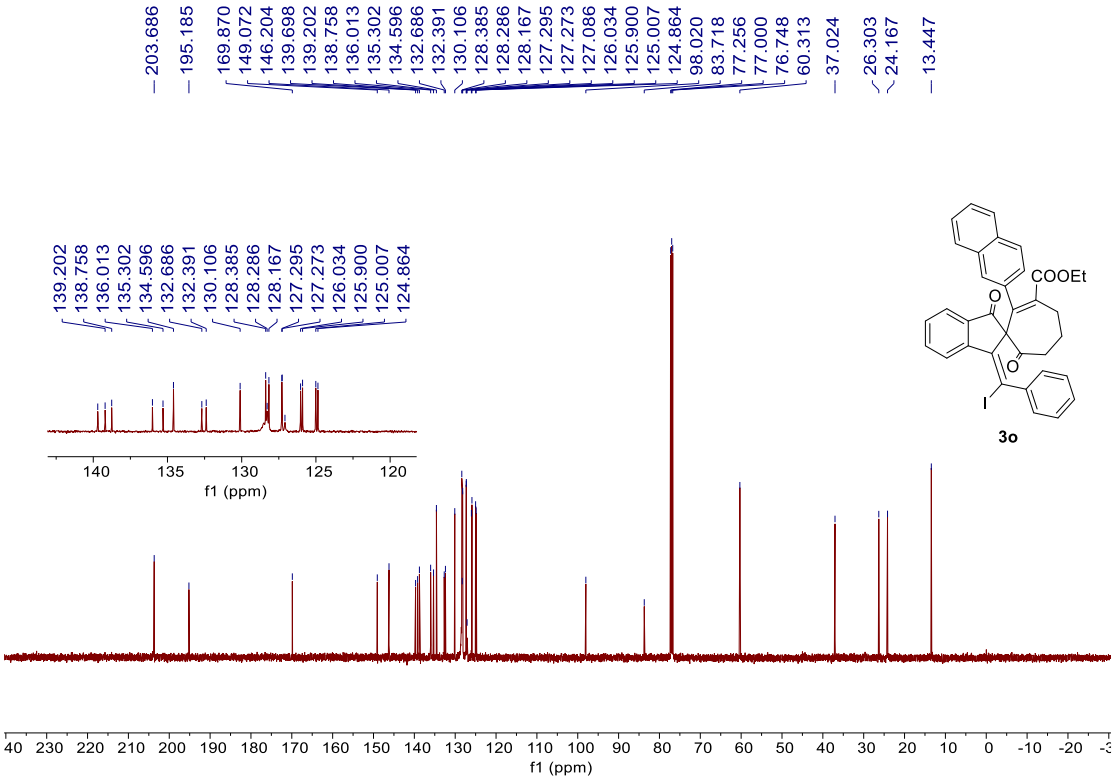
^{13}C NMR (125 MHz, $CDCl_3$)



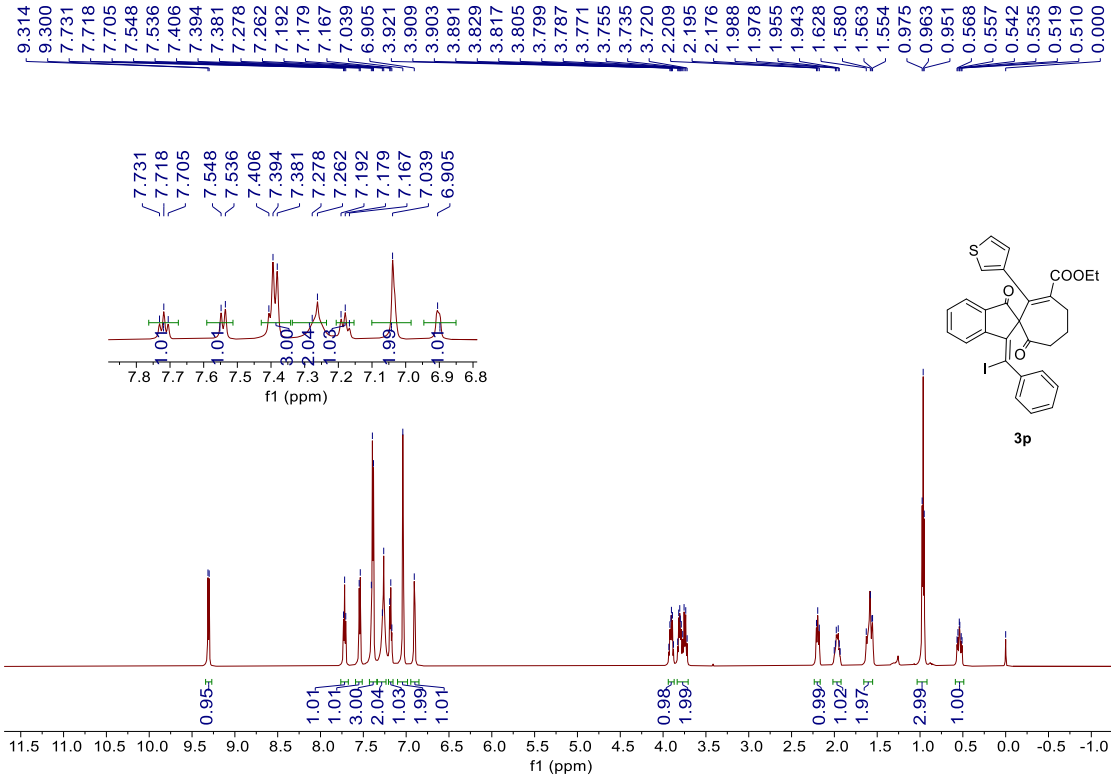
^{1}H NMR (500 MHz, $CDCl_3$)



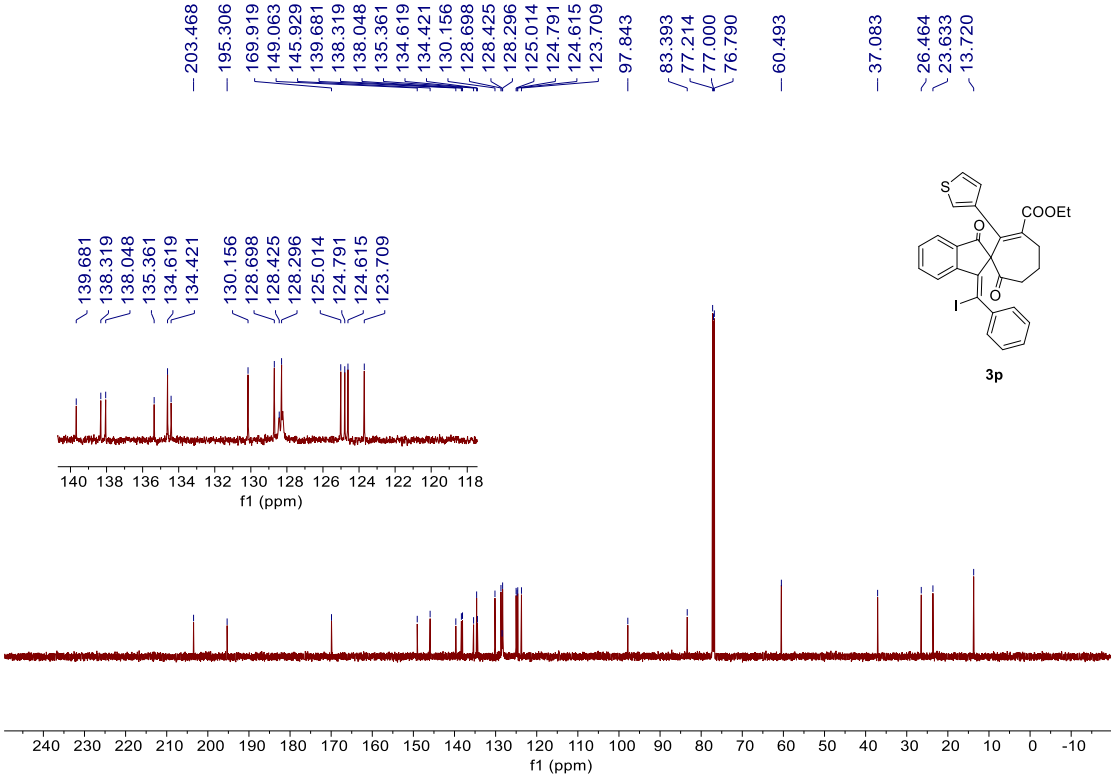
^{13}C NMR (125 MHz, $CDCl_3$)



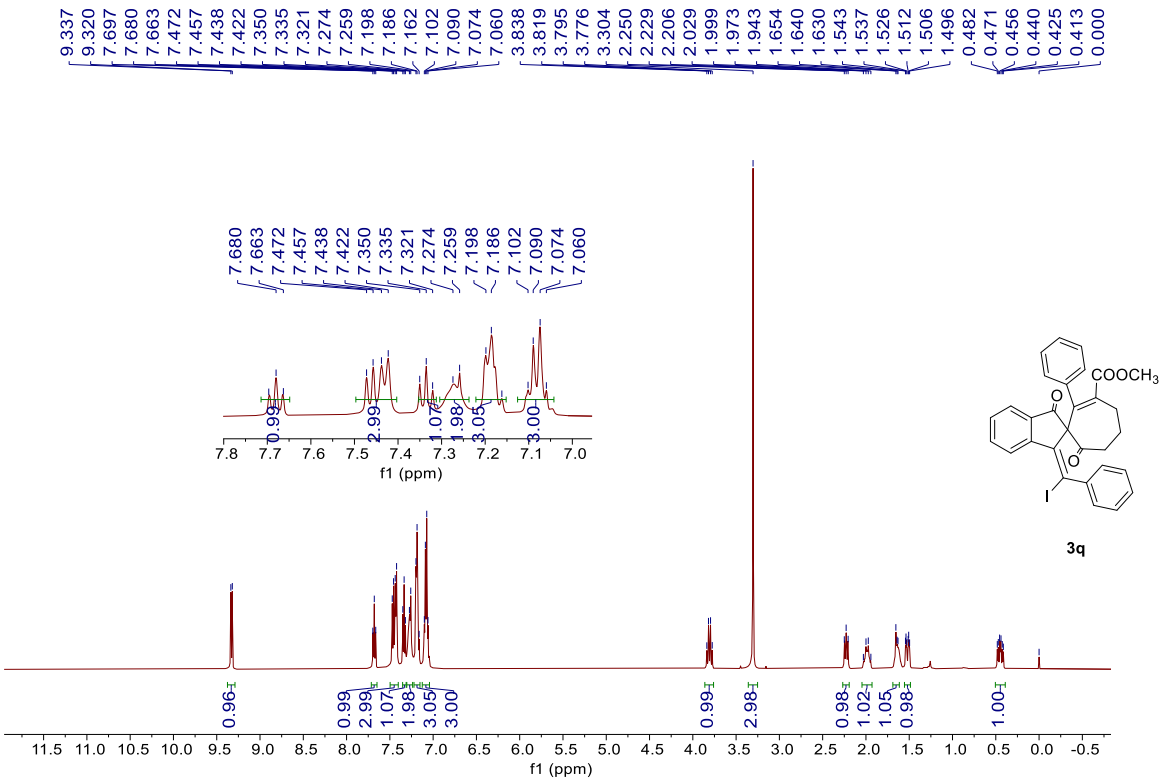
^{1}H NMR (600 MHz, $CDCl_3$)



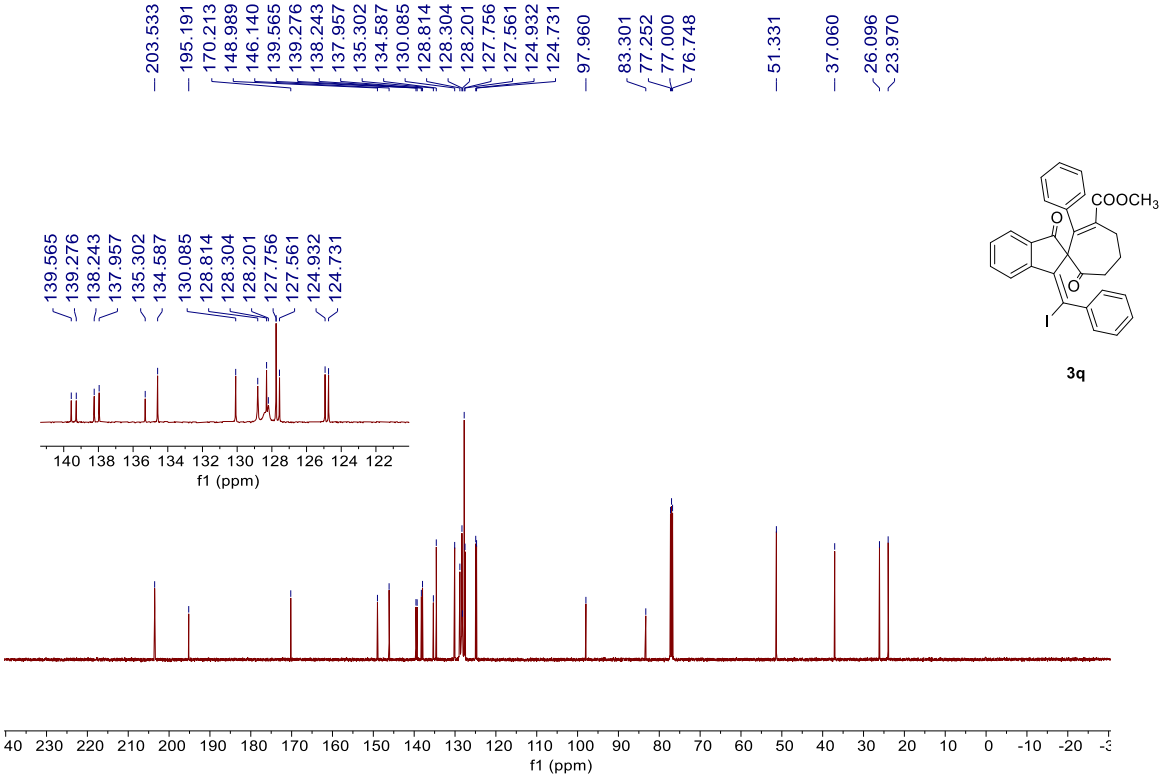
^{13}C NMR (150 MHz, $CDCl_3$)



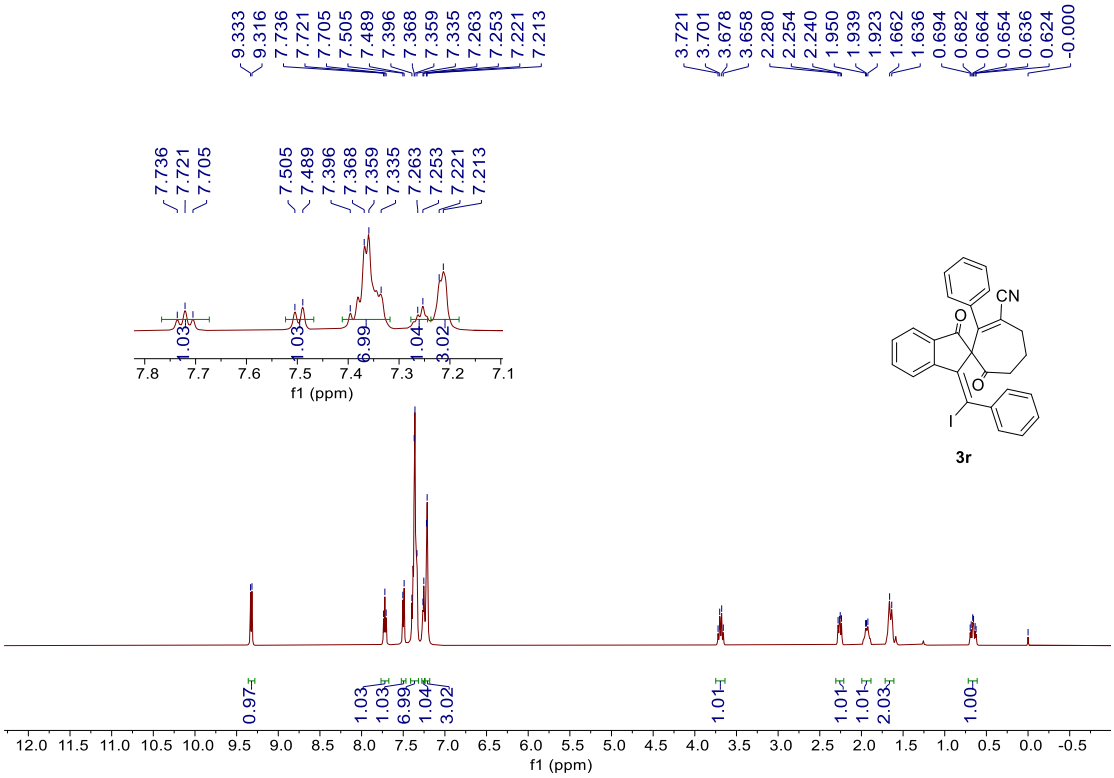
^{1}H NMR (500 MHz, $CDCl_3$)



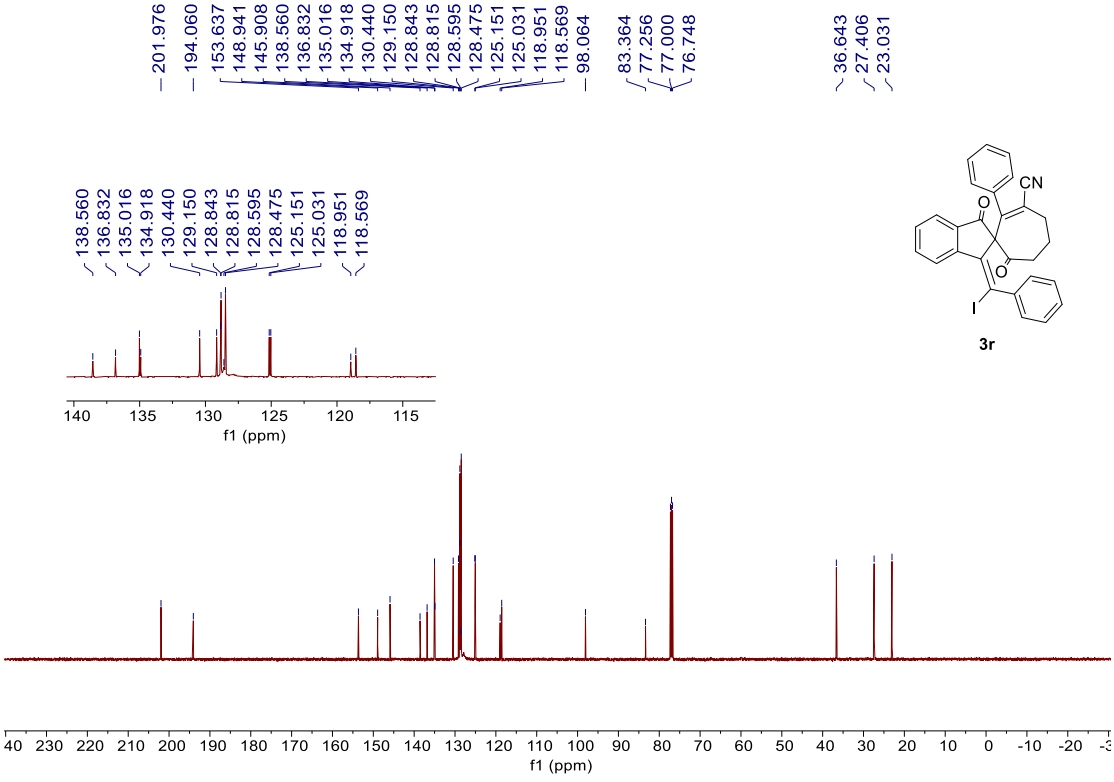
^{13}C NMR (125 MHz, $CDCl_3$)



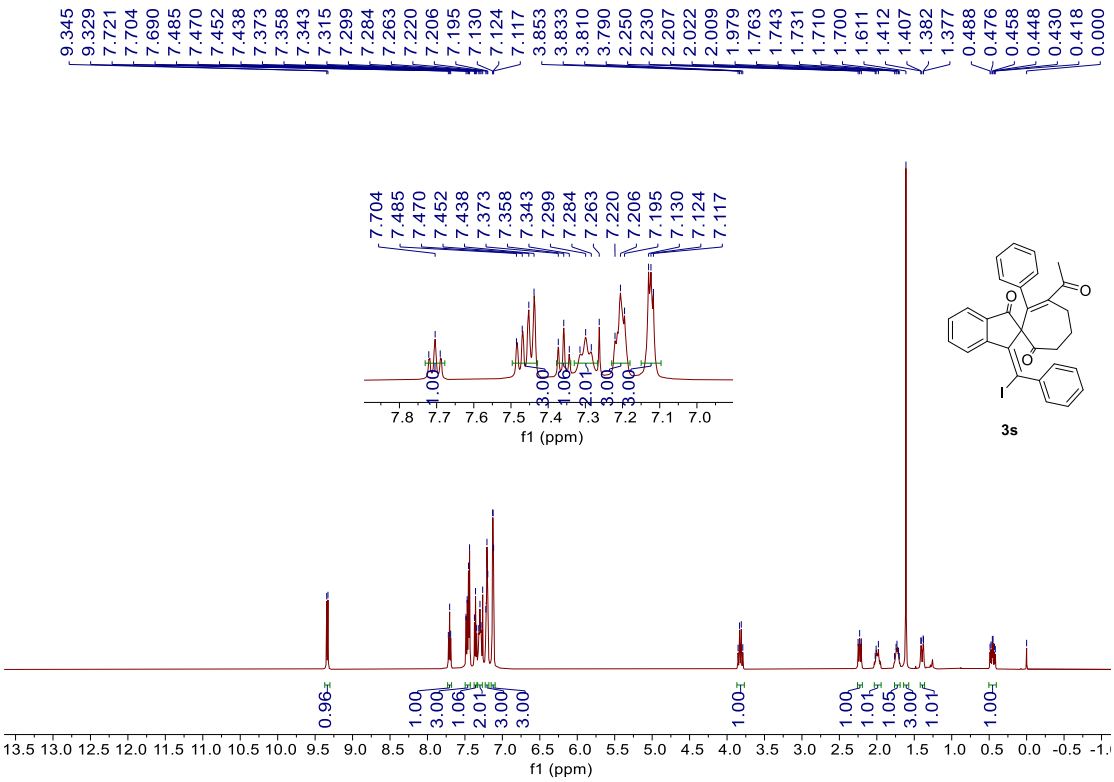
^{1}H NMR (500 MHz, $CDCl_3$)



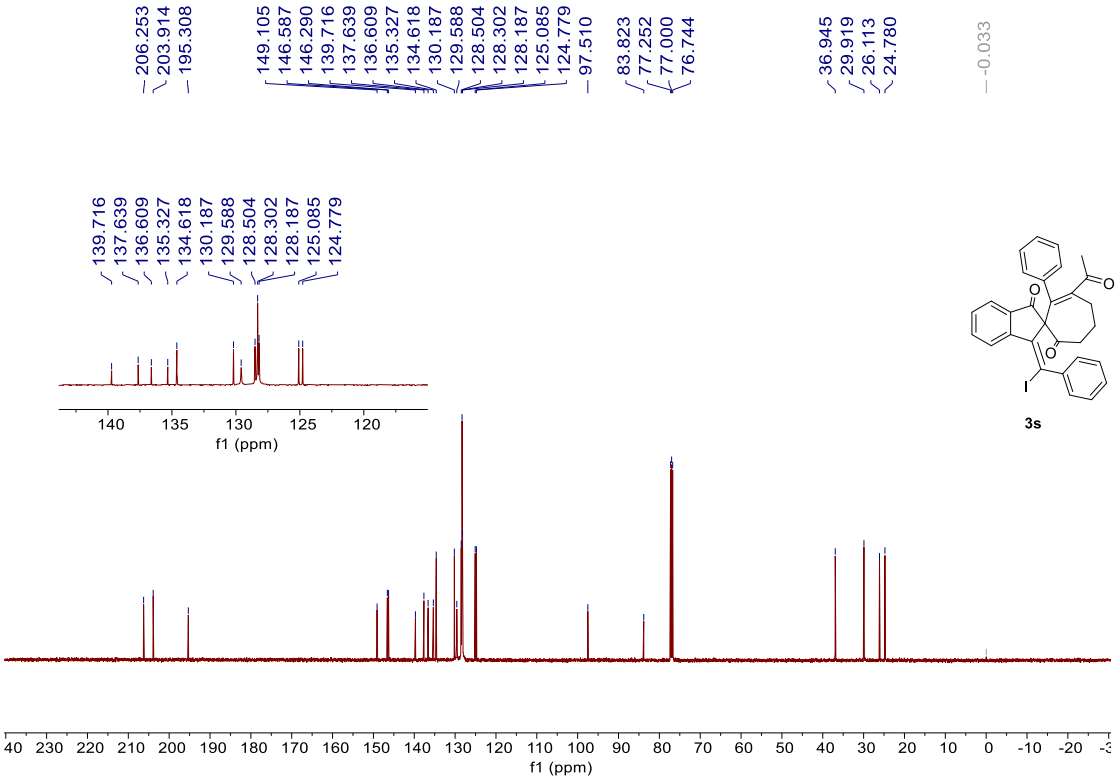
^{13}C NMR (125 MHz, $CDCl_3$)



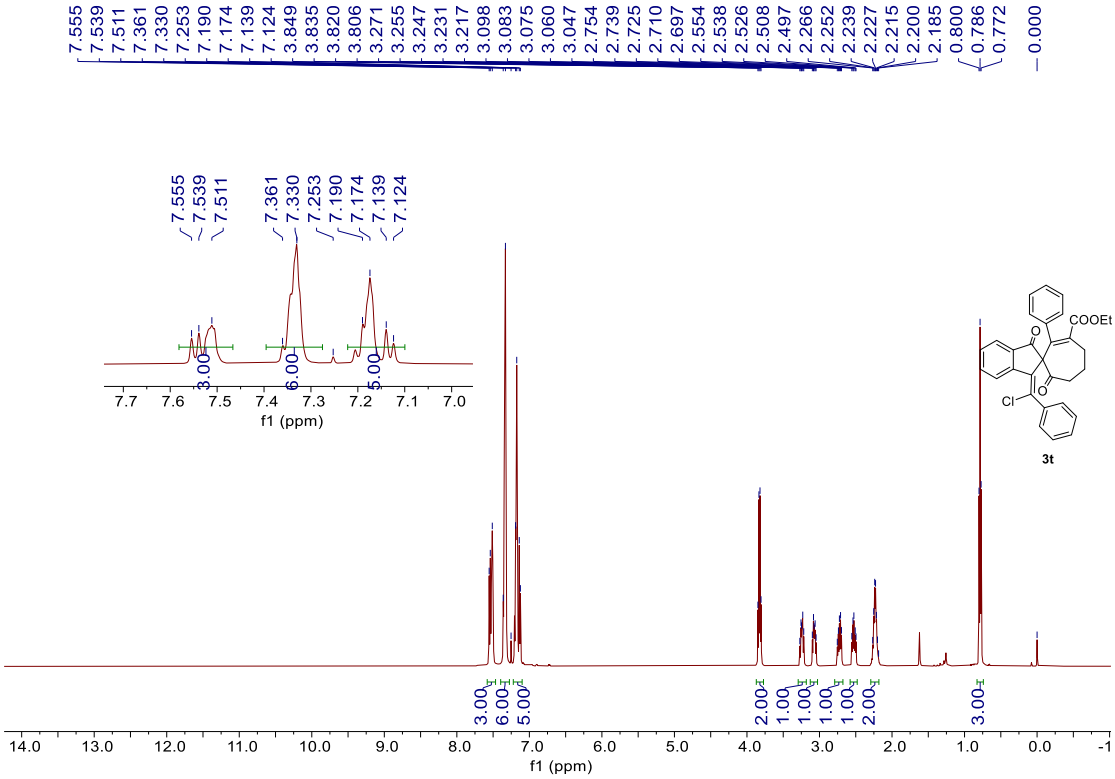
^{1}H NMR (500 MHz, $CDCl_3$)



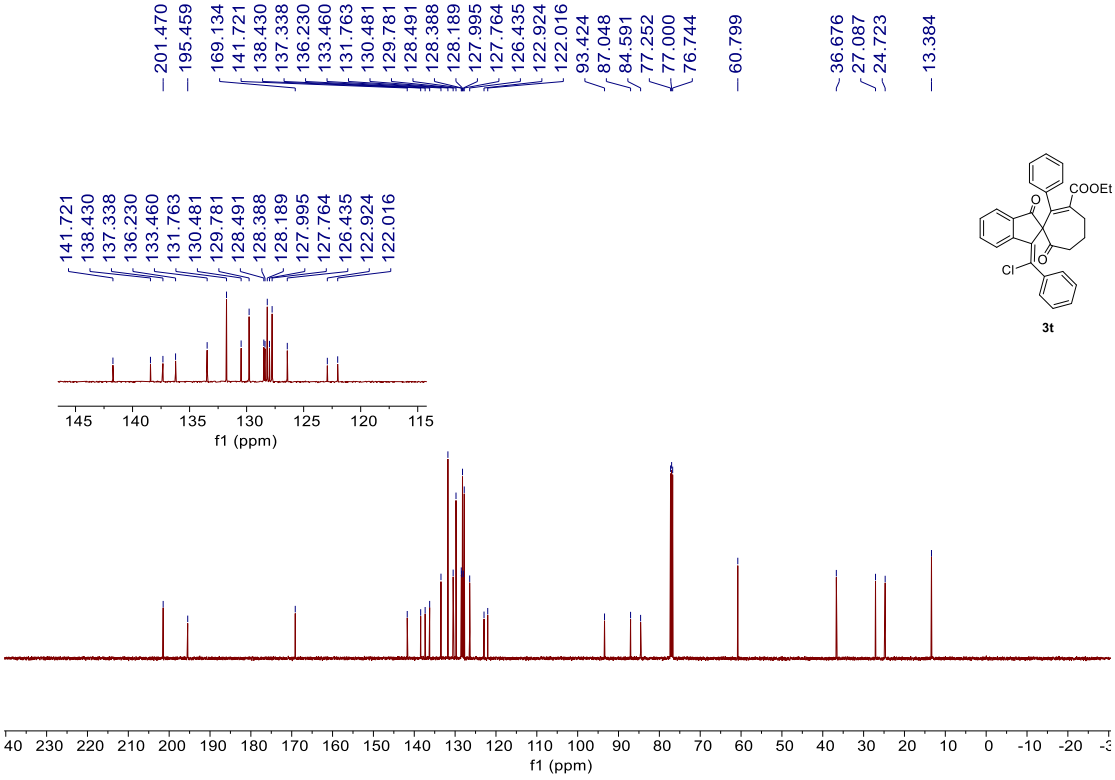
^{13}C NMR (125 MHz, $CDCl_3$)



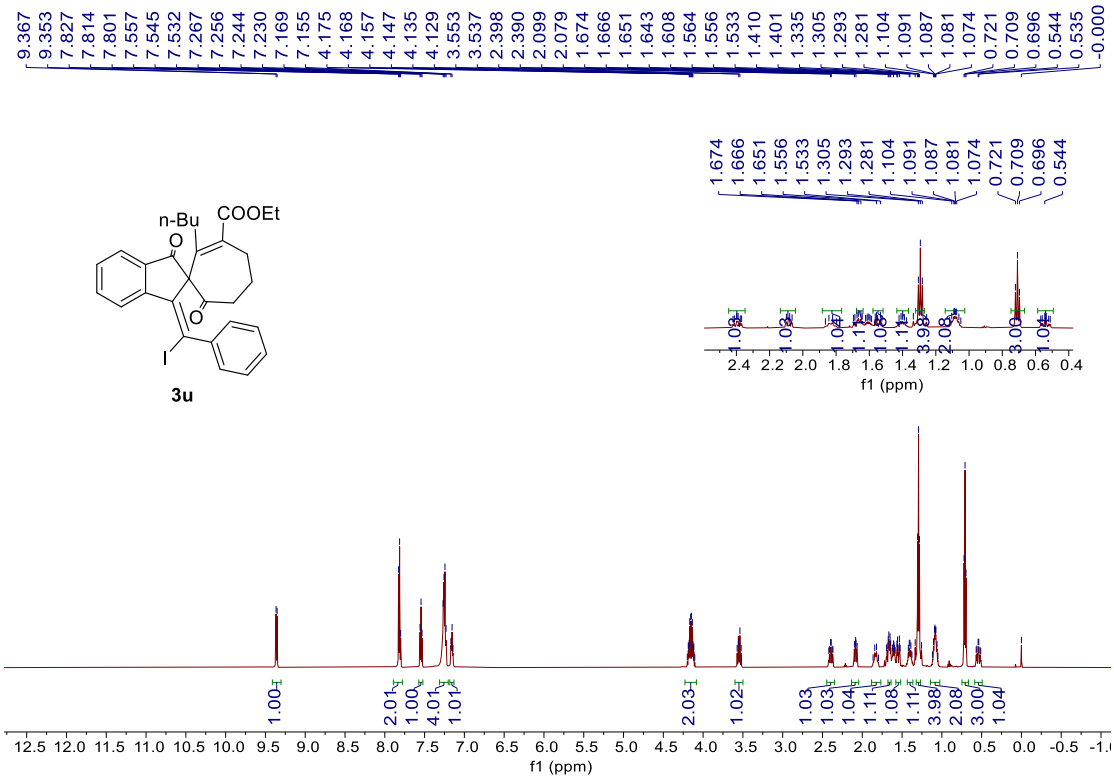
^{1}H NMR (500 MHz, $CDCl_3$)



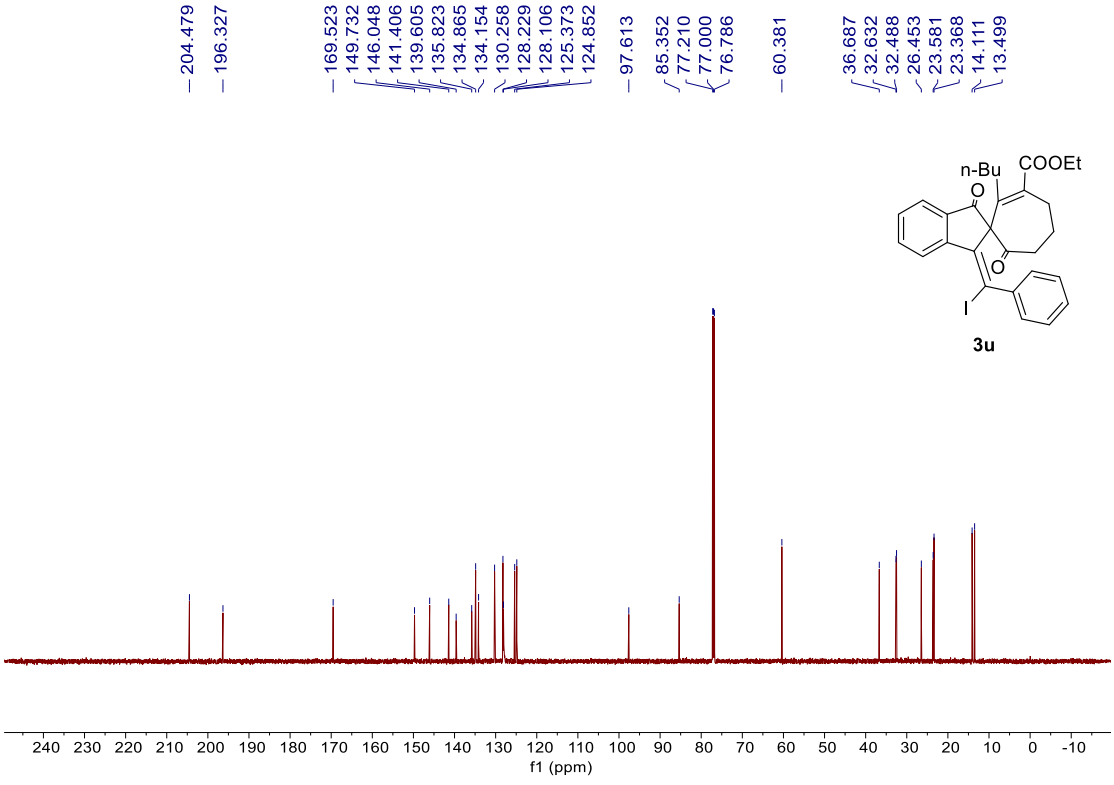
^{13}C NMR (125 MHz, $CDCl_3$)



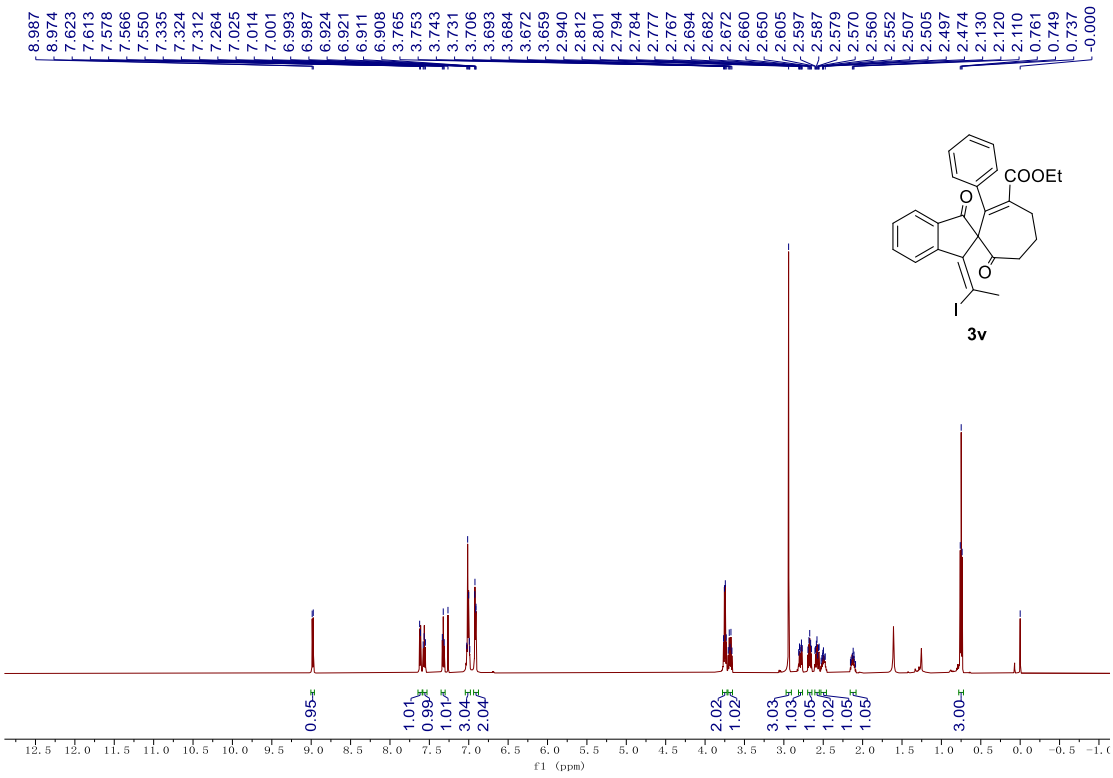
^{1}H NMR (600 MHz, $CDCl_3$)



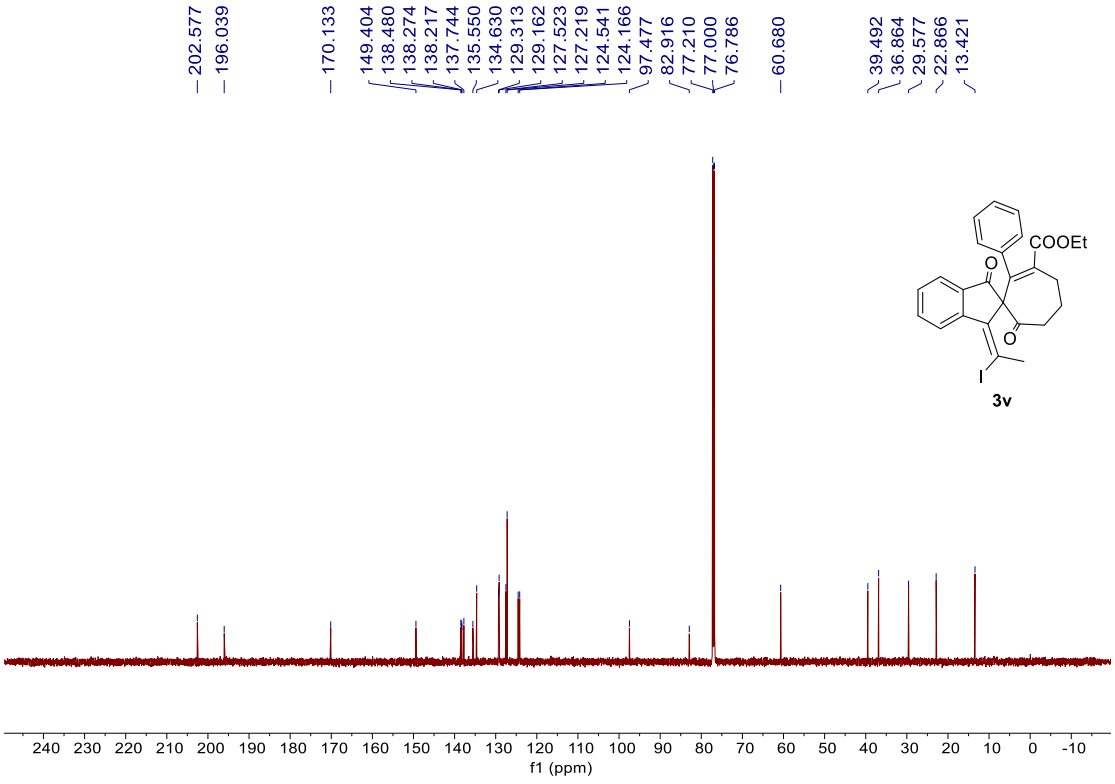
^{13}C NMR (150 MHz, $CDCl_3$)



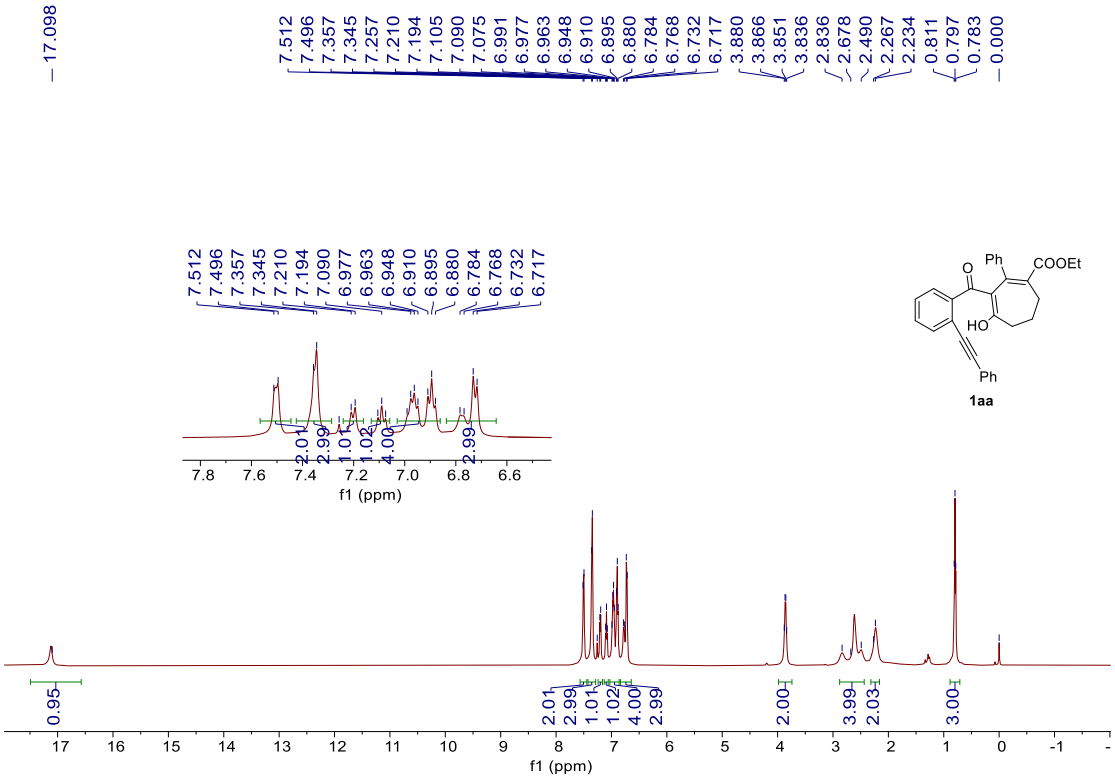
^{1}H NMR (600 MHz, $CDCl_3$)



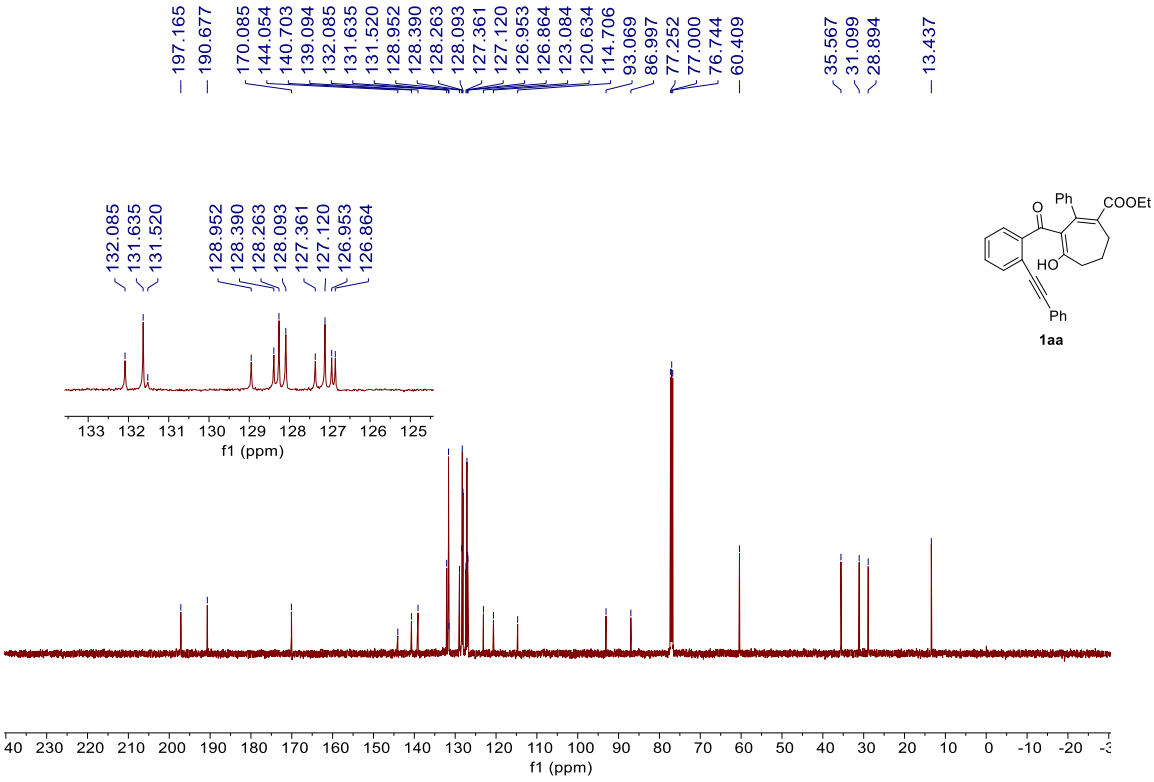
^{13}C NMR (150 MHz, $CDCl_3$)



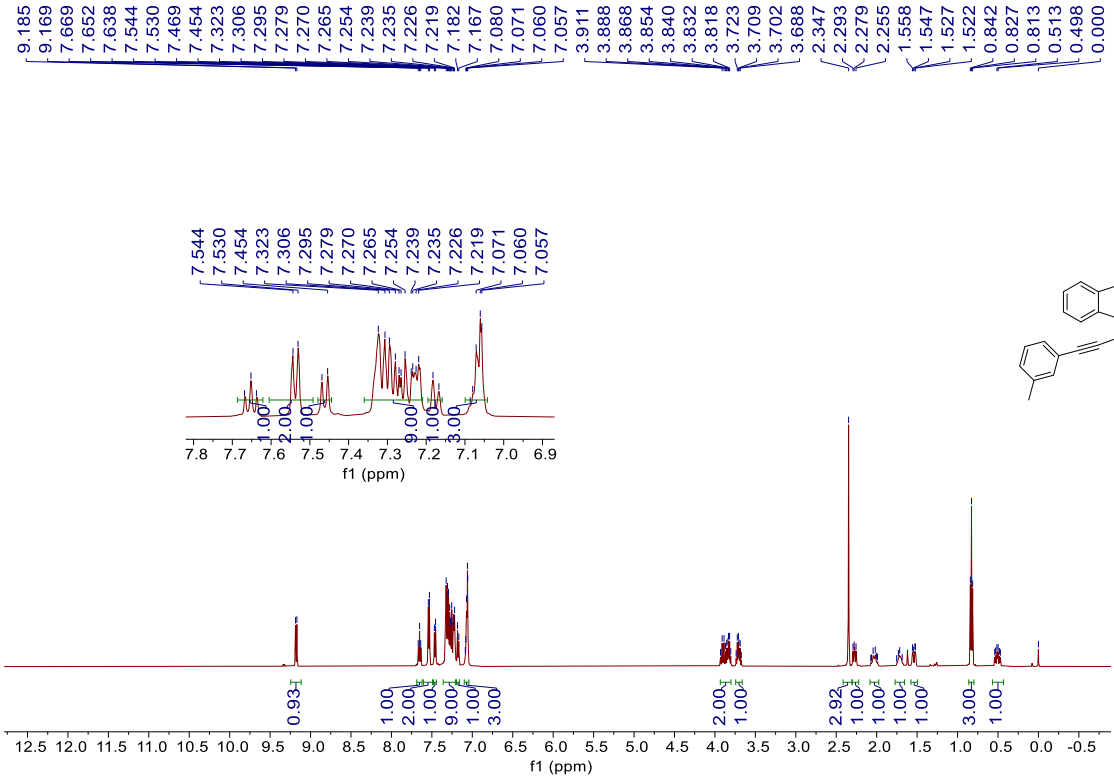
^{1}H NMR (500 MHz, $CDCl_3$)



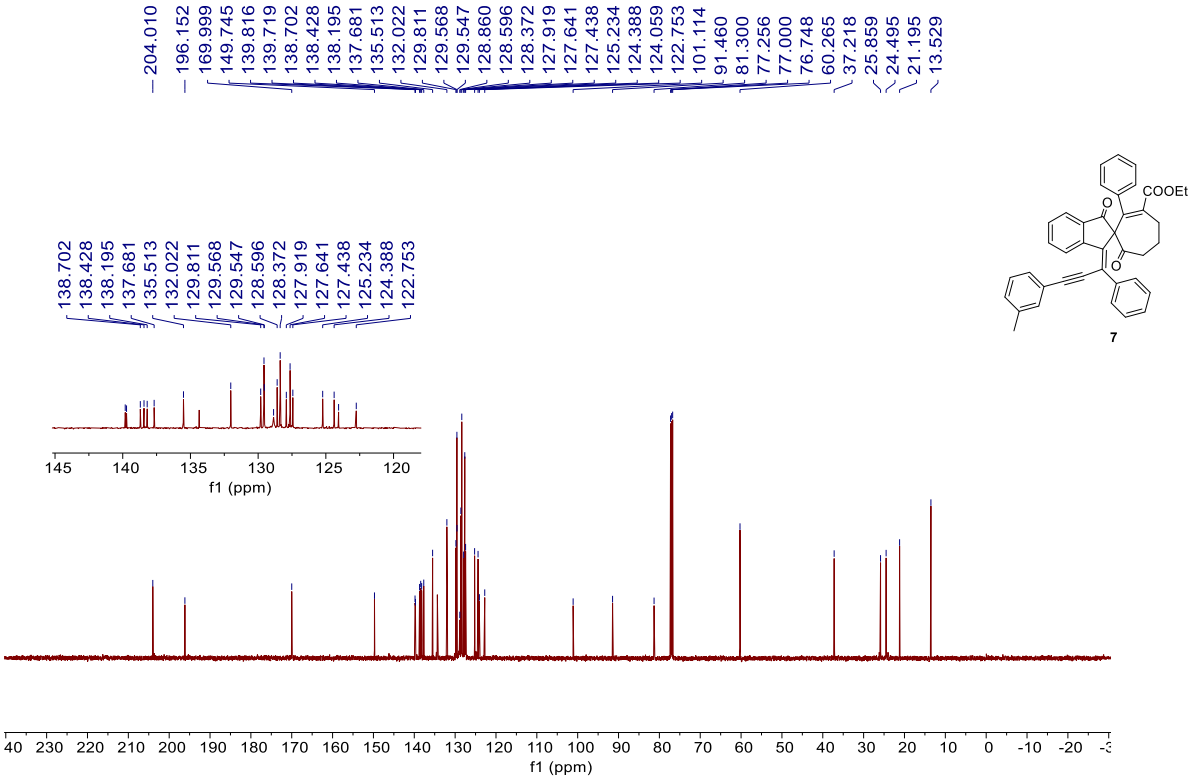
^{13}C NMR (125 MHz, $CDCl_3$)



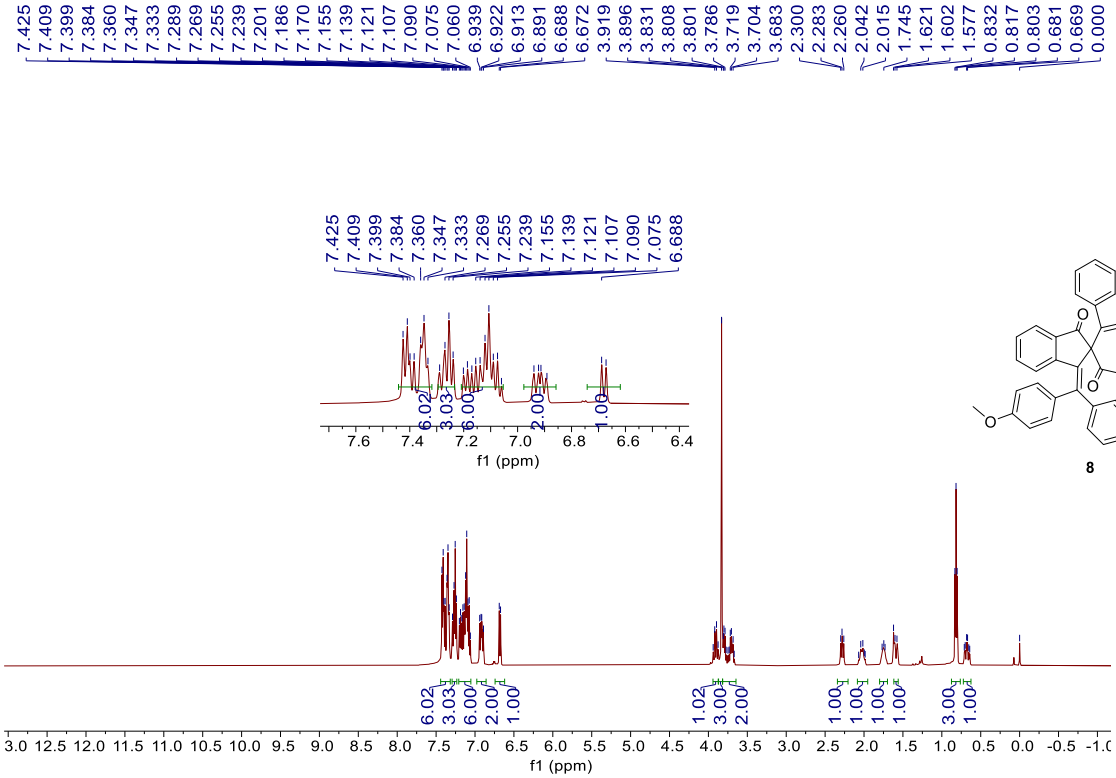
^{1}H NMR (500 MHz, $CDCl_3$)



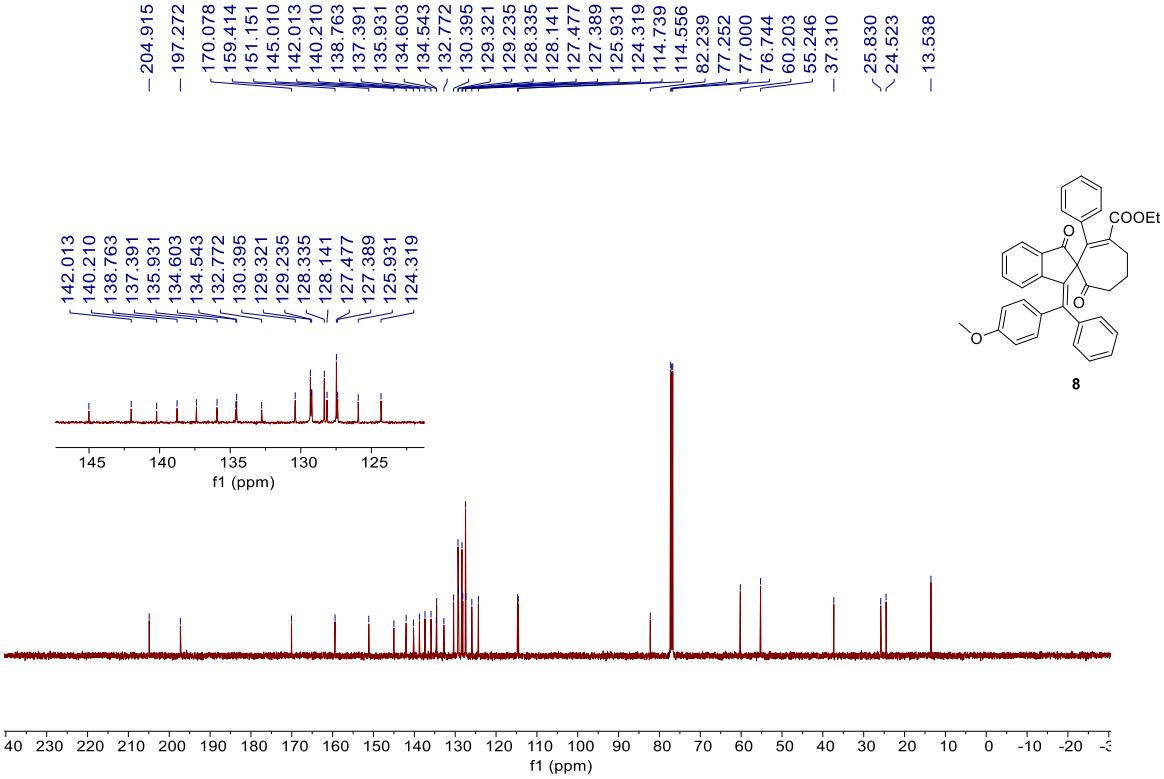
^{13}C NMR (125 MHz, $CDCl_3$)



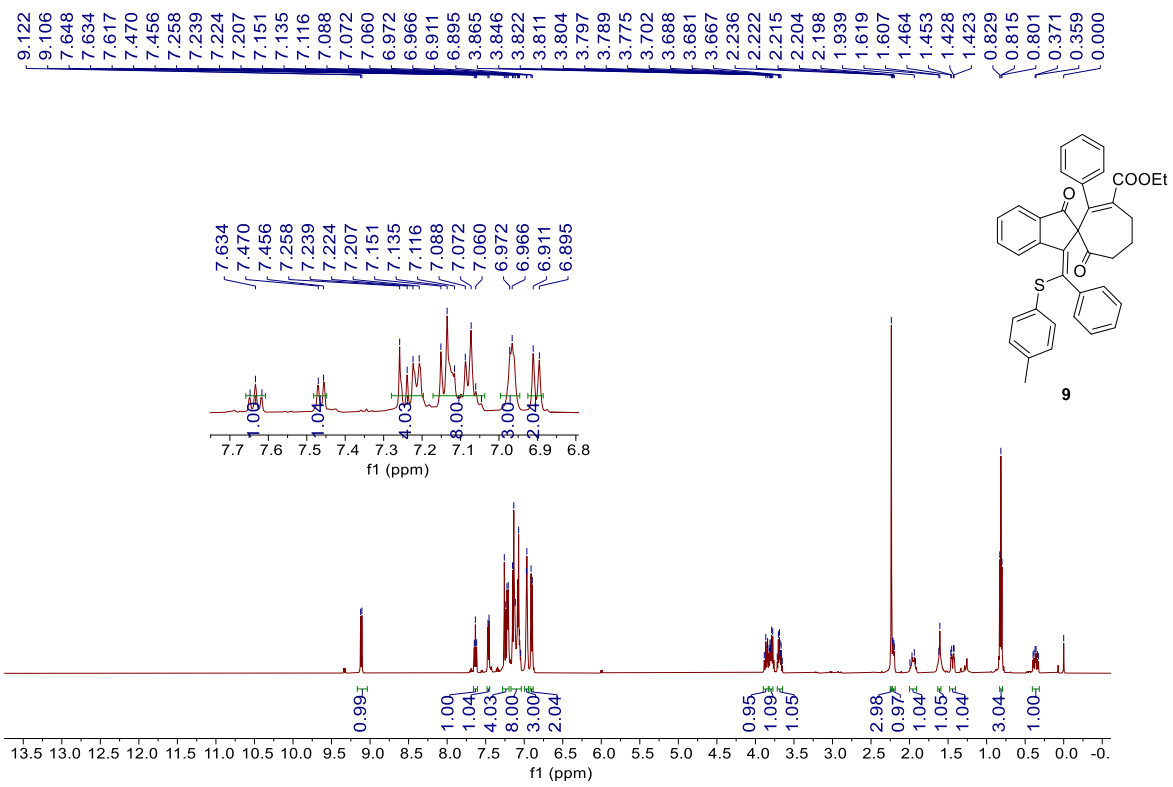
^{1}H NMR (500 MHz, $CDCl_3$)



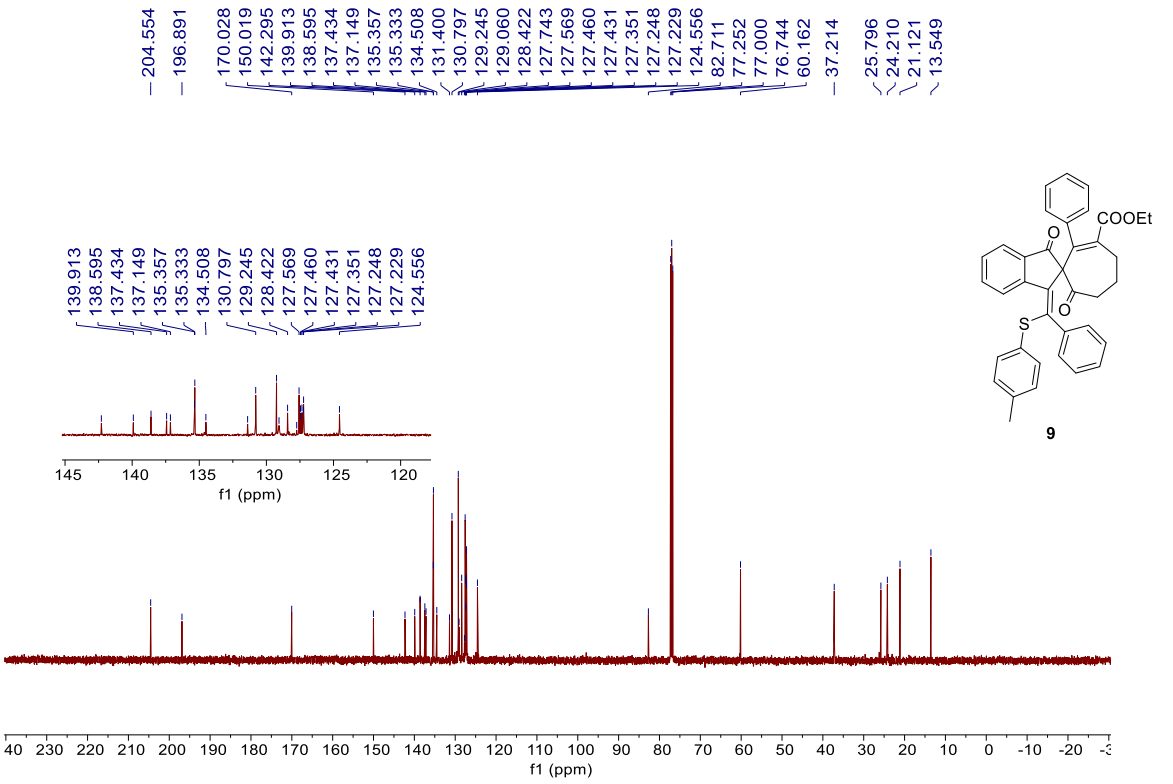
^{13}C NMR (125 MHz, $CDCl_3$)



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



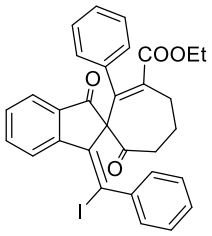
^{13}C NMR (125 MHz, $CDCl_3$)



10. X-ray crystallography of compound 3a.

Ethyl (E)-1'-(iodo(phenyl)methylene)-3',7-dioxo-2-phenyl-1',3'-dihydrospiro[cycloheptane-1,2'-inden]-2-ene-3-carboxylate **(3a)**

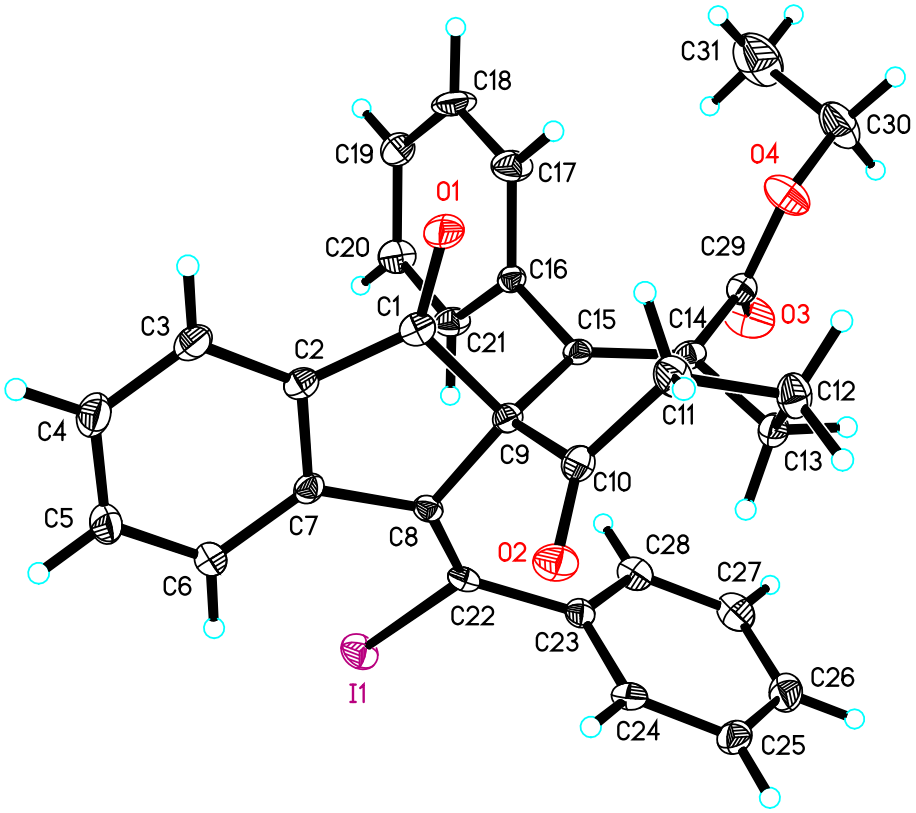
(Ortep ellipsoids are depicted at the 50% level)



3a

Table S1. Crystal data and structure refinement for 3a.

Identification code	**3a**
Empirical formula	$C_{31}H_{25}IO_4$
Formula weight	588.41
Temperature	213(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Pca 21
Unit cell dimensions	a = 17.4166(4) Å,α= 90°. b = 10.3859(3) Å, β= 90°. c = 27.8098(8) Å, γ = 90°.
Volume	5030.4(2) $Å^3$
Z	8
Density (calculated)	1.554 Mg/m3
Absorption coefficient	1.309 mm^{-1}
F(000)	2368
Crystal size	0.160× 0.130 ×0.090 mm^3
Theta range for data collection	1.961 to 25.996°.
Index ranges	-21<=h<=21, -12<=k<=12, -34<=l<=34
Reflections collected	67394
Independent reflections	9844 [R(int) = 0.0569]
Completeness to theta = 25.242°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.5728
Data / restraints / parameters	9844 / 1 / 651
Goodness-of-fit on F^2	1.035
Final R indices [I>2sigma(I)]	R_1 = 0.0335, wR_2 = 0.0750
R indices (all data)	R_1 = 0.0434, wR_2 = 0.0799
Extinction coefficient	n/a
Largest diff. peak and hole	1.535 and -0.764 e.$Å^{-3}$


C31
C18
C30
C19
C17
O4
O1
C20
C16
C29
C1
C15
C14
O3
C3
C2
C21
C12
C11
C4
C9
C10
C13
C5
C7
C8
O2
C28
C6
C27
C22
C23
C26
I1
C24
C25