De novo synthesis of 6-6-5 fused-systems through electrochemical decarboxylation and radical domino additions

Chengcheng Yuan,[a] Guanru Liu,[a] Wenjing Guan,[a] Jinlin Hang, [a] Zheng Fang,[a] Chengkou Liu,*[,a] and Kai Guo*[a,b]

[a]College of Biotechnology and Pharmaceutical Engineering, Nanjing Tech University, Nanjing, 211816, China. E-mail: liuchengkou@njtech.edu.cn; guok@njtech.edu.cn.

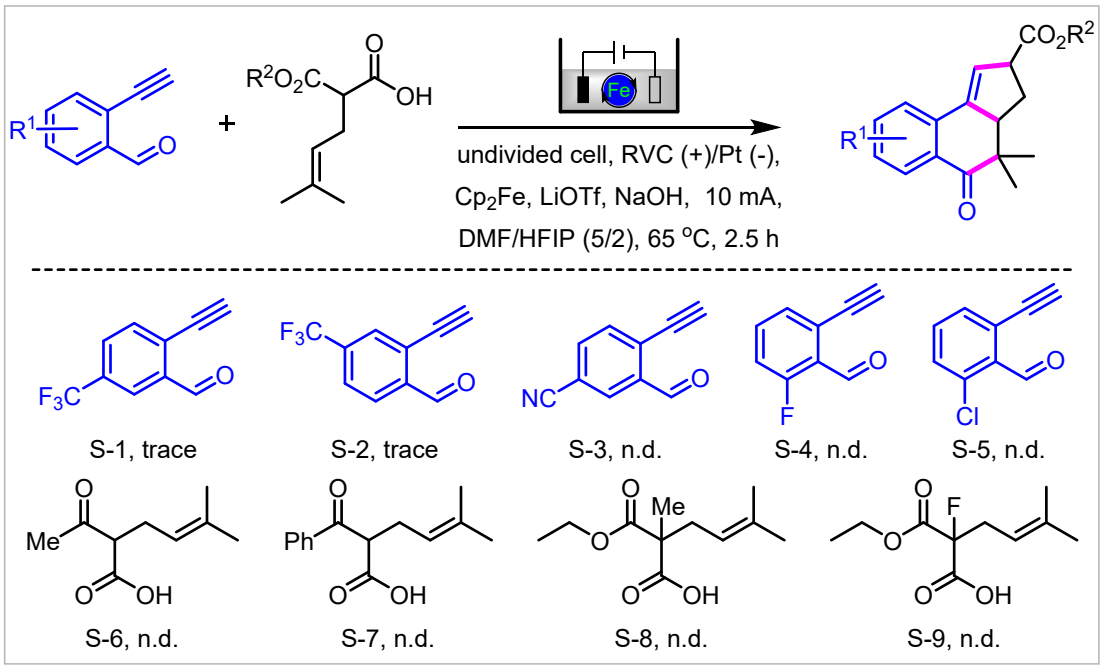
[b]State Key Laboratory of Materials-Oriented Chemical Engineering, Nanjing Tech University, Nanjing, 211816, China.

Table of Contents

1. General information

Commercially available reagents and solvents were of reagent grade quality without further purification. Analytical thin-layer chromatography (TLC) was performed on 0.2 mm coated silica gel plates (HSGF 254) and visualized using a UV lamp (254 or 365 nm). Flash column chromatography was performed using silicycle silica gel (200-300 mesh). ^{1}H NMR and ^{13}C NMR were recorded on magnet system 400'54 ascend purchased from Bruker Biospin AG. HRMS (ESI) spectra were recorded on Agilent Q-TOF 6520.

Electrochemical decarboxylation and three-step radical addition to give the corresponding 6-6-5 fused-system was carried out in an undivided cell equipped with a RVC anode and a platinum plate cathode under open air. The carbon cloth, graphite rod (⌀ 6 mm), platinum plate, Ni plate and Fe plate were purchased from Shanghai Jing Chong Electronic Technology Development Co., Ltd. Reticulated vitreous carbon (RVC) was purchased from Gaoss Union (Tianjin) Photoelectric Technology Co., Ltd. And, electrolysis was conducted under an AXIOMET AX3003P potentiostat in constant current mode. Cyclic voltammogram experiments were investigated using a Metrohm Autolab PGSTAT204 workstation and Nova 2.0 software.

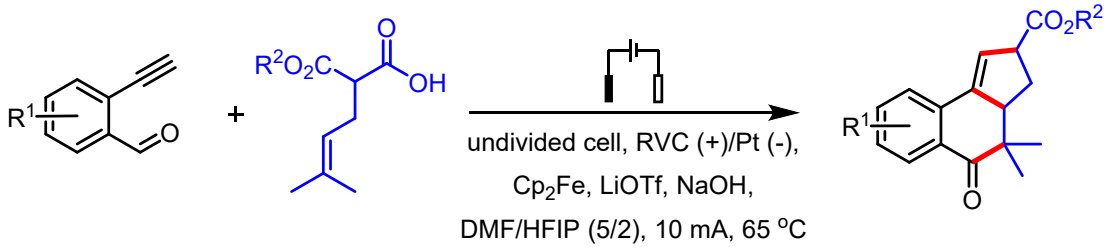


Scheme S1 Unsuccessful and low yielding examples.

2. Unsuccessful and low yielding examples

The unsuccessful and low yielding examples were shown in Scheme **S1**.

3. General procedure for the electrosynthesis of 6-6-5 fused-systems



In an undivided cell equipped with a RVC (100 PPI, 10 mm x 10 mm x 12 mm) anode and a Pt (10 mm x 10 mm x 0.1 mm) cathode, *o*-ethynylbenzaldehyde (0.2 mmol, 1.0 eq), γ,δ-unsaturated carboxylic acid (0.6 mmol, 3.0 eq), Cp_2Fe (0.05 mmol, 0.25 eq, 9.3 mg), NaOH (0.8 mmol, 4.0 eq, 32.0 mg) and LiOTf (0.3 mmol, 1.5 eq, 46.8 mg) were dissolved in a mixed solvent of DMF/HFIP (5/2, 7 mL). The mixture above was stirred and electrolyzed at a constant current of 10 mA under 65 °C for about 2.5 h. The reaction solution was diluted with ethyl acetate (100 mL) and washed with saturated NaCl aqueous solution (50 mL) and H_2O (100 mL x 6). The separated organic layer was dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure to give the crude product, which was purified by column chromatographic separation (petroleum ether/ethyl acetate: 200:1) to obtain the desired product.

4. Mechanistic studies

4.1 Cyclic voltammetry experiments

4.1.1 Cyclic voltammetry experiments of substrates and radical trapping agents

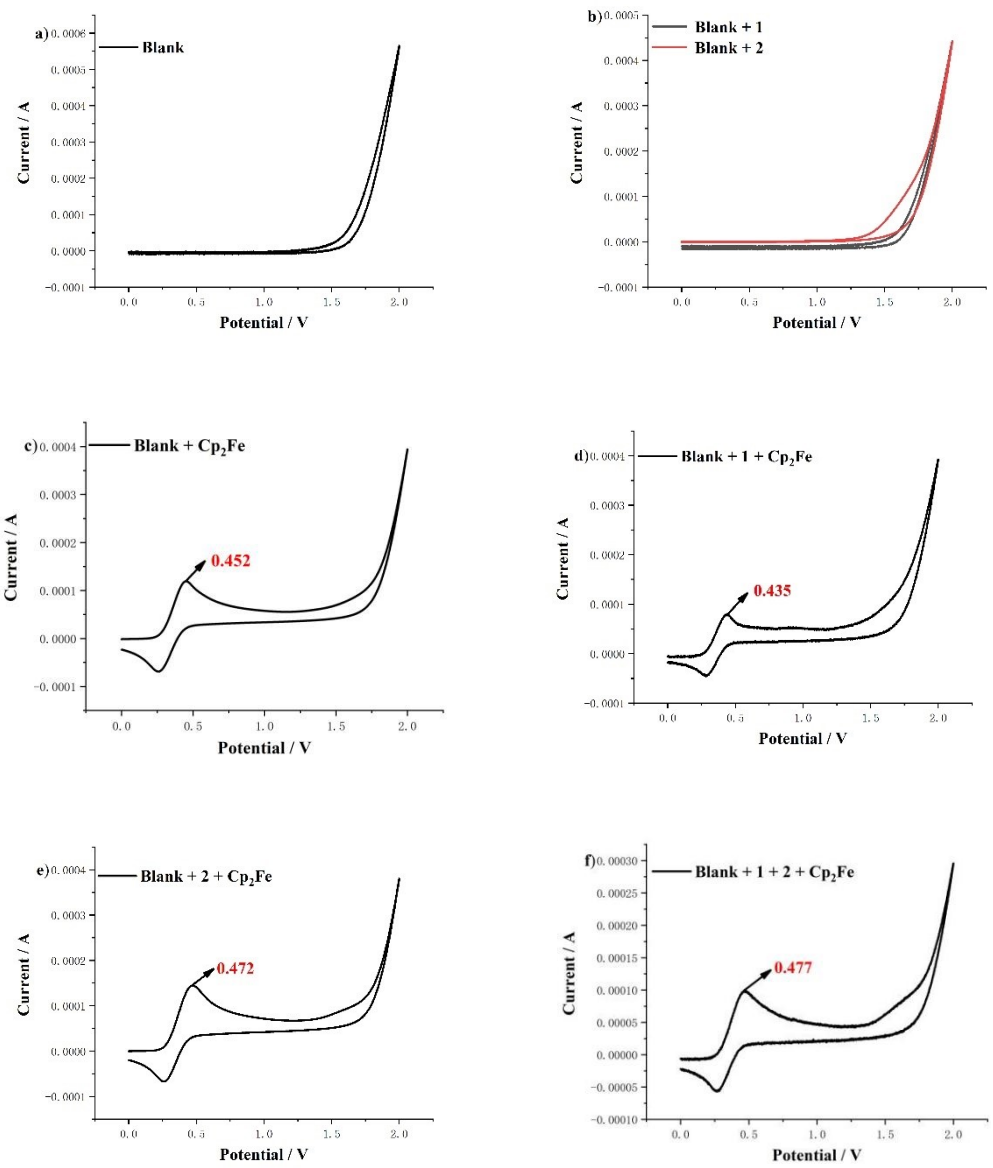


Figure S1 Cyclic voltammetry experiments of substrates

IUPAC Convention, 100 mVs-1, rt: a) blank; b) black: 2-ethynylbenzaldehyde **1** (0.2 mmol, 26.0 mg), red: 2-(ethoxycarbonyl)-5-methylhex-4-enoic acid **2** (0.6 mmol, 120.1 mg); c) Cp_2Fe (0.05 mmol, 9.3 mg); d) 2-ethynylbenzaldehyde **1** (0.2 mmol, 26.0 mg) and Cp_2Fe (0.05 mmol, 9.3 mg); e) 2-(ethoxycarbonyl)-5-methylhex-4-enoic acid **2** (0.6 mmol, 120.1 mg) and Cp_2Fe (0.05 mmol, 9.3 mg); f) 2-ethynylbenzaldehyde **1** (0.2 mmol, 26.0 mg), 2-(ethoxycarbonyl)-5- methylhex-4-enoic acid **2** (0.6 mmol, 120.1 mg) and Cp_2Fe (0.05 mmol, 9.3 mg).

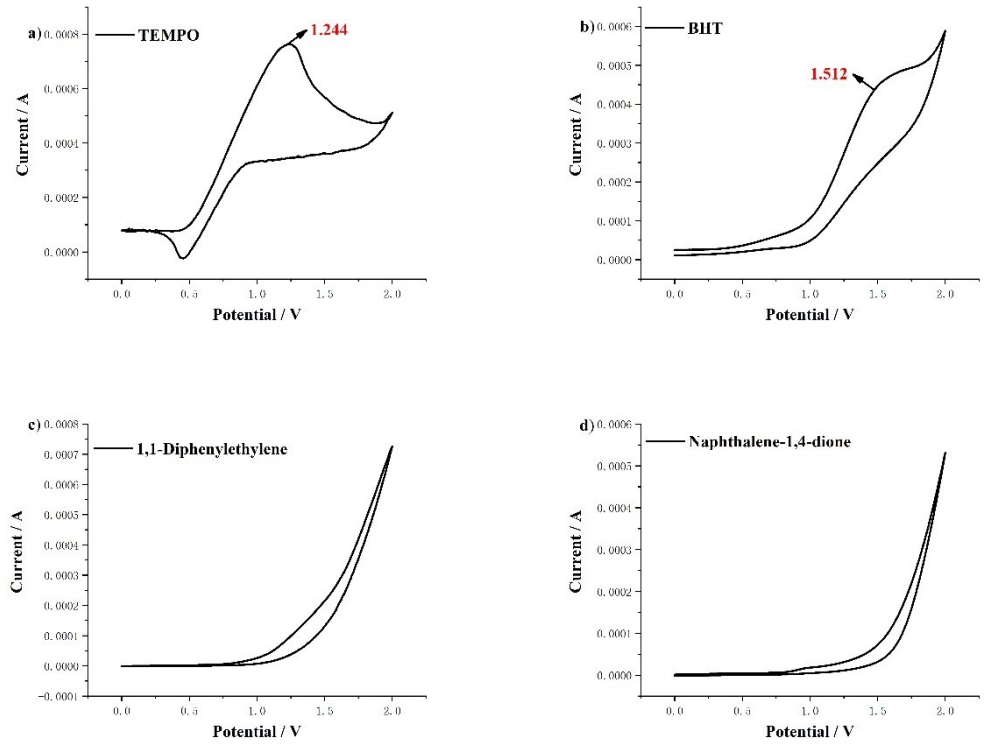
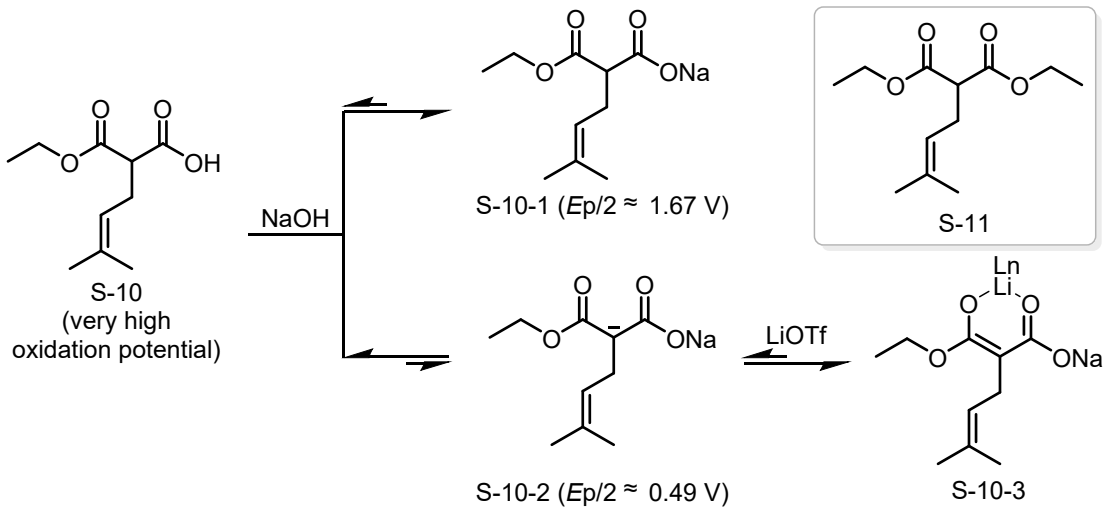


Figure S2 Cyclic voltammetry experiments of the radical trapping agents IUPAC Convention, 100 mVs-1, rt: a) TEMPO (0.2 mmol, 31.2 mg); b) BHT (0.2 mmol, 44.1 mg); c) 1,1-diphenylethylene (0.2 mmol, 36.1 mg); d) 1,4-naphthoquinone (0.2 mmol, 31.6 mg).

The undivided cell was equipped with glassy-carbon disk working electrode (diameter, 3.0 mm) and Pt wire auxiliary electrode. The Ag/AgCl was used as reference electrode. The scan range was 0.0 V to 2.0 V. The scan rate was 100 mVs^{-1}. A mixed solvent of DMF/HFIP (5/2, 7 mL) containing NaOH (0.8 mmol, 32.0 mg) and LiOTf (0.3 mmol, 46.8 mg) were poured into the electrochemical cell in all experiments. The electrode was used without polishing and the solvent was used without deoxygenation.

4.1.2 Cyclic voltammetry experiments of carboxylic acid S-10 and 1,3-dicarbonyl compound S-11



Scheme S2 Oxidation potential of carboxylic acid and 1,3-dicarbonyl compound

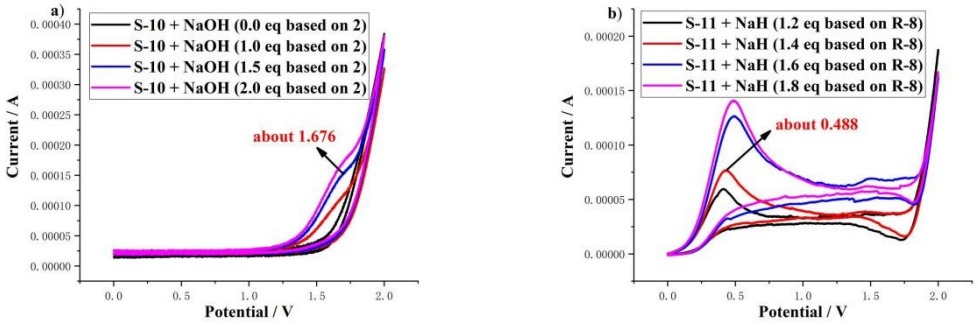


Figure S3 Cyclic voltammetry experiments of carboxylic acid and 1,3-dicarbonyl compound. IUPAC Convention, 100 mVs^{-1}, rt. a) black: **S-10** (0.2 mmol, 1.0 eq, 40.0 mg); red: **S-10** (0.2 mmol, 1.0 eq, 40.0 mg) and NaOH (0.2 mmol, 1.0 eq, 8.0 mg); blue: **S-10** (0.2 mmol, 1.0 eq, 40.0 mg) and NaOH (0.3 mmol, 1.5 eq, 12.0 mg); pink: **S-10** (0.2 mmol, 1.0 eq, 40.0 mg) and NaOH (0.4 mmol, 2.0 eq, 16.0 mg); b) black: **S-11** (0.2 mmol, 1 eq, 45.6 mg) and NaH (0.24 mmol, 1.2 eq, 9.6 mg); red: **S-11** (0.2 mmol, 1 eq, 45.6 mg) and NaH (0.28 mmol, 1.4 eq, 11.2 mg); blue: **S-11** (0.2 mmol, 1 eq, 45.6 mg) and NaH (0.32 mmol, 1.6 eq, 12.8 mg); pink: **S-11** (0.2 mmol, 1 eq, 45.6 mg) and NaH (0.36 mmol, 1.8 eq, 14.4 mg).

The undivided cell was equipped with glassy-carbon disk working electrode (diameter, 3.0 mm) and Pt wire auxiliary electrode. The Ag/AgCl was used as reference electrode. The scan range was 0.0 V to 2.0 V. The scan rate was 100 mVs^{-1}. A mixed solvent of DMF/HFIP (5/2, 7 mL) containing $^{n}Bu_4NPF_6$ (0.4 mmol, 155.0 mg) was poured into the electrochemical cell in all experiments. The electrode was used without polishing and the solvent was used without deoxygenation.

4.2 Radical-trapping experiments

4.2. 1 1,1-diphenylethylene was added

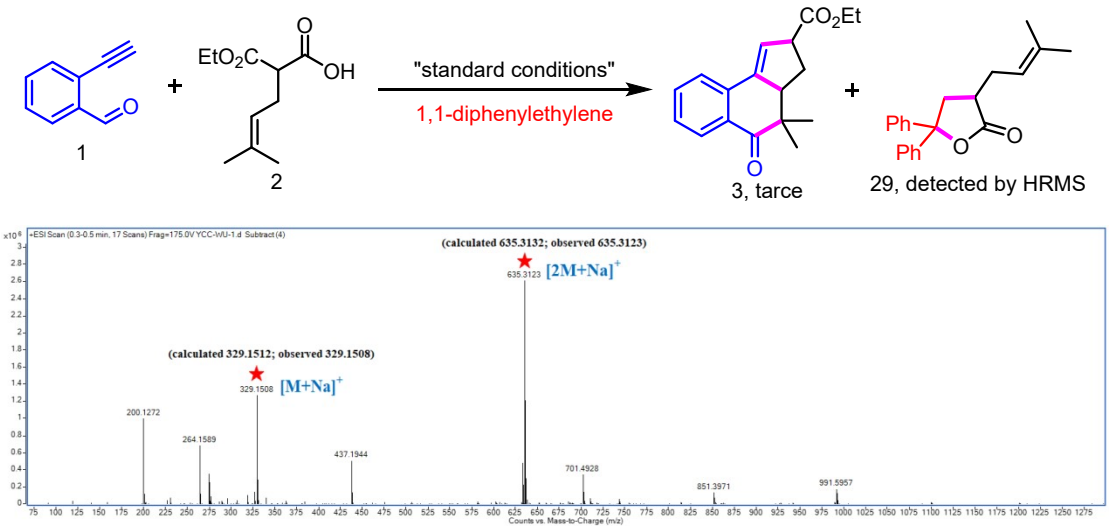
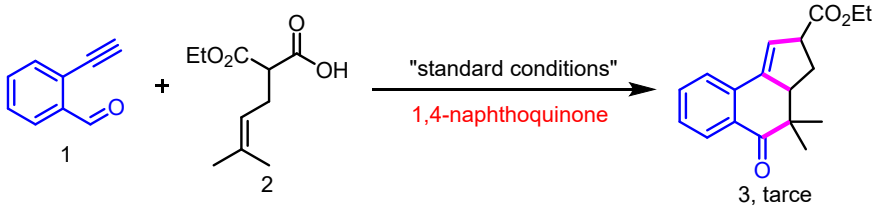


Figure S4 HRMS (ESI) analysis of radical-trapping intermediate

In an undivided cell equipped with a RVC (100 PPI, 10 mm x 10 mm x 12 mm) anode and a Pt (10 mm x 10 mm x 0.1 mm) cathode, 2-ethynylbenzaldehyde **1** (0.2 mmol, 1.0 eq, 26.0 mg), 2-(ethoxycarbonyl)-5-methylhex-4-enoic acid **2** (0.6 mmol, 3.0 eq, 120.1 mg), Cp_2Fe (0.05 mmol, 0.25 eq, 9.3 mg), NaOH (0.8 mmol, 4.0 eq, 32.0 mg), LiOTf (0.3 mmol, 1.5 eq, 46.8 mg) and 1,1-diphenylethylene (0.6 mmol, 3.0 eq, 108.2 mg) were dissolved in a mixed solvent of DMF/HFIP (5/2, 7 mL). The mixture above was stirred and electrolyzed at a constant current of 10 mA for about 6 h under 65 °C with only trace amounts of desired product **3** detected. Moreover, the corresponding radical trapping product **29** was detected by HRMS (HRMS (ESI-TOF)

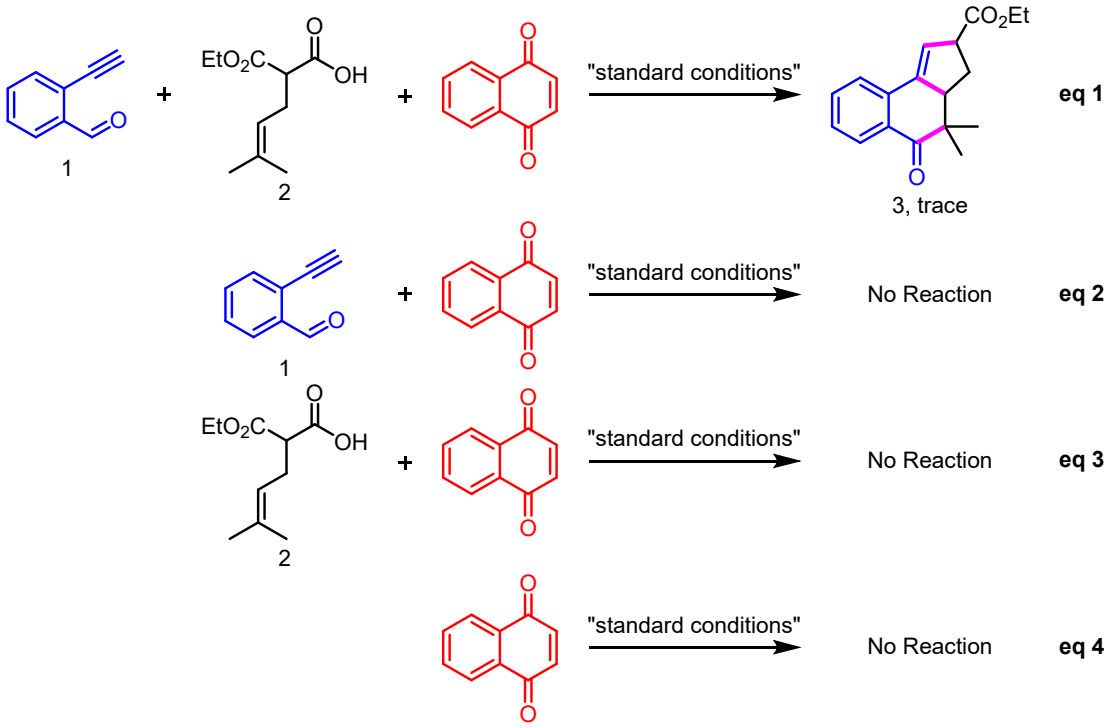
HRMS (ESI-TOF) Calcd for $C_{21}H_{22}O_2Na$ $[M+Na]^+$: 329.1512; found: 329.1508, Calcd for $C_{42}H_{44}O_4Na$ $[2M+Na]^+$: 635.3132; found: 635.3123.

4.2.2 1,4-naphthoquinone was added



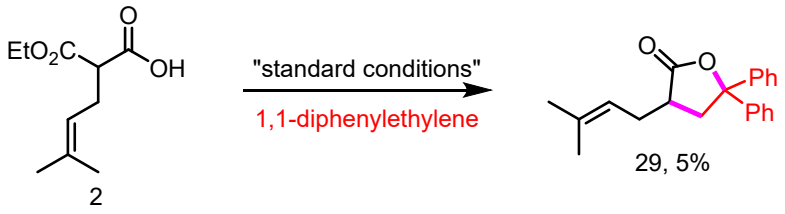
In an undivided cell equipped with a RVC (100 PPI, 10 mm x 10 mm x 12 mm) anode and a Pt (10 mm x 10 mm x 0.1 mm) cathode, 2-ethynylbenzaldehyde **1** (0.2 mmol, 1.0 eq, 26.0 mg), 2-(ethoxycarbonyl)-5-methylhex-4-enoic acid **2** (0.6 mmol, 3.0 eq, 120.1 mg), Cp_2Fe (0.05 mmol, 0.25 eq, 9.3 mg), NaOH (0.8 mmol, 4.0 eq, 32.0 mg), LiOTf (0.3 mmol, 1.5 eq, 46.8 mg) and 1,4-naphthoquinone (0.6 mmol, 3.0 eq, 94.9 mg) were dissolved in a mixed solvent of DMF/HFIP (5/2, 7 mL). The mixture above was stirred and electrolyzed at a constant current of 10 mA for about 6 h under 65 °C with only trace amounts of desired product **3** detected. And, no corresponding radical trapping product was detected.

Moreover, the reactions between 1,4-naphthoquinone and substrates were carried out (Scheme **S3**). It was found that no coupling product between 1,4-naphthoquinone and **1** or between 1,4-naphthoquinone and **2** was observed (eq **1** to **3**). Moreover, no new product was detected when 1,4-naphthoquinone was electrolyzed solely (eq **4**).

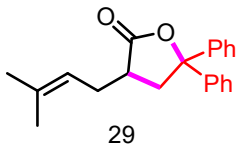


Scheme S3 The reaction between 1,4-naphthoquinone and substrates

4.2.3 1,1-diphenylethylene was added in the absence of 1



In an undivided cell equipped with a RVC (100 PPI, 10 mm x 10 mm x 12 mm) anode and a Pt (10 mm x 10 mm x 0.1 mm) cathode, 2-(ethoxycarbonyl)-5-methylhex -4-enoic acid **2** (0.6 mmol, 3.0 eq, 120.1 mg), Cp_2Fe (0.05 mmol, 0.25 eq, 9.3 mg), NaOH (0.8 mmol, 4.0 eq, 32.0 mg), LiOTf (0.3 mmol, 1.5 eq, 46.8 mg) and 1,1-diphenylethylene (0.6 mmol, 3.0 eq, 108.2 mg) were dissolved in a mixed solvent of DMF/HFIP (5/2, 7 mL). The mixture above was stirred and electrolyzed at a constant current of 10 mA for 6 h under 65 °C, the corresponding radical trapping product **29** was obtained with 5% yield.



29

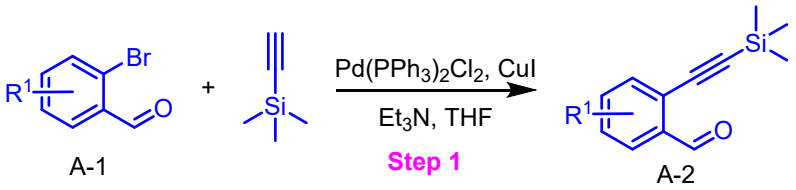
3-(3-methylbut-2-en-1-yl)-5,5-diphenyldihydrofuran-2(3*H*)-one (**29**):

Colourless oil; Eluent:petroluem ether/ethyl acetate 200:1; 5%, 9.2 mg; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 - 7.43 (m, 2H), 7.41 - 7.39 (m, 2H), 7.36 - 7.31 (m, 4H), 7.28 - 7.23 (m, 2H), 5.08 (tt, *J* = 7.3, 1.4 Hz, 1H), 3.13 (dd, *J* = 12.4, 7.7 Hz, 1H), 2.69 - 2.57 (m, 1H), 2.55 - 2.52 (m, 1H), 2.49 - 2.46 (m, 1H), 2.26 - 2.19 (m, 1H), 1.69 (s, 3H), 1.59 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.7, 144.0, 142.8, 134.8, 128.6, 128.5, 127.81, 127.77, 125.40, 125.35, 120.1, 87.5, 41.4, 40.6, 28.2, 25.8, 17.9; HRMS (ESI-TOF) Calcd for $C_{21}H_{22}O_2Na$ $[M+Na]^+$: 329.1512; found: 329.1508.

5. Synthesis of substrates

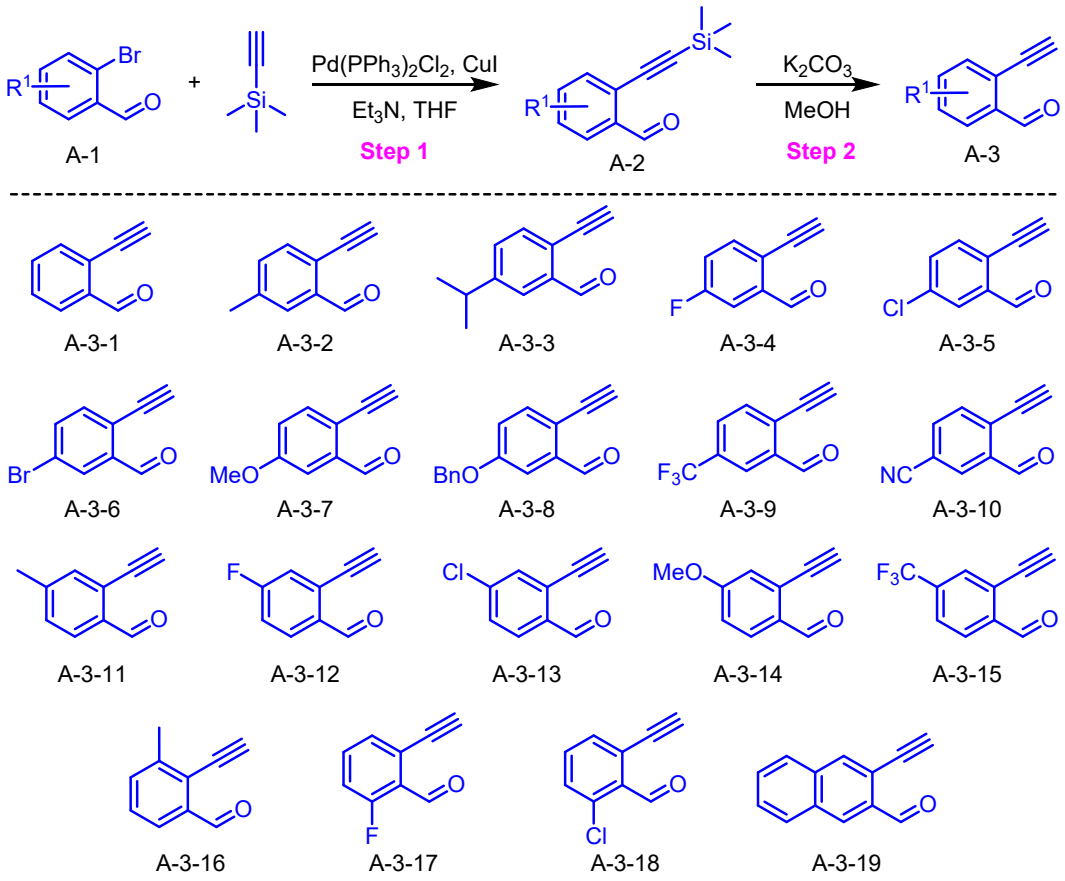
5.1 General procedure for the synthesis of 2-ethynylbenzaldehydes (Scheme S4, A-3-1 to A-3-19)

Step 1: Synthesis of intermediates **A-2**.[1]



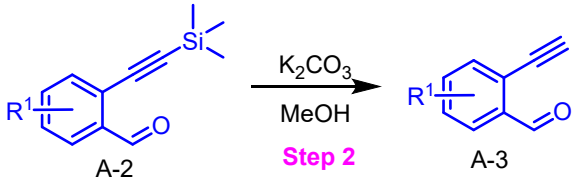
The substituted *o*-bromobenzaldehyde compounds **A-1** (10 mmol, 1 eq), $Pd(PPh_3)_2Cl_2$ (0.3 mmol, 0.03 eq, 210.6 mg), CuI (0.5 mmol, 0.05 eq, 95.2 mg), Et_3N (10 mL) and dry THF (20 mL) were added in a 250 mL round bottom flask under nitrogen. The mixture was stirred for 15 min at room temperature, then ethynyltrimethylsilane (12 mmol, 1.2 eq, 1176.2 mg) was added slowly to the mixtures above. Upon completion of the reaction by TLC, the reaction solution was diluted with DCM (300 mL) and washed with saturated NH_4Cl aqueous solution (100 mL) and H_2O (300 mL). The separated organic layer was dried with anhydrous Na_2SO_4 and filtered.

The filtrate was concentrated under reduced pressure to give the crude product, which was purified by column chromatographic separation (petroleum ether/ethyl acetate: 100:1) to obtain the desired product **A-2**.



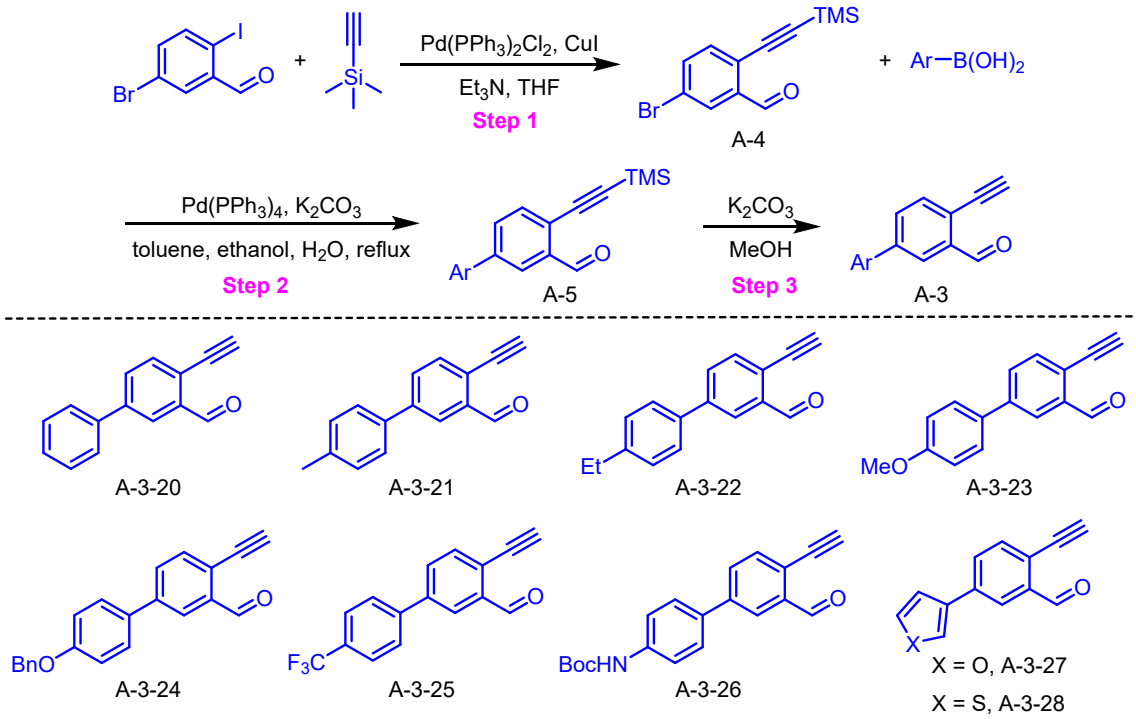
Scheme S4 General schemes for the synthesis of 2-ethynylbenzaldehydes (**A-3-1** to **A-3-19**)

Step 2: Synthesis of substrates **A-3**.[1]



To the suspension of K_2CO_3 (0.5 mmol, 0.1 eq, 69.1 mg) in MeOH (5 mL) was added the corresponding **A-2** (5 mmol, 1 eq). The resultant mixture was stirred at room temperature for about 15 min. Upon completion of the reaction by TLC, the mixture was concentrated under reduced pressure to give the crude product, which was purified

by column chromatographic separation (petroleum ether/ethyl acetate: 4:1) to obtain the desired product **A-3**.

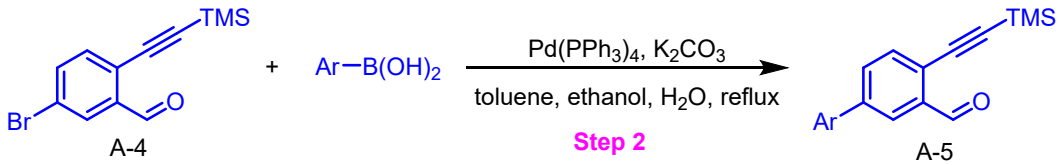


Scheme S5 General schemes for the synthesis of 2-ethynylbenzaldehydes (**A-3-20** to **A-3-28**)

5.2 General procedure for the synthesis of 2-ethynylbenzaldehydes (Scheme S5, A-3-20 to A-3-28).

Step 1: Synthesis of intermediates **A-4**: see the synthesis of intermediates **A-2**.

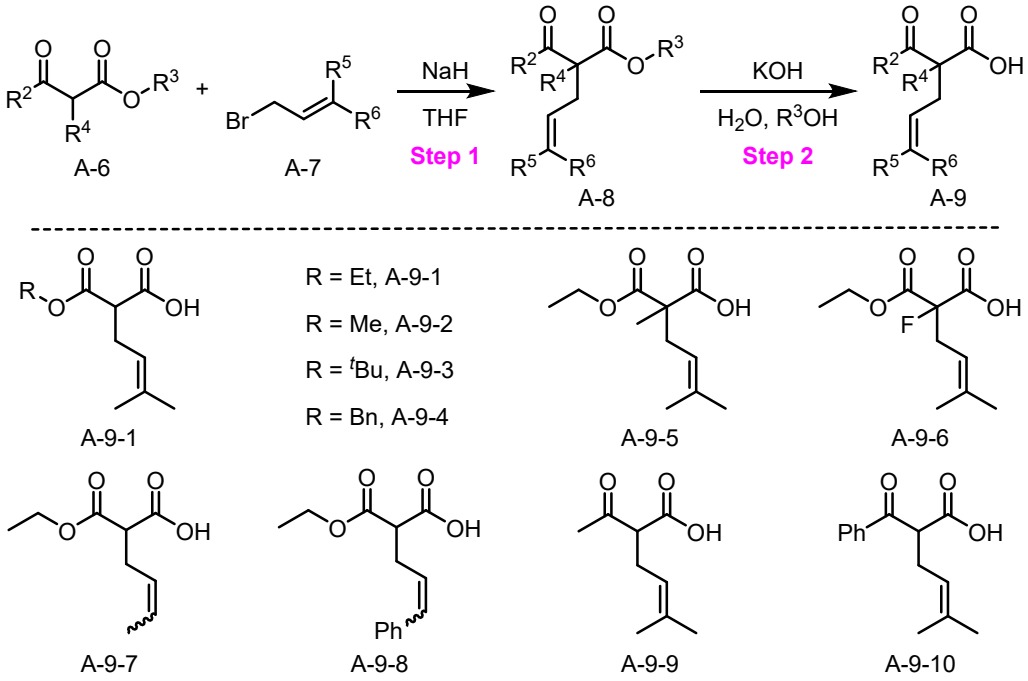
Step 2: Synthesis of intermediates **A-5**.[2]



To a solution of the **A-4** (5 mmol, 1 eq, 1400.0 mg) and the boric acid compound (5.5 mmol, 1.1 eq) in toluene (20 mL), ethanol (5 mL) and water (5 mL), $Pd(PPh_3)_4$ (0.15 mmol, 0.03 eq, 173.3 mg) and K_2CO_3 (12.5 mmol, 2.5 eq, 1700.0 mg) were added. The resulting mixture was heated to reflux for about 12 h under a nitrogen atmosphere.

Upon completion of the reaction, the reaction solution was diluted with DCM (300 mL) and washed with saturated NH_4Cl aqueous solution (100 mL) and H_2O (300 mL). The separated organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The filtrate was concentrated under reduced pressure to give the crude product, which was purified by column chromatographic separation (petroleum ether/ethyl acetate: 100:1) to obtain the desired product **A-5**.

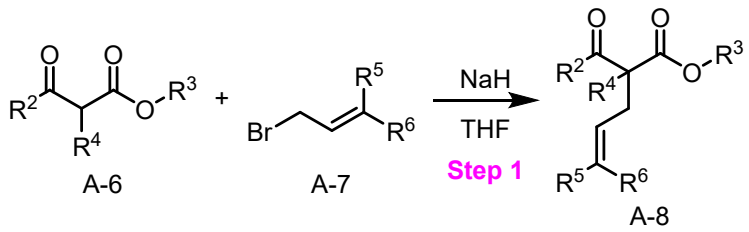
Step 3: Synthesis of intermediates **A-3-20 to A-3-28**: see the synthesis of intermediates **A-3** (**A-3-1** to **A-3-19**).



Scheme S6 General schemes for the synthesis of γ,δ-unsaturated carboxylic acids

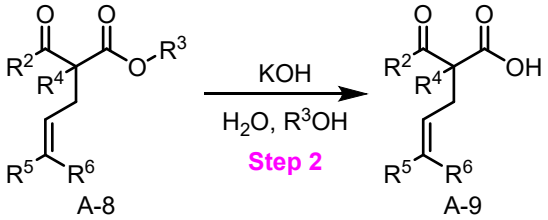
5.3 General procedure for the synthesis of γ,δ-unsaturated carboxylic acid (Scheme S6)

Step 1: Synthesis of intermediates **A-8**.[3]



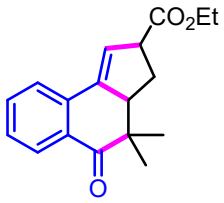
The corresponding activated methylene compound **A-6** (10 mmol, 1 eq), NaH (11 mmol, 1.1 eq, 264.0 mg) were dissolved in dry THF (30 mL). The reaction mixture was stirred under 0 °C for 1 h, then **A-7** (11 mmol, 1.1 eq) was added slowly. The mixture was warmed up to room temperature and allowed to stir for 12 - 24 h. Upon completion of the reaction by TLC, the reaction solution was diluted with ethyl acetate (300 mL) and washed with H_2O (300 mL). The organic phase was concentrated under reduced pressure to give the crude product, which was purified by column chromatographic separation (petroleum ether/ethyl acetate: 400:1) to give the desired product **A-8**.

Step 2: Synthesis of **A-9**.[4]



The corresponding **A-8** (5 mmol, 1 eq) and R^3OH (4 mL) were added to the KOH aqueous solution (6 mmol, 1.2 eq, 2.5 M) at 0 °C, then the mixture was warmed up to room temperature and allowed to stir for 12 - 24 h. Upon completion of the reaction by TLC, the solvent was removed under reduced pressure. the concentrate was diluted with water (10 mL) and extracted with DCM (20 mL x 3) to remove unreacted **A-8**. The aqueous layer was acidized with HCl aqueous solution to adjust pH to 2 and then re-extracted with DCM (30 mL x 3). The separated organic layer was dried with anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure to give the crude product, which was purified by column chromatographic separation (petroleum ether/ethyl acetate: 20:1) to obtain the desired product **A-9**.

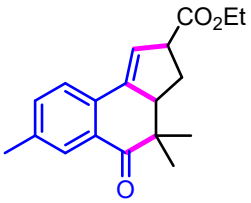
6. Characterization data for electrolysis products



3

ethyl 4,4-dimethyl-5-oxo-3,3a,4,5-tetrahydro-2*H*-cyclopenta[*a*]naphthalene-2-carboxylate (**3**):

Yellow oil; Eluent: petroluem ether/ethyl acetate 200:1; 47.1 mg, *d.r.* = 2.3:1, 83%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.0 - 7.97 (m, 1H), 7.66 - 7.62 (m, 1H), 7.54 - 7.49 (m, 1H), 7.40 - 7.35 (m, 1H), 6.34 (t, *J* = 2.4 Hz, 0.7H), 6.30 (t, *J* = 2.8 Hz, 0.3H), 4.25 - 4.14 (m, 2H), 3.83 - 3.77 (m, 1H), 3.37 (tt, *J* = 8.2, 2.5 Hz, 0.35H), 3.20 (tt, *J* = 8.6, 2.8 Hz, 0.65H), 2.50 - 2.44 (m, 0.3H), 2.39 - 2.32 (m, 0.7H), 2.21 - 2.06 (m, 1H), 1.33 - 1.28 (m, 3H), 1.24 - 1.23(m, 3H), 0.97 - 0.92 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.2, 174.0, 140.4, 135.0, 133.1, 129.7, 128.6, 128.2, 124.6, 123.7, 61.0, 52.8, 50.5, 46.0, 27.0, 21.9, 19.1, 14.3; HRMS (ESI-TOF) Calcd for $C_{18}H_{20}O_3Na$ $[M+Na]^+$: 307.1305; found: 307.1330.

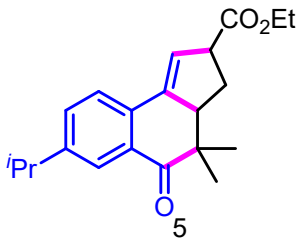


4

ethyl 4,4,7-trimethyl-5-oxo-3,3a,4,5-tetrahydro-2*H*-cyclopenta[*a*]naphthalene-2-carboxylate (**4**):

Yellow oil; Eluent: petroluem ether/ethyl acetate 200:1; 47.1 mg, *d.r.* = 2.3:1, 79%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 - 7.78 (m, 1H), 7.56 - 7.52 (m, 1H), 7.34 - 7.31 (m, 1H), 6.28 (t, *J* = 2.4 Hz, 0.7H), 6.23 (t, *J* = 2.8 Hz, 0.3H), 4.25 - 4.16 (m, 2H), 3.81 - 3.76 (m, 1H), 3.35 (tt, *J* = 8.2, 2.2 Hz, 0.3H), 3.18 (tt, *J* = 8.5, 2.7 Hz, 0.7H), 2.47 - 2.45 (m, 0.3H), 2.39 (s, 3H), 2.36 - 2.32 (m, 0.7H), 2.19 - 2.07 (m, 1H), 1.33 - 1.28 (m, 3H), 1.23 - 1.23 (m, 3H), 0.96 - 0.91 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.5, 174.1, 140.3, 138.7, 134.1, 132.4, 129.5, 128.3, 124.6, 122.6, 60.9, 52.8, 50.4, 46.0,

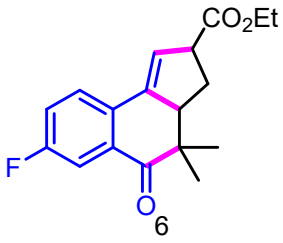
27.0, 21.9, 21.3, 19.1, 14.3; HRMS (ESI-TOF) Calcd for $C_{19}H_{22}O_3Na$ $[M+Na]^+$: 321.1461; found: 321.1491.



5

ethyl 7-isopropyl-4,4-dimethyl-5-oxo-3,3a,4,5-tetrahydro-2*H*-cyclopenta[*a*]-naphthalene-2-carboxylate (**5**):

Yellow oil; Eluent: petroluem ether/ethyl acetate 200:1; 48.9 mg, *d.r.* = 1.9:1, 75%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 - 7.91 (m, 1H), 7.47 - 7.46 (m, 1H), 7.26 - 7.23 (m, 1H), δ 6.35 (t, *J* = 2.4 Hz, 0.65H), 6.29 (t, *J* = 2.8 Hz, 0.35H), 4.25 - 4.15 (m, 2H), 3.83 - 3.77 (m, 1H), 3.35 (tt, *J* = 8.3, 2.5 Hz, 0.4H), 3.19 (tt, *J* = 8.5, 2.7 Hz, 0.6H), 2.99 - 2.92 (m, 1H), 2.49 - 2.43 (m, 0.4H), 2.39 - 2.31 (m, 0.6H), 2.20 - 2.06 (m, 1H), 1.34 - 1.32 (m, 3H), 1.31 - 1.27 (m, 6H), 1.23 - 1.22 (m, 3H), 0.97 - 0.92 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.0, 174.1, 154.5, 140.7, 135.0, 128.5, 127.3, 123.3, 122.5, 122.2, 61.0, 53.0, 50.5, 46.0, 34.4, 27.0, 23.6, 21.9, 19.2, 14.3; HRMS (ESI-TOF) Calcd for $C_{21}H_{26}O_4$ Na $[M+Na]^+$: 349.1774; found: 349.1835.

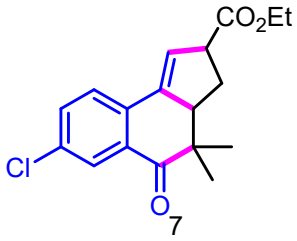


6

ethyl 7-fluoro-4,4-dimethyl-5-oxo-3,3a,4,5-tetrahydro-2*H*-cyclopenta[*a*]naphthalene -2-carboxylate (**6**):

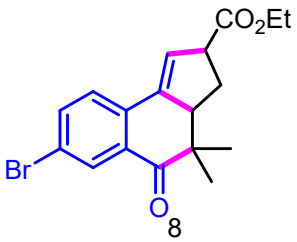
Yellow oil; Eluent: petroluem ether/ethyl acetate 200:1; 42.9 mg, *d.r.* = 1.5:1, 71%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 - 7.60 (m, 2H), 7.24 - 7.19 (m, 1H), 6.28 (t, *J* = 2.2 Hz, 0.6H), 6.24 (t, *J* = 2.6 Hz, 0.4H), 4.24 - 4.13 (m, 2H), 3.81 - 3.76 (m, 1H), 3.35 (tt, *J* = 8.2, 2.1 Hz, 0.4H), 3.18 (tt, *J* = 8.5, 2.5 Hz, 0.6H), 2.50 - 2.46 (m, 0.4H), 2.44 - 2.31 (m, 0.6H), 2.20 - 2.05 (m, 1H), 1.33 - 1.28 (m, 3H), 1.23 - 1.23 (m, 3H),

0.96 - 0.91 (m, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.09, -111.22; ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.1, 173.9, 164.0, 139.3, 131.6 (d, J = 6.5 Hz), 131.4 (d, J = 5.2 Hz), 126.9 (d, J = 7.3 Hz), 123.5, 120.9, 114.3 (d, J = 2.9 Hz), 61.0, 52.8, 50.4, 46.0, 27.0, 21.8, 19.0, 14.3; HRMS (ESI-TOF) Calcd for $C_{18}H_{19}O_3Na$ $[M+Na]^+$: 325.1210; found: 325.1283.



ethyl 7-chloro-4,4-dimethyl-5-oxo-3,3a,4,5-tetrahydro-2*H*-cyclopenta[*a*]naphthalene -2-carboxylate (**7**):

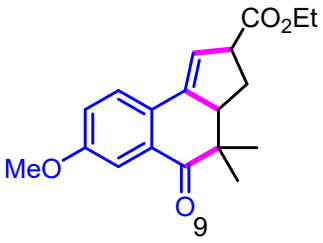
Yellow oil; Eluent: petroluem ether/ethyl acetate 200:1; 46.4 mg, *d.r.* = 1.5:1, 73%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 - 7.93 (m, 1H), 7.60 - 7.56 (m, 1H), 7.48 - 7.44 (m, 1H), 6.34 (t, J = 2.4 Hz, 0.6H), 6.29 (t, J = 2.8 Hz, 0.4H), 4.25 - 4.13 (m, 2H), 3.82 - 3.76 (m, 1H), 3.34 (tt, J = 8.2, 2.4 Hz, 0.4H), 3.18 (tt, J = 8.6, 2.7 Hz, 0.6H), 2.50 - 2.44 (m, 0.4H), 2.39 - 2.32 (m, 0.6H), 2.20 - 2.05 (m, 1H), 1.33 - 1.28 (m, 3H), 1.23 - 1.23 (m, 3H), 0.95 - 0.90 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.0, 173.7, 139.3, 134.8, 133.3, 133.2, 130.9, 128.0, 126.2, 124.5, 61.1, 52.6, 50.5, 46.0, 26.9, 21.8, 19.0, 14.3; HRMS (ESI-TOF) Calcd for $C_{18}H_{19}NO_3ClNa$ $[M+Na]^+$: 341.0915; found: 341.0917.



ethyl 7-bromo-4,4-dimethyl-5-oxo-3,3a,4,5-tetrahydro-2*H*-cyclopenta[*a*]naphthalene -2-carboxylate (**8**):

Yellow oil; Eluent: petroluem ether/ethyl acetate 200:1; 52.3 mg, *d.r.* = 1.5:1, 72%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 - 8.10 (m, 1H), 7.64 - 7.60 (m, 1H), 7.54 - 7.49

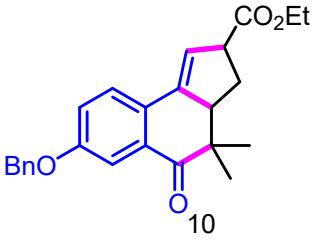
(m, 1H), 6.36 (t, J = 2.4 Hz, 0.6H), 6.31 (t, J = 2.8 Hz, 0.4H), 4.25 - 4.16 (m, 2H), 3.81 - 3.75 (m, 1H), 3.35 (tt, J = 8.2, 2.4 Hz, 0.4H), 3.19 (tt, J = 8.7, 2.7 Hz, 0.6H), 2.51 - 2.44 (m, 0.4H), 2.40 - 2.32 (m, 0.6H), 2.20 - 2.08 (m, 1H), 1.33 - 1.29 (m, 3H), 1.23 - 1.23 (m, 3H), 0.95 - 0.91 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.8, 173.7, 139.4, 136.0, 133.7, 131.2, 126.4, 124.6, 123.9, 122.8, 61.1, 52.6, 50.5, 46.0, 26.9, 21.8, 19.0, 14.3; HRMS (ESI-TOF) Calcd for $C_{18}H_{19}O_3BrNa$ $[M+Na]^+$: 385.0410; found: 385.0410.



9

ethyl 7-methoxy-4,4-dimethyl-5-oxo-3,3a,4,5-tetrahydro-2*H*-cyclopenta[*a*]-naphthalene-2-carboxylate (**9**):

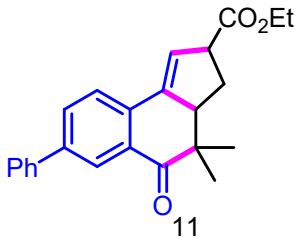
Yellow oil; Eluent: petroluem ether/ethyl acetate 200:1; 52.1 mg, *d.r.* = 3.3:1, 83%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 - 7.54 (m, 1H), 7.45 - 7.43 (m, 1H), 7.10 - 7.06 (m, 1H), 6.19 (t, J = 2.4 Hz, 0.77H), 6.15 (t, J = 2.8 Hz, 0.23H), 4.24 - 4.14 (m, 2H), 3.85 (s, 3H), 3.80 - 3.74 (m, 1H), 3.34 (tt, J = 8.3, 2.4 Hz, 0.26H), 3.17 (tt, J = 8.6, 2.7 Hz, 0.74H), 2.47 - 2.41 (m, 0.24H), 2.36 - 2.28 (m, 0.76H), 2.18 - 2.05 (m, 1H), 1.32 - 1.28 (m, 3H), 1.23 - 1.22 (m, 3H), 0.96 - 0.91 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.2, 174.2, 159.9, 139.9, 130.9, 128.4, 126.2, 121.6, 121.6, 109.9, 60.9, 55.5, 52.9, 50.4, 46.0, 26.9, 22.0, 19.2, 14.3; HRMS (ESI-TOF) Calcd for $C_{19}H_{22}O_4Na$ $[M+Na]^+$: 337.1410; found: 337.1419.



10

ethyl 7-(benzyloxy)-4,4-dimethyl-5-oxo-3,3a,4,5-tetrahydro-2*H*-cyclopenta[*a*]-naphthalene-2-carboxylate (**10**):

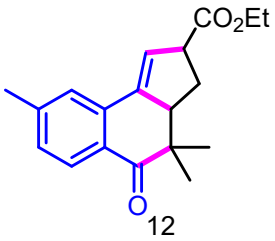
Yellow oil; Eluent: petroluem ether/ethyl acetate 200:1; 64.7 mg, *d.r.* = 2.3:1, 82%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 - 7.54 (m, 2H), 7.46 - 7.38 (m, 5H), 7.18 - 7.14 (m, 1H), 6.20 (t, *J* = 2.4 Hz, 0.7H), 6.16 (t, *J* = 2.8 Hz, 0.3H), 5.11 (s, 2H), 4.24 - 4.13 (m, 2H), 3.81 - 3.74 (m, 1H), 3.35 (tt, *J* = 8.3, 2.4 Hz, 0.29H), 3.17 (tt, *J* = 8.6, 2.7 Hz, 0.71H), 2.48 - 2.42 (m, 0.26H), 2.37 - 2.29 (m, 0.74H), 2.19 - 2.04 (m, 1H), 1.33 - 1.23 (m, 6H), 0.97 - 0.92 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.2, 174.2, 159.1, 139.9, 136.4, 130.9, 128.7, 128.2, 127.7, 126.3, 122.2, 121.7, 121.0, 111.1, 70.2, 60.9, 52.8, 50.4, 46.0, 26.9, 22.0, 19.2, 14.3; HRMS (ESI-TOF) Calcd for $C_{25}H_{26}O_4Na$ $[M+Na]^+$: 413.1723; found: 413.1771.



11

ethyl 4,4-dimethyl-5-oxo-7-phenyl-3,3a,4,5-tetrahydro-2*H*-cyclopenta[*a*]naphthalene -2-carboxylate (**11**):

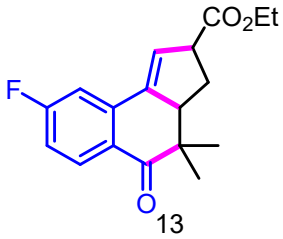
Yellow oil; Eluent: petroluem ether/ethyl acetate 200:1; 53.3 mg, *d.r.* = 1.9:1, 74%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.24 - 8.22 (m, 1H), 7.78 - 7.69 (m, 2H), 7.65 - 7.63 (m, 2H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 6.38 (t, *J* = 2.4 Hz, 0.65H), 6.33 (t, *J* = 2.8 Hz, 0.35H), 4.26 - 4.15 (m, 2H), 3.85 - 3.80 (m, 1H), 3.40 (tt, *J* = 8.2, 2.4 Hz, 0.4H), 3.23 (tt, *J* = 8.5, 2.7 Hz, 0.6H), 2.53 - 2.46 (m, 0.4H), 2.41 - 2.34 (m, 0.6H), 2.23 - 2.11 (m, 1H), 1.34 - 1.29 (m, 3H), 1.27 - 1.26 (m, 3H), 1.00 - 0.96 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.2, 173.9, 141.4, 141.0, 140.1, 139.8, 133.8, 131.6, 130.0, 128.9, 127.8, 127.0, 126.5, 125.2, 123.8, 123.0, 61.0, 52.8, 50.6, 46.1, 27.0, 21.9, 19.1, 14.3; HRMS (ESI-TOF) Calcd for $C_{24}H_{24}O_3Na$ $[M+Na]^+$: 383.1618; found: 383.1619.



12

ethyl 4,4,8-trimethyl-5-oxo-3,3a,4,5-tetrahydro-2*H*-cyclopenta[*a*]naphthalene-2-carboxylate (**12**):

Yellow oil; Eluent: petroluem ether/ethyl acetate 200:1; 43.5 mg, *d.r.* = 2.3:1, 73%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 - 7.87 (m, 1H), 7.45 - 7.42 (m, 1H), 7.20 - 7.17 (m, 1H), 6.32 (t, *J* = 2.4 Hz, 0.7H), 6.27 (t, *J* = 2.8 Hz, 0.3H), 4.24 - 4.15 (m, 2H), 3.81 - 3.76 (m, 1H), 3.34 (tt, *J* = 8.2, 2.4 Hz, 0.3H), 3.18 (tt, *J* = 8.5, 2.7 Hz, 0.7H), 2.47 - 2.45 (m, 0.3H), 2.40 - 2.40 (m, 3H), 2.36 - 2.33 (m, 0.7H), 2.20 - 2.12 (m, 1H), 1.33 - 1.29 (m, 3H), 1.23 - 1.22 (m, 3H), 0.95 - 0.91 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.1, 174.0, 143.8, 140.5, 135.0, 129.8, 128.3, 127.5, 124.8, 123.4, 60.9, 52.9, 50.5, 46.0, 26.9, 21.9, 21.8, 19.2, 14.3; HRMS (ESI-TOF) Calcd for $C_{19}H_{22}O_3Na$ $[M+Na]^+$: 321.1461; found: 321.1475.

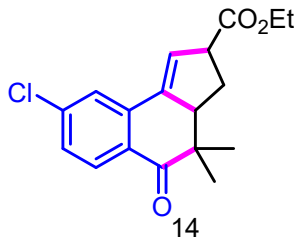


13

ethyl 8-fluoro-4,4-dimethyl-5-oxo-3,3a,4,5-tetrahydro-2*H*-cyclopenta[*a*]naphthalene-2-carboxylate (**13**):

Yellow oil; Eluent: petroluem ether/ethyl acetate 200:1; 42.3 mg, *d.r.* = 1.5:1, 70%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 - 7.99 (m, 1H), 7.29 - 7.27 (m, 0.62H), 7.24 - 7.24 (m, 0.38H), 7.08 - 7.02 (m, 1H), 6.35 (t, *J* = 2.4 Hz, 0.6H), 6.30 (t, *J* = 2.7 Hz, 0.4H), 4.25 - 4.14 (m, 2H), 3.83 - 3.77 (m, 1H), 3.35 (tt, *J* = 8.2, 2.4 Hz, 0.4H), 3.19 (tt, *J* = 8.5, 2.7 Hz, 0.6H), 2.51 - 2.44 (m, 0.4H), 2.40 - 2.32 (m, 0.6H), 2.21 - 2.08 (m, 1H), 1.33 - 1.29 (m, 3H), 1.23 - 1.22 (m, 3H), 0.95 - 0.91 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.8, 173.7, 164.4, 139.7 (d, *J* = 2.6 Hz), 137.6, 131.3, 126.3 (d, *J* = 2.6 Hz), 125.3, 116.5 (d, *J* = 7.8 Hz), 110.8 (t, *J* = 22.5 Hz), 61.1, 52.7, 50.5, 45.9, 27.0, 21.8,

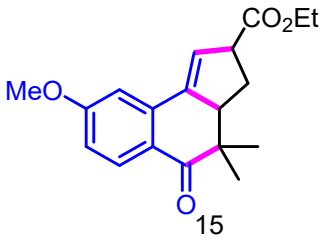
19.1, 14.3; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -105.15, -105.17; HRMS (ESI-TOF) Calcd for $C_{18}H_{19}O_3FNa$ $[M+Na]^+$: 325.1210; found: 325.1278.



14

ethyl 8-chloro-4,4-dimethyl-5-oxo-3,3a,4,5-tetrahydro-2*H*-cyclopenta[*a*]naphthalene -2-carboxylate (**14**):

Yellow oil; Eluent: petroluem ether/ethyl acetate 200:1; 46.4 mg, *d.r.* = 3:1, 73%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 - 7.91 (m, 1H), 7.62 - 7.59 (m, 1H), 7.35 - 7.31 (m, 1H), δ 6.37 (t, *J* = 2.4 Hz, 0.75H), 6.32 (t, *J* = 2.8 Hz, 0.25H), 4.25 - 4.16 (m, 2H), 3.80 (tt, *J* = 8.5, 2.8 Hz, 1H), 3.35 (tt, *J* = 8.2, 2.5 Hz, 0.25H), 3.19 (tt, *J* = 8.5, 2.7 Hz, 0.75H), 2.48 (ddd, *J* = 13.6, 8.5, 2.5 Hz, 0.25H), 2.36 (dt, *J* = 13.4, 8.6 Hz, 0.75H), 2.22 - 2.08 (m, 1H), 1.33 - 1.29 (m, 3H), 1.23 - 1.23 (m, 3H), 0.95 - 0.91 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.1, 173.4, 139.5, 139.3, 136.4, 130.0, 128.9, 128.0, 125.3, 124.5, 61.1, 52.7, 50.5, 46.0, 26.9, 21.8, 19.0, 14.3; HRMS (ESI-TOF) Calcd for $C_{18}H_{19}O_3ClNa$ $[M+Na]^+$: 341.0915; found: 341.0925.

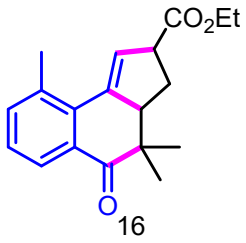


15

ethyl 8-methoxy-4,4-dimethyl-5-oxo-3,3a,4,5-tetrahydro-2*H*-cyclopenta[*a*]-naphthalene-2-carboxylate (**15**):

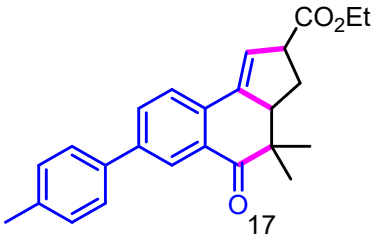
Yellow oil; Eluent: petroluem ether/ethyl acetate 200:1; 51.5 mg, *d.r.* = 4:1, 82%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (dd, *J* = 8.8, 4.3 Hz, 1H), 7.04 (dd, *J* = 6.5, 2.5 Hz, 1H), 6.91 (dt, *J* = 8.8, 3.1 Hz, 1H), 6.33 (t, *J* = 2.4 Hz, 0.8H), 6.27 (t, *J* = 2.8 Hz, 0.2H), 4.24 - 4.18 (m, 2H), 3.88 - 3.88 (m, 3H), 3.79 (td, *J* = 8.6, 7.3, 4.4 Hz, 1H), 3.34 (tt, *J* = 8.2, 2.5 Hz, 0.2H), 3.19 (tt, *J* = 8.5, 2.7 Hz, 0.8H), 2.49 - 2.43 (m, 0.2H), 2.39 -

2.31 (m, 0.8H), 2.20 - 2.10 (m, 1H), 1.33 - 1.29 (m, 3H), 1.22 - 1.21 (m, 3H), 0.95 - 0.91 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.2, 173.9, 163.3, 140.6, 137.0, 130.6, 123.9, 123.5, 115.6, 107.9, 61.0, 55.5, 53.0, 50.4, 45.8, 27.0, 22.0, 19.4, 14.3; HRMS (ESI-TOF) Calcd for $C_{19}H_{22}O_4Na$ $[M+Na]^+$: 337.1410; found: 337.1423.



ethyl 4,4,9-trimethyl-5-oxo-3,3a,4,5-tetrahydro-2*H*-cyclopenta[*a*]naphthalene-2-carboxylate (**16**):

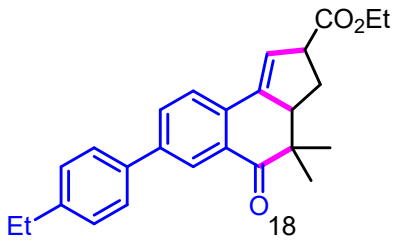
Yellow oil; Eluent: petroluem ether/ethyl acetate 200:1; 41.7 mg, *d.r.* = 3:1, 70%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 - 7.94 (m, 1H), 7.42 - 7.39 (m, 1H), 7.20 - 7.27 (m, 0.85H), 7.25 (s, 0.15H), 66.28 (t, *J* = 2.3 Hz, 0.75H), 6.22 (t, *J* = 2.5 Hz, 0.25H), 4.24 - 4.18 (m, 2H), 3.91 (ddt, *J* = 9.6, 7.3, 2.3 Hz, 0.75H), 3.83 (dq, *J* = 7.4, 2.3 Hz, 0.25H), 3.32 (ddt, *J* = 9.5, 5.0, 2.3 Hz, 0.25H), 3.24 (ddt, *J* = 9.1, 7.2, 2.1 Hz, 0.75H), 2.55 - 2.53 (m, 3H), 2.41 - 2.28 (m, 1H), 2.21 - 2.07 (m, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.25 - 1.23 (m, 3H), 0.97 - 0.94 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.4, 174.0, 139.5, 136.3, 136.2, 134.2, 131.0, 128.4, 127.7, 126.7, 61.0, 55.3, 51.4, 46.2, 25.5, 23.5, 22.0, 18.7, 14.3; HRMS (ESI-TOF) Calcd for $C_{19}H_{22}O_3Na$ $[M+Na]^+$: 321.1461; found: 321.1456.



ethyl 4,4-dimethyl-5-oxo-7-(*p*-tolyl)-3,3a,4,5-tetrahydro-2*H*-cyclopenta[*a*]-naphthalene-2-carboxylate (**17**):

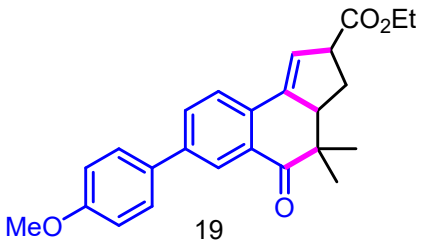
Yellow oil; Eluent: petroluem ether/ethyl acetate 200:1; 57.6 mg, *d.r.* = 2.3:1, 77%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 (dd, *J* = 4.3, 1.9 Hz, 1H), 7.77 - 7.66 (m, 2H),

7.54 (d, J = 8.1 Hz, 2H), 7.27 (s, 1H), 7.25 (s, 1H), 6.36 (t, J = 2.4 Hz, 0.7H), 6.32 (t, J = 2.8 Hz, 0.3H), 4.26 - 4.15 (m, 2H), 3.82 (tt, J = 7.6, 2.3 Hz, 1H), 3.40 (tt, J = 8.3, 2.4 Hz, 0.3H), 3.22 (tt, J = 8.5, 2.7 Hz, 0.7H), 2.52 - 2.46 (m, 0.4H), 2.40 (s, 3H), 2.40 - 2.33 (m, 0.6H), 2.23 - 2.10 (m, 1H), 1.33 - 1.31 (m, 3H), 1.26 - 1.26 (m, 3H), 1.00 - 0.95 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.3, 174.0, 141.3, 140.2, 137.8, 136.9, 133.6, 131.4, 130.0, 129.6, 126.8, 126.2, 125.4, 125.2, 123.6, 122.8, 61.0, 52.8, 50.6, 46.1, 29.7, 27.0, 21.1, 19.1, 14.3; HRMS (ESI-TOF) Calcd for $C_{25}H_{26}O_3Na$ $[M+Na]^+$: 397.1774; found: 397.1736.



ethyl 7-(4-ethylphenyl)-4,4-dimethyl-5-oxo-3,3a,4,5-tetrahydro-2*H*-cyclopenta[*a*]-naphthalene-2-carboxylate (**18**):

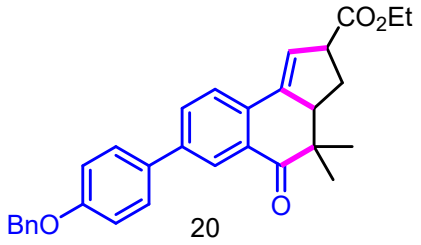
Yellow oil; Eluent: petroluem ether/ethyl acetate 200:1; 58.2 mg, *d.r.* = 1.5:1, 75%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.22 (dd, J = 4.4, 1.8 Hz, 1H), 7.77 - 7.67 (m, 2H), 7.56 (d, J = 8.1 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 6.36 (t, J = 2.4 Hz, 0.6H), 6.32 (t, J = 2.8 Hz, 0.4H), 4.26 - 4.17 (m, 2H), 3.84 - 3.79 (m, 1H), 3.40 (tt, J = 8.2, 2.3 Hz, 0.4H), 3.22 (tt, J = 8.5, 2.6 Hz, 0.6H), 2.70 (q, J = 7.6 Hz, 2H), 2.52 - 2.46 (m, 0.4H), 2.41 - 2.33 (m, 0.6H), 2.23 - 2.08 (m, 1H), 1.34 - 1.29 (m, 6H), 1.28 - 1.26 (m, 3H), 1.00 - 0.95 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.3, 174.0, 144.1, 141.4, 141.0, 140.2, 137.2, 133.6, 131.5, 130.0, 128.5, 126.9, 126.2, 125.2, 123.6, 122.8, 61.0, 52.8, 50.6, 46.1, 28.6, 27.0, 21.9, 19.2, 15.6, 14.3; HRMS (ESI-TOF) Calcd for $C_{26}H_{28}O_3Na$ $[M+Na\,]^+$: 411.1931; found: 411.1933.



19

ethyl 7-(4-methoxyphenyl)-4,4-dimethyl-5-oxo-3,3a,4,5-tetrahydro-2*H*-cyclopenta -[*a*]-naphthalene-2-carboxylate (**19**):

Yellow oil; Eluent: petroluem ether/ethyl acetate 200:1; 62.4 mg, *d.r.* = 2.3:1, 80%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18 (dd, *J* = 4.2, 1.7 Hz, 1H), 7.73 - 7.71 (m, 2H), 7.59 - 7.57 (m, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 6.35 (t, *J* = 2.4 Hz, 0.7H), 6.31 (t, *J* = 2.8 Hz, 0.3H), 4.26 - 4.17 (m, 2H), 3.86 (s, 3H), 3.83 - 3.78 (m, 1H), 3.39 (tt, *J* = 8.3, 2.4 Hz, 0.3H), 3.22 (tt, *J* = 8.5, 2.7 Hz, 0.7H), 2.52 - 2.46 (m, 0.3H), 2.41 - 2.33 (m, 0.7H), 2.16 - 2.10 (m, 1H), 1.34 - 1.29 (m, 3H), 1.26 - 1.26 (m, 3H), 1.00 - 0.95 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.3, 174.0, 159.6, 141.0, 140.2, 133.2, 132.3, 131.2, 130.0, 128.0, 125.9, 125.4, 125.2, 123.4, 122.7, 114.4, 61.0, 55.4, 52.8, 50.5, 46.1, 27.0, 21.9, 19.1, 14.3; HRMS (ESI-TOF) Calcd for $C_{25}H_{26}O_4Na$ $[M+Na]^+$: 413.1723; found: 413.1721.

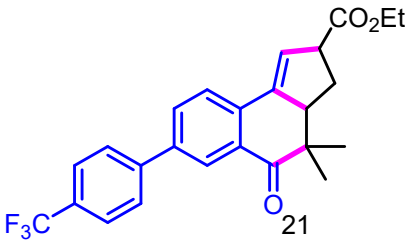


20

ethyl 7-(4-(benzyloxy)phenyl)-4,4-dimethyl-5-oxo-3,3a,4,5-tetrahydro-2*H*-cyclopenta -[*a*]-naphthalene-2-carboxylate (**20**):

Yellow oil; Eluent: petroluem ether/ethyl acetate 200:1; 75.5 mg, *d.r.* = 1.9:1, 81%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18 (dd, *J* = 4.3, 1.7 Hz, 1H), 7.74 - 7.66 (m, 2H), 7.59 - 7.57 (m, 2H), 7.47 - 7.32 (m, 5H), 7.06 (d, *J* = 8.7 Hz, 2H), 6.36 (t, *J* = 2.4 Hz, 0.65H), 6.31 (t, *J* = 2.8 Hz, 0.35H), 5.12 (s, 2H), 4.26 - 4.15 (m, 2H), 3.84 - 3.79 (m, 1H), 3.39 (tt, *J* = 8.1, 2.3 Hz, 0.4H), 3.22 (tt, *J* = 8.5, 2.6 Hz, 0.6H), 2.52 - 2.46 (m,

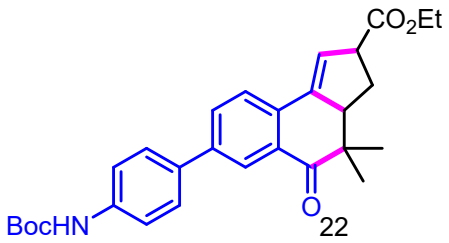
0.4H), 2.41 - 2.33 (m, 0.6H), 2.20 - 2.08 (m, 1H), 1.34 - 1.29 (m, 3H), 1.26 - 1.26 (m, 3H), 1.00 - 0.95 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.3, 174.0, 158.8, 141.0, 140.1, 136.8, 133.3, 132.5, 131.2, 130.0, 128.7, 128.1, 127.5, 125.9, 125.2, 123.5, 122.7, 115.3, 70.1, 61.0, 52.8, 50.5, 46.1, 27.0, 21.9, 19.2, 14.3; HRMS (ESI-TOF) Calcd for $C_{31}H_{30}O_4Na$ $[M+Na]^+$: 489.2036; found: 489.2127.



21

ethyl 4,4-dimethyl-5-oxo-7-(4-(trifluoromethyl)phenyl)-3,3a,4,5-tetrahydro-2*H*-cyclopenta-[*a*]-naphthalene-2-carboxylate (**21**):

Yellow oil; Eluent: petroluem ether/ethyl acetate 200:1; 53.9 mg, *d.r.* = 1:1, 63%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.24 - 8.23 (m, 1H), 7.77 - 7.70 (m, 6H), 6.42 (t, *J* = 2.4 Hz, 0.5H), 6.37 (t, *J* = 2.8 Hz, 0.5H), 4.27 - 4.16 (m, 2H), 3.87 - 3.81 (m, 1H), 3.41 (tt, *J* = 8.2, 2.4 Hz, 0.4H), 3.24 (tt, *J* = 8.6, 2.7 Hz, 0.6H), 2.54 - 2.48 (m, 0.4H), 2.43 - 2.35 (m, 0.6H), 2.24 - 2.12 (m, 1H), 1.35 - 1.30 (m, 3H), 1.28 - 1.27 (m, 3H), 1.01 - 0.96 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.0, 173.8, 143.3, 140.8, 139.9 (t, *J* = 4.7 Hz), 134.7, 131.6, 130.2 (t, *J* = 12.4 Hz), 127.3, 125.9 (q, *J* = 3.6 Hz), 125.7, 125.5, 124.6, 123.8, 61.0, 52.7, 50.6, 46.1, 27.0, 21.9, 19.1, 14.3; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.46; HRMS (ESI-TOF) Calcd for $C_{25}H_{23}NO_3F_3Na$ $[M+Na]^+$: 451.1492; found: 451.1492.

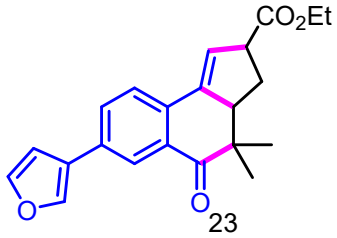


22

ethyl 7-(4-((*tert*-butoxycarbonyl)amino)phenyl)-4,4-dimethyl-5-oxo-3,3a,4,5-tetrahydro-2*H*-cyclopenta[*a*]naphthalene-2-carboxylate (**22**):

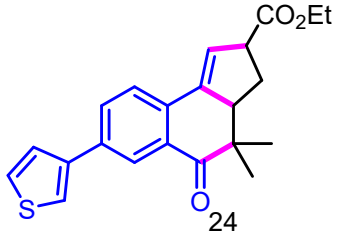
Yellow oil; Eluent: petroluem ether/ethyl acetate 200:1; 67.5 mg, *d.r.* = 1.5:1, 71%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.20 - 8.18 (m, 1H), 7.75 - 7.67 (m, 2H), 7.59 - 7.57

(m, 2H), 7.47 - 7.45 (m, 2H), 6.60 (s, 1H), 6.36 (t, J = 2.3 Hz, 0.6H), 6.32 (t, J = 2.8 Hz, 0.4H), 4.26 - 4.15 (m, 2H), 3.85 - 3.79 (m, 1H), 3.39 (tt, J = 8.0, 2.2 Hz, 0.4H), 3.22 (tt, J = 8.5, 2.7 Hz, 0.6H), 2.52 - 2.46 (m, 0.4H), 2.41 - 2.33 (m, 0.6H), 2.22 - 2.10 (m, 1H), 1.54 (s, 9H), 1.34 - 1.29 (m, 3H), 1.28 - 1.26 (m, 3H), 1.00 - 0.95 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.3, 174.0, 152.6, 141.0, 140.8, 141.0, 140.1, 138.3, 133.5, 131.2, 130.0, 127.5, 125.2, 123.6, 118.8, 80.8, 61.0, 52.8, 50.5, 46.1, 28.4, 27.0, 22.0, 19.1, 14.3; HRMS (ESI-TOF) Calcd for $C_{29}H_{33}O_5NNa$ $[M+Na]^+$: 498.2251; found: 498.2249.



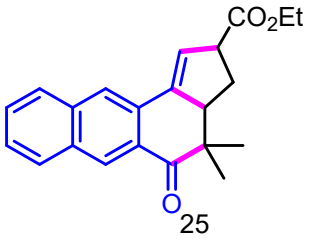
ethyl 7-(furan-3-yl)-4,4-dimethyl-5-oxo-3,3a,4,5-tetrahydro-2*H*-cyclopenta-[*a*]naphthalene-2-carboxylate (**23**):

Yellow oil; Eluent: petroluem ether/ethyl acetate 200:1; 50.4 mg, *d.r.* = 1.5:1, 72%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 - 8.08 (m, 1H), 7.81 (s, 1H), 7.68 - 7.64 (m, 2H), 7.49 (t, J = 1.6 Hz, 1H), 6.76 (s, 1H), 6.35 (t, J = 2.4 Hz, 0.6H), 6.30 (t, J = 2.7 Hz, 0.4H), 4.26 - 4.15 (m, 2H), 3.84 - 3.79 (m, 1H), 3.38 (tt, J = 8.2, 2.3 Hz, 0.4H), 3.21 (tt, J = 8.6, 2.7 Hz, 0.6H), 2.51 - 2.45 (m, 0.4H), 2.40 - 2.33 (m, 0.6H), 2.22 - 2.07 (m, 1H), 1.36 - 1.29 (m, 3H), 1.28 - 1.25 (m, 3H), 0.99 - 0.94 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.3, 174.0, 144.0, 140.0, 139.1, 133.5, 132.8, 130.3, 130.0, 125.5, 125.0, 123.5, 122.8, 108.6, 61.0, 52.7, 50.5, 46.0, 27.0, 21.9, 19.1, 14.3; HRMS (ESI-TOF) Calcd for $C_{22}H_{22}O_4Na$ $[M+Na]^+$: 373.1410; found: 373.1412.



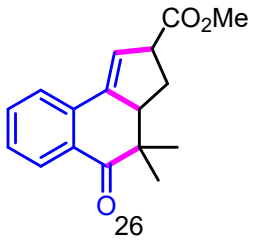
ethyl 4,4-dimethyl-5-oxo-7-(thiophen-3-yl)-3,3a,4,5-tetrahydro-2*H*-cyclopenta-[*a*]naphthalene-2-carboxylate (**24**):

Yellow oil; Eluent: petroluem ether/ethyl acetate 200:1; 52.0 mg, *d.r.* = 1.5:1, 71%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.22 - 8.20 (m, 1H), 7.78 - 7.74 (m, 1H), 7.69 - 7.65 (m, 1H), 7.55 - 7.55 (m, 1H), 7.46 - 7.44 (m, 1H), 7.42 - 7.40 (m, 1H), 6.36 (t, *J* = 2.4 Hz, 0.6H), 6.31 (t, *J* = 2.8 Hz, 0.4H), 4.26 - 4.17 (m, 2H), 3.84 - 3.79 (m, 0.9H), 3.72 (d, *J* = 7.0 Hz, 0.1H), 3.39 (tt, *J* = 8.2, 2.4 Hz, 0.4H), 3.22 (tt, J = 8.6, 2.7 Hz, 0.6H), 2.52 - 2.46 (m, 0.4H), 2.41 - 2.33 (m, 0.6H), 2.22 - 2.08 (m, 1H), 1.34 - 1.26 (m, 3H), 1.26 (d, *J* = 2.1 Hz, 3H), 0.97 (d, *J* = 19.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.3, 174.0, 141.1, 140.1, 136.0, 133.6, 130.9, 130.0, 126.6, 126.1, 125.7, 125.3, 123.7, 121.1, 61.0, 52.7, 50.5, 46.1, 27.0, 21.9, 19.1, 14.3; HRMS (ESI-TOF) Calcd for $C_{22}H_{22}O_3SNa$ $[M+Na]^+$: 389.1182; found: 389.1188.



ethyl 4,4-dimethyl-5-oxo-3,3a,4,5-tetrahydro-2*H*-cyclopenta[*a*]anthracene-2-carboxylate (**25**):

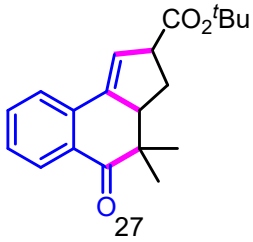
Yellow oil; Eluent: petroluem ether/ethyl acetate 200:1; 46.1 mg, *d.r.* = 1.9:1, 69%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.61 - 8.51 (m, 1H), 8.09 (dd, *J* = 8.7, 3.3 Hz, 1H), 7.88 - 7.77 (m, 2H), 7.63 - 7.57 (m, 2H), 6.58 (t, *J* = 2.1 Hz, 0.65H), 6.47 (t, *J* = 2.3 Hz, 0.35H), 4.24 (dq, *J* = 41.2, 7.1 Hz, 2H), 4.10 - 4.06 (m, 0.6H), 3.92 (tq, *J* = 6.8, 2.5 Hz, 0.4H), 3.48 - 3.34 (m, 0.94H), 3.23 (s, 0.06H), 2.53 - 2.42 (m, 1H), 2.37 - 2.22 (m, 1H), 1.39 - 1.25 (m, 6H), 1.00 (d, *J* = 2.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.2, 173.6, 138.4, 136.3, 135.5, 129.7, 128.9, 128.8, 128.6, 128.5, 128.2, 127.1, 127.0, 123.9, 61.0, 56.9, 51.8, 47.5, 25.2, 22.5, 18.8, 14.3; HRMS (ESI-TOF) Calcd for $C_{22}H_{22}O_3Na$ $[M+Na]^+$: 357.1461; found: 357.1465.



26

methyl 4,4-dimethyl-5-oxo-3,3a,4,5-tetrahydro-2*H*-cyclopenta[*a*]naphthalene-2-carboxylate (**26**):

Yellow oil; Eluent: petroluem ether/ethyl acetate 200:1; 41.0 mg, *d.r.* = 1.5:1, 76%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 - 7.97 (m, 1H), 7.65 - 7.61 (m, 1H), 7.51 (tdd, *J* = 7.8, 3.6, 1.4 Hz, 1H), 7.40 - 7.35 (m, 1H), 6.34 (t, *J* = 2.4 Hz, 0.6H), 6.29 (t, *J* = 2.8 Hz, 0.4H), 3.81 (ddd, *J* = 8.9, 5.9, 2.6 Hz, 1H), 3.77 (s, 2H), 3.71 (s, 1H), 3.36 (tt, *J* = 8.2, 2.4 Hz, 0.4H), 3.23 - 3.17 (m, 0.6H), 2.48 (ddd, *J* = 13.6, 8.4, 2.4 Hz, 0.4H), 2.36 (dt, *J* = 13.3, 8.5 Hz, 0.6H), 2.21 - 2.09 (m, 1H), 1.23 (d, *J* = 2.7 Hz, 3H), 0.94 (d, *J* = 17.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.2, 174.4, 140.5, 134.9, 133.1, 129.7, 128.7, 128.2, 124.6, 123.5, 52.8, 52.1, 50.3, 46.0, 27.0, 21.9, 19.1; HRMS (ESI-TOF) Calcd for $C_{17}H_{18}O_3Na$ $[M+Na]^+$: 293.1148; found: 293.1179.

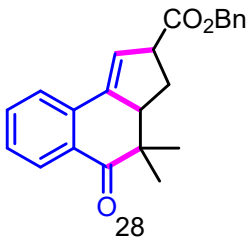


27

tert-butyl 4,4-dimethyl-5-oxo-3,3a,4,5-tetrahydro-2*H*-cyclopenta[*a*]naphthalene-2 -carboxylate (**27**):

Yellow oil; Eluent: petroluem ether/ethyl acetate 200:1; 45.6 mg, *d.r.* = 4:1, 73%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 - 7.97 (m, 1H), 7.66 - 7.62 (m, 1H), 7.53 - 7.48 (m, 1H), 7.39 - 7.34 (m, 1H), 6.30 (t, *J* = 2.4 Hz, 0.8H), 6.27 (t, *J* = 2.8 Hz, 0.2H), 3.70 (dt, *J* = 6.0, 2.7 Hz, 1H), 3.34 - 3.27 (m, 0.2H), 3.18 (tt, *J* = 8.5, 2.7 Hz, 0.8H), 2.42 - 2.38 (m, 0.2H), 2.34 - 2.27 (m, 0.8H), 2.17 - 2.02 (m, 1H), 1.48 (d, *J* = 13.1 Hz, 9H), 1.23 (s, 3H), 0.94 (d, *J* = 23.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.3, 173.2, 140.1, 135.2, 133.1, 129.7, 128.5, 128.2, 124.6, 124.3, 81.0, 52.8, 51.62, 46.0, 28.2,

26.9, 21.9, 19.0; HRMS (ESI-TOF) Calcd for $C_{20}H_{24}O_3Na$ $[M+Na]^+$: 335.1618; found: 335.1618.



benzyl 4,4-dimethyl-5-oxo-3,3a,4,5-tetrahydro-2*H*-cyclopenta[*a*]naphthalene-2-carboxylate (**28**):

Yellow oil; Eluent: petroluem ether/ethyl acetate 200:1; 51.2 mg, *d.r.* = 1.5:1, 74%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 - 7.96 (m, 1H), 7.62 (t, *J* = 7.9 Hz, 1H), 7.54 - 7.48 (m, 1H), 7.39 - 7.35 (m, 6H), 6.35 (t, *J* = 2.4 Hz, 0.6H), 6.31 (t, *J* = 2.8 Hz, 0.4H), 5.21 (s, 1H), 5.16 - 5.12 (m, 1H), 3.89 - 3.83 (m, 1H), 3.38 (tt, *J* = 8.2, 2.4 Hz, 0.4H), 3.21 (tt, *J* = 8.6, 2.7 Hz, 0.6H), 2.53 - 2.47 (m, 0.4H), 2.41 - 2.34 (m, 0.6H), 2.24 - 2.09 (m, 1H), 1.23 (d, *J* = 4.1 Hz, 3H), 0.94 (d, *J* = 13.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.2, 173.8, 160.0, 140.6, 135.9, 134.9, 133.1, 129.7, 128.7, 128.6, 128.4, 128.2, 128.1, 124.6, 123.4, 122.7, 66.8, 52.8, 50.5, 46.0, 27.0, 21.9, 19.1; HRMS (ESI-TOF) Calcd for $C_{23}H_{22}O_3Na$ $[M+Na]^+$:369.1461; found: 369.1460.

7. X-ray crystallography studies of compound 20

Table **S1** Crystal data and structure refinement for **20**

Empirical formula	$C_{31}H_{30}O_4$
Formula weight	466.55
Temperature/K	193.00
Crystal system	triclinic
Space group	P-1
a/Å	6.6573(6)

b/Å	11.2660(8)
c/Å	16.8729(14)
α/°	97.191(3)
β/°	93.243(3)
γ/°	102.955(3)
Volume/Å^3	1218.88(17)
Z	2
ρcalcg/cm^3	1.271
μ/mm^{-1}	0.083
F(000)	496.0
Crystal size/mm^3	0.12× 0.11 × 0.09
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.174 to 50.686
Index ranges	-8 ≤ h ≤ 8, -13 ≤ k ≤ 13, -20 ≤ l ≤ 20
Reflections collected	45709
Independent reflections	4441 [Rint = 0.1032, Rsigma = 0.0502]
Data/restraints/parameters	4441/0/320
Largest diff. peak/hole / e Å^{-3}	0.84/-0.30

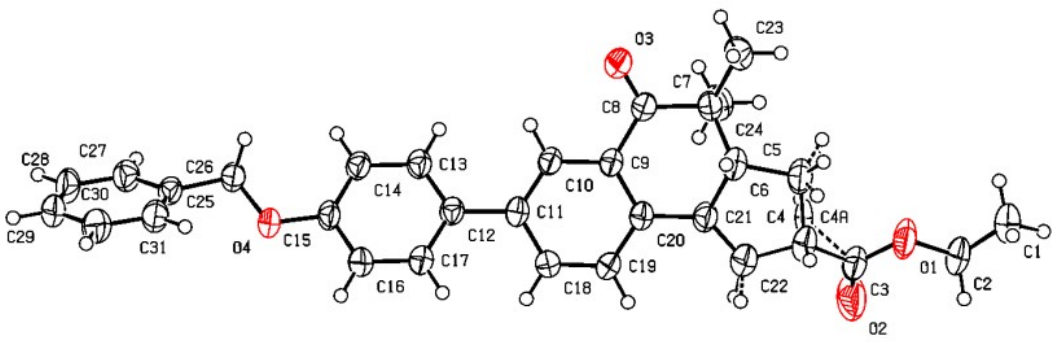


Figure **S5** Structure of **20** by X-Ray crystallographic (CCDC = 2367475)

Single crystal suitable for X-ray diffraction was obtained by slow evaporation of a solution of compound **20** ($CDCl_3$) in a nuclear magnetic tube.

8. References

1. S. K. Pagire, P. Kreitmeier and O. Reiser, *Angew. Chem., Int. Ed.*, 2017, **56**, 10928-10932.

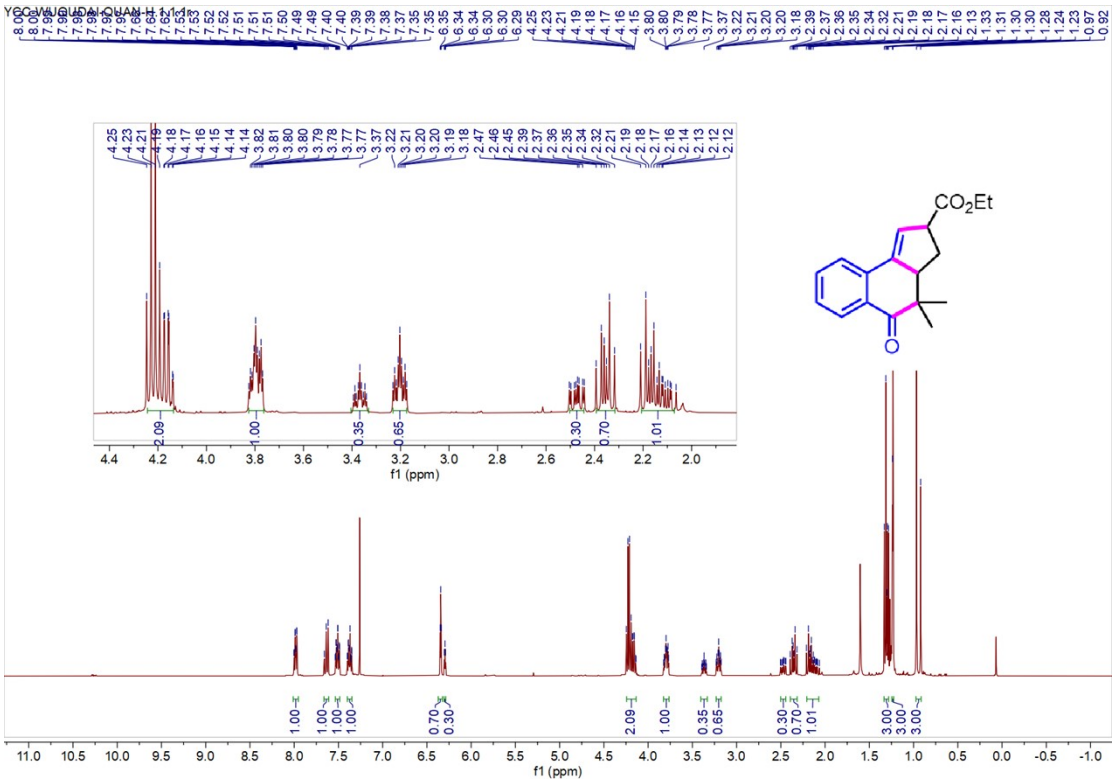
2. R. K. Mohamed, S. Mondal, J. V. Guerrera, T. M. Eaton, T. E. Albrecht-Schmitt, M. Shatruk and I. V. Alabugin, *Angew. Chem., Int. Ed.*, 2016, **55**, 12054-12058.

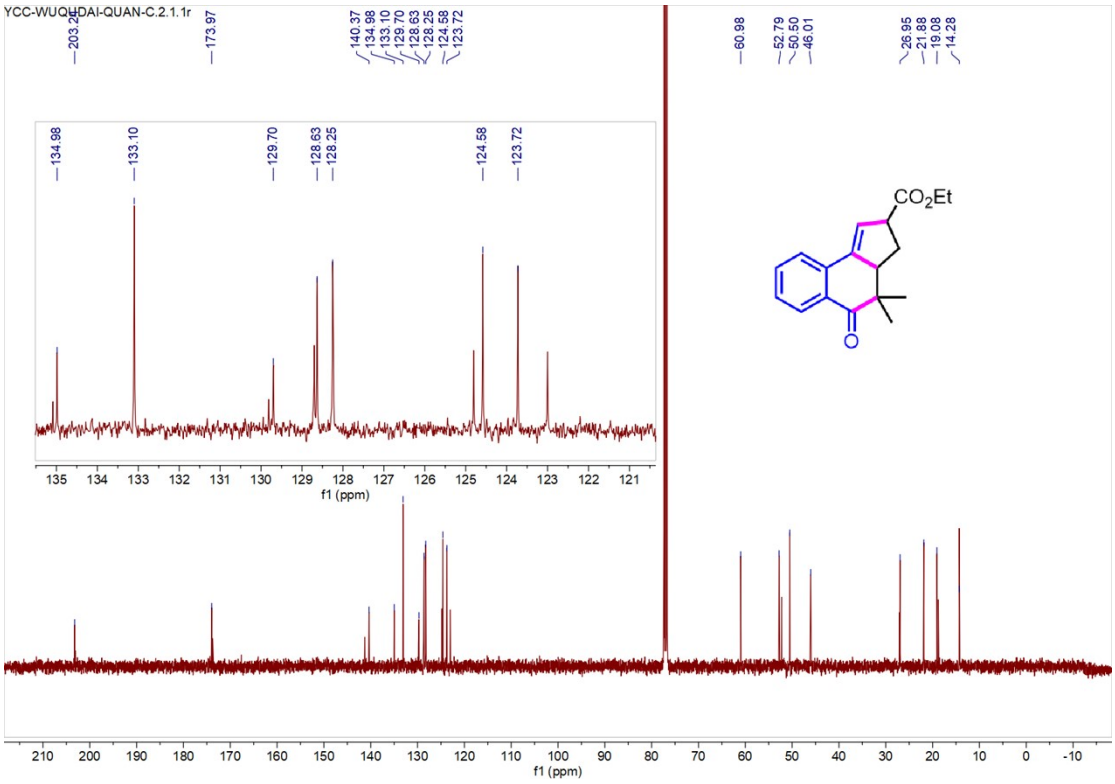
3. H. X. Feng, Y. Y. Wang, J. Chen, L. Zhou, *Adv. Synth. Catal.*, 2015, **357**, 940-944.

4. T. Bixa, R. Hunter, A. Andrijevic, W. Petersen, H. Su and F. Dhoro, *J. Org. Chem.*, 2015, **80**, 762-769.

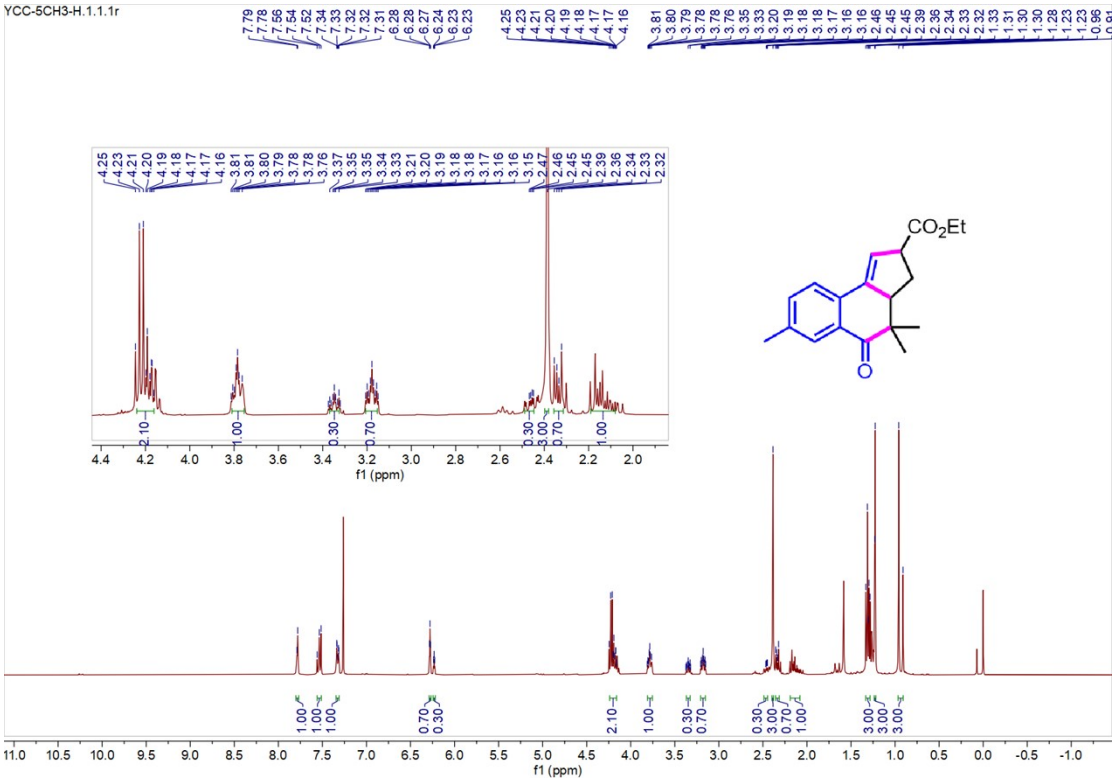
9. NMR Spectra for Electrolysis Products

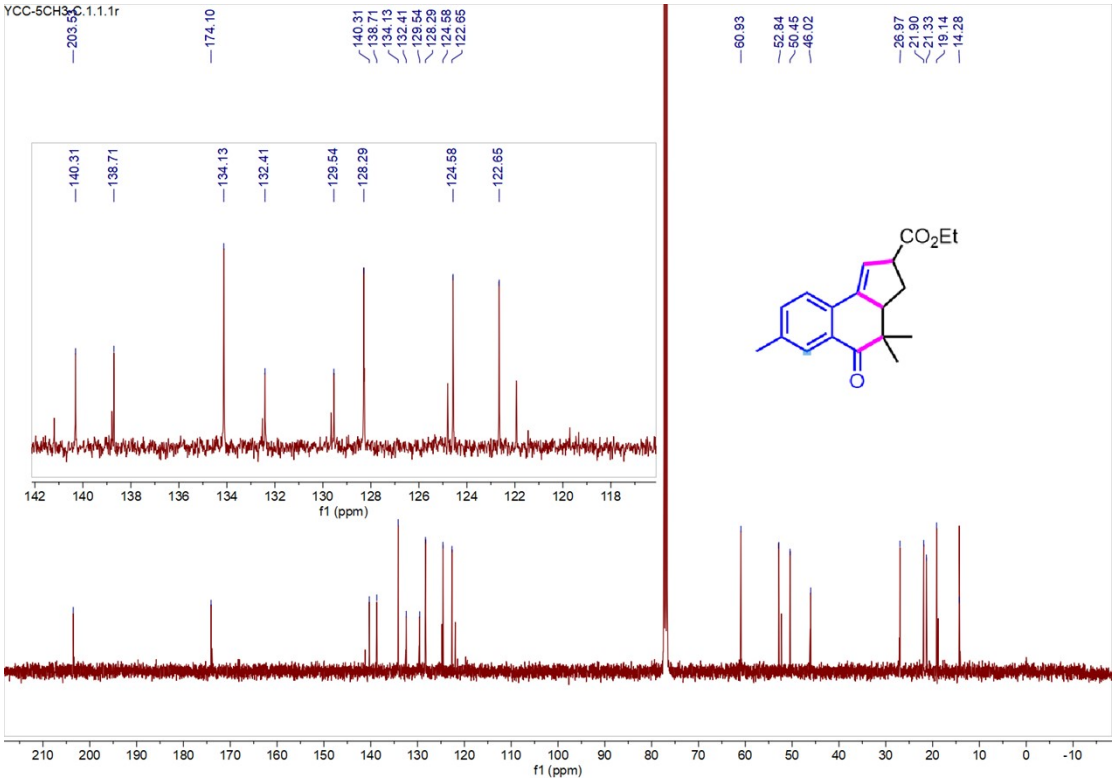
ethyl 4,4-dimethyl-5-oxo-3,3a,4,5-tetrahydro-2*H*-cyclopenta[*a*]naphthalene-2-carboxylate (**3**):



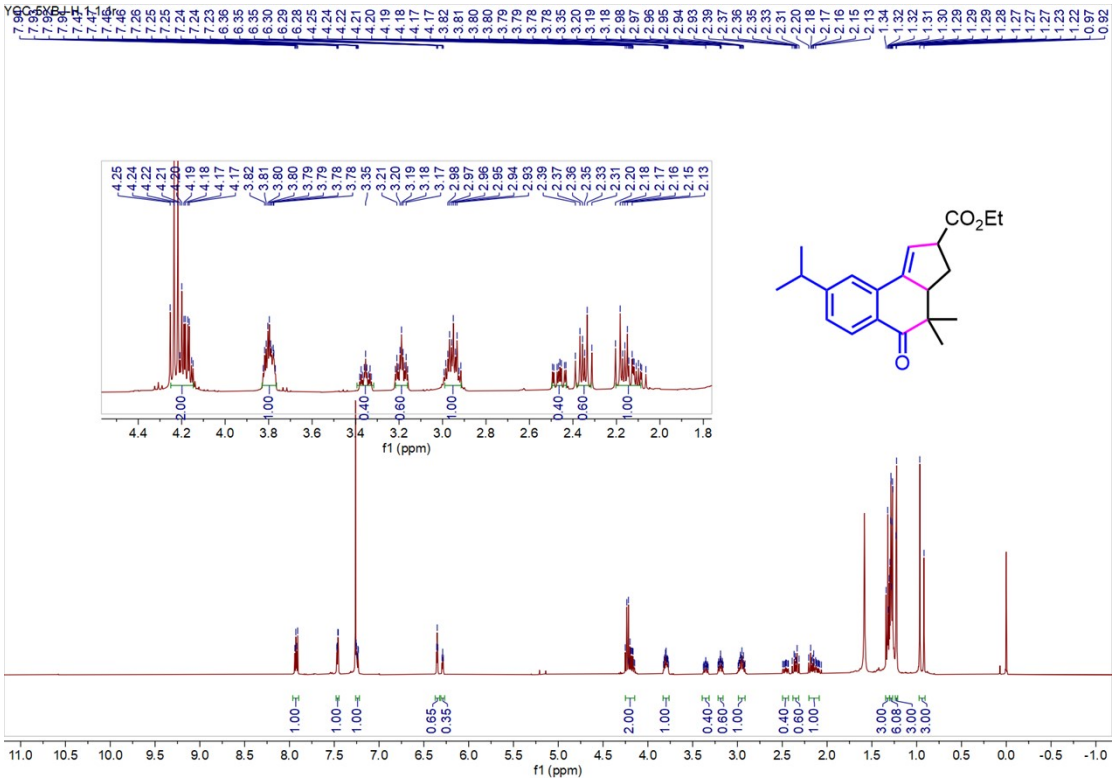


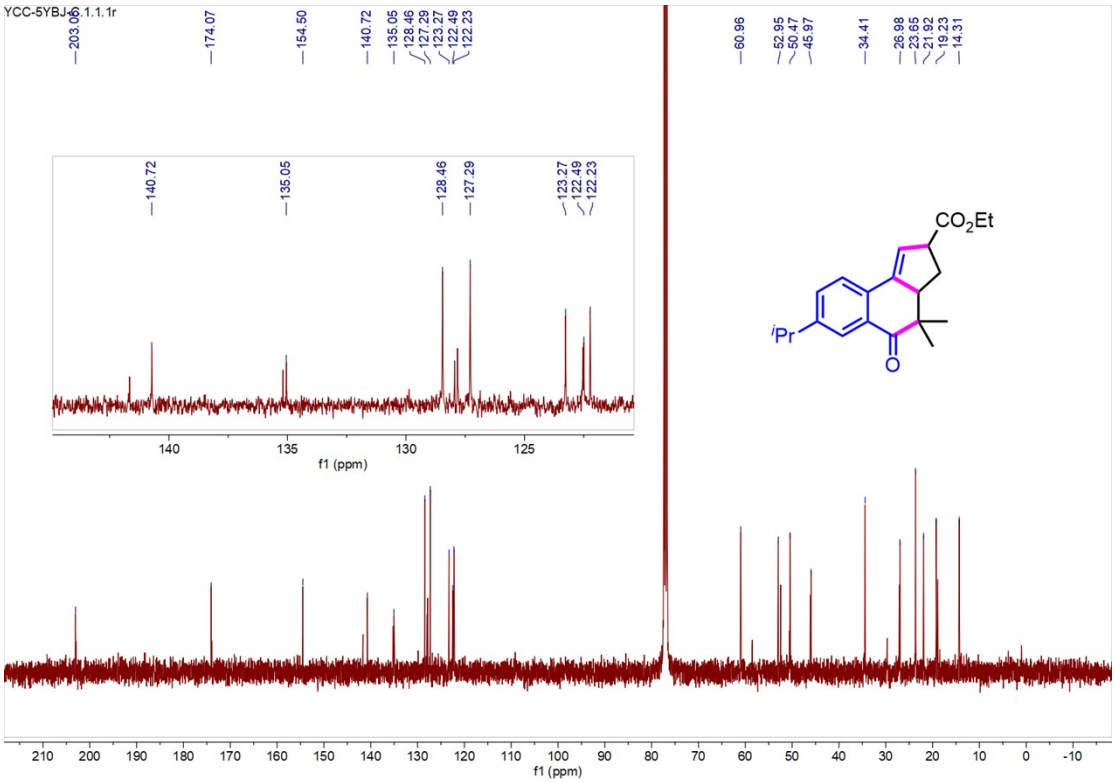
ethyl 4,4,7-trimethyl-5-oxo-3,3a,4,5-tetrahydro-2*H*-cyclopenta[*a*]naphthalene-2-carboxylate (**4**):



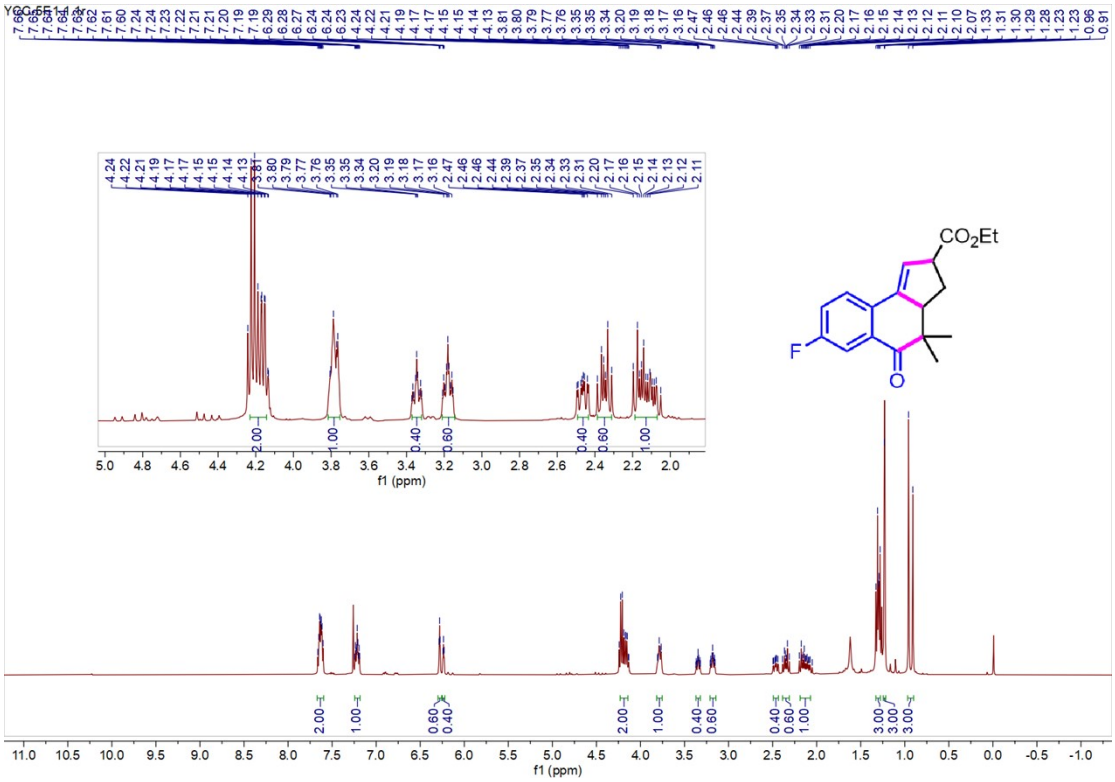


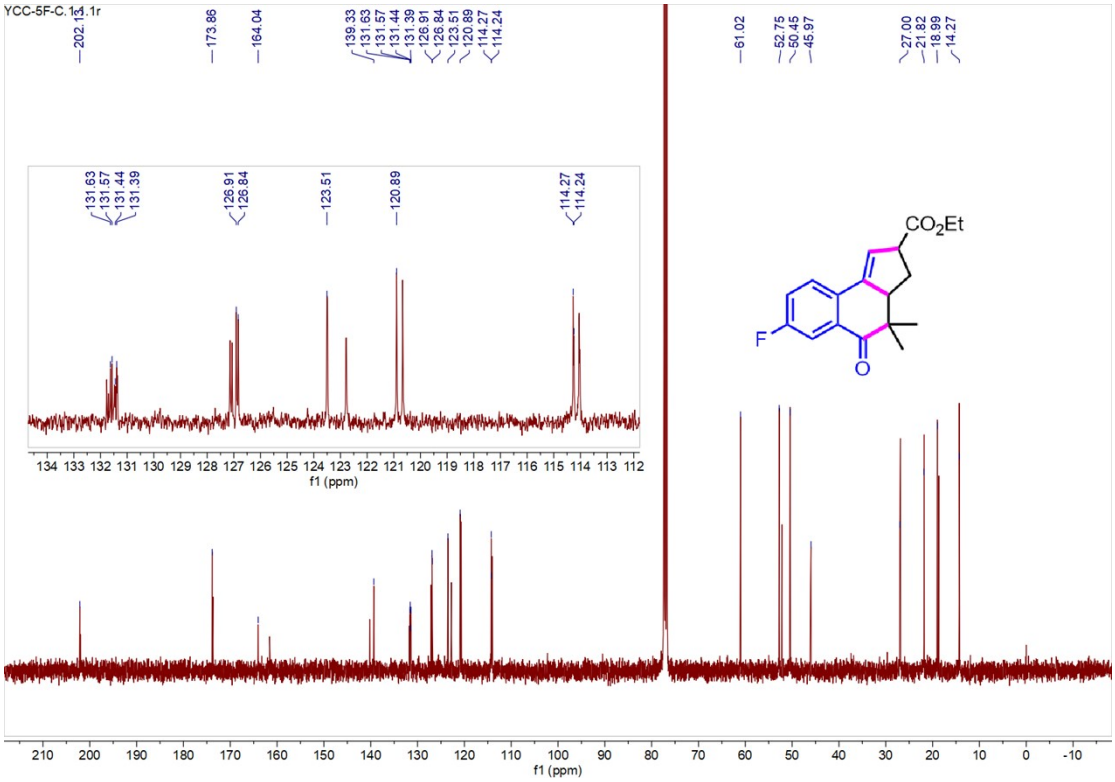
ethyl 7-isopropyl-4,4-dimethyl-5-oxo-3,3a,4,5-tetrahydro-2*H*-cyclopenta[*a*]-naphthalene-2-carboxylate (**5**):

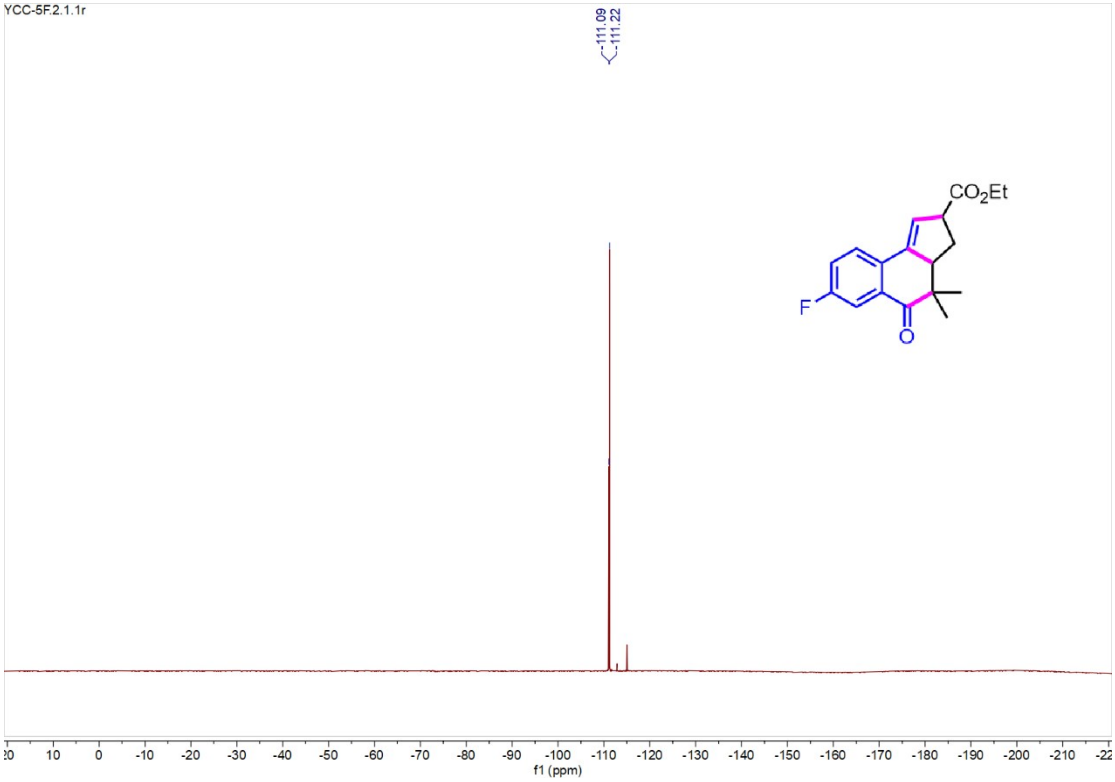




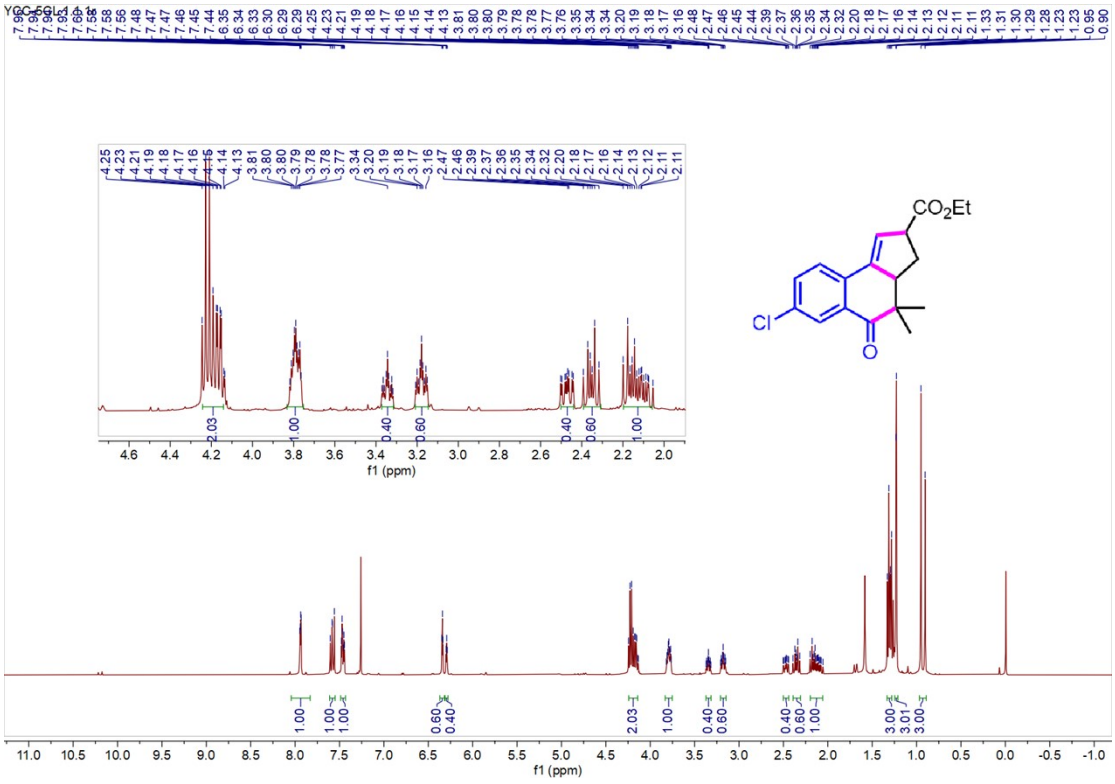
ethyl 7-fluoro-4,4-dimethyl-5-oxo-3,3a,4,5-tetrahydro-2*H*-cyclopenta[*a*]naphthalene -2-carboxylate (**6**):

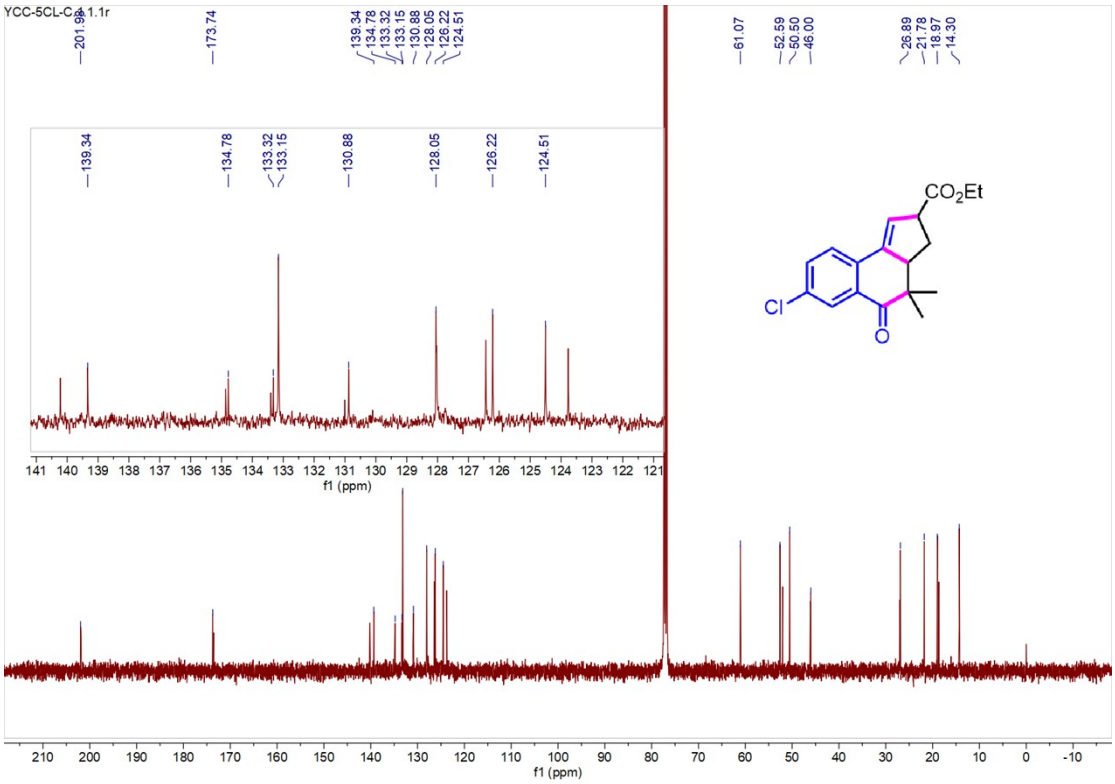




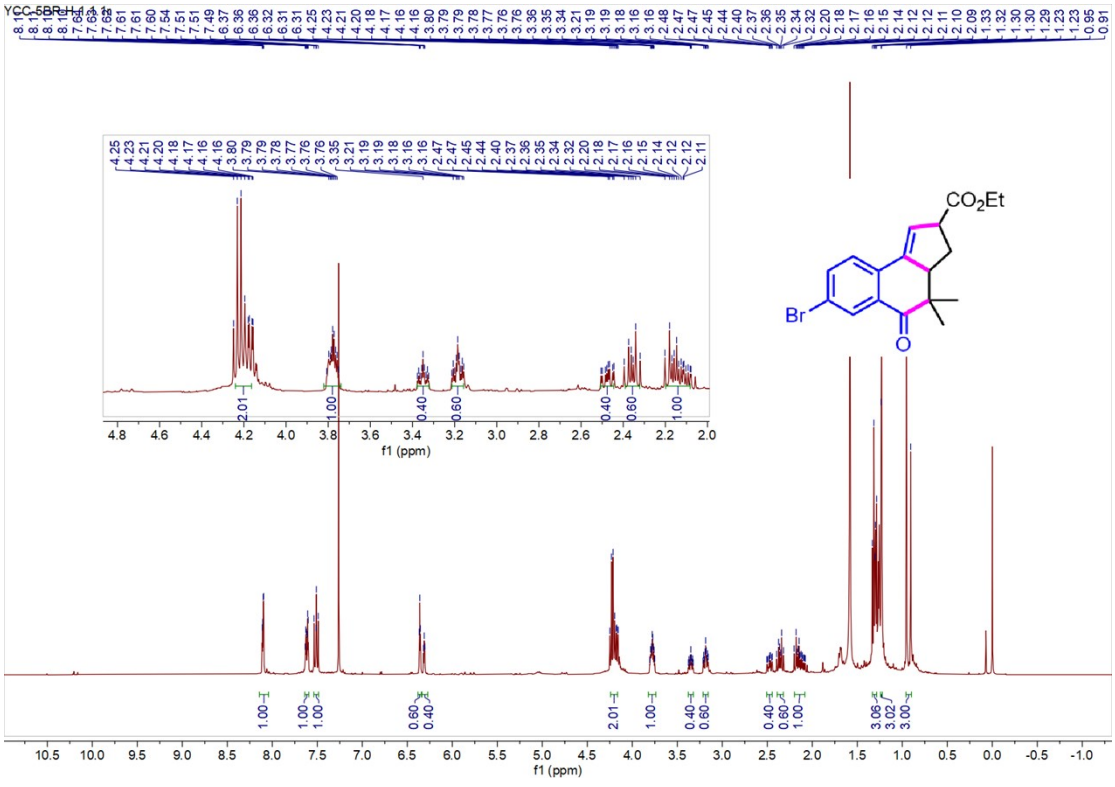


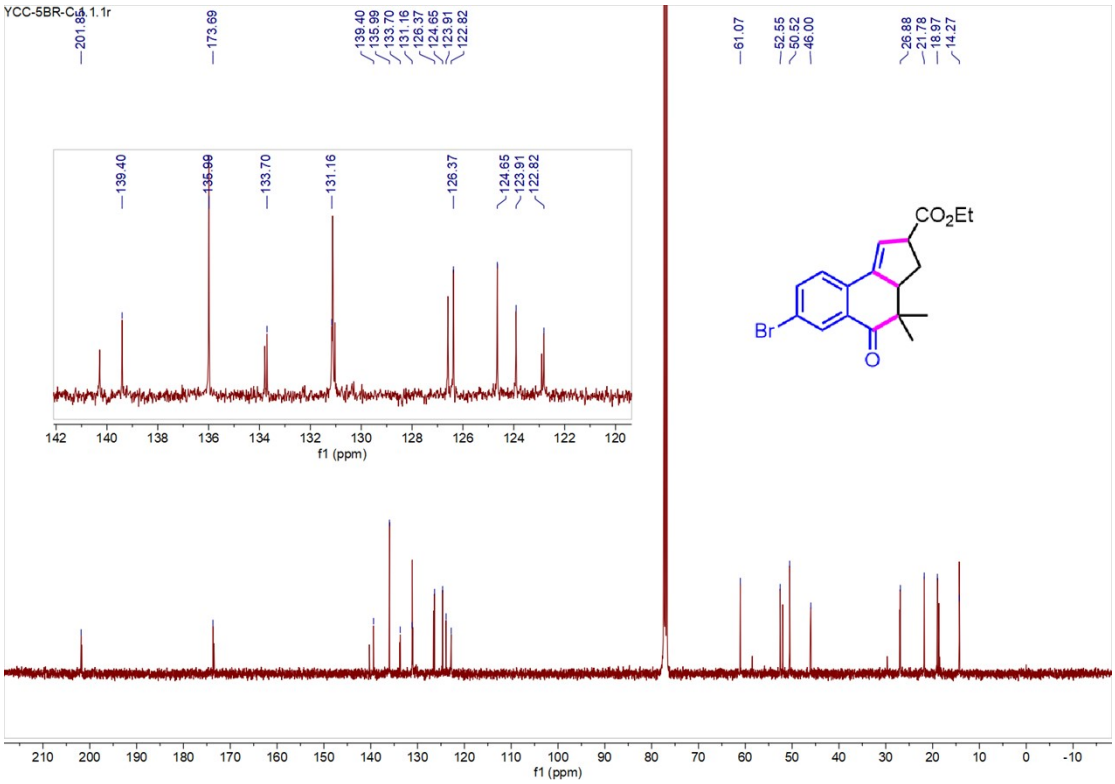
ethyl 7-chloro-4,4-dimethyl-5-oxo-3,3a,4,5-tetrahydro-2*H*-cyclopenta[*a*]naphthalene -2-carboxylate (**7**):



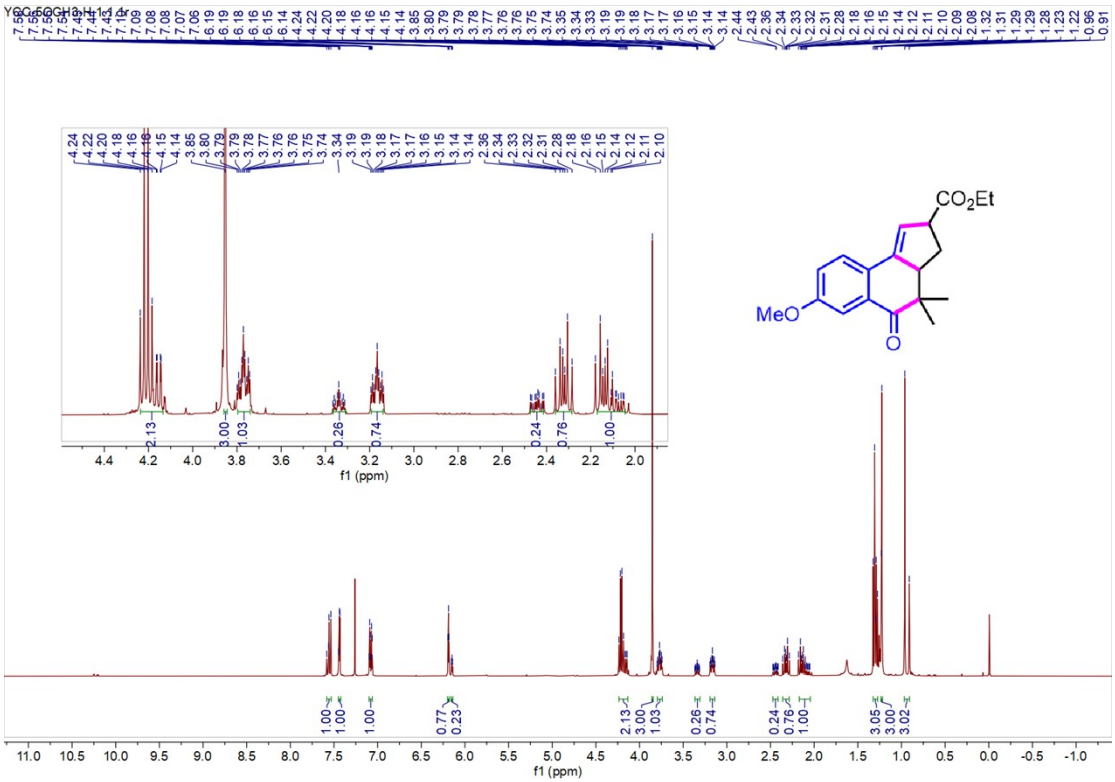


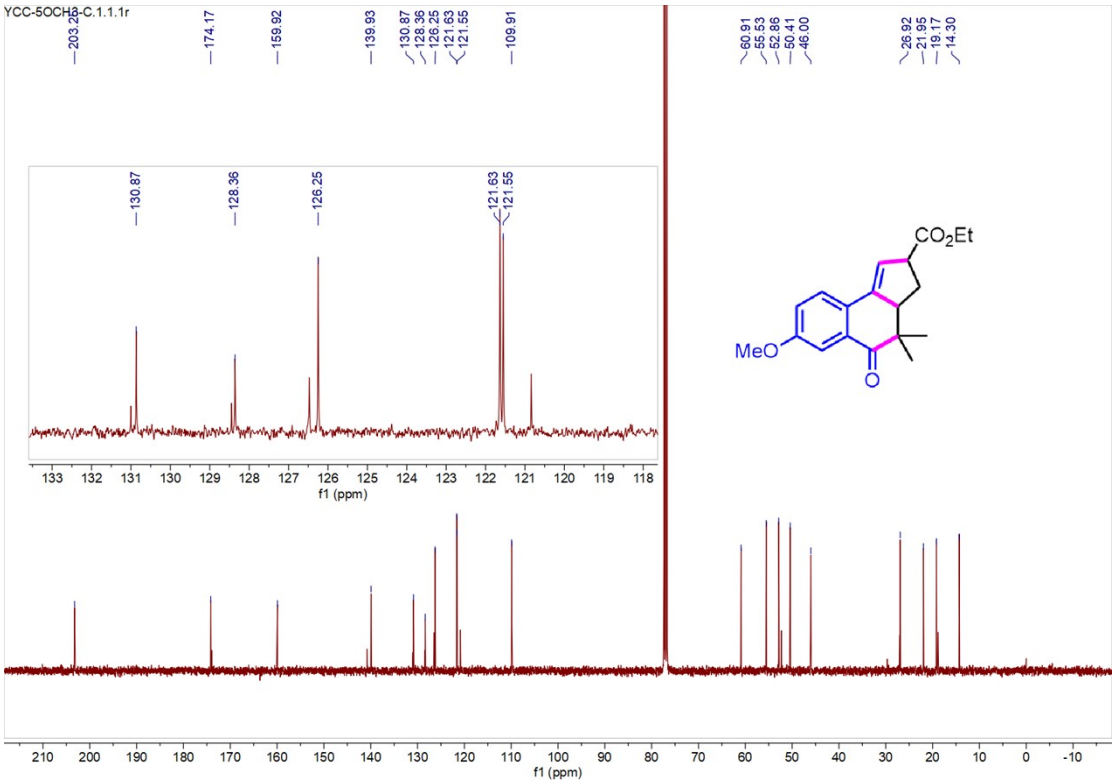
ethyl 7-bromo-4,4-dimethyl-5-oxo-3,3a,4,5-tetrahydro-2*H*-cyclopenta[*a*]naphthalene -2-carboxylate (**8**):



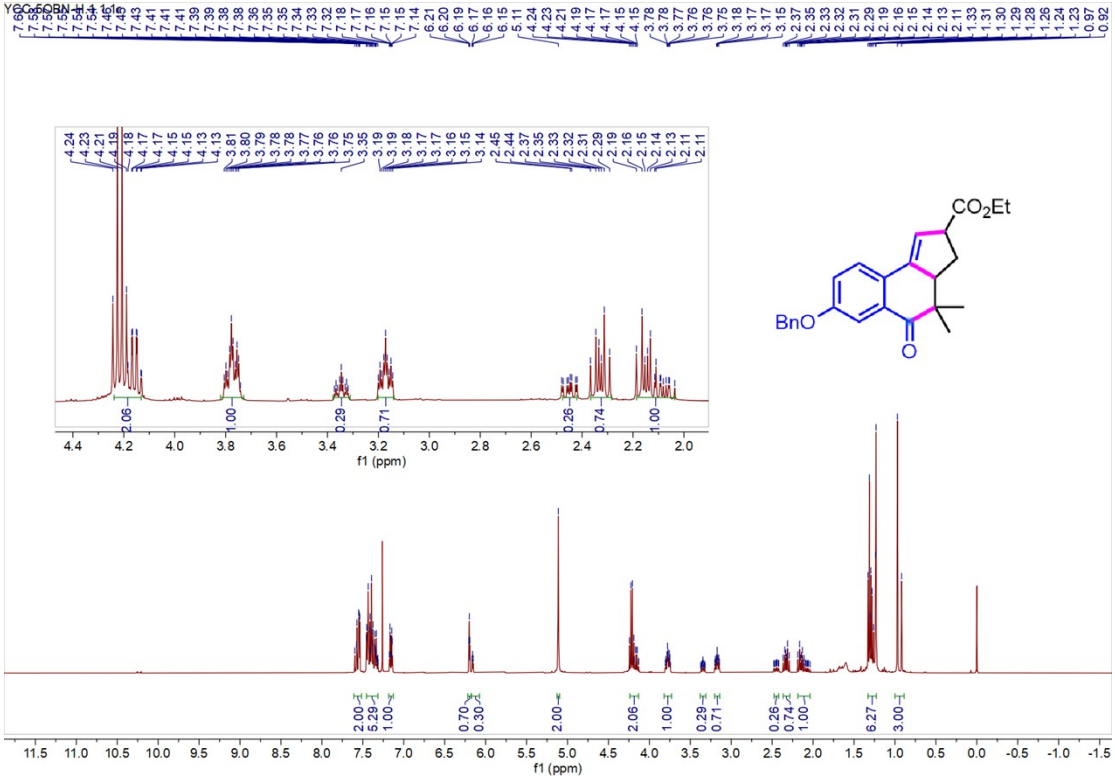


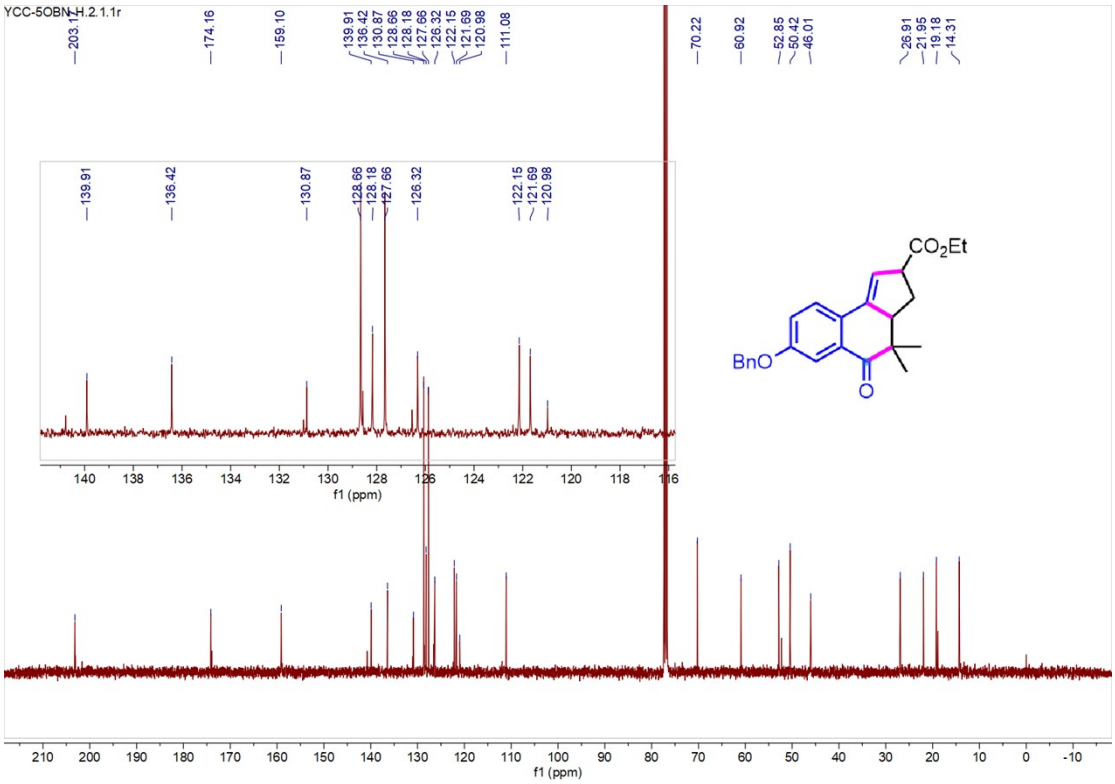
ethyl 7-methoxy-4,4-dimethyl-5-oxo-3,3a,4,5-tetrahydro-2*H*-cyclopenta[*a*]-naphthalene-2-carboxylate (**9**):



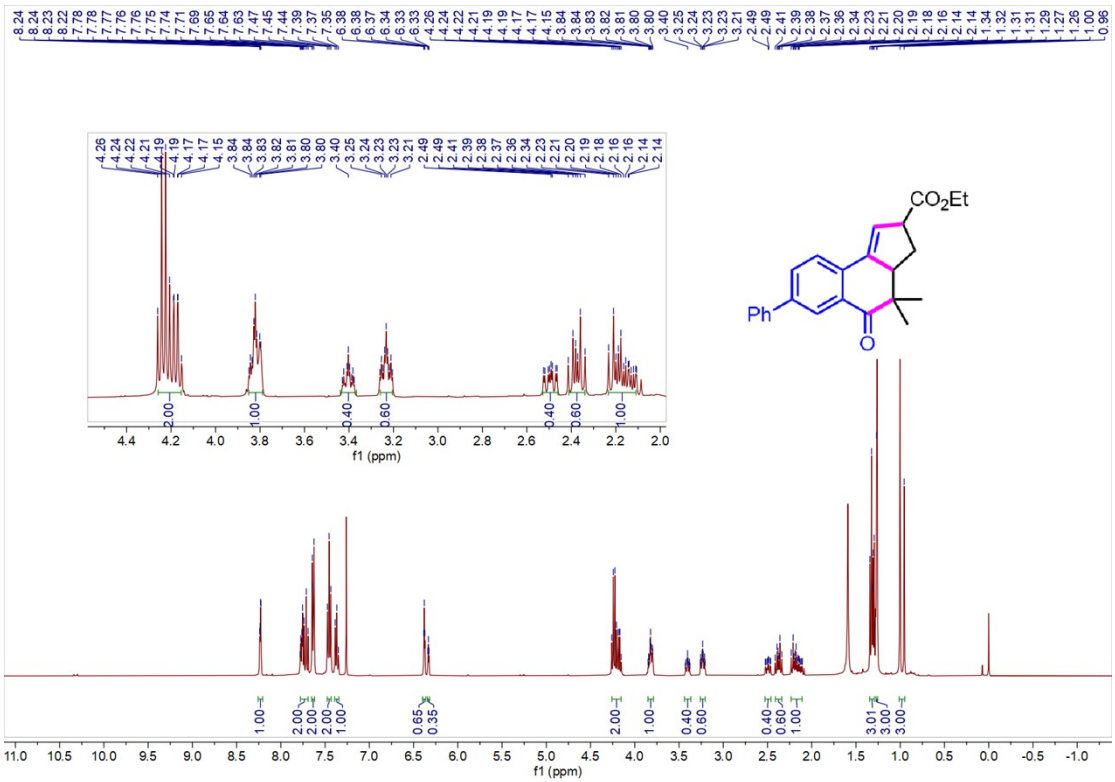


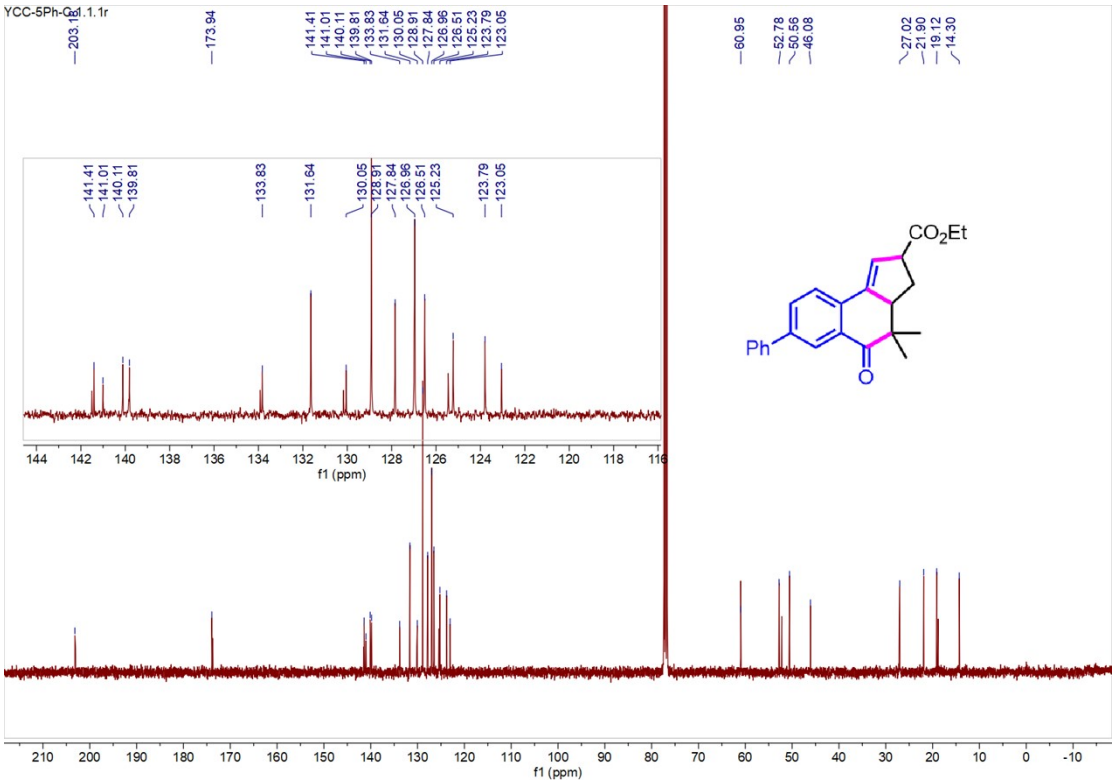
ethyl 7-(benzyloxy)-4,4-dimethyl-5-oxo-3,3a,4,5-tetrahydro-2*H*-cyclopenta[*a*]-naphthalene-2-carboxylate (**10**):



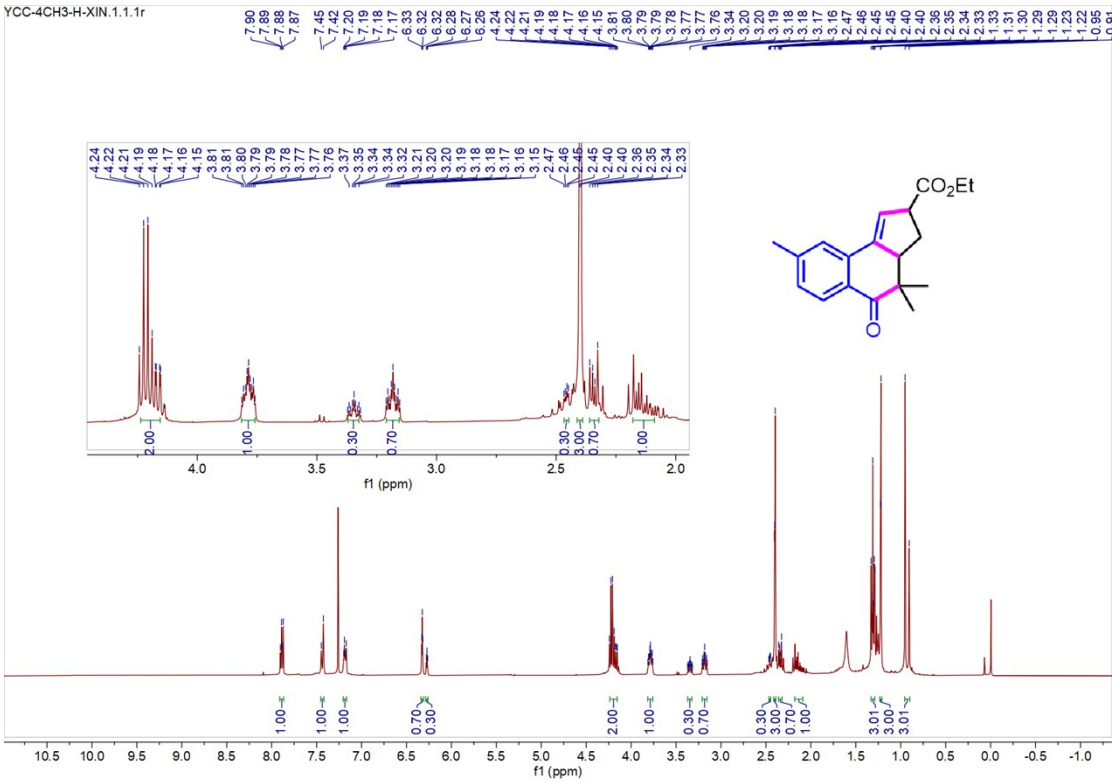


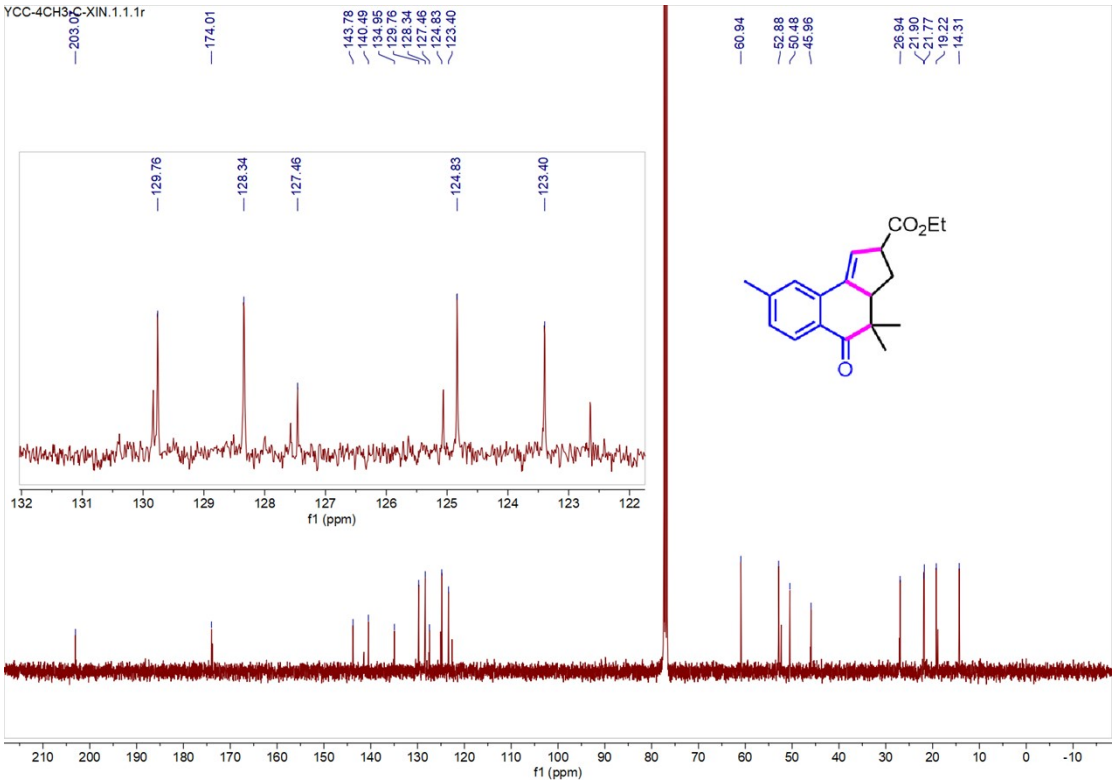
ethyl 4,4-dimethyl-5-oxo-7-phenyl-3,3a,4,5-tetrahydro-2*H*-cyclopenta[*a*]naphthalene -2-carboxylate (**11**):



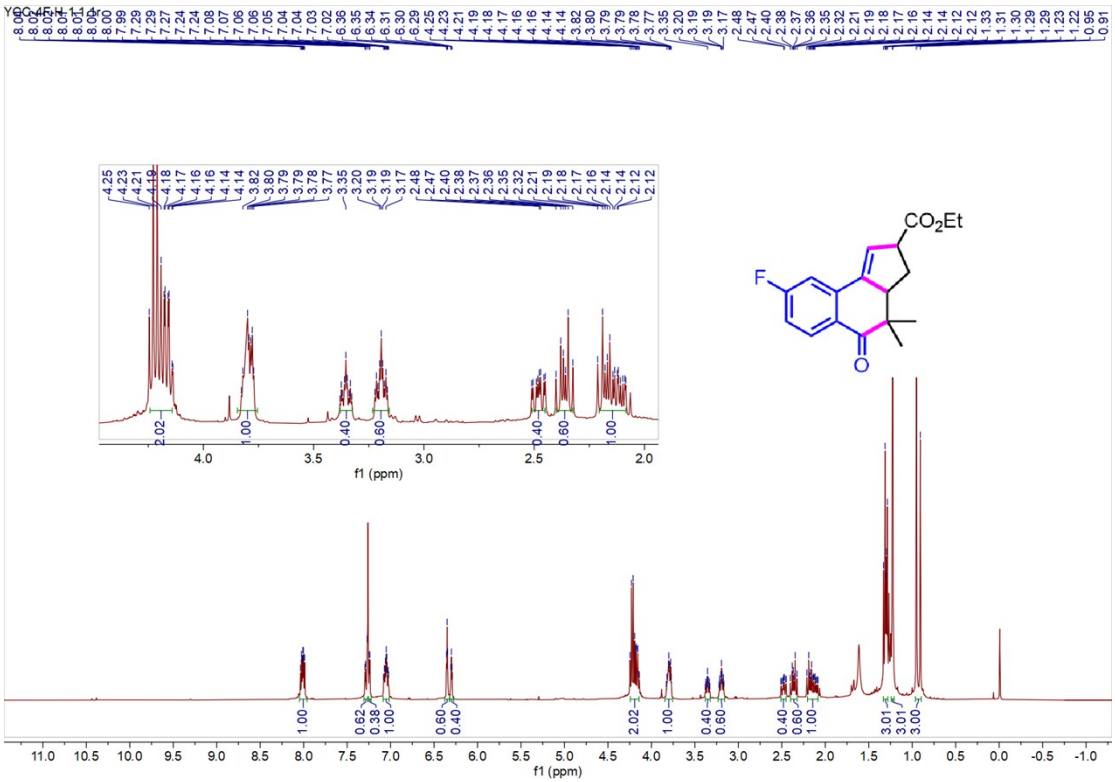


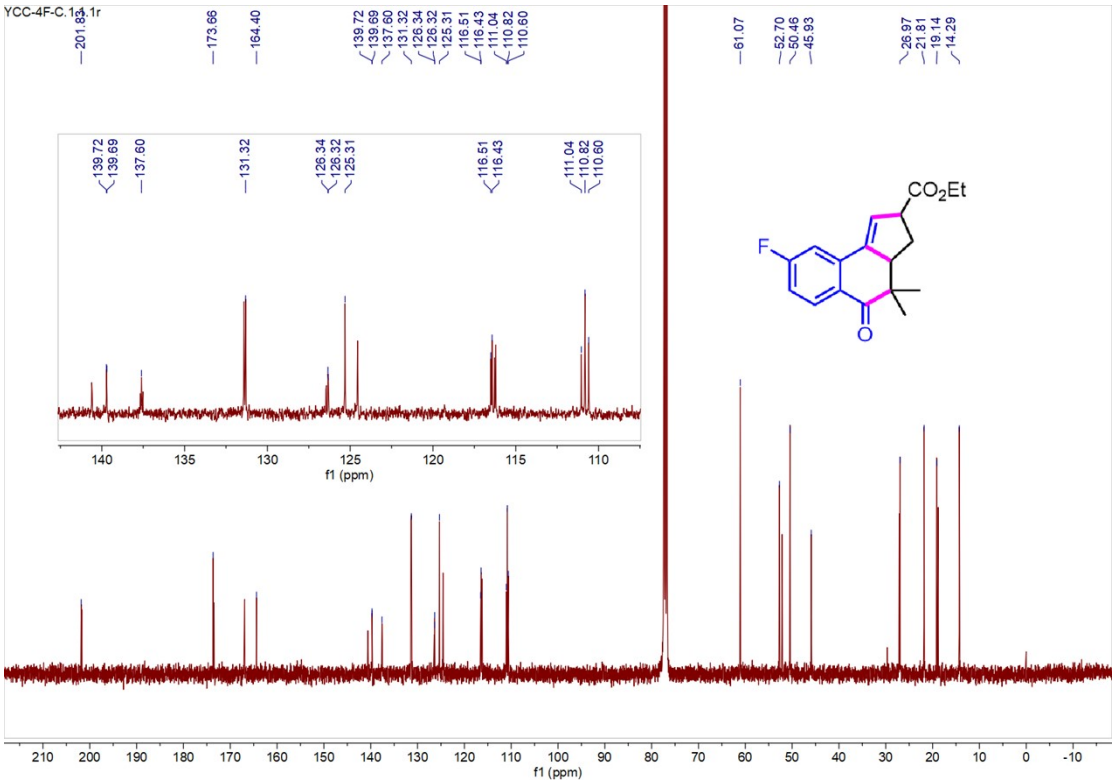
ethyl 4,4,8-trimethyl-5-oxo-3,3a,4,5-tetrahydro-2*H*-cyclopenta[*a*]naphthalene-2-carboxylate (**12**):

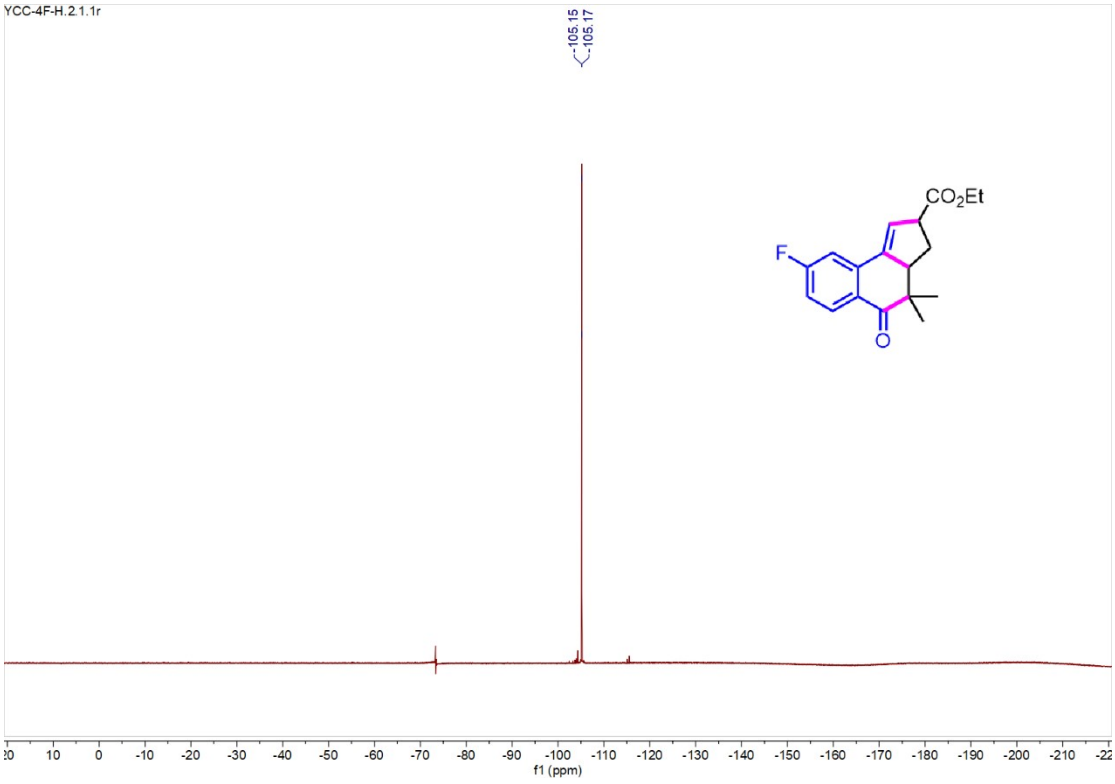




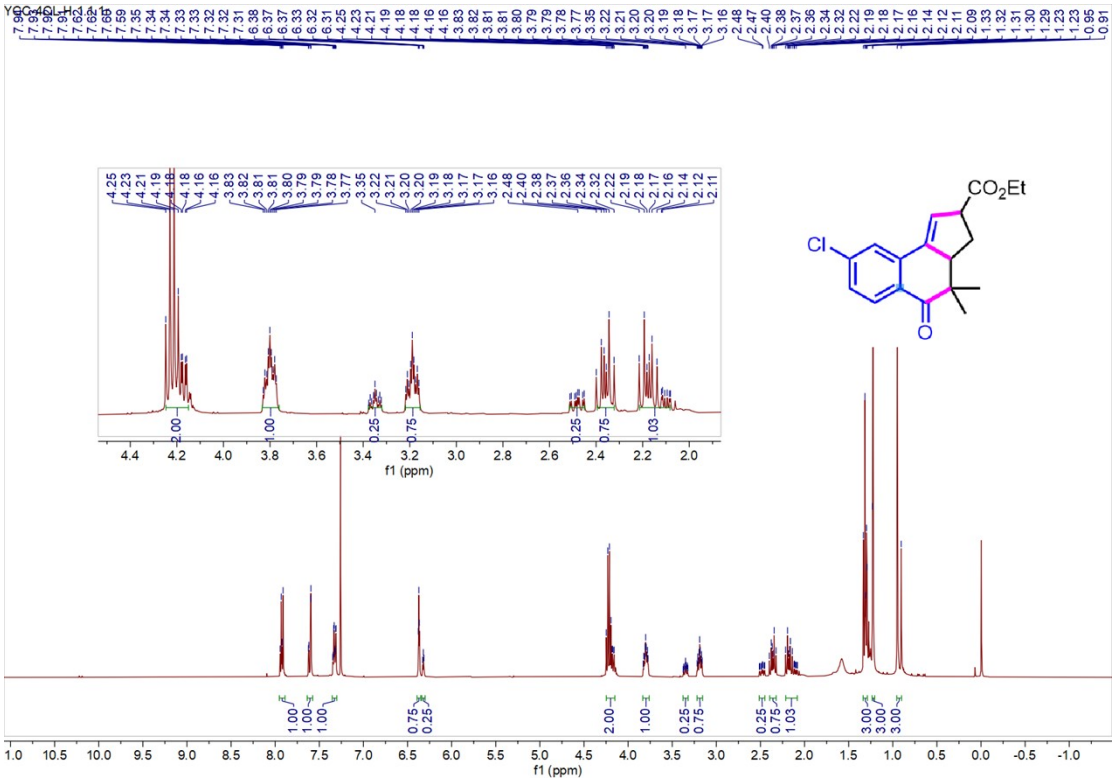
ethyl 8-fluoro-4,4-dimethyl-5-oxo-3,3a,4,5-tetrahydro-2*H*-cyclopenta[*a*]naphthalene -2-carboxylate (**13**):

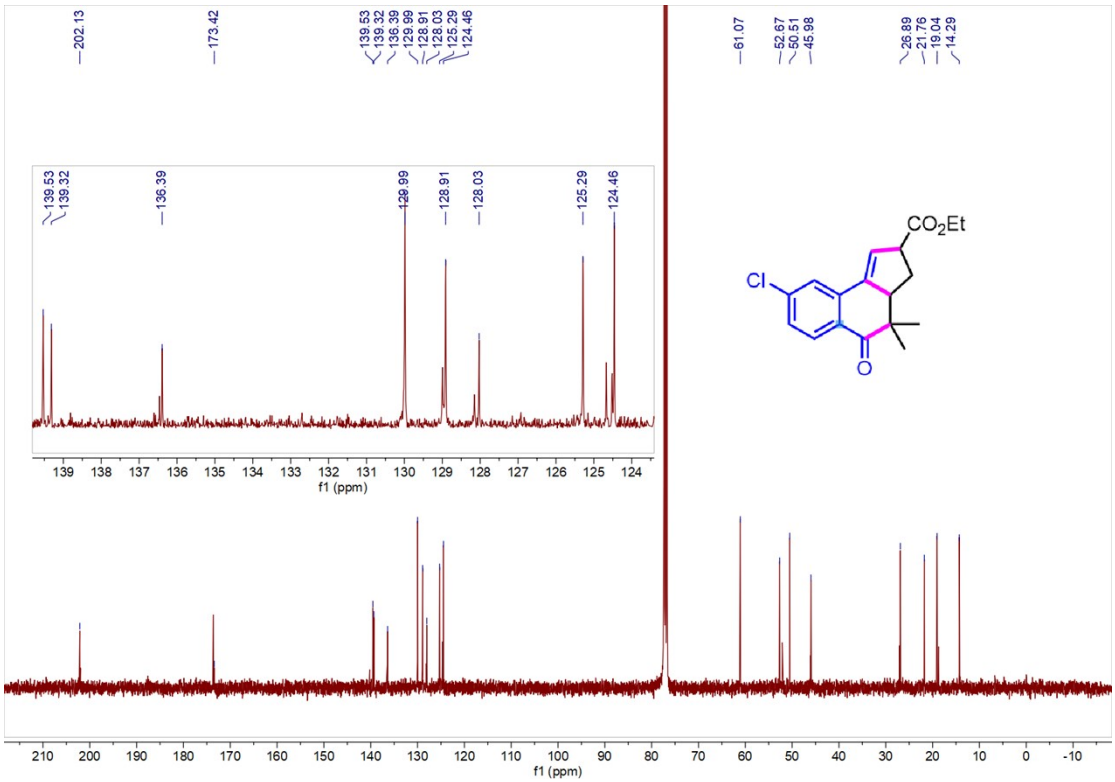



YCC-4F-C.1a.1r
201.83
173.66
164.40
139.72
139.69
137.60
131.32
126.34
126.32
125.31
116.51
116.43
111.04
110.82
110.60
61.07
52.70
50.46
45.93
26.97
21.81
19.14
14.29
CO2Et
F
O
f1 (ppm)

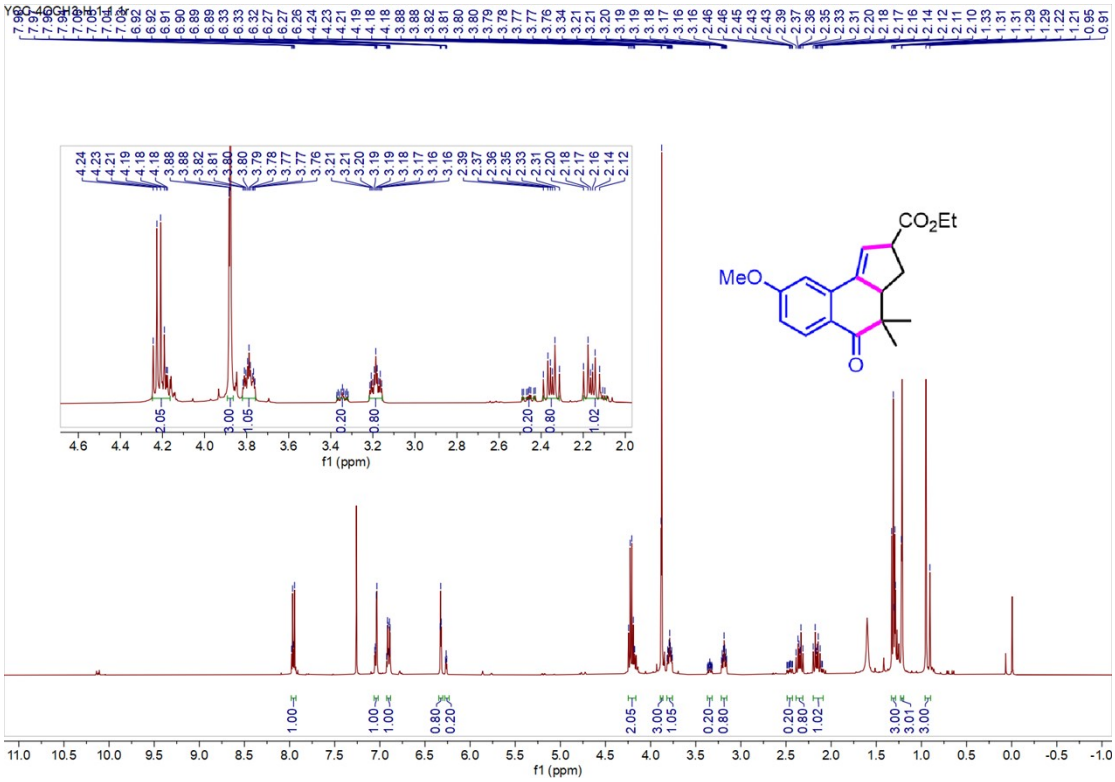

YCC-4F-H.2.1.1r
105.15
105.17
CO2Et
F
O
f1 (ppm)

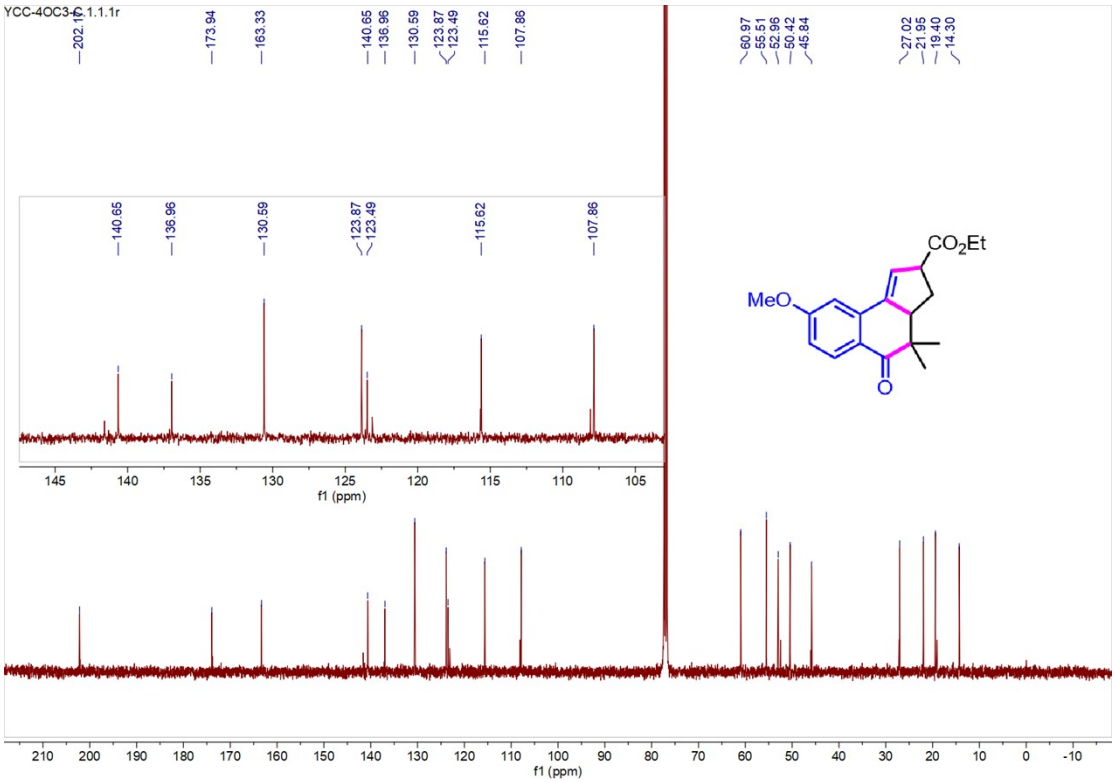
ethyl 8-chloro-4,4-dimethyl-5-oxo-3,3a,4,5-tetrahydro-2*H*-cyclopenta[*a*]naphthalene -2-carboxylate (**14**):



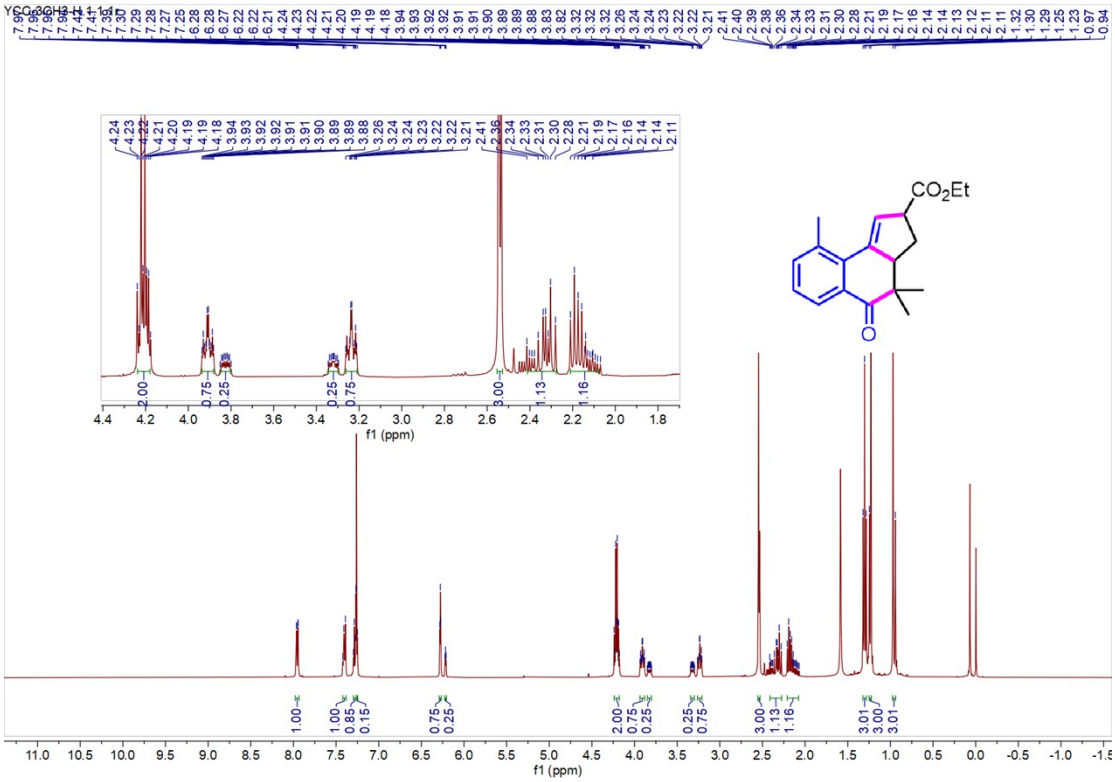


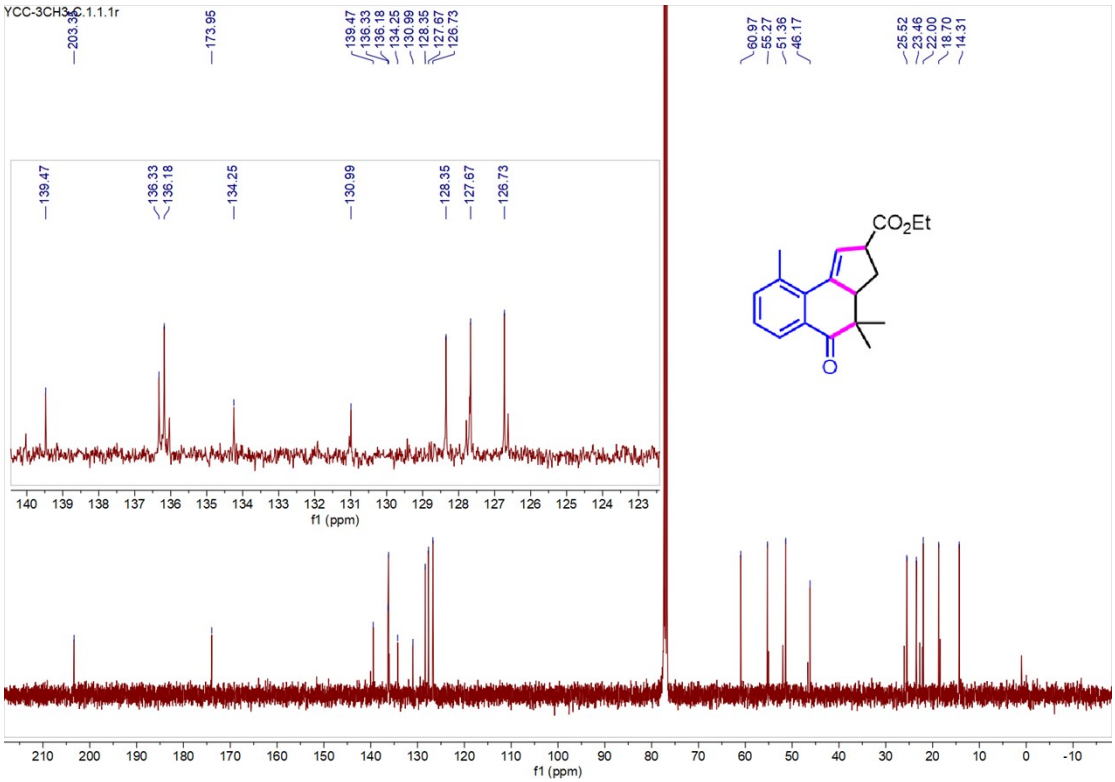
ethyl 8-methoxy-4,4-dimethyl-5-oxo-3,3a,4,5-tetrahydro-2*H*-cyclopenta[*a*]-naphthalene-2-carboxylate (**15**):



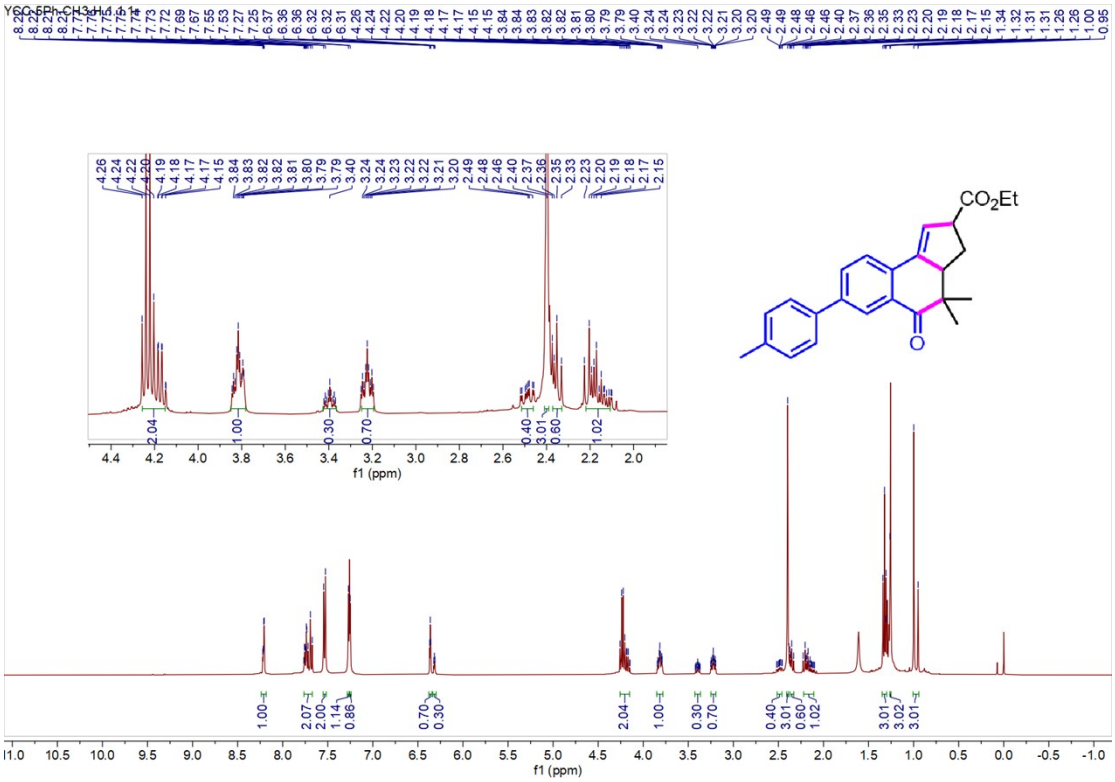


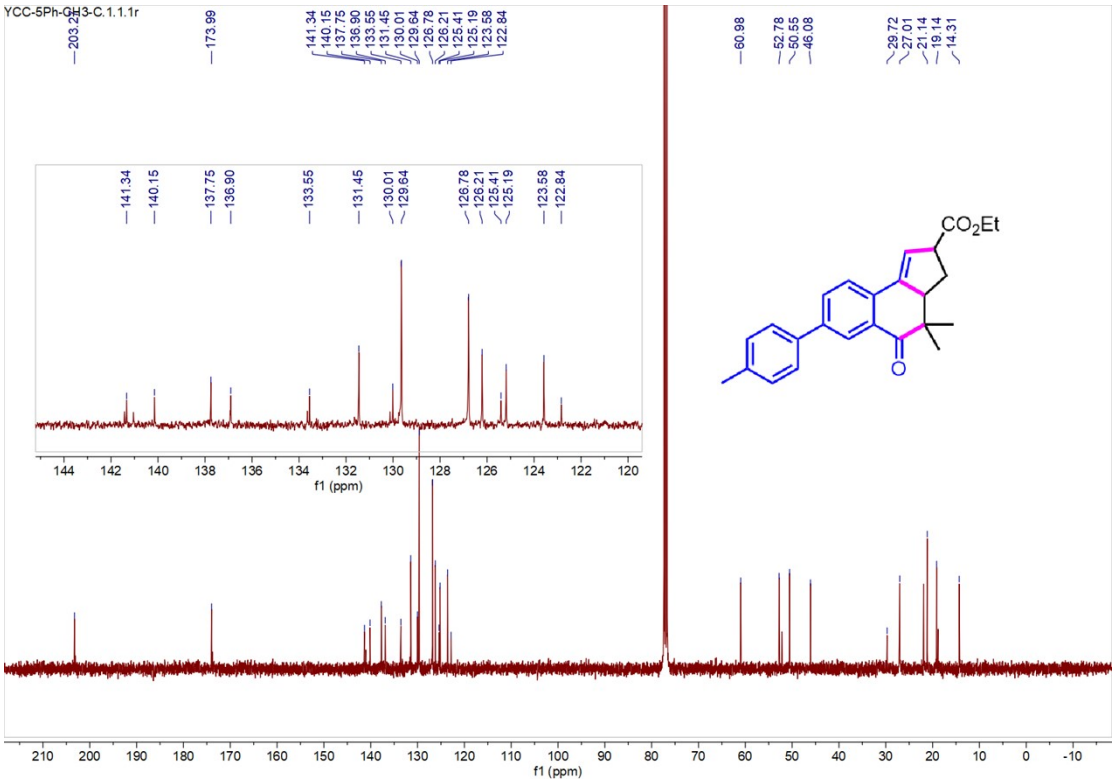
ethyl 4,4,9-trimethyl-5-oxo-3,3a,4,5-tetrahydro-2*H*-cyclopenta[*a*]naphthalene-2-carboxylate (**16**):



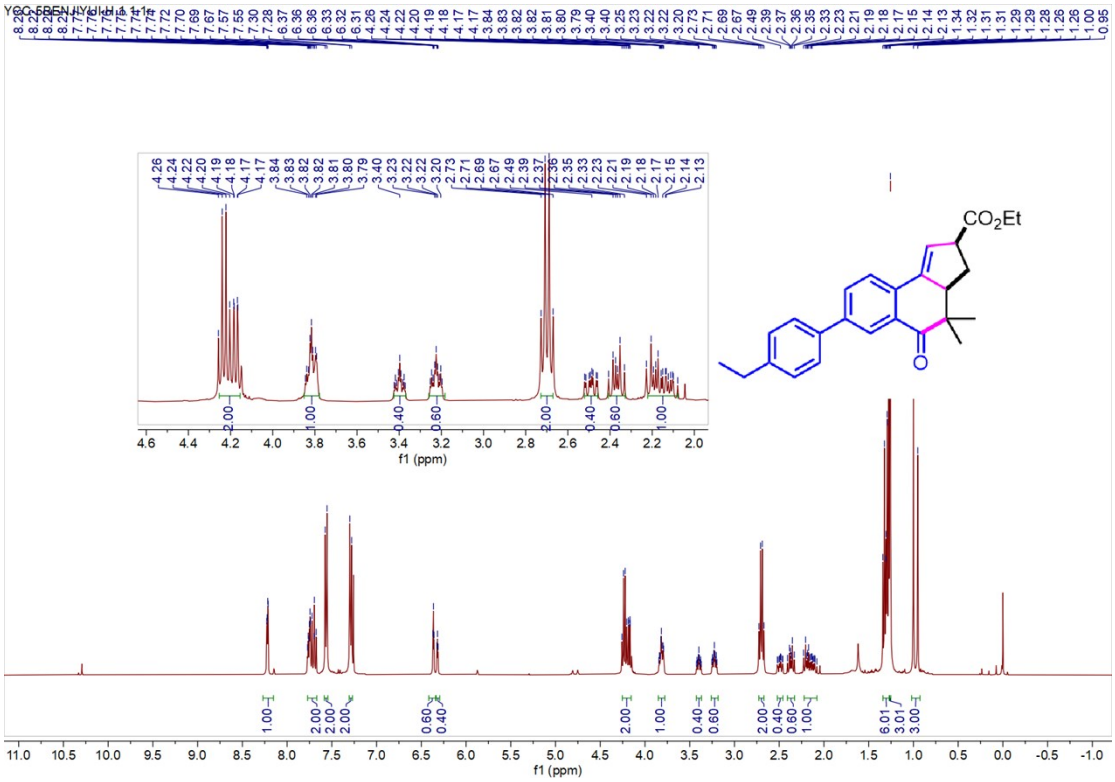


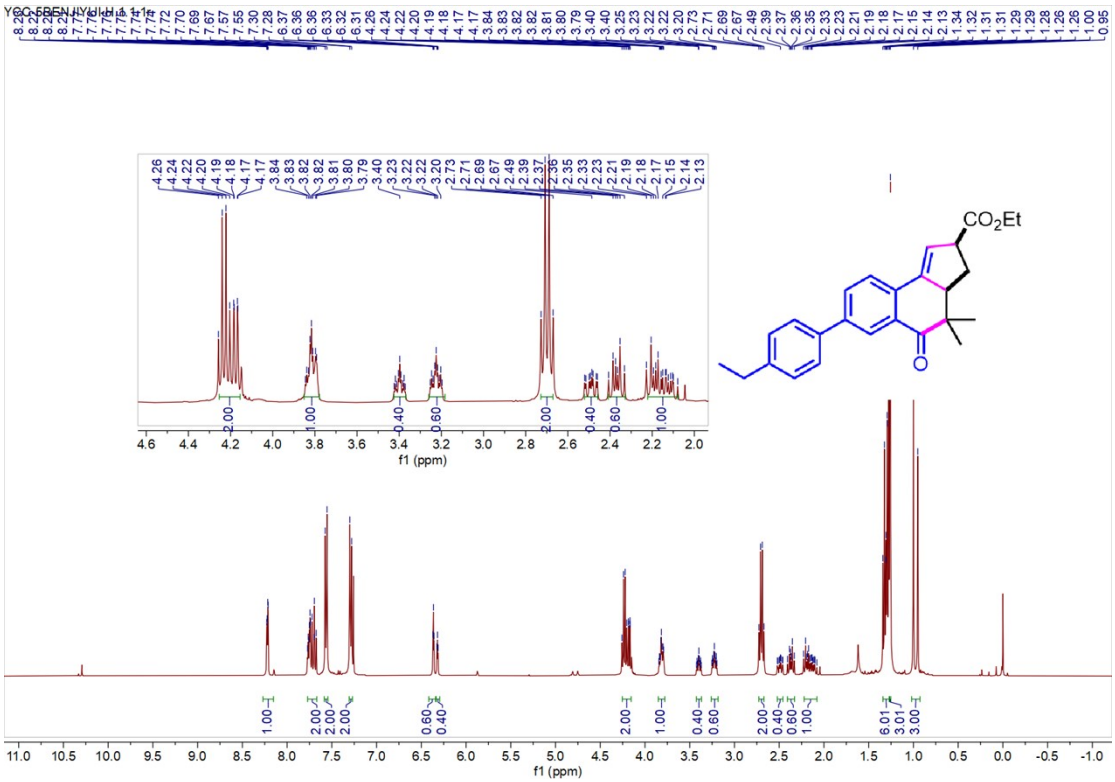
ethyl 4,4-dimethyl-5-oxo-7-(*p*-tolyl)-3,3a,4,5-tetrahydro-2*H*-cyclopenta[*a*]-naphthalene-2-carboxylate (**17**):



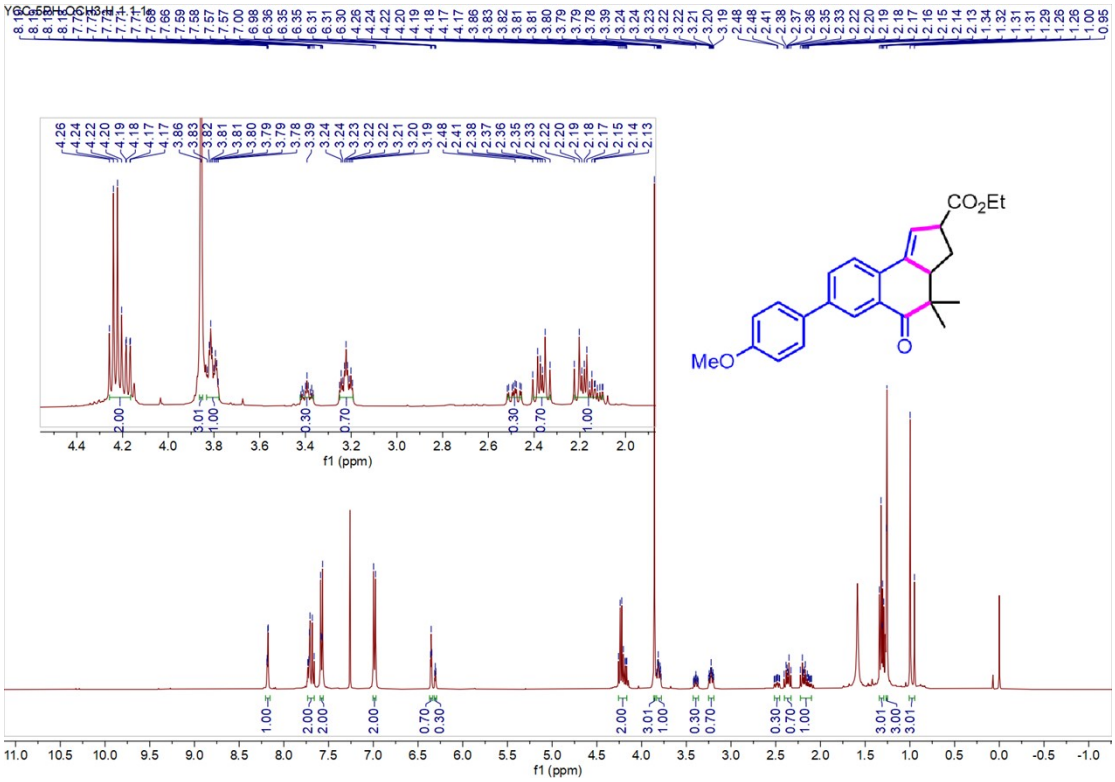


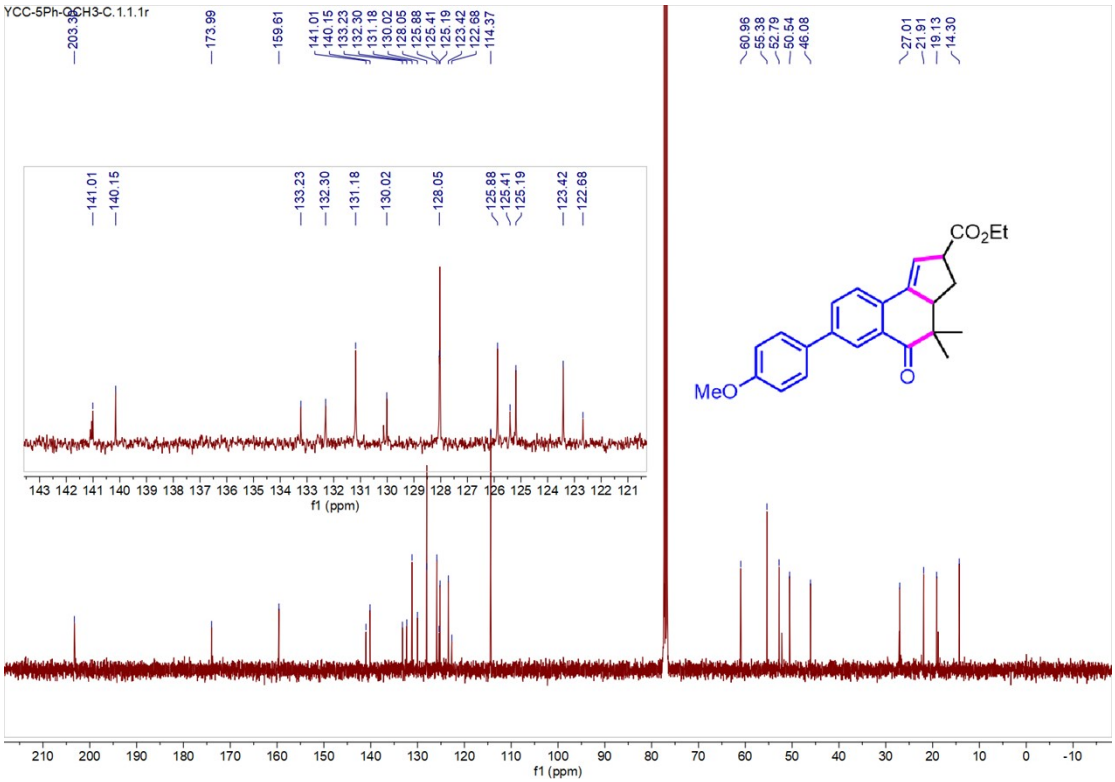
ethyl 7-(4-ethylphenyl)-4,4-dimethyl-5-oxo-3,3a,4,5-tetrahydro-2*H*-cyclopenta[*a*]-naphthalene-2-carboxylate (**18**):



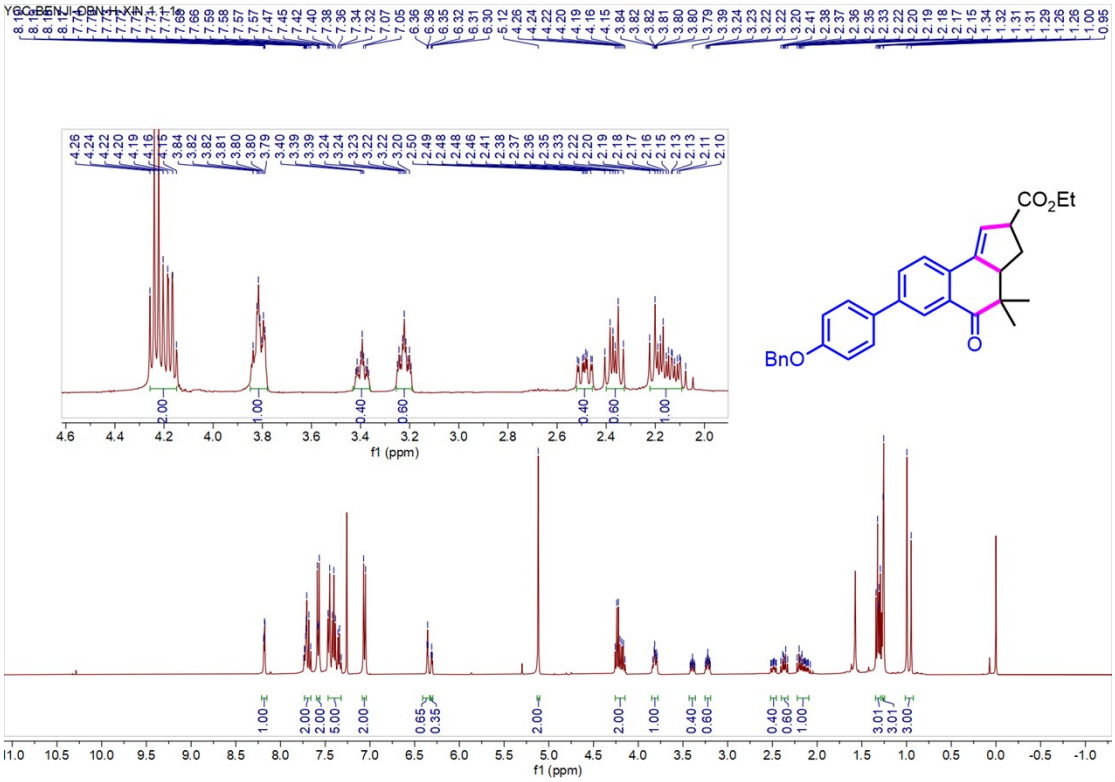


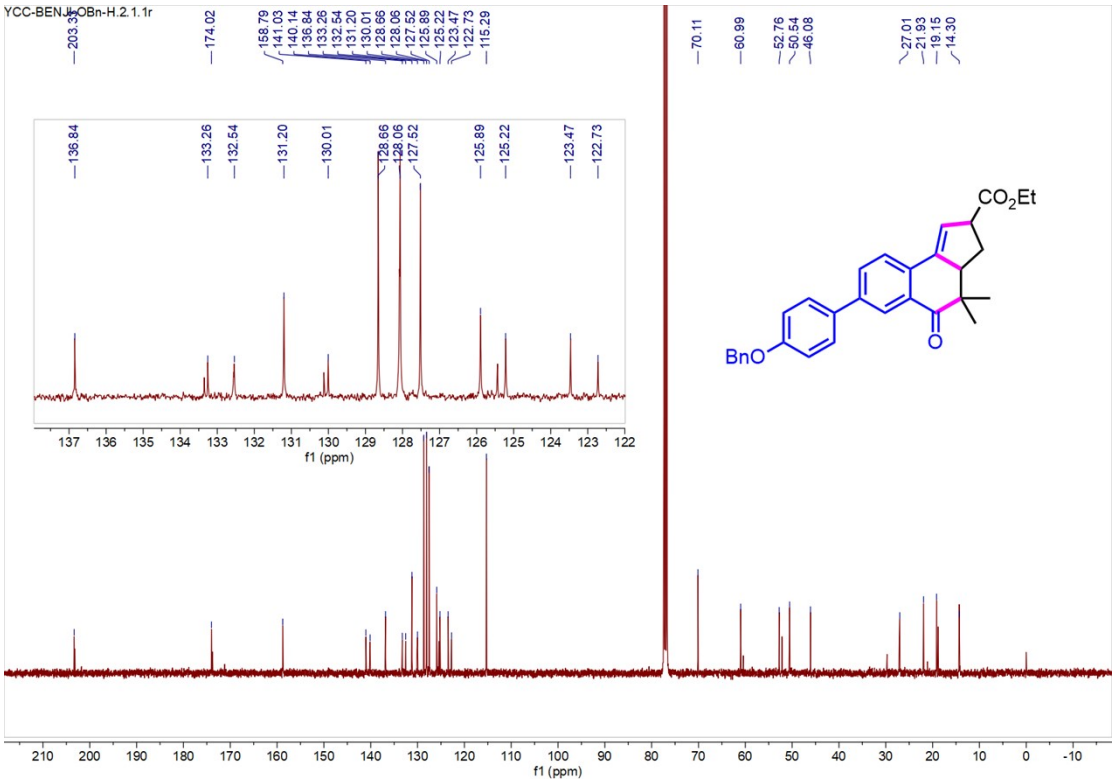
ethyl 7-(4-methoxyphenyl)-4,4-dimethyl-5-oxo-3,3a,4,5-tetrahydro-2*H*-cyclopenta -[*a*]-naphthalene-2-carboxylate (**19**):



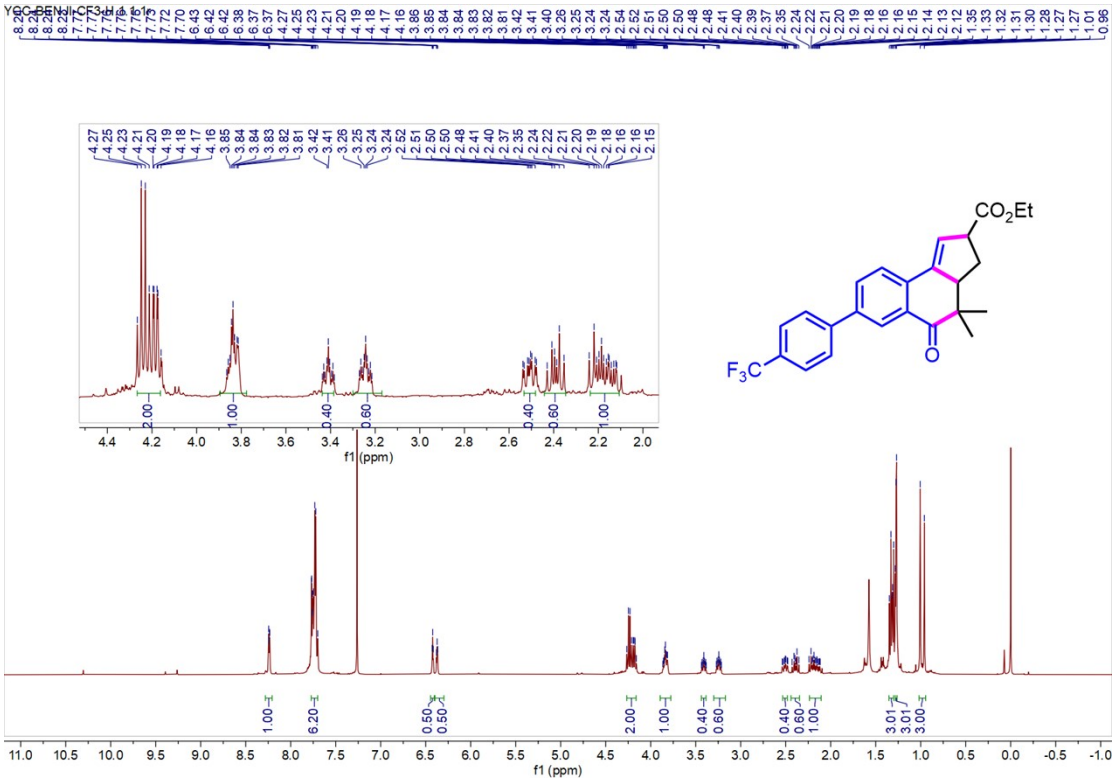


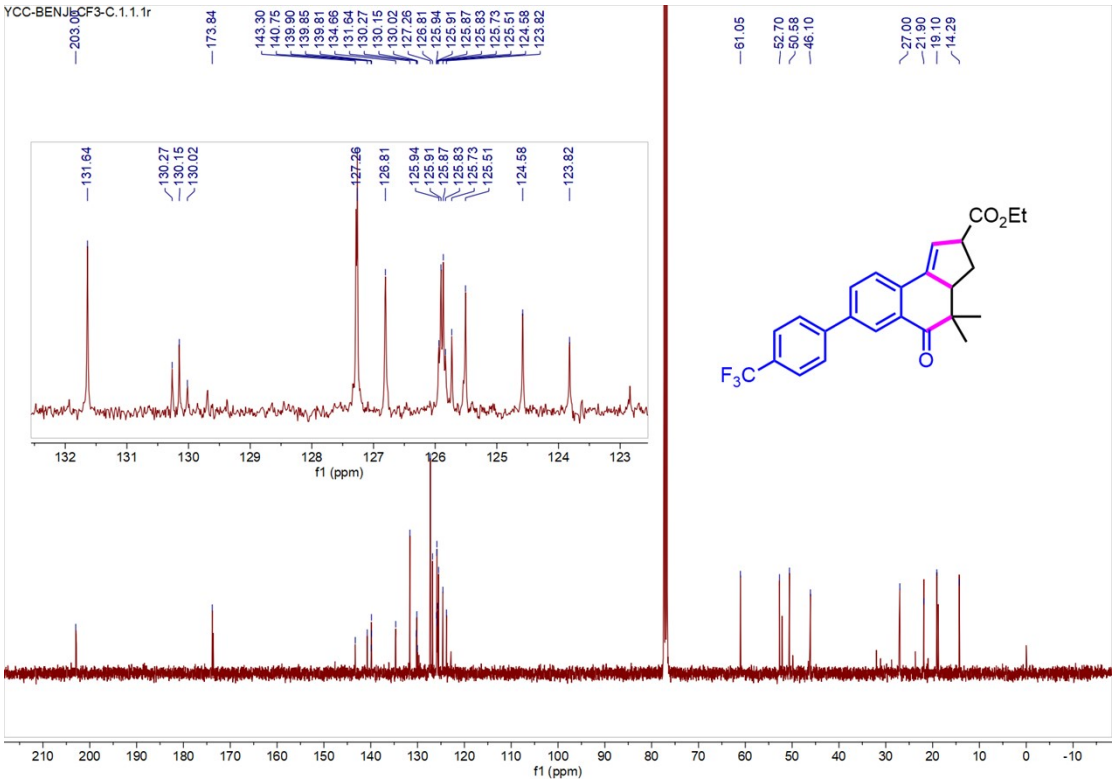
ethyl 7-(4-(benzyloxy)phenyl)-4,4-dimethyl-5-oxo-3,3a,4,5-tetrahydro-2*H*-cyclopenta-[*a*]-naphthalene-2-carboxylate (**20**):

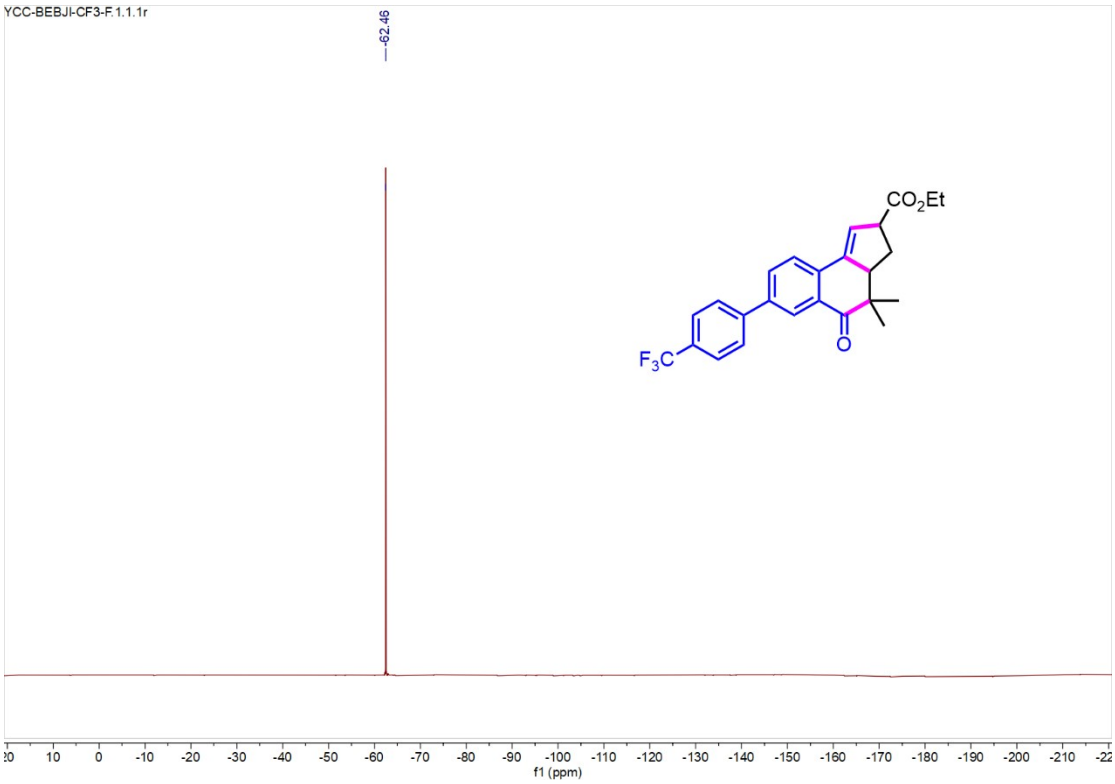




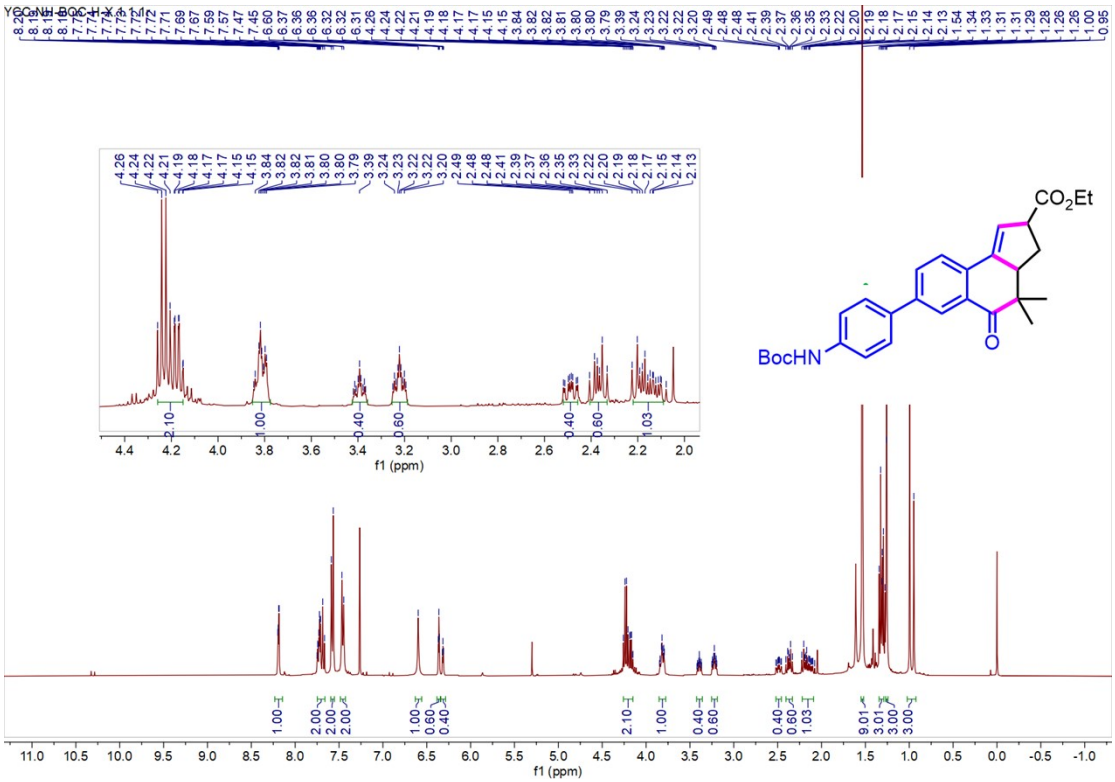
ethyl 4,4-dimethyl-5-oxo-7-(4-(trifluoromethyl)phenyl)-3,3a,4,5-tetrahydro-2*H*-cyclopenta-[*a*]-naphthalene-2-carboxylate (**21**):

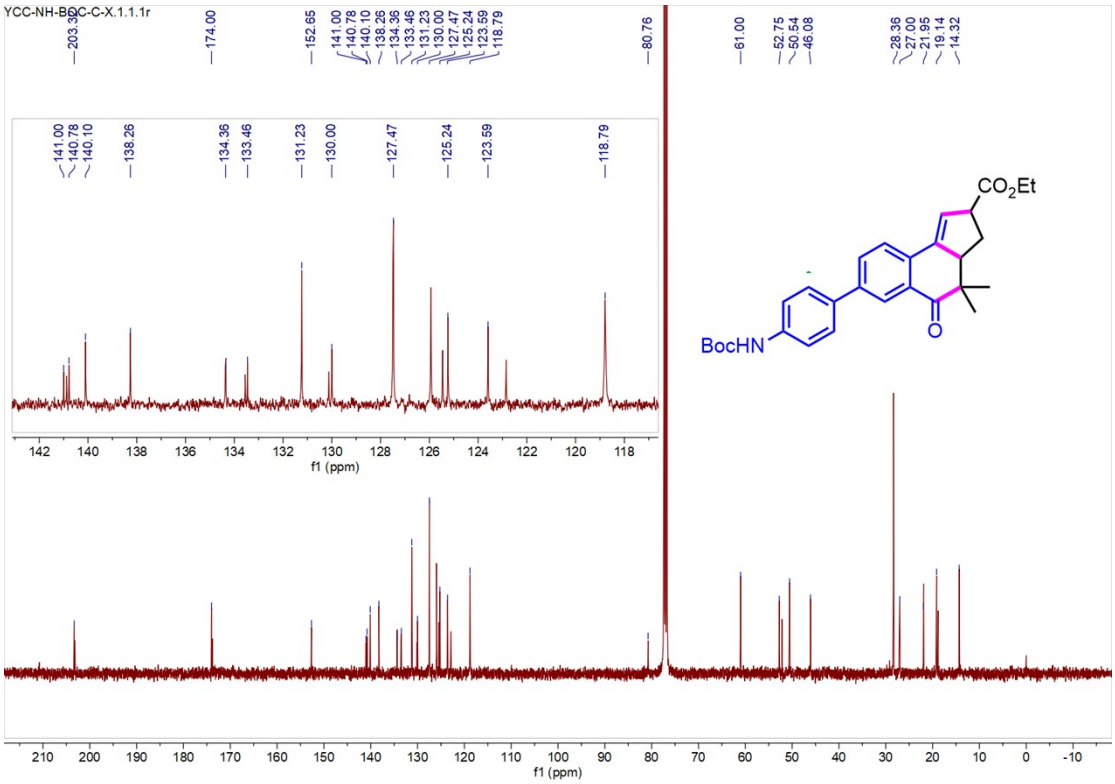




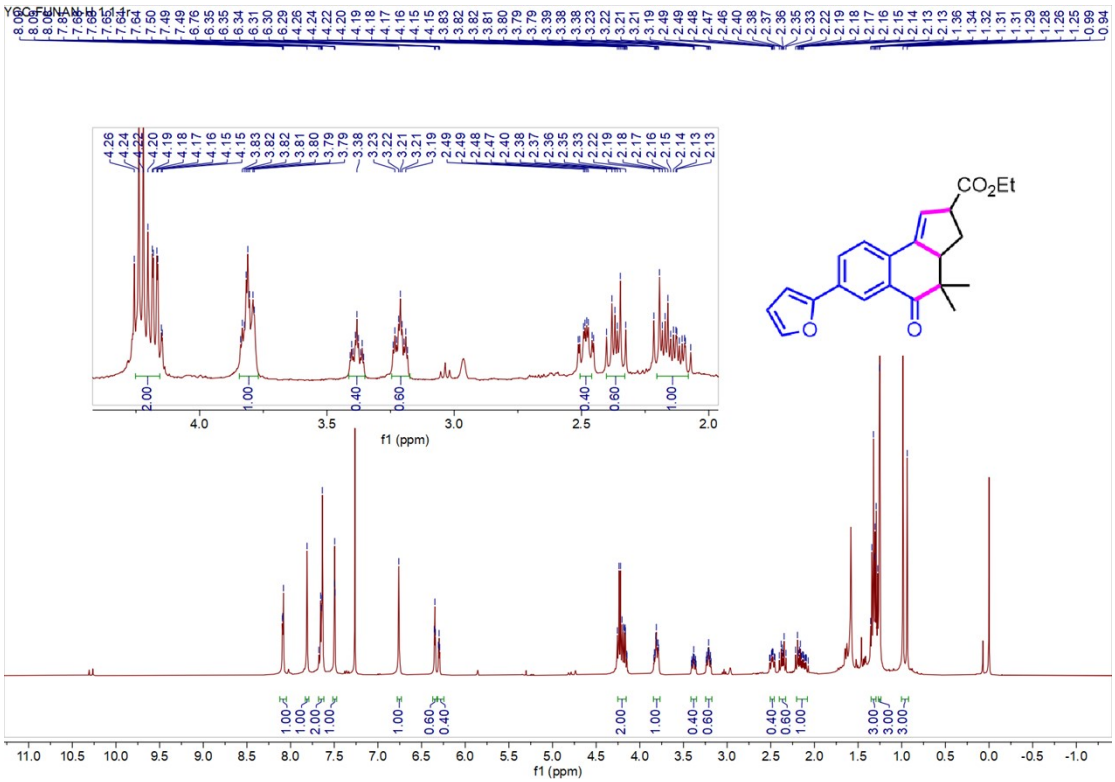


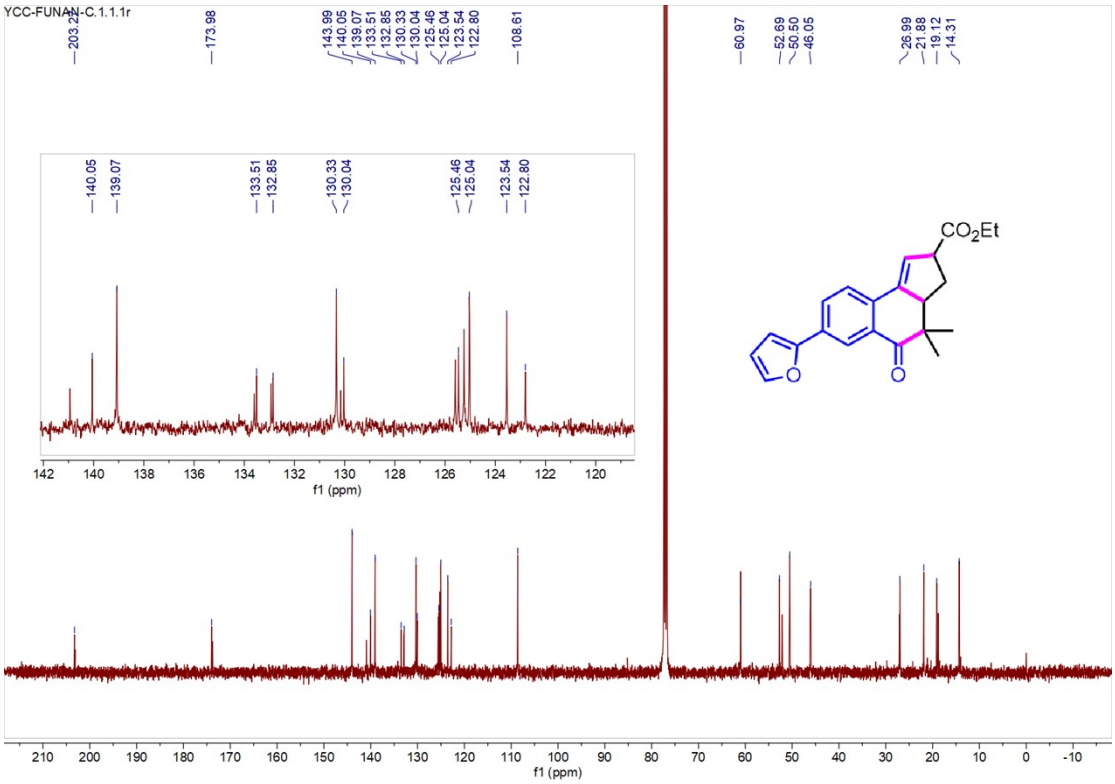
ethyl 7-(4-((*tert*-butoxycarbonyl)amino)phenyl)-4,4-dimethyl-5-oxo-3,3a,4,5-tetrahydro-2*H*-cyclopenta[*a*]naphthalene-2-carboxylate (**22**):



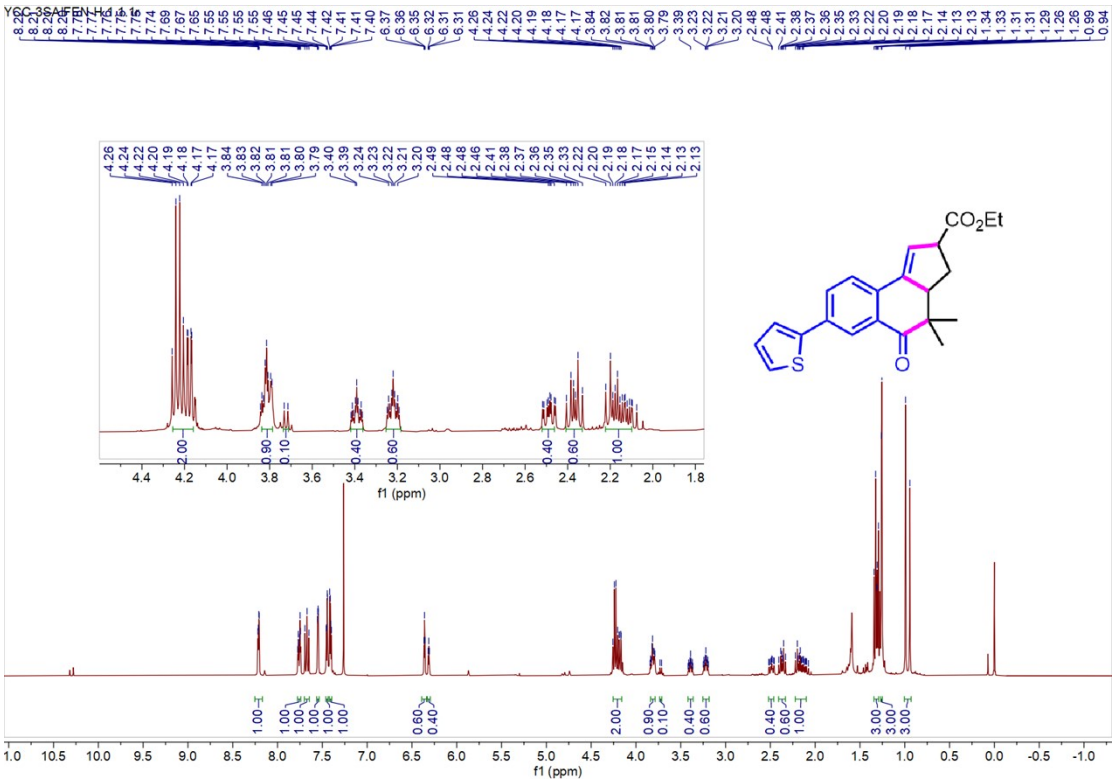


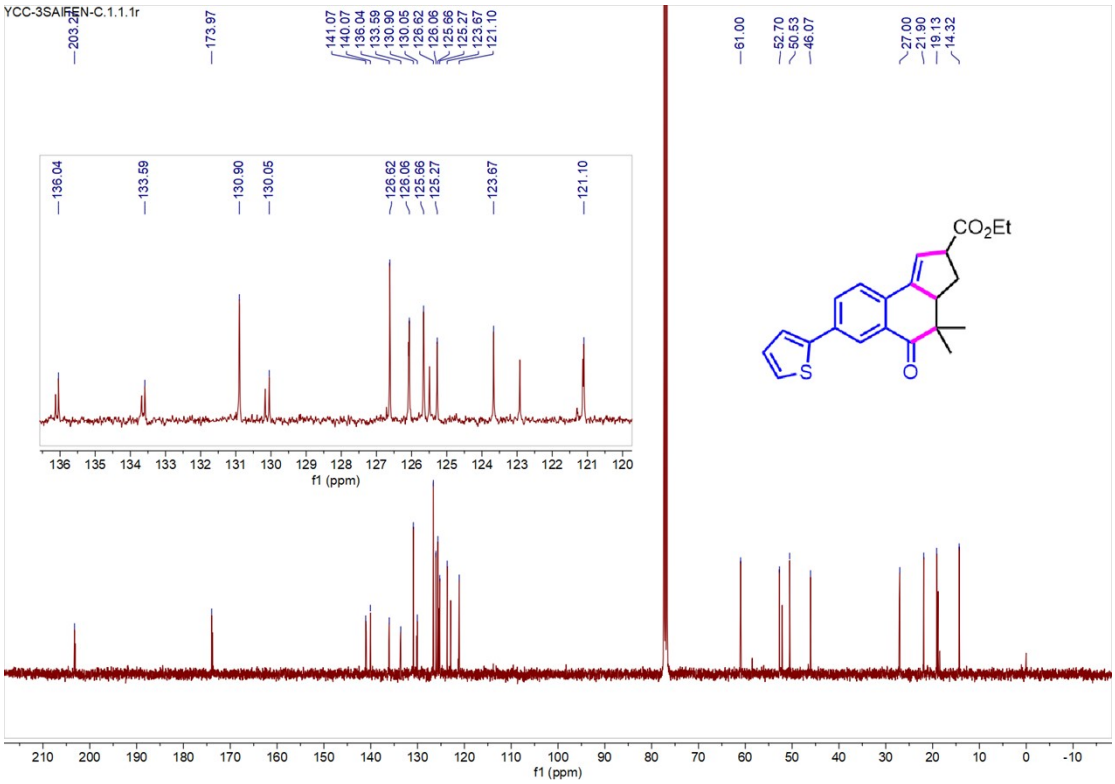
ethyl 7-(furan-3-yl)-4,4-dimethyl-5-oxo-3,3a,4,5-tetrahydro-2*H*-cyclopenta-[*a*]naphthalene-2-carboxylate (**23**):



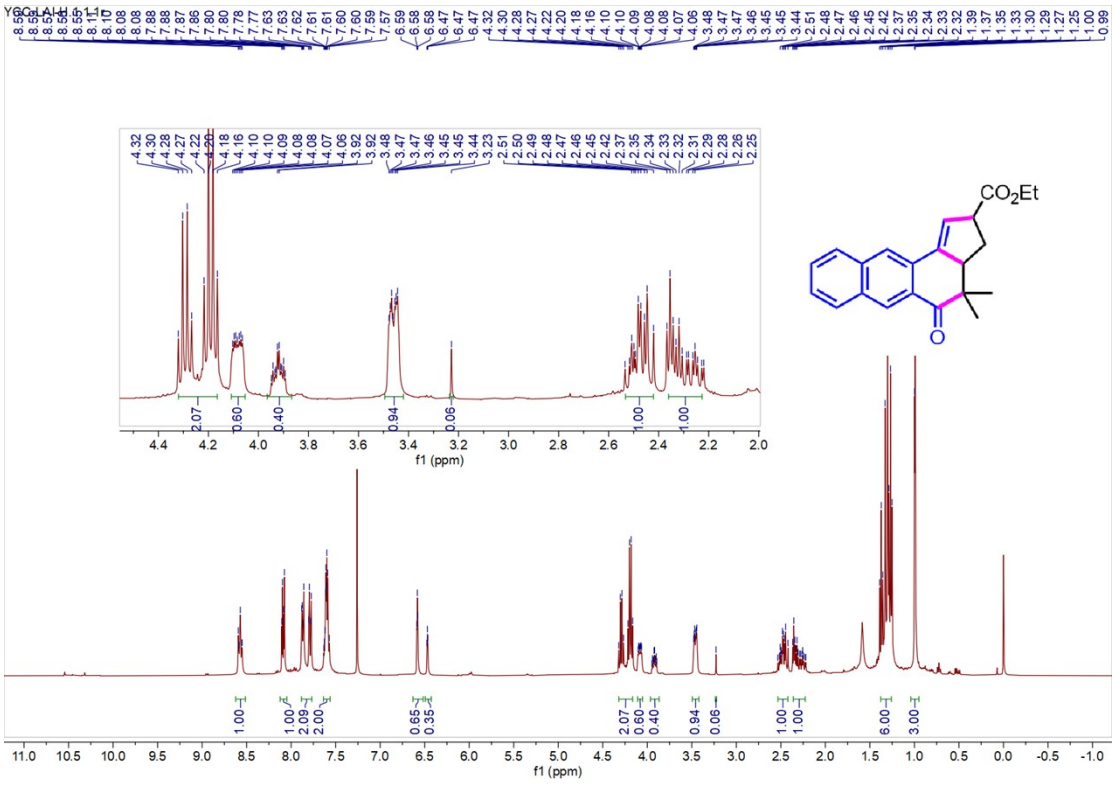


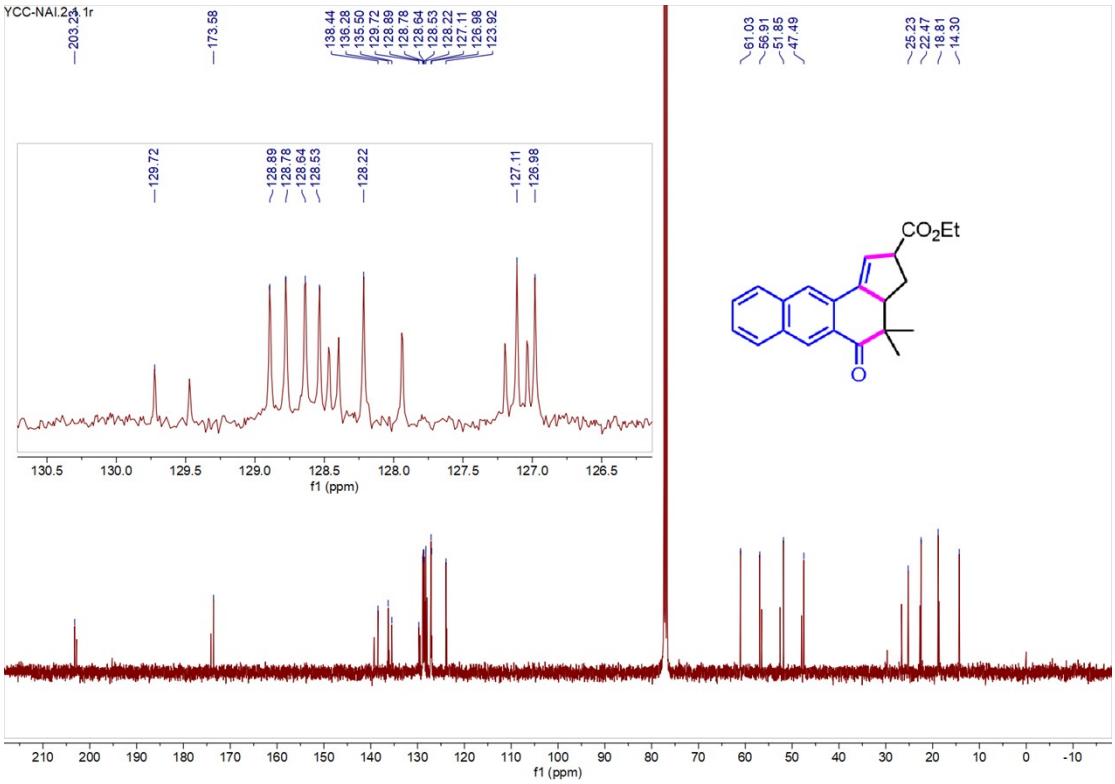
ethyl 4,4-dimethyl-5-oxo-7-(thiophen-3-yl)-3,3a,4,5-tetrahydro-2*H*-cyclopenta-[*a*]naphthalene-2-carboxylate (**24**):



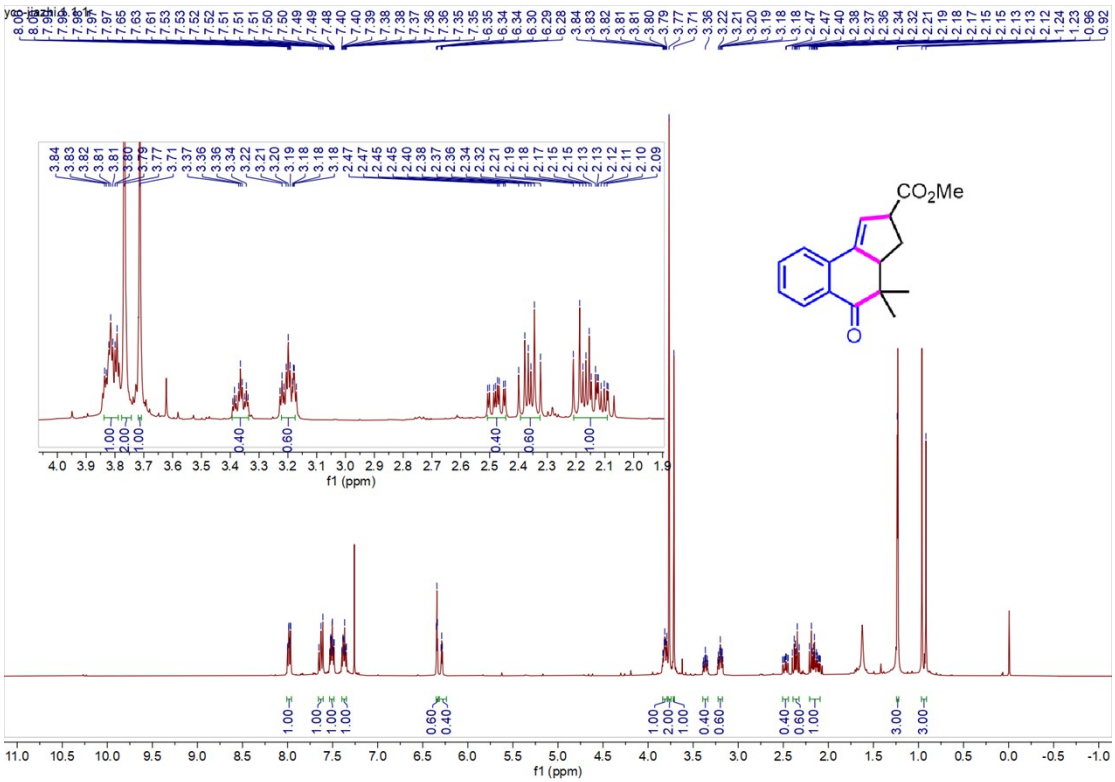


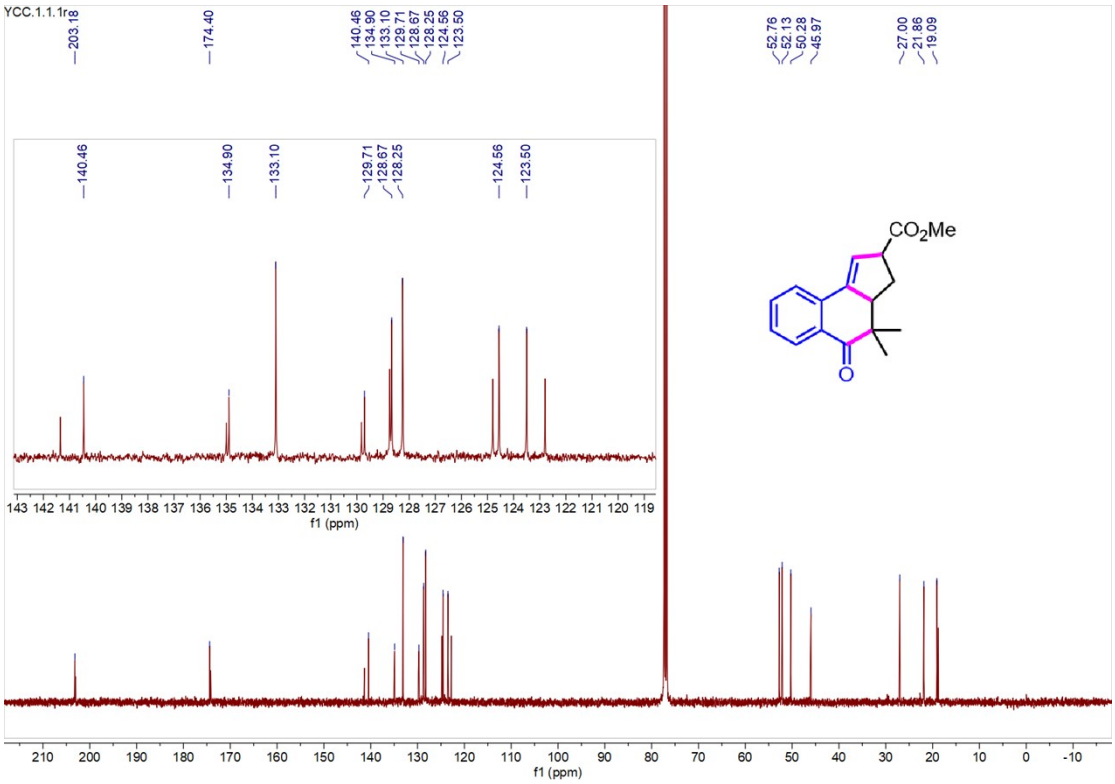
ethyl 4,4-dimethyl-5-oxo-3,3a,4,5-tetrahydro-2*H*-cyclopenta[*a*]anthracene-2-carboxylate (**25**):



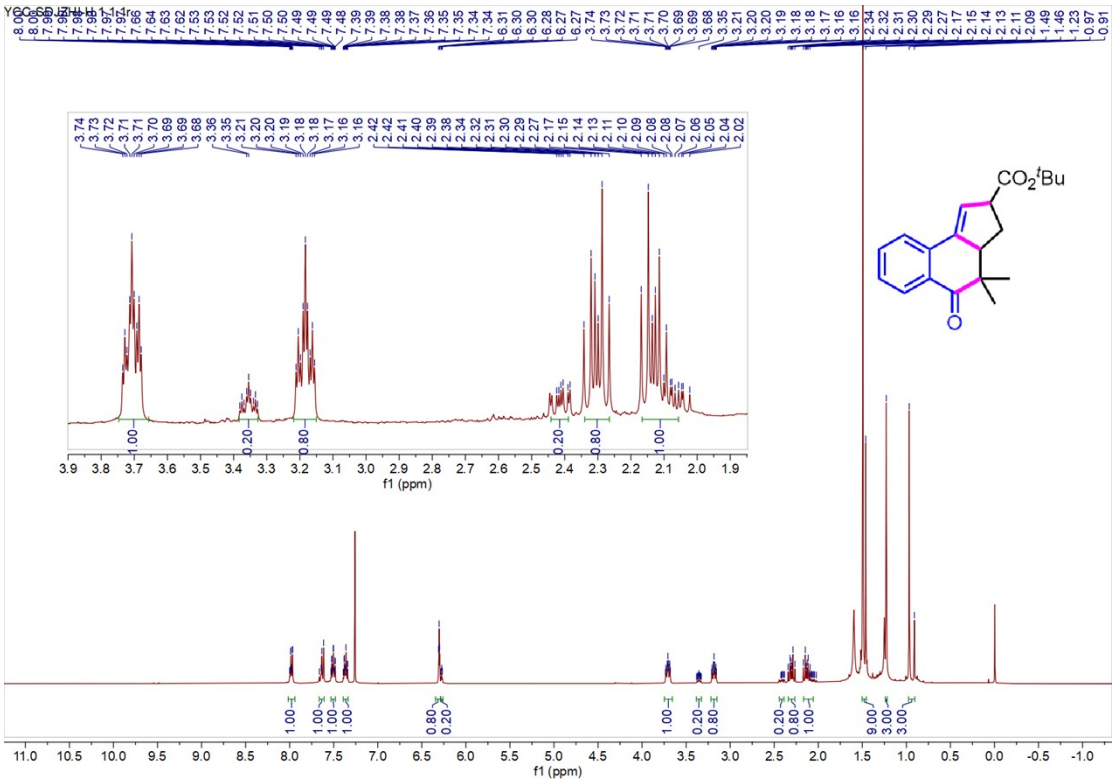


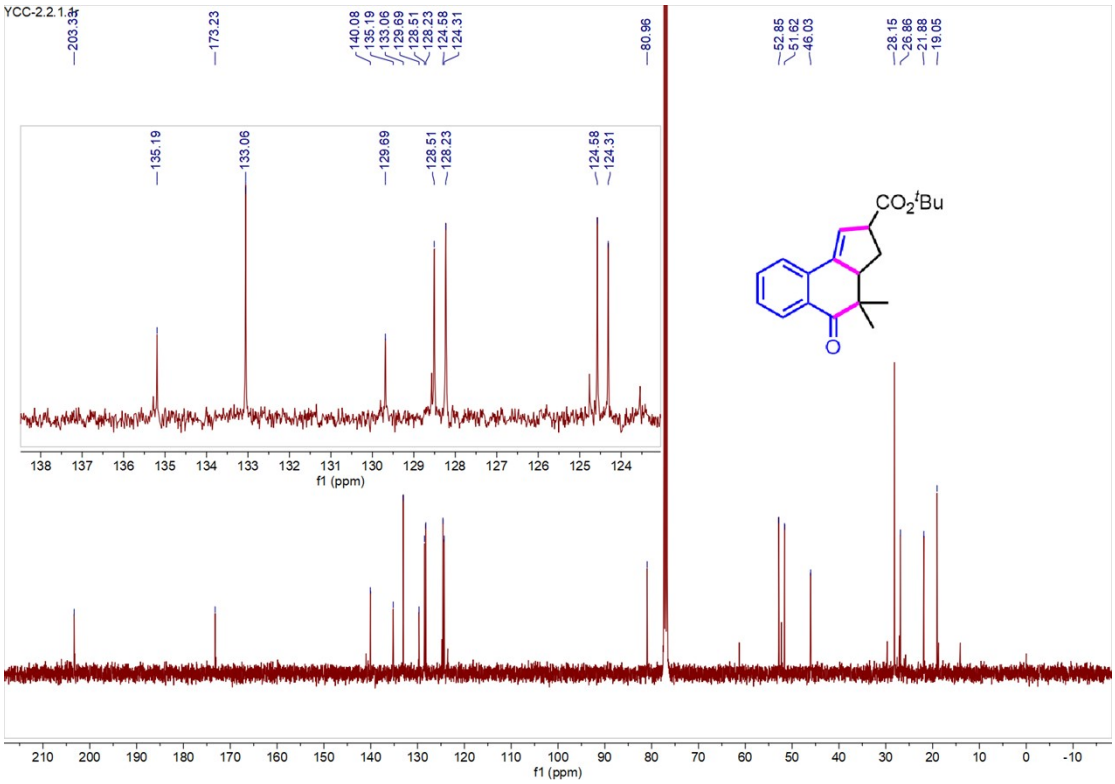
methyl 4,4-dimethyl-5-oxo-3,3a,4,5-tetrahydro-2*H*-cyclopenta[*a*]naphthalene-2-carboxylate (**26**):



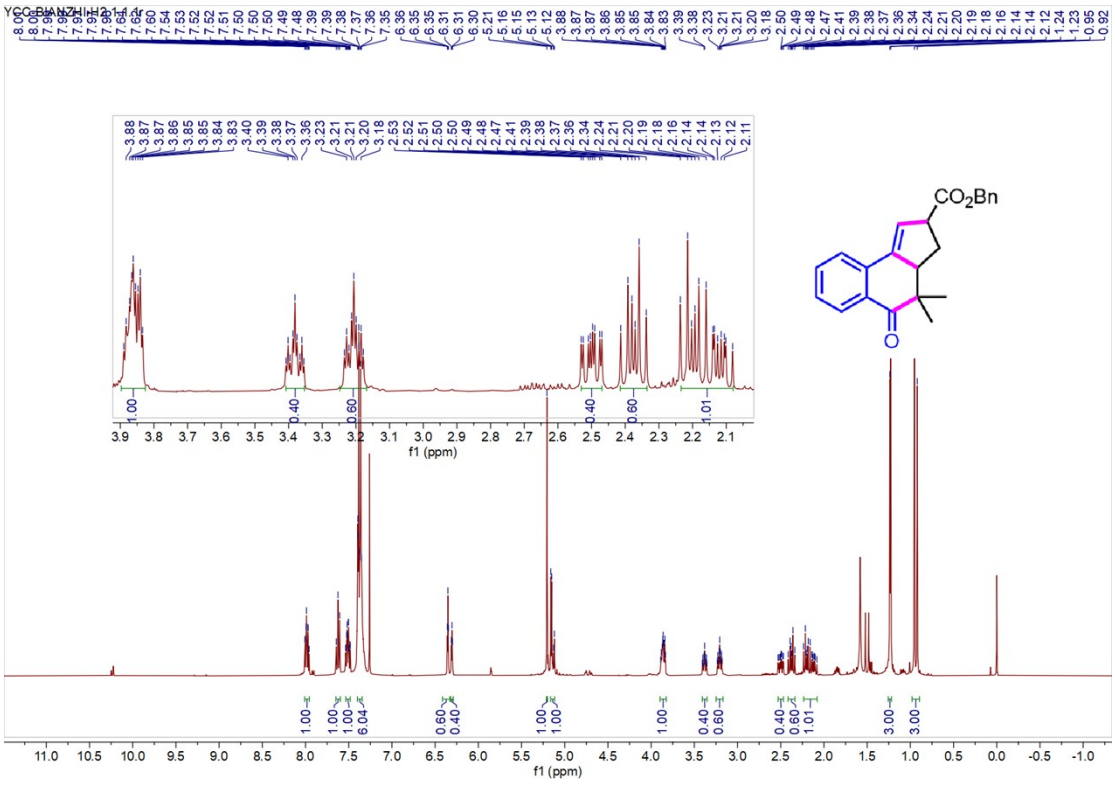


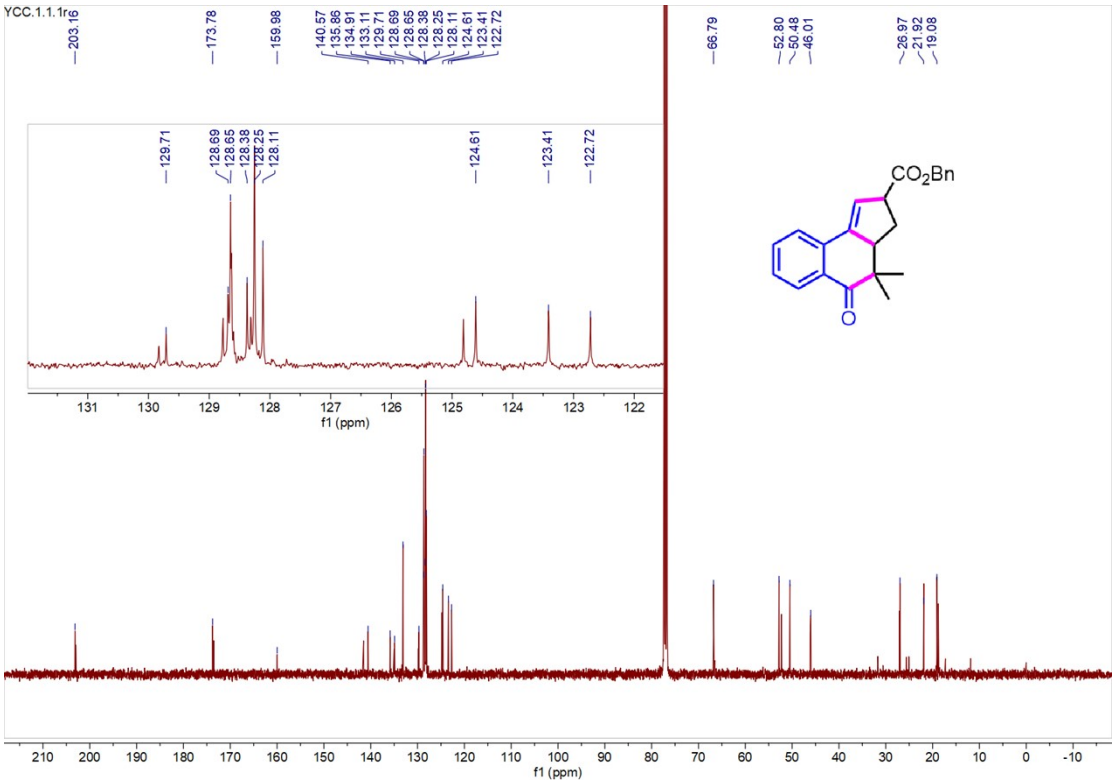
tert-butyl 4,4-dimethyl-5-oxo-3,3a,4,5-tetrahydro-2*H*-cyclopenta[*a*]naphthalene-2-carboxylate (**27**):



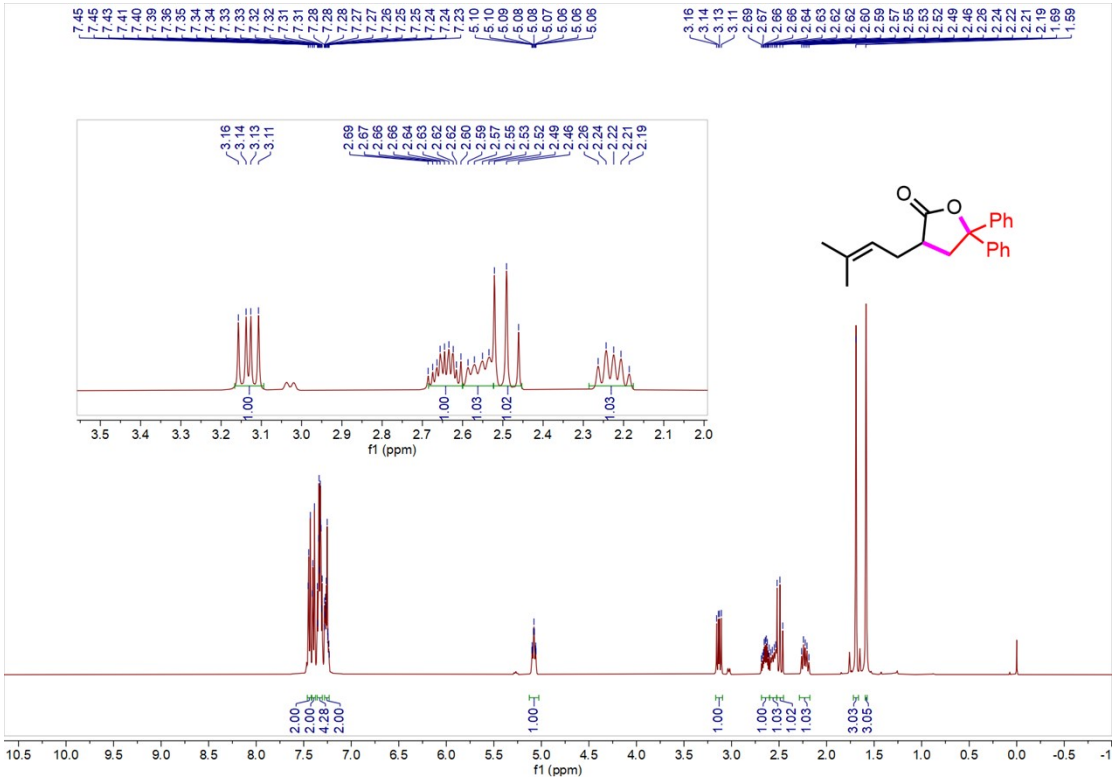


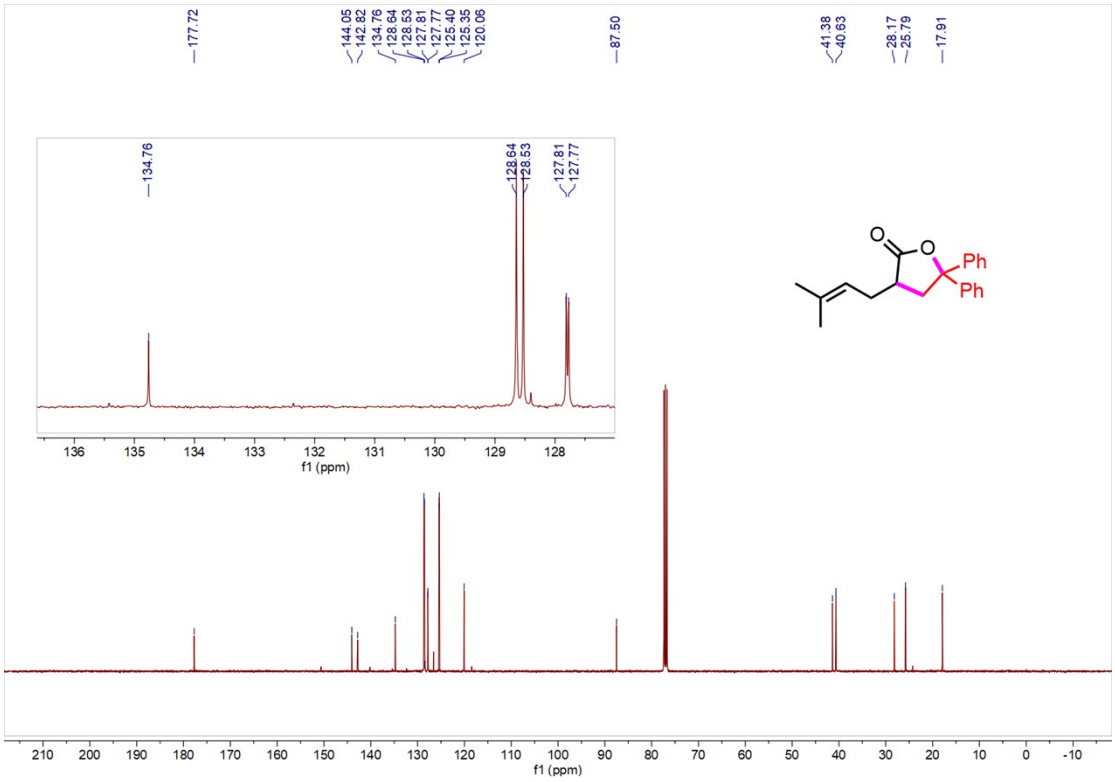
benzyl 4,4-dimethyl-5-oxo-3,3a,4,5-tetrahydro-2*H*-cyclopenta[*a*]naphthalene-2-carboxylate (**28**):





3-(3-methylbut-2-en-1-yl)-5,5-diphenyldihydrofuran-2(3*H*)-one (**29**):




177.72
144.05
142.82
134.76
128.64
128.53
127.81
127.77
125.40
125.35
120.06
87.50
41.38
40.63
28.17
25.79
17.91
134.76
128.64
128.53
127.81
127.77
Ph
Ph
f1 (ppm)
f1 (ppm)