Electronic Supplementary Material (ESI) for Chemical Communications.

Organocatalytic [10+4] Cycloadditions for the Synthesis of Functionalised Benzo[*a*]azulenes

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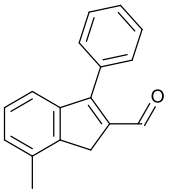
Supporting Information

General methods

NMR spectra were acquired on a Bruker AVANCE III HD spectrometer running at 400 MHz for ^{1}H, 101 MHz for ^{13}C and 376 MHz for ^{19}F. Chemical shifts (δ) are reported in ppm relative to residual solvent signals ($CDCl_3$, 7.26 ppm for ^{1}H NMR, $CDCl_3$, 77.0 ppm for ^{13}C NMR). Chemical shifts (δ) for ^{19}F NMR are reported in ppm relative to $CFCl_3$ as external reference. The following abbreviations are used to indicate the multiplicity in NMR spectra: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. ^{13}C NMR spectra were acquired in broad band decoupled mode. Mass spectra were recorded on a Bruker Maxis Impact-TOF-MS with electrospray ionization (ESI) (referenced to the mass of the charged species). UV/Vis spectra were recorded on a Genesys 10S UV-Vis spectrophotometer. The spectra were measured in CH_2Cl_2 in a quartz cuvette (1 cm) at 298 K. The absorption maxima (λ_{max}) are reported in nm with the extinction coefficient (ε) M^{-1} cm^{-1} in brackets. Analytical thin layer chromatography (TLC) was performed using pre-coated aluminum-backed plates (Merck Kieselgel 60 F_{254}) and visualized by ultraviolet radiation and/or staining with $KMnO_4$ or vanillin. For flash column chromatography (FC) silica gel (Silica gel 60, 230-400 mesh) was used. Unless otherwise noted, analytical grade solvents and commercially available reagents were used without further purification.

Synthesis of indene-2-carbaldehydes **1**

The two-step synthesis of indene-2-carbaldehydes **1** from 1-indanones have previously been reported in the literature.[1] Data for compounds **1a**-**c,g**-**j** were in accordance with those in the literature,[1] as well as those for **1l-1p**.[2]



1d

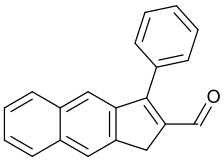
7-Methyl-3-phenyl-1*H*-indene-2-carbaldehyde 1d

7-Methyl-3-phenyl-1*H*-indene-2-carbaldehyde was obtained as a yellow solid from 4-methylindan-1-one (5 mmol scale) following the reported procedure in 86% yield over two steps.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.92 (s, 1H), 7.56–7.52 (m, 5H), 7.41–7.35 (m, 1H), 7.35–7.25 (m, 2H), 3.72 (s, 2H), 2.45 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.4, 159.4, 143.4, 143.2, 140.2, 134.3, 132.2, 130.2, 129.6 (2C), 129.2, 128.7 (2C), 127.4, 121.1, 35.0, 18.6.

HRMS (ESI+) calcd for $[C_{17}H_{14}O+H]^+$: 235.1117; found: 235.1117.



1e

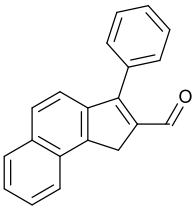
3-Phenyl-1*H*-cyclopenta[*b*]naphthalene-2-carbaldehyde 1e

A solution of α,α,α',α'-tetrabromo-*o*-xylene (5.1 g, 12.2 mmol, 1 equiv.), NaI (11.9 g, 79.8 mmol, 6.5 equiv.), and cyclopent-2-enone (1.0 g, 12.2 mmol, 1 equiv.) in DMF was heated for 18 h at 80 °C, cooled, diluted with CH_2Cl_2, and shaken with 20% aq. solution of sodium metabisulphite. The aq. phase was extracted with CH_2Cl_2 and the combined organic layers were washed with brine, dried over $MgSO_4$, and the solvent was removed in vacuum. The residue was purified by FC on silica gel (pentane:Et_2O 19:1) to give 1.53 g (8.42 mmol, 69% yield) of 5,6-benzoindan-3-one as a slightly yellow solid. This indanone was then converted into the titled indene-2-carbaldehyde following the reported procedure. The desired compound was obtained as an orange solid in 77% yield over two steps.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.99 (s, 1H), 7.97 (d, *J* = 11.6 Hz, 2H), 7.87 (dd, *J* = 12.5, 8.1 Hz, 2H), 7.63-7.57 (m, 5H), 7.50 (dddd, *J* = 21.9, 8.1, 6.8, 1.3 Hz, 2H), 3.91 (d, *J* = 1.1 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.6, 158.5, 142.6, 141.3, 140.3, 134.0, 132.6, 132.0, 129.6 (2C), 129.4, 128.8 (2C), 128.7, 127.8, 126.7, 125.7, 123.3, 122.8, 35.0.

HRMS (ESI+) calcd for $[C_{20}H_{14}O+H]^+$: 271.1117; found: 271.1126.



1f

3-Phenyl-1*H*-cyclopenta[*a*]naphthalene-2-carbaldehyde 1f

A well-stirred mixture of 2-naphthaldehyde (4.81 g, 30 mmol, 1 equiv.), malonic acid (6.41 g, 60 mmol, 2 equiv.), and piperidine (2.4 mL, 26.2 mmol, 85 mol%) in pyridine (36 mL) was refluxed for 2 h. After cooling, the reaction mixture was poured into conc. HCl (65 mL) containing crushed ice. The fluffy white precipitate was collected by suction filtration and dried to give 3-(1-naphthyl)acrylic acid (66% yield) as a white solid. A solution of 3-(1-naphthyl)acrylic acid (4.0 g, 20 mmol, 1 equiv.), ammonium formate (12.7 g, 202 mmol, 10.1 equiv.) and palladium (645 mg, 0.61 mmol, 3 mol%) in EtOAc (100 mL) was refluxed for 3 h. It was then filtered over Celite while boiling hot. The filter cake was rinsed with more boiling hot EtOAc. The filtrate was then evaporated under reduced pressure to afford 3-(1-naphthyl)propanoic acid (94% yield) without further purification. A solution of 3-(1-

[1] B. S. Donslund, N. I. Jessen, G. Bertuzzi, M. Giardinetti, T. A. Palazzo, M. L. Christensen, K. A. Jørgensen, *Angew. Chem. Int. Ed.*, 2018, **57**, 13182

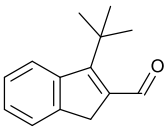
[2] B. S. Donslund, A. Monleón, T. A. Palazzo, M. L. Christensen, A. Dahlgaard, J. D. Erickson, K. A. Jørgensen, *Angew. Chem. Int. Ed.*, 2018, **57**, 1246

naphthyl)propanoic acid (3.8 g, 20 mmol) in TfOH (20 mL) was stirred at rt for 2 h. Crushed ice was added slowly and the reaction mixture was extracted with Et_2O. The organic layer was washed sequentially with aq. $NaHCO_3$, water, and brine, and dried (Na_2SO_4). The residue obtained by evaporation was subjected to FC on silica gel (pentane:EtOAc 9:1) to furnish 4,5-benzoindan-3-one (10%). This indanone was then transformed into the titled indene-2-carbaldehyde following the reported procedure (51% yield, orange solid).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.93 (s, 1H), 8.09 (d, *J* = 8.3 Hz, 1H), 7.91 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.83 (d, *J* = 8.5 Hz, 1H), 7.58 (dddd, *J* = 13.5, 8.3, 5.3, 3.2 Hz, 8H), 4.16 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.7, 160.0, 143.1, 140.9, 140.1, 133.7, 132.1, 130.0, 129.6 (2C), 129.4, 128.9, 128.8 (2C), 128.2, 127.0, 126.9, 124.4, 120.6, 35.1.

HRMS (ESI+) calcd for $[C_{20}H_{14}O+H]^+$: 271.1117; found: 271.1118.



1k

3-(*tert*-Butyl)-1*H*-indene-2-carbaldehyde 1k

To indene (1.17 mL, 10 mmol, 1 equiv.), *tert*-butylbromide (5.62 mL, 50 mmol, 5 equiv.) and 22 mL of a 50% w/w aq. solution of KOH was added NBu_4Cl (0.284 mL, 1 mmol, 10 mol%). This mixture was then stirred at 60 °C for 75 min and then at 100 °C for 45 min. After cooling back to rt, it was diluted with water and extracted several times with pentane to yield 3-(*tert*-butyl)-1*H*-indene as a liquid of sufficient purity for the next step. This indene was then formylated following the standard procedure. Column on silica gel using a gradient from pentane:CH_2Cl_2 1:1 to 2:8 afforded the named compound in 36% yield as a pale-yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.62 (s, 1H), 7.97–7.83 (m, 1H), 7.54–7.47 (m, 1H), 7.38–7.31 (m, 2H), 3.70 (s, 2H), 1.65 (d, *J* = 0.7 Hz, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.6, 164.1, 145.0, 143.8, 140.1, 127.7, 126.1, 125.9, 124.6, 37.8, 37.7, 32.0 (3C).

HRMS (ESI+) calcd for $[C_{14}H_{16}O+H]^+$: 201.1274; found: 201.1269.

Synthesis of chromen-4-ones **2**

Synthesis of 3-formylchromen-4-ones via Vilsmeier-Haack reaction

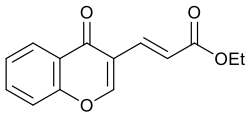
To dry DMF (1.7 mL, 22 mmol, 4.4 equiv.) in a flame-dried flask under argon was added $POCl_3$ (2 mL, 22 mmol, 4.4 equiv.) dropwise at 0 °C. Upon stirring for 10 min at 0 °C, the Vilsmeier-Haack reagent crystallized. To this white solid was added dry $CHCl_3$ (3.3 mL) and the 2'-hydroxyacetophenone (5 mmol, 1 equiv.). This mixture was stirred at rt until all the Vilsmeier-Haack reagent was dissolved then refluxed for 16 h. It was then poured into crushed ice (70 g) and stirred for 30 min. Mixture was then diluted with H_2O (100 mL) and CH_2Cl_2 (30 mL). Layers were separated, and the aq. layer was extracted with CH_2Cl_2 (4 x 30 mL). Combined organic layers were dried over $MgSO_4$ and evaporated. Most of the time, the obtained 3-formylchromen-4-one was of sufficient purity for the next step. When not, it was purified by FC on silica gel using a pentane/EtOAc mixture as eluent.

Procedure for the Wittig reaction

Conditions A: To the 3-formylchromen-4-one (1 equiv.) in dry toluene (0.25 M) under argon at 0 °C was added portionwise the Wittig reagent (1.3 equiv.). The mixture was stirred for 90 min while being allowed to warm up to rt. Toluene was then removed under reduced pressure and the crude compound was then directly purified by FC on silica gel.

Conditions B: To the 3-formylchromen-4-one (1 equiv.) in absolute EtOH (0.2 M) was added the Wittig reagent (1.5 equiv.). The mixture was then refluxed until full conversion. EtOH was then removed under reduced pressure and the crude compound was then directly purified by FC on silica gel.

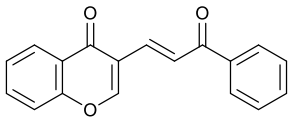
Characterization of chromen-4-ones **2**



2a

Ethyl (*E*)-3-(4-oxo-4*H*-chromen-3-yl)acrylate 2a

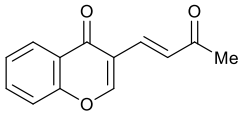
Synthesized from 3-formylchromen-4-one (1.742 g, 10 mmol) and ethyl (triphenylphosphoranylidene)acetate (5.226 g, 15 mmol) using conditions B. The crude compound was purified by FC on silica gel (Et_2O:EtOAc 10:1) to afford the desired compound as a white solid in 61% yield. Data were in accordance with those found in the literature.[3]



2b

(*E*)-3-(3-Oxo-3-phenylprop-1-en-1-yl)-4*H*-chromen-4-one 2b

Synthesized from 3-formylchromen-4-one (1.742 g, 10 mmol) and (triphenylphosphoranylidene)acetophenone (5.706 g, 15 mmol) using conditions B. The crude compound was purified by FC on silica gel (Et_2O:EtOAc 10:1) to afford the desired compound as a white solid in 34% yield. Data were in accordance with those found in the literature.[3]

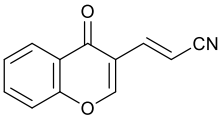


2c

(*E*)-3-(3-Oxobut-1-en-1-yl)-4*H*-chromen-4-one 2c

Synthesized from 3-formylchromen-4-one (522 mg, 3 mmol) and (triphenylphosphoranylidene)propanone (1.433 g, 4.5 mmol) using conditions B. The crude compound was purified by FC on silica gel using a gradient from pure CH_2Cl_2 to CH_2Cl_2:Et_2O 95:5 to afford the desired compound as a slightly yellow solid in 87% yield. Data were in accordance with those found in the literature.[3]

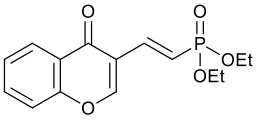
[3] A.-T. Dang, D. O. Miller, L. N. Dawe, G. J. Bodwell, *Org. Lett.*, 2008, **10**, 233-236



2d

(*E*)-3-(4-Oxo-4*H*-chromen-3-yl)acrylonitrile 2d

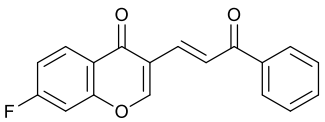
Synthesized from 3-formylchromen-4-one (522 mg, 3 mmol) and (triphenylphosphoranylidene)acetonitrile (1.356 g, 4.5 mmol) using conditions B. The crude compound was purified by FC on silica gel using a gradient from pentane:CH_2Cl_2 2:8 to pure CH_2Cl_2 to afford the desired compound as a slightly yellow solid in 33% yield. Data were in accordance with those found in the literature.[3]



2e

Diethyl (*E*)-(2-(4-oxo-4*H*-chromen-3-yl)vinyl)phosphonate 2e

To tetraethyl methylenebis(phosphonate) (0.75 mL, 3 mmol, 3 equiv.) in dry THF (46 mL) at -78 °C was added *n*BuLi (1.9 mL, 3 mmol, 3 equiv.). The mixture was stirred for 20 min at -78 °C then a solution of 3-formylchromen-4-one (174 mg, 1 mmol, 1 equiv.) in dry THF (25 mL) was added dropwise. The resulting mixture was then stirred for 2 h at 0 °C then quenched with sat. aq. NH_4Cl. The mixture was then concentrated under vacuum and extracted with Et_2O (x 3). The combined organic layers were washed with water and brine, dried over Na_2SO_4 and evaporated. The crude compound was purified by FC on silica gel using a gradient from pure Et_2O to Et_2O:EtOAc 8:2 to afford the desired compound as a yellow solid in 43% yield. Data were in accordance with those found in the literature.[4]



2f

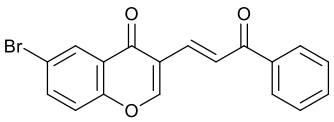
(*E*)-7-Fluoro-3-(3-oxo-3-phenylprop-1-en-1-yl)-4*H*-chromen-4-one 2f

Synthesized from 7-fluoro-3-formylchromen-4-one (961 mg, 5 mmol) (derived from 4'-fluoro-2'-hydroxyacetophenone) and (triphenylphosphoranylidene)acetophenone (2.47 g, 6.5 mmol) using conditions A. The crude compound was purified by FC on silica gel using a gradient from pentane:EtOAc 95:5 to 85:15. The obtained solid was dissolved into the minimum amount of CH_2Cl_2 then pentane was added until a precipitate appeared. This solid was filtered and dried to afford the desired compound as a pale yellow solid in 6% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 15.3 Hz, 1H), 8.37–8.29 (m, 1H), 8.19 (s, 1H), 8.16–8.08 (m, 2H), 7.64–7.56 (m, 1H), 7.55–7.44 (m, 3H), 7.21 (d, *J* = 8.4 Hz, 2H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -101.7.

HRMS (ESI+) calcd for $[C_{18}H_{11}FO_3+Na]^+$: 317.0584; found: 317.0589.



2g

(*E*)-6-Bromo-3-(3-oxo-3-phenylprop-1-en-1-yl)-4*H*-chromen-4-one 2g

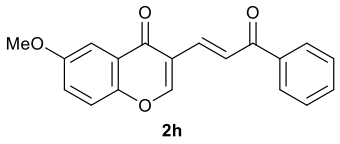
Synthesized from 6-bromo-3-formylchromen-4-one (1.265 g, 5 mmol) (derived from 5'-bromo-2'-hydroxyacetophenone) and (triphenylphosphoranylidene)acetophenone (2.47 g, 6.5 mmol) using conditions A. The crude compound was purified by FC on silica gel using a gradient from pentane:EtOAc 95:5 to 85:15. The obtained solid was dissolved into the minimum amount of CH_2Cl_2 then pentane was added until a precipitate appeared. This solid was filtered and dried to afford the desired compound as a pale yellow solid in 21% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 15.4 Hz, 1H), 8.41 (d, *J* = 2.4 Hz, 1H), 8.20 (s, 1H), 8.12–8.06 (m, 2H), 7.78 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.63–7.55 (m, 1H), 7.54–7.36 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.4, 174.9, 158.8, 154.2, 137.7, 137.0, 134.7, 133.1, 128.9, 128.7 (2C), 128.6 (2C), 126.1, 125.5, 120.1, 119.7, 119.5.

HRMS (ESI+) calcd for $[C_{18}H_{11}BrO_3+Na]^+$: 376.9784 (^{79}Br), 378.9763 (^{81}Br); found: 376.9784 (^{79}Br), 378.9763 (^{81}Br).

[4] D. Kim, S. Hong, *Org. Lett.*, 2011, **13**, 4466-4469



2h

(*E*)-6-Methoxy-3-(3-oxo-3-phenylprop-1-en-1-yl)-4*H*-chromen-4-one 2h

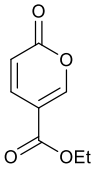
Synthesized from 3-formyl-6-methoxychromen-4-one (1.021 g, 5 mmol) (derived from 2'-hydroxy-5'-methoxyacetophenone) and (triphenylphosphoranylidene)acetophenone (2.47 g, 6.5 mmol) using conditions A. The crude compound was purified by FC on silica gel using a gradient from pentane:EtOAc 9:1 to 8:2. The obtained solid was dissolved into the minimum amount of CH_2Cl_2 then pentane was added until a precipitate appeared. This solid was filtered and dried to afford the desired compound as a pale orange solid in 29% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 15.3 Hz, 1H), 8.20 (s, 1H), 8.14–8.09 (m, 2H), 7.66 (d, *J* = 3.1 Hz, 1H), 7.62–7.55 (m, 1H), 7.53–7.48 (m, 3H), 7.45 (d, *J* = 9.1 Hz, 1H), 7.30 (dd, *J* = 9.1, 3.1 Hz, 1H), 3.92 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.6, 176.2, 158.7, 157.5, 150.3, 137.9, 135.5, 133.0, 128.7 (2C), 128.6 (2C), 125.5, 124.9, 124.1, 119.6, 118.7, 105.2, 55.9.

HRMS (ESI+) calcd for $[C_{19}H_{14}O_4+Na]^+$: 329.0784; found: 329.0790.

Synthesis of α-pyrone **5a**



5a

Ethyl 2-oxo-2*H*-pyran-5-carboxylate 5a

Ethyl 3,3-(diethoxy)propanoate (4 mL, 20 mmol, 1 equiv.), $FeCl_3$ (487 mg, 3 mmol, 15 mol%), AcOH (80 mL) and EtOH (10 mL) were introduced into a flask. The reaction mixture was then refluxed for 16 h. Solvent was then removed under reduced pressure. The residue was diluted with H_2O (2 L) and extracted several times with EtOAc. The combined organic layers were dried over $MgSO_4$ and evaporated. The crude compound was then purified by FC on silica gel using a mixture of pentane:EtOAc 9:1 as eluent, to afford the desired compound as a pale yellow solid (whose melting point is around rt) in 56% yield.

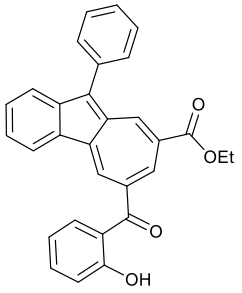
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (dd, *J* = 2.6, 1.1 Hz, 1H), 7.80 (dd, *J* = 9.8, 2.6 Hz, 1H), 6.34 (dd, *J* = 9.8, 1.1 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8, 159.8, 157.9, 141.6, 115.1, 112.1, 61.5, 14.1.

HRMS (ESI+) calcd for $[C_8H_8O_4+H]^+$: 169.0495; found: 169.0496.

General procedure for the organocatalyzed [10+4] cycloaddition reaction between indene-2-carbaldehydes **1** and chromen-4-ones **2**

In a vial were successively introduced *p*MeOBzOH (2.3 mg, 0.015 mmol, 15 mol%), $CDCl_3$ filtered over Al_2O_3 (0.4 mL), molecular sieves (MS) 4Å (3 beads), **2** (0.15 mmol, 1.5 equiv.), **1** (0.1 mmol, 1 equiv.) and pyrrolidine **3c** (1.2 µL, 0.015 mmol, 15 mol%). The vial was capped, and the mixture was stirred at 40 °C for 1-3 d. The crude compound was then directly loaded onto a column and purified by FC on silica gel.



4aa

Ethyl 6-(2-hydroxybenzoyl)-10-phenylbenzo[*a*]azulene-8-carboxylate 4aa

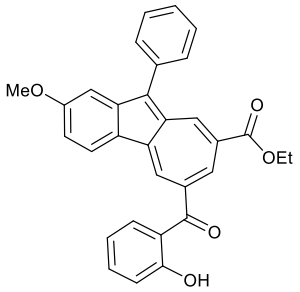
Synthesized from **1a** and **2a** according to the general procedure in 1 d. The crude compound was purified by FC on silica gel using a gradient from pentane:CH_2Cl_2 6:4 to pure CH_2Cl_2, affording **4aa** as a brown solid in 65% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.87 (s, 1H), 9.21 (d, *J* = 1.5 Hz, 1H), 8.58 (d, *J* = 1.4 Hz, 1H), 8.48 (dd, *J* = 8.0, 1.0 Hz, 1H), 8.33 (d, *J* = 1.8 Hz, 1H), 8.02 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.83–7.75 (m, 1H), 7.72–7.66 (m, 4H), 7.63 (t, *J* = 7.6 Hz, 2H), 7.58–7.50 (m, 2H), 7.14 (d, *J* = 8.4 Hz, 1H), 6.96–6.87 (m, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.9, 167.2, 163.3, 141.8, 141.7, 139.4, 138.3, 137.3, 136.6, 134.1, 133.4, 133.1, 132.9, 131.4, 130.1 (2C), 129.7, 129.0 (2C), 128.3, 127.2, 125.3, 122.8, 121.3, 121.0, 118.9, 118.8, 118.7, 61.9, 14.2.

UV/Vis λ_{max} (CH_2Cl_2)/nm 227 (24800), 263 (31200), 330 (40100), 439 (12100), 463 (13100).

HRMS (ESI-) calcd for $[C_{30}H_{21}O_4]^-$: 445.1445; found: 445.1445.



4ba

Ethyl 6-(2-hydroxybenzoyl)-2-methoxy-10-phenylbenzo[*a*]azulene-8-carboxylate 4ba

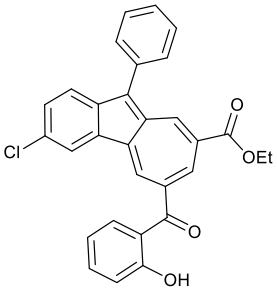
Synthesized from **1b** and **2a** according to the general procedure in 1 d. The crude compound was purified by FC on silica gel using a gradient from pentane:CH_2Cl_2 6:4 to pure CH_2Cl_2, affording **4ba** as a brown solid in 45% yield.

^{1}H NMR (400 MHz, $CDCl_3$) 11.90 (s, 1H), 9.20 (d, *J* = 1.6 Hz, 1H), 8.52 (d, *J* = 1.6 Hz, 1H), 8.39 (dd, *J* = 8.7, 1.3 Hz, 1H), 8.35 (q, *J* = 1.6 Hz, 1H), 7.71–7.60 (m, 5H), 7.57-7.50 (m, 2H), 7.37 (d, *J* = 2.1 Hz, 1H), 7.30–7.25 (m, 1H), 7.15–7.11 (m, 1H), 6.94–6.87 (m, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 3.94 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.2, 167.4, 163.3, 161.9, 143.8, 140.2, 138.5, 137.1, 136.5, 135.9, 134.2, 133.3, 132.8, 132.5, 130.0 (2C), 129.0 (2C), 128.2, 127.3, 125.9, 122.8 (2C), 118.9, 118.9, 118.6, 115.9, 102.0, 61.8, 55.7, 14.2.

UV/Vis λ_{max} (CH_2Cl_2)/nm 228 (24300), 269 (34100), 362 (50900), 451 (7500), 481 (7300).

HRMS (ESI-) calcd for $[C_{31}H_{23}O_5]^-$: 475.1551; found: 475.1547.



4ca

Ethyl 3-chloro-6-(2-hydroxybenzoyl)-10-phenylbenzo[*a*]azulene-8-carboxylate 4ca

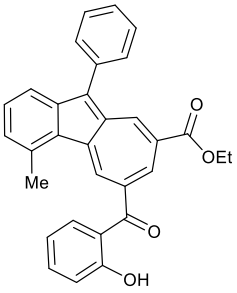
Synthesized from **1c** and **2a** according to the general procedure in 1 d. The crude compound was purified by FC on silica gel using a gradient from pentane:CH_2Cl_2 6:4 to pure CH_2Cl_2, affording **4ca** as a brown solid in 33% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.82 (s, 1H), 9.17 (d, *J* = 1.6 Hz, 1H), 8.51 (d, *J* = 1.6 Hz, 1H), 8.41 (d, *J* = 1.9 Hz, 1H), 8.34 (d, *J* = 1.8 Hz, 1H), 7.93 (d, *J* = 8.5 Hz, 1H), 7.74–7.50 (m, 8H), 7.14 (dd, *J* = 8.5, 1.1 Hz, 1H), 6.93 (ddd, *J* = 8.2, 7.2, 1.1 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.5, 167.0, 163.4, 142.2, 139.8, 138.4, 138.1, 137.7, 136.7, 134.3, 133.6, 133.0 (2C), 131.7, 131.5, 130.1, 130.0 (2C), 129.1 (2C), 128.5, 128.3, 123.2, 122.1, 121.0, 119.0, 118.8, 118.7, 62.0, 14.2.

UV/Vis λ_{max} (CH_2Cl_2)/nm 227 (32800), 265 (36000), 334 (45800), 438 (15200), 461 (16700).

HRMS (ESI-) calcd for $[C_{30}H_{20}ClO_4]^-$: 479.1056 (^{35}Cl), 481.1048 (^{37}Cl); found: 479.1060 (^{35}Cl), 481.1056 (^{37}Cl).



4da

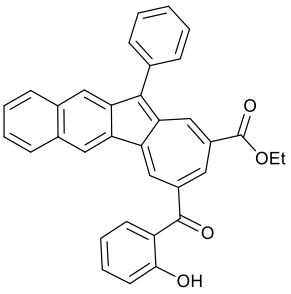
Ethyl 6-(2-hydroxybenzoyl)-4-methyl-10-phenylbenzo[*a*]azulene-8-carboxylate 4da

Synthesized from **1d** and **2a** according to the general procedure in 1 d. The crude compound was purified by FC on silica gel using a gradient from pentane:CH_2Cl_2 6:4 to pure CH_2Cl_2, affording **4da** as a brown solid in 83% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.87 (s, 1H), 9.18 (d, *J* = 1.7 Hz, 1H), 8.78 (d, *J* = 1.4 Hz, 1H), 8.32 (d, *J* = 1.8 Hz, 1H), 7.90 (d, *J* = 7.9 Hz, 1H), 7.73 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.71–7.59 (m, 5H), 7.58–7.48 (m, 3H), 7.13 (d, *J* = 8.4 Hz, 1H), 6.95–6.89 (m, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 3.00 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.2, 167.2, 163.3, 142.5, 141.9, 140.4, 139.0, 137.1, 136.5, 135.4, 134.2, 133.2, 133.1, 131.8, 131.0, 130.8, 130.4 (2C), 129.1, 128.9 (2C), 128.8, 128.2, 122.3, 119.5, 118.8 (2C), 118.7, 61.8, 22.9, 14.2.

HRMS (ESI-) calcd for $[C_{31}H_{23}O_4]^-$: 459.1602; found: 459.1605.



4ea

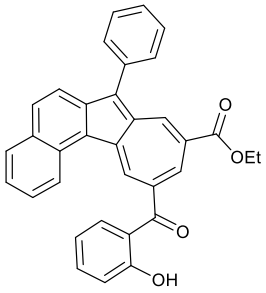
Ethyl 7-(2-hydroxybenzoyl)-11-phenylnaphtho[2,3-*a*]azulene-9-carboxylate 4ea

Synthesized from **1e** and **2a** according to the general procedure in 1 d. The crude compound was purified by FC on silica gel using a gradient from pentane:CH_2Cl_2 1:1 to pure CH_2Cl_2, affording **4ea** as a brown solid in 82% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.87 (s, 1H), 8.85 (d, *J* = 1.5 Hz, 1H), 8.83 (s, 1H), 8.28 (s, 1H), 8.20 (d, *J* = 1.5 Hz, 1H), 8.15 (d, *J* = 7.3 Hz, 1H), 8.05 (d, *J* = 7.5 Hz, 1H), 7.92 (t, *J* = 1.5 Hz, 1H), 7.76 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.73-7.71 (m, 2H), 7.65 (t, *J* = 7.6 Hz, 2H), 7.62-7.53 (m, 4H), 7.14 (dd, *J* = 8.5, 0.9 Hz, 1H), 6.93 (td, *J* = 7.6, 1.1 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.7, 166.9, 163.4, 141.9, 141.3, 139.5, 139.3, 136.6, 135.8, 134.7, 134.0, 133.9, 133.8, 132.9, 132.8, 131.2, 129.7 (2C), 129.1 (2C), 129.0, 128.5, 128.4, 126.7, 125.4, 124.2, 123.3, 120.7, 118.9, 118.8, 118.7 (2C), 61.8, 14.2.

HRMS (ESI-) calcd for $[C_{34}H_{23}O_4]^-$: 495.1602; found: 495.1603.



4fa

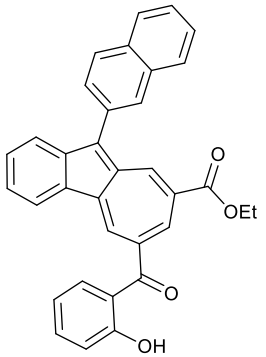
Ethyl 11-(2-hydroxybenzoyl)-7-phenylnaphtho[1,2-*a*]azulene-9-carboxylate 4fa

Synthesized from **1f** and **2a** according to the general procedure in 2 d. The crude compound was purified by FC on silica gel using a gradient from pentane:CH_2Cl_2 6:4 to pure CH_2Cl_2, affording **4fa** as a brown solid in 42% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.95 (s, 1H), 9.67 (d, *J* = 1.5 Hz, 1H), 9.46 (d, *J* = 1.7 Hz, 1H), 9.00 (d, *J* = 8.4 Hz, 1H), 8.71 (t, *J* = 1.6 Hz, 1H), 8.12–7.99 (m, 3H), 7.79 (ddd, *J* = 8.4, 7.0, 1.4 Hz, 1H), 7.75–7.62 (m, 6H), 7.57 (ddd, *J* = 8.9, 7.2, 1.6 Hz, 2H), 7.17 (dd, *J* = 8.4, 1.1 Hz, 1H), 6.93 (ddd, *J* = 8.2, 7.1, 1.2 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.4, 167.4, 163.4, 142.8, 140.8, 138.0, 137.6, 137.2, 136.5, 134.0, 133.8, 133.5, 133.0, 132.6, 132.1, 131.9, 130.8 (2C), 130.1, 129.9, 128.9 (2C), 128.5, 128.2, 127.1, 125.7, 124.5, 121.8, 120.2, 119.1, 118.9, 118.7, 61.9, 14.3.

HRMS (ESI-) calcd for $[C_{34}H_{23}O_4]^-$: 495.1602; found: 495.1605.



4ga

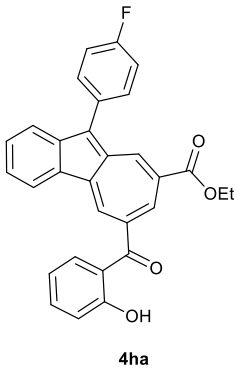
Ethyl 6-(2-hydroxybenzoyl)-10-(naphth-2-yl)benzo[*a*]azulene-8-carboxylate 4ga

Synthesized from **1g** and **2a** according to the general procedure in 1 d. The crude compound was purified by FC on silica gel using a gradient from pentane:CH_2Cl_2 6:4 to pure CH_2Cl_2, affording **4ga** as a brown solid in 83% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.88 (s, 1H), 9.29 (d, *J* = 1.3 Hz, 1H), 8.61 (d, *J* = 1.2 Hz, 1H), 8.51 (dd, *J* = 8.0, 1.0 Hz, 1H), 8.35 (q, *J* = 1.4 Hz, 1H), 8.17 (s, 1H), 8.08 (dd, *J* = 8.1, 6.7 Hz, 2H), 8.00–7.96 (m, 2H), 7.84–7.77 (m, 2H), 7.73–7.68 (m, 2H), 7.62–7.53 (m, 3H), 7.14 (d, *J* = 8.4 Hz, 1H), 6.93 (tt, *J* = 8.1, 1.1 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.9, 167.2, 163.4, 141.8 (2C), 139.5, 138.2, 137.4, 136.6, 133.7, 133.5, 133.1 (2C), 133.0, 131.7, 131.6, 129.8, 129.3, 128.6, 128.2, 127.9, 127.8, 127.3, 126.6, 126.5, 125.4, 123.0, 121.3, 121.1, 118.9, 118.8, 118.7, 61.9, 14.2.

HRMS (ESI-) calcd for $[C_{34}H_{23}O_4]^-$: 495.1602; found: 495.1606.



4ha

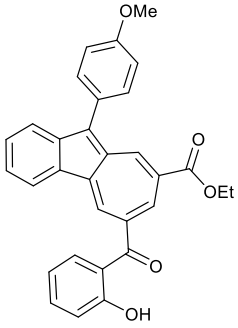
Ethyl 10-(4-fluorophenyl)-6-(2-hydroxybenzoyl)benzo[*a*]azulene-8-carboxylate 4ha

Synthesized from **1h** and **2a** according to the general procedure in 1 d. The crude compound was purified by FC on silica gel using a gradient from pentane:CH_2Cl_2 7:3 to pure CH_2Cl_2, affording **4ha** as a golden-brown solid in 98% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.89 (s, 1H), 9.14 (d, *J* = 1.6 Hz, 1H), 8.59 (d, *J* = 1.6 Hz, 1H), 8.49 (d, *J* = 7.9 Hz, 1H), 8.33 (t, *J* = 1.5 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.79 (td, *J* = 7.5, 0.8 Hz, 1H), 7.71-7.64 (m, 4H), 7.56 (td, *J* = 7.8, 1.6 Hz, 1H), 7.33 (tt, *J* = 8.7, 2.1 Hz, 2H), 7.14 (dd, *J* = 8.6, 0.8 Hz, 1H), 6.92 (td, *J* = 7.6, 0.9 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -113.1.

HRMS (ESI-) calcd for $[C_{30}H_{20}FO_4]^-$: 463.1357; found: 463.1357.



4ia

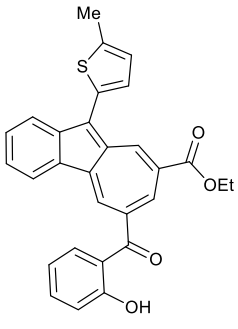
Ethyl 6-(2-hydroxybenzoyl)-10-(4-methoxyphenyl)benzo[*a*]azulene-8-carboxylate 4ia

Synthesized from **1i** and **2a** according to the general procedure in 1 d. The crude compound was purified by FC on silica gel using a gradient from pentane:CH_2Cl_2 6:4 to 2:8, affording **4ia** as a golden-brown solid in 82% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.87 (s, 1H), 9.19 (d, *J* = 1.6 Hz, 1H), 8.53 (d, *J* = 1.6 Hz, 1H), 8.47 (d, *J* = 7.9 Hz, 1H), 8.30 (t, *J* = 1.5 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.78 (td, *J* = 7.6, 0.8 Hz, 1H), 7.71-7.61 (m, 4H), 7.55 (td, *J* = 7.9, 1.6 Hz, 1H), 7.18-7.12 (m, 3H), 6.92 (td, *J* = 7.6, 1.1 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 3.95 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 210.9, 167.3, 163.3, 159.7, 142.1, 141.8, 139.4, 138.3, 137.4, 136.5, 133.4, 133.1, 132.8, 131.3 (2C), 131.1, 129.7, 126.8, 126.4, 125.3, 122.4, 121.2, 121.1, 118.9 (2C), 118.7, 114.5 (2C), 61.8, 55.4, 14.3.

HRMS (ESI-) calcd for $[C_{31}H_{23}O_5]^-$: 475.1556; found: 475.1560.



4ja

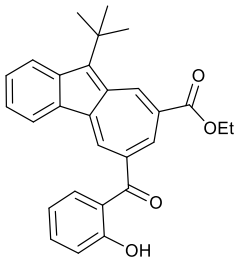
Ethyl 6-(2-hydroxybenzoyl)-10-(5-methylthiophen-2-yl)benzo[*a*]azulene-8-carboxylate 4ja

Synthesized from **1j** and **2a** according to the general procedure in 1 d. The crude compound was purified by FC on silica gel using a gradient from pentane:CH_2Cl_2 6:4 to pentane:CH_2Cl_2 3:7, affording **4ja** as a brown solid in 85% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.85 (s, 1H), 9.51 (d, *J* = 1.1 Hz, 1H), 8.51 (t, *J* = 1.2 Hz, 1H), 8.45 (d, *J* = 7.9 Hz, 1H), 8.32–8.28 (m, 2H), 7.82 (t, *J* = 7.5 Hz, 1H), 7.71–7.65 (m, 2H), 7.58–7.52 (m, 1H), 7.32 (d, *J* = 3.5 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 6.99 (dt, *J* = 3.5, 1.1 Hz, 1H), 7.92 (td, *J* = 7.5, 0.9 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 2.65 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.7, 167.3, 163.3, 142.2, 142.0, 141.2, 139.5, 137.6, 136.6, 133.4, 133.1 (2C), 133.0, 131.5, 130.9, 129.9, 128.2, 127.0, 126.3, 125.4, 122.9, 121.3, 121.1, 118.9, 118.8, 118.7, 61.9, 15.5, 14.3.

HRMS (ESI-) calcd for $[C_{29}H_{21}O_4S]^-$: 465.1166; found: 465.1167.



4ka

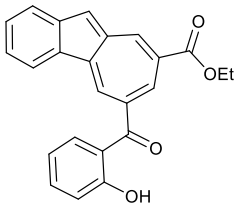
Ethyl 10-(*tert*-butyl)-6-(2-hydroxybenzoyl)benzo[*a*]azulene-8-carboxylate 4ka

Synthesized from **1k** and **2a** according to the general procedure in 3 d. The crude compound was purified by FC on silica gel using a gradient from pentane:CH_2Cl_2 75:25 to pentane:CH_2Cl_2 6:4, affording **4ka** as a dark green gooey compound in 70% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.88 (s, 1H), 9.88 (d, *J* = 1.4 Hz, 1H), 8.45 (d, *J* = 1.7 Hz, 1H), 8.42 (d, *J* = 7.9 Hz, 1H), 8.36 (d, *J* = 8.3 Hz, 1H), 8.26 (t, *J* = 1.7 Hz, 1H), 7.73 (td, *J* = 7.4, 0.9 Hz, 1H), 7.67 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.54 (ddd, *J* = 8.7, 7.2, 1.7 Hz, 1H), 7.12 (dd, *J* = 8.4, 1.0 Hz, 1H), 6.90 (ddd, *J* = 8.3, 7.2, 1.1 Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.86 (s, 9H), 1.41 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.8, 167.7, 163.3, 145.7, 142.5, 142.1, 140.2, 136.5, 136.4, 134.3, 133.1, 132.7, 129.8, 128.8, 125.2, 124.2, 123.6, 121.1, 121.0, 118.9, 118.8, 118.6, 61.9, 37.1, 32.7 (3C), 14.3.

HRMS (ESI-) calcd for $[C_{28}H_{25}O_4]^-$: 425.1758; found: 425.1758.



4la

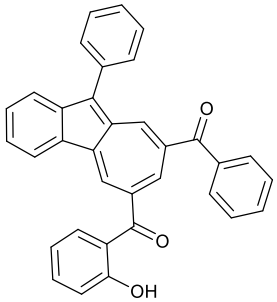
Ethyl 6-(2-hydroxybenzoyl)benzo[*a*]azulene-8-carboxylate 4la

Synthesized from **1l** and **2a** according to the general procedure in 2 d. The crude compound was purified by FC on silica gel using a gradient from pentane:CH_2Cl_2 6:4 to pure CH_2Cl_2, affording **4la** as a brown solid in 18% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.86 (s, 1H), 9.13 (d, *J* = 1.6 Hz, 1H), 8.57 (d, *J* = 1.4 Hz, 1H), 8.43 (d, *J* = 8.0 Hz, 1H), 8.36 (t, *J* = 1.6 Hz, 1H), 7.99 (d, *J* = 7.9 Hz, 1H), 7.82 (s, 1H), 7.80–7.74 (m, 1H), 7.69–7.60 (m, 2H), 7.55 (ddd, *J* = 8.6, 7.1, 1.7 Hz, 1H), 7.13 (dd, *J* = 8.4, 1.1 Hz, 1H), 6.91 (ddd, *J* = 8.2, 7.1, 1.2 Hz, 1H), 4.42 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.1, 167.2, 163.4, 142.8, 142.2, 139.0, 136.6, 136.5, 135.9, 134.2, 133.2, 132.9, 129.7, 127.3, 126.5, 124.9, 122.6, 121.8, 121.4, 118.9, 118.8, 118.7, 62.0, 14.4.

HRMS (ESI-) calcd for $[C_{24}H_{17}O_4]^-$: 369.1132; found: 369.1130.



4ab

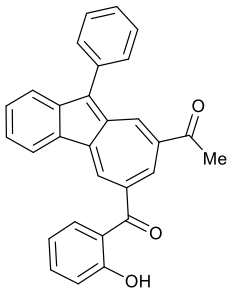
(8-Benzoyl-10-phenylbenzo[*a*]azulen-6-yl)(2-hydroxyphenyl)methanone 4ab

Synthesized from **1a** and **2b** according to the general procedure in 1 d. The crude compound was purified by FC on silica gel using a gradient from pentane:CH_2Cl_2 6:4 to pure CH_2Cl_2, affording **4ab** as a brown foam in 60% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.86 (s, 1H), 8.71 (d, *J* = 1.6 Hz, 1H), 8.58 (d, *J* = 1.5 Hz, 1H), 8.49 (d, *J* = 7.9 Hz, 1H), 8.12 (t, *J* = 1.5 Hz, 1H), 7.99 (d, *J* = 7.9 Hz, 1H), 7.80-7.67 (m, 5H), 7.59-7.52 (m, 4H), 7.47 (t, *J* = 7.5 Hz, 4H), 7.40 (tt, *J* = 7.4, 1.3 Hz, 1H), 7.12 (dd, *J* = 8.4, 0.7 Hz, 1H), 6.92 (td, *J* = 7.6, 1.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.8, 197.1, 163.4, 142.7, 141.6, 140.0, 138.7, 137.5, 137.3, 136.7, 133.8, 133.7, 133.5, 133.1, 132.3, 131.1, 130.8, 129.8 (2C), 129.7 (2C), 128.9 (2C), 128.4 (2C), 128.2, 127.1, 125.5, 121.3, 120.9, 119.0, 118.7 (2C), 99.9.

HRMS (ESI-) calcd for $[C_{34}H_{21}O_3]^-$: 477.1496; found: 477.1500.



4ac

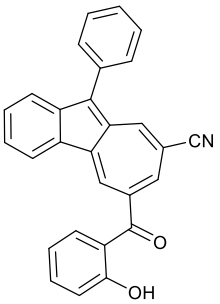
1-(6-(2-Hydroxybenzoyl)-10-phenylbenzo[*a*]azulen-8-yl)ethan-1-one 4ac

Synthesized from **1a** and **2c** according to the general procedure in 1 d. The crude compound was purified by FC on silica gel using a gradient from pentane:CH_2Cl_2 6:4 to 2:8, affording **4ac** as a dark green solid in 94% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.87 (s, 1H), 8.96 (d, *J* = 1.5 Hz, 1H), 8.52 (d, *J* = 1.5 Hz, 1H), 8.46 (d, *J* = 7.9 Hz, 1H), 8.26 (t, *J* = 1.5 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.77 (td, *J* = 7.5, 0.8 Hz, 1H), 7.70-7.63 (m, 6H), 7.55 (t, *J* = 7.4 Hz, 2H), 7.13 (dd, *J* = 8.4, 0.8 Hz, 1H), 6.91 (td, *J* = 7.6, 1.0 Hz, 1H), 2.55 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.0, 197.7, 163.4, 141.6, 140.9, 139.6, 139.0, 136.7, 135.8, 134.0, 133.6, 133.3, 133.1, 131.3, 130.2, 129.9 (2C), 129.8, 129.1 (2C), 128.5, 127.1, 125.6, 121.3, 121.0, 119.0, 118.8, 118.7, 26.5.

HRMS (ESI-) calcd for $[C_{29}H_{19}O_3]^-$: 415.1340; found: 415.1340.



4ad

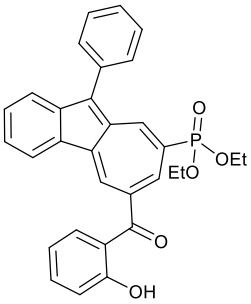
6-(2-Hydroxybenzoyl)-10-phenylbenzo[*a*]azulene-8-carbonitrile 4ad

Synthesized from **1a** and **2d** according to the general procedure in 1 d. The crude compound was purified by FC on silica gel using a gradient from pentane:CH_2Cl_2 6:4 to 2:8, affording **4ad** as a dark green solid in 72% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.67 (s, 1H), 8.48-8.45 (m, 3H), 8.00 (d, *J* = 7.9 Hz, 1H), 7.82 (td, *J* = 7.6, 0.5 Hz, 1H), 7.73 (td, *J* = 7.5, 0.7 Hz, 1H), 7.67-7.55 (m, 7H), 7.49 (t, *J* = 1.2 Hz, 1H), 7.15 (dd, *J* = 8.4, 0.5 Hz, 1H), 6.95 (td, *J* = 7.6, 0.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.4, 163.4, 144.2, 141.9, 140.3, 139.1, 137.1, 136.4, 134.8, 133.3, 133.2, 132.7, 131.2, 130.6, 129.9 (2C), 129.3 (2C), 128.8, 126.4, 126.1, 121.5, 121.4, 121.0, 119.2, 118.9, 118.3, 105.4.

HRMS (ESI-) calcd for $[C_{28}H_{16}NO_2]^-$: 398.1187; found: 398.1190.



4ae

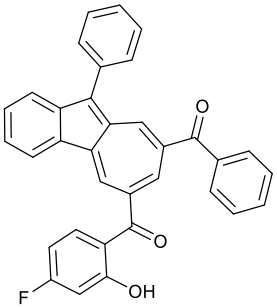
Diethyl (6-(2-hydroxybenzoyl)-10-phenylbenzo[*a*]azulen-8-yl)phosphonate 4ae

Synthesized from **1a** and **2e** according to the general procedure in 1 d. The crude compound was purified by FC on silica gel using a gradient from pentane:EtOAc 7:3 to 6:4, affording **4ae** as a green oil in 83% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.86 (s, 1H), 8.84 (dd, *J* = 21.5, 1.1 Hz, 1H), 8.53 (d, *J* = 1.5 Hz, 1H), 8.48 (d, *J* = 7.9 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.80-7.75 (m, 2H), 7.70-7.48 (m, 8H), 7.13 (dd, *J* = 8.4, 0.9 Hz, 1H), 6.91 (td, *J* = 7.6, 1.1 Hz, 1H), 4.20-4.06 (m, 4H), 1.30 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.6 (d, *J* = 0.6 Hz), 163.4, 143.9 (d, *J* = 10.9 Hz), 141.8 (d, *J* = 1.8 Hz), 140.2, 137.7 (2C), 137.6, 136.7, 134.0 (d, *J* = 18.0 Hz), 133.9, 133.1, 133.0, 131.7 (d, *J* = 22.3 Hz), 129.9 (2C), 129.8, 129.1 (2C), 128.3, 126.8 (d, *J* = 0.5 Hz), 125.3, 121.3, 121.3 (d, *J* = 186.0 Hz), 121.0, 118.8 (d, *J* = 13.5 Hz), 118.7, 62.4 (d, *J* = 5.6 Hz, 2C), 16.3 (d, *J* = 6.6 Hz, 2C).

HRMS (ESI-) calcd for $[C_{31}H_{26}O_5P]^-$: 509.1523; found: 509.1520.



4af

(8-Benzoyl-10-phenylbenzo[*a*]azulen-6-yl)(4-fluoro-2-hydroxyphenyl)methanone 4af

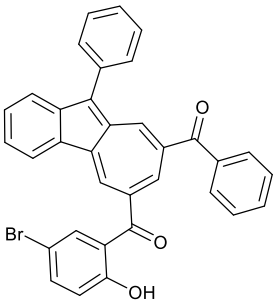
Synthesized from **1a** and **2f** according to the general procedure in 1 d. The crude compound was purified by FC on silica gel using a gradient from pentane:CH_2Cl_2 6:4 to pure CH_2Cl_2, affording **4af** as a brown solid in 72% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.25 (d, *J* = 1.5 Hz, 1H), 8.70 (d, *J* = 1.6 Hz, 1H), 8.54 (d, *J* = 1.6 Hz, 1H), 8.49 (dt, *J* = 8.0, 1.0 Hz, 1H), 8.07 (t, *J* = 1.6 Hz, 1H), 7.99 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.81–7.74 (m, 4H), 7.70 (ddd, *J* = 8.0, 7.1, 1.1 Hz, 1H), 7.57 (ddt, *J* = 8.7, 3.3, 1.7 Hz, 3H), 7.47 (tdd, *J* = 7.6, 3.3, 2.2 Hz, 4H), 7.42–7.37 (m, 1H), 6.80 (dd, *J* = 10.3, 2.5 Hz, 1H), 6.64 (ddd, *J* = 8.9, 8.0, 2.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.8, 197.1, 167.9 (d, *J* = 258.3 Hz), 166.0, 165.9, 142.9, 141.7, 140.2, 138.9, 137.3 (2C), 135.6 (d, *J* = 11.6 Hz), 133.7, 133.5 (2C), 132.4, 131.0, 130.6, 129.9, 129.8 (2C), 129.7 (2C), 128.9 (2C), 128.4 (2C), 128.3, 126.8, 125.6, 121.2 (d, *J* = 28.9 Hz), 115.8 (d, *J* = 2.2 Hz), 107.4 (d, *J* = 22.1 Hz), 105.4 (d, *J* = 24.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -98.4.

HRMS (ESI-) calcd for $[C_{34}H_{20}FO_4]^-$: 495.1402; found: 495.1399.



4ag

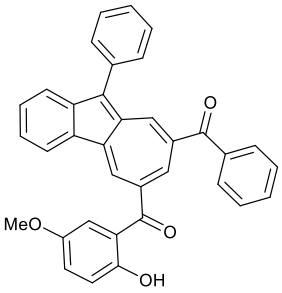
(8-Benzoyl-10-phenylbenzo[*a*]azulen-6-yl)(5-bromo-2-hydroxyphenyl) methanone 4ag

Synthesized from **1a** and **2g** according to the general procedure in 1 d. The crude compound was purified by FC on silica gel using a gradient from pentane:CH_2Cl_2 6:4 to pure CH_2Cl_2, affording **4ag** as a brown solid in 58% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.70 (s, 1H), 8.75 (d, *J* = 1.6 Hz, 1H), 8.53 (d, *J* = 1.6 Hz, 1H), 8.50 (dt, *J* = 7.9, 1.0 Hz, 1H), 8.06 (t, *J* = 1.6 Hz, 1H), 8.00 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.83 (d, *J* = 2.5 Hz, 1H), 7.82–7.77 (m, 3H), 7.71 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 7.64–7.54 (m, 4H), 7.52–7.46 (m, 4H), 7.43–7.38 (m, 1H), 7.02 (d, *J* = 8.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.9, 196.9, 162.2, 143.2, 141.7, 140.2, 139.3, 139.2, 137.6, 137.2, 134.9, 133.7, 133.6, 133.0, 132.4, 131.2, 130.6, 130.0, 129.8 (2C), 129.7 (2C), 128.9 (2C), 128.5 (2C), 128.3, 126.5, 125.7, 121.3, 121.1, 120.7, 120.2, 110.6.

HRMS (ESI-) calcd for $[C_{34}H_{20}BrO_3]^-$: 555.0601 (^{79}Br), 557.0581 (^{81}Br); found: 555.0593 (^{79}Br), 557.0579 (^{81}Br).



4ah

(8-Benzoyl-10-phenylbenzo[*a*]azulen-6-yl)(2-hydroxy-5-methoxyphenyl) methanone 4ah

Synthesized from **1a** and **2h** according to the general procedure in 1 d. The crude compound was purified by FC on silica gel using a gradient from pentane:CH_2Cl_2 6:4 to pure CH_2Cl_2 to CH_2Cl_2:Et_2O 98:2, affording **4ah** as a brown solid in 19% yield.

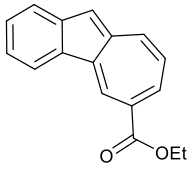
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.39 (s, 1H), 8.62 (d, *J* = 1.6 Hz, 1H), 8.53 (d, *J* = 1.6 Hz, 1H), 8.43 (td, *J* = 7.8, 1.0 Hz, 1H), 8.11 (t, *J* = 1.6 Hz, 1H), 7.92 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.73–7.69 (m, 3H), 7.63 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 7.52–7.47 (m, 3H), 7.42–7.37 (m, 4H), 7.35–7.31 (m, 1H), 7.14–7.09 (m, 2H), 6.99 (dd, *J* = 8.6, 0.8 Hz, 1H), 3.66 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.3, 197.1, 157.8, 151.7, 142.7, 141.7, 140.0, 138.7, 137.7, 137.2, 133.8, 133.6 (2C), 132.4, 131.1, 130.8, 129.8 (5C), 128.9 (2C), 128.4 (2C), 128.2, 127.1, 125.5, 124.9, 121.3, 121.0, 119.6, 118.1, 115.3, 56.0.

HRMS (ESI-) calcd for $[C_{35}H_{23}O_4]^-$: 507.1602; found: 507.1601.

General procedure for the organocatalyzed [10+4] cycloaddition reaction between indene-2-carbaldehydes **1** and α-pyrone **5a**

In a 4 mL vial containing a magnetic stirring bar, **5a** (25.2 mg, 0.15 mmol, 1.5 equiv.), catalyst **3b** (5.6 mg, 0.015 mmol, 15 mol%) and NaOAc (1.2 mg, 0.015 mmol, 15 mol%) were dissolved in $CDCl_3$ (0.4 mL). Indene-2-carbaldehyde (**1l**-**1q**) (0.1 mmol, 1 equiv.) was added. Generation of an intensely dark green product was visible within short time. The reaction mixture was stirred for 6-7 d at rt. The [10+4] cycloadducts were purified directly *via* FC on silica gel.



6la

Ethyl benzo[*a*]azulene-6-carboxylate 6la

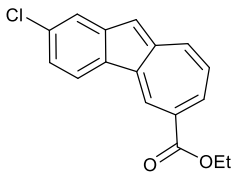
Synthesized from **1l** and **5a.** The crude compound was purified by FC on silica gel using a gradient from pentane:CH_2Cl_2 8:2 to pentane:CH_2Cl_2 7:3, affording **6la** as a dark green solid in 64% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (d, *J* = 1.4 Hz, 1H), 8.52 (d, *J* = 8.0 Hz, 1H), 8.28 (dt, *J* = 9.3, 1.2 Hz, 1H), 8.13 (d, *J* = 10.6 Hz, 1H), 7.91 (d, *J* = 7.9 Hz, 1H), 7.75–7.66 (m, 1H), 7.60–7.54 (m, 1H), 7.48 (s, 1H), 6.91 (dd, *J* = 10.7, 9.3 Hz, 1H), 4.46 (q, *J* = 7.1 Hz, 2H), 1.47 (t, *J* = 7.1 Hz, 3H).

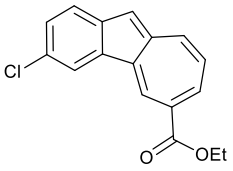
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 142.3, 140.5, 138.5 (2C), 138.2, 133.1, 128.9, 126.8, 125.8, 123.1, 121.8, 121.2, 120.8, 119.7, 61.7, 14.4.

UV/Vis λ_{max} (CH_2Cl_2)/nm 231 (14800), 304 (31700), 317 (36200), 329 (33900), 379 (3200), 400 (4500), 424 (3700).

HRMS (ESI+) calcd for $[C_{17}H_{14}O_2+Na]^+$: 273.0886; found: 273.0885.



6ma



6na

Ethyl 2-chlorobenzo[*a*]azulene-6-carboxylate 6ma and ethyl 3-chlorobenzo[*a*]azulene-6-carboxylate 6na

Synthesized from **5a** and either **1m** or **1n**. Both setups yielded an inseparable 1:1.9 regioisomeric mixture of **6ma**:**6na**. The crude mixture was purified by FC on silica gel using a gradient from pentane:CH_2Cl_2 of 8:2 to 2:8. When **1m** was used as a starting material, the reaction was carried out according to the general procedure over 6 d, yielding 25% of the mixture. When **1n** was used as a starting material, the reaction was carried out according to the general procedure over 6 d, yielding 25% of the mixture.

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

Major (**6na**): δ 8.99 (t, *J* = 1.3 Hz, 1H), 8.44 (d, *J* = 1.8 Hz, 1H), 8.35–8.26 (m, 1H), 8.17–8.08 (m, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.65 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.42 (s, 1H), 7.01–6.88 (m, 1H), 4.46 (q, *J* = 7.1 Hz, 2H), 1.47 (t, *J* = 7.1 Hz, 3H).

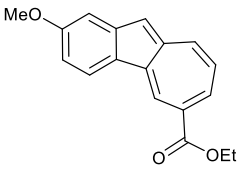
Minor (**6ma**): δ 9.03 (t, *J* = 1.3 Hz, 1H), 8.41 (d, *J* = 8.5 Hz, 1H), 8.35–8.26 (m, 1H), 8.17–8.08 (m, 1H), 7.87 (d, *J* = 1.8 Hz, 1H), 7.50 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.39 (s, 1H), 7.01–6.88 (m, 1H), 4.46 (q, *J* = 7.1 Hz, 2H), 1.47 (t, *J* = 7.1, 3H).

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

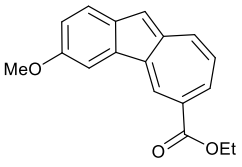
Major (**6na**): δ 167.5, 140.9, 140.4, 139.4, 138.6, 137.5, 134.0, 129.3, 127.9, 126.0, 123.5, 122.2, 121.8, 121.0, 119.0, 61.9, 14.4.

Minor (**6ma**): δ 167.6, 143.2, 140.3, 139.3, 138.7, 137.8, 135.0, 131.1, 129.0, 127.5, 126.3, 122.6, 122.3, 120.4, 118.5, 61.9, 14.4.

HRMS (ESI+) calcd for $[C_{17}H_{13}ClO_2+H]^+$: 285.0677 (^{35}Cl), 287.0647 (^{37}Cl); found: 285.0684 (^{35}Cl), 287.0640 (^{37}Cl) (from setup with **1m**) and 285.0681 (^{35}Cl), 287.0655 (^{37}Cl) (from setup with **1n**).



6oa



6pa

Ethyl 2-methoxybenzo[*a*]azulene-6-carboxylate 6oa and ethyl 3-methoxybenzo[*a*]azulene-6-carboxylate 6pa

Synthesized from **5a** and either **1o** or **1p**. Setup yielded an inseparable 1:7.6 regioisomeric mixture of **6oa**:**6pa**. The crude mixture was purified by FC on silica gel using a gradient from pentane:CH_2Cl_2 8:2 to 2:8. When **1o** was used as a starting material, the reaction was carried out according to the general procedure over 7 d, yielding 29% of the mixture. When **1p** was used as a starting material, the reaction was carried out according to the general procedure over 7 d, yielding 34% of the mixture.

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

Major (**6pa**): δ 9.03-8.98 (m, 1H), 8.31-8.22 (m, 1H), 8.08 (d, *J* = 10.6 Hz, 1H), 7.92 (d, *J* = 2.2 Hz, 1H), 7.83 (d, *J* = 8.6 Hz, 1H), 7.43 (s, 1H), 7.37 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.84–6.75 (m, 1H), 4.45 (q, *J* = 7.1 Hz, 2H), 4.02 (s, 3H), 1.46 (t, *J* = 7.1 Hz, 3H).

Minor (**6oa**): δ 9.03-8.98 (m, 1H), 8.42 (d, *J* = 8.7 Hz, 1H), 8.31-8.22 (m, 1H), 8.14 (d, *J* = 10.6 Hz, 1H), 7.43 (s, 1H), 7.31 (d, *J* = 2.3 Hz, 1H), 7.17 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.01-6.93 (m, 1H), 4.45 (q, *J* = 7.1 Hz, 2H), 3.98 (s, 3H), 1.46 (t, *J* = 7.1, 3H).

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

Major (**6pa**): δ 168.0, 156.8, 141.0, 139.0, 137.6, 137.4, 136.8, 134.3, 127.3, 124.6, 121.8, 120.4, 119.6, 119.3, 102.9, 61.7, 55.8, 14.4.

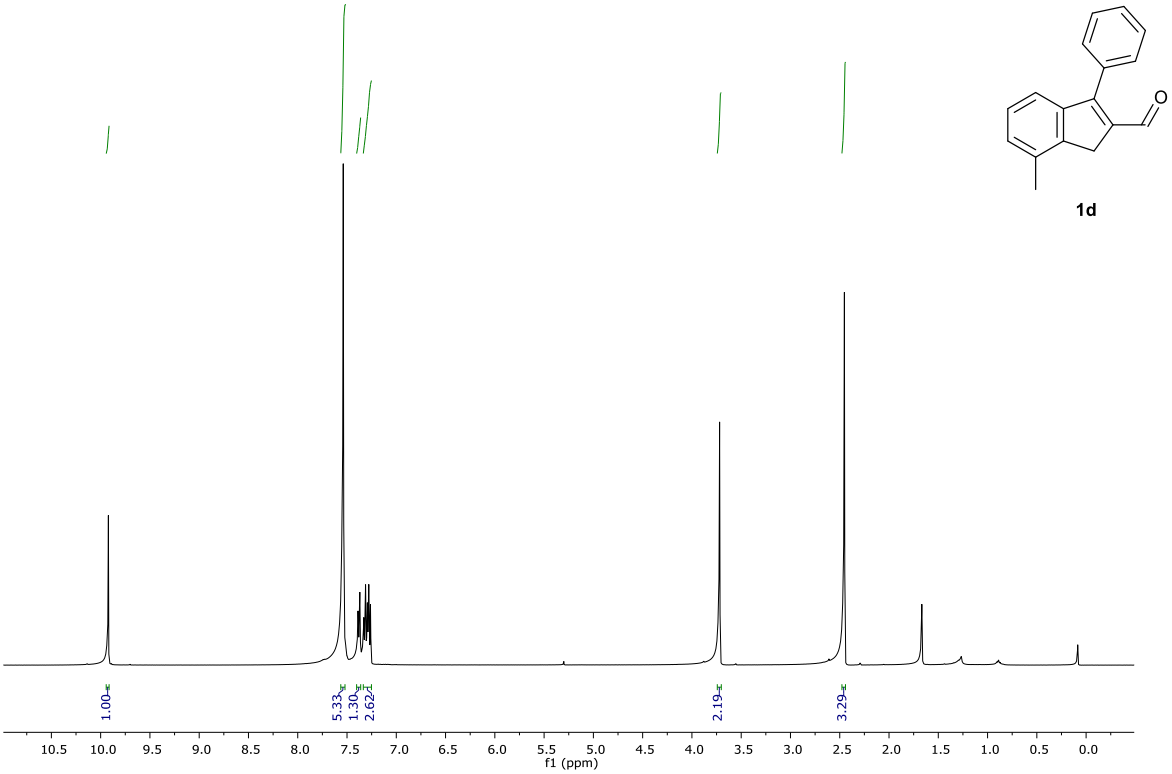
Minor (**6oa**): δ 163.3, 161.2, 144.3, 139.1, 139.1, 137.7, 137.0, 127.1, 125.8, 125.5, 122.6, 121.9, 118.7, 113.6, 102.0. 61.7, 55.5, 14.4.

HRMS (ESI+) calcd for $[C_{18}H_{16}O_3+H]^+$: 281.1172; found: 281.1163 (from setup with **1o**) and 281.1174 (from setup with **1p**).

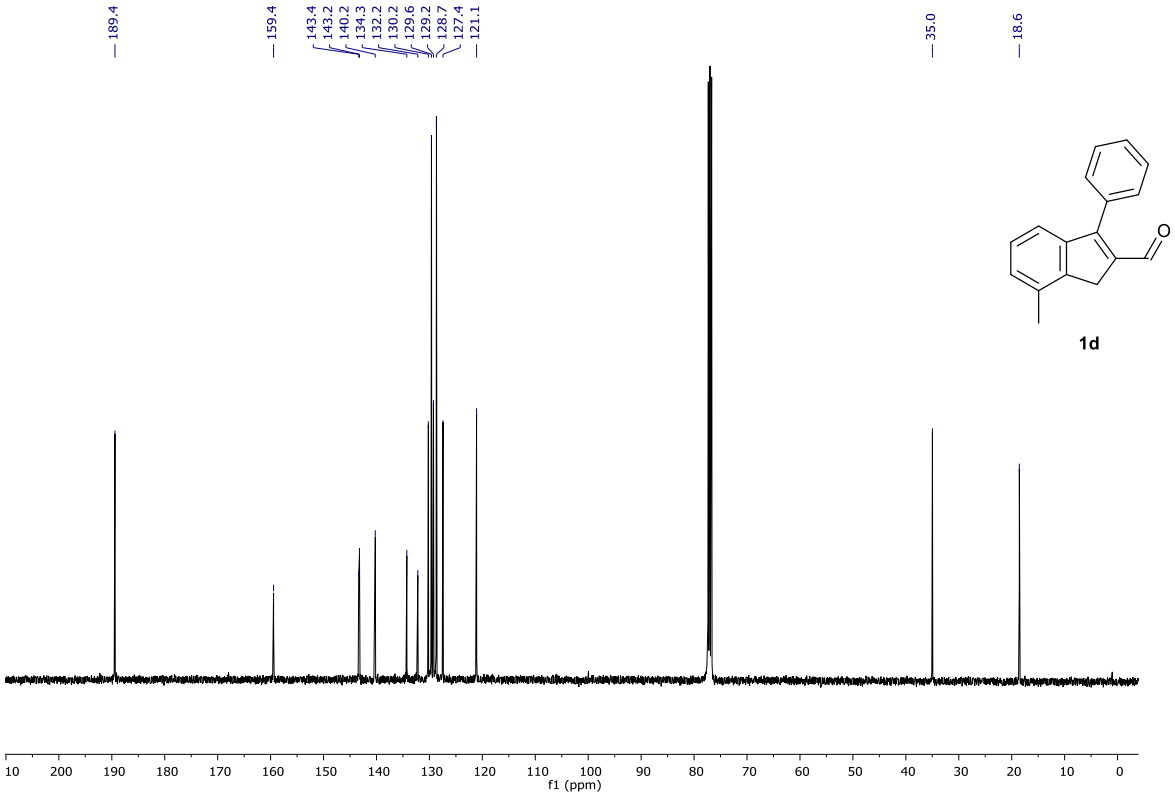
NMR spectra

1d

^{1}H NMR

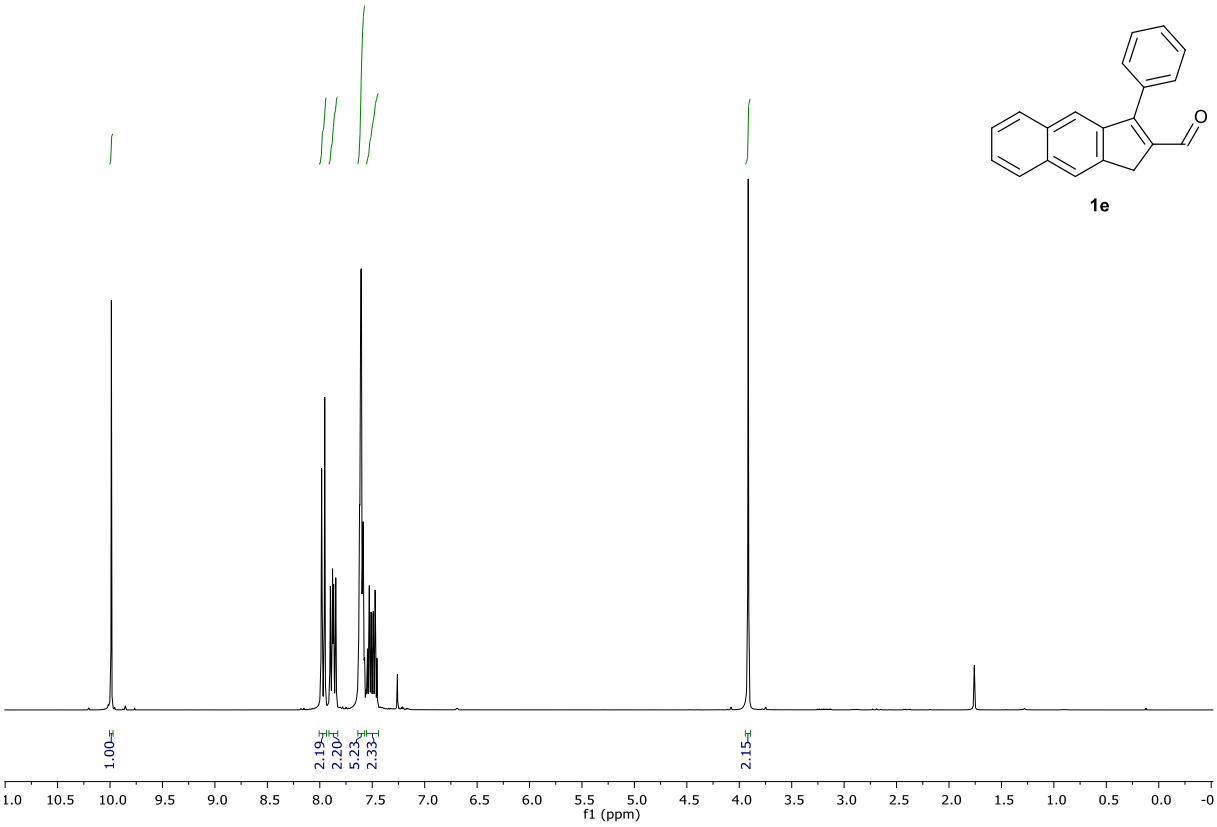


^{13}C NMR

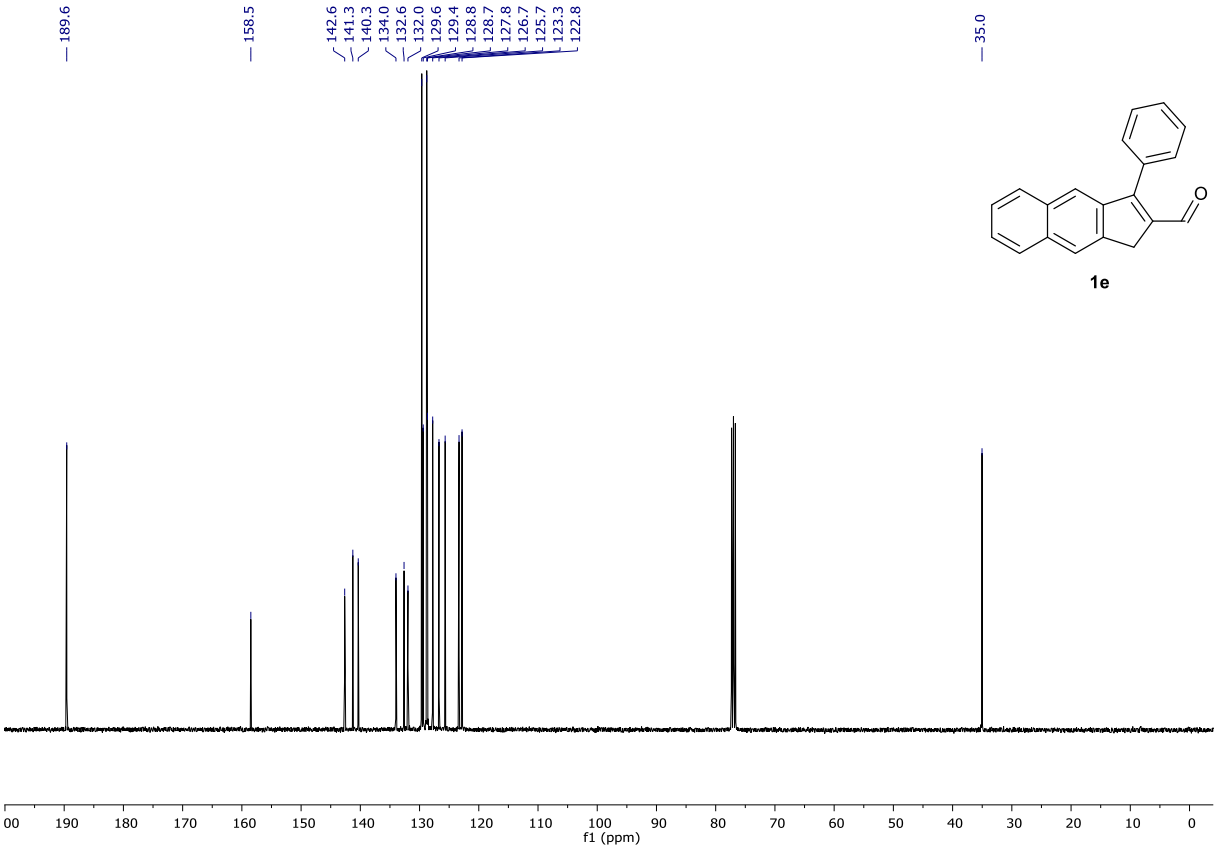


1e

^{1}H NMR

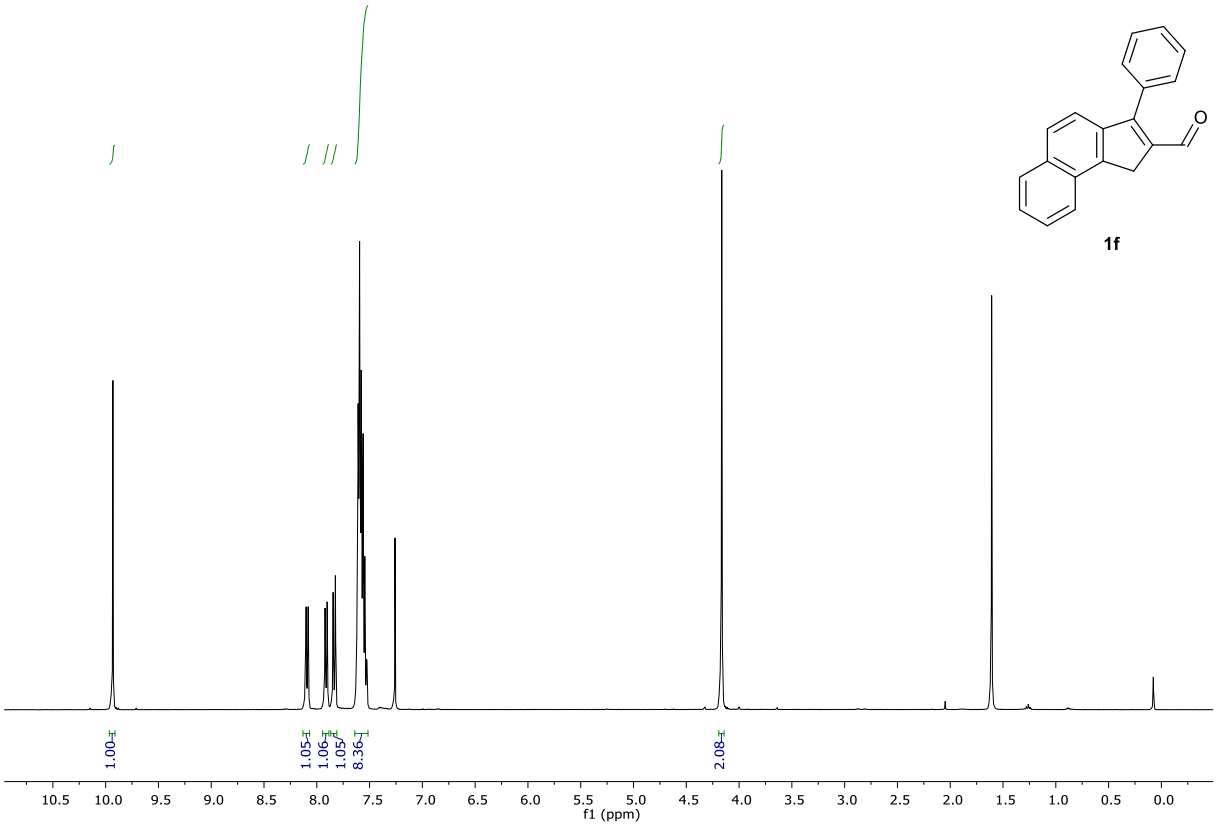


^{13}C NMR

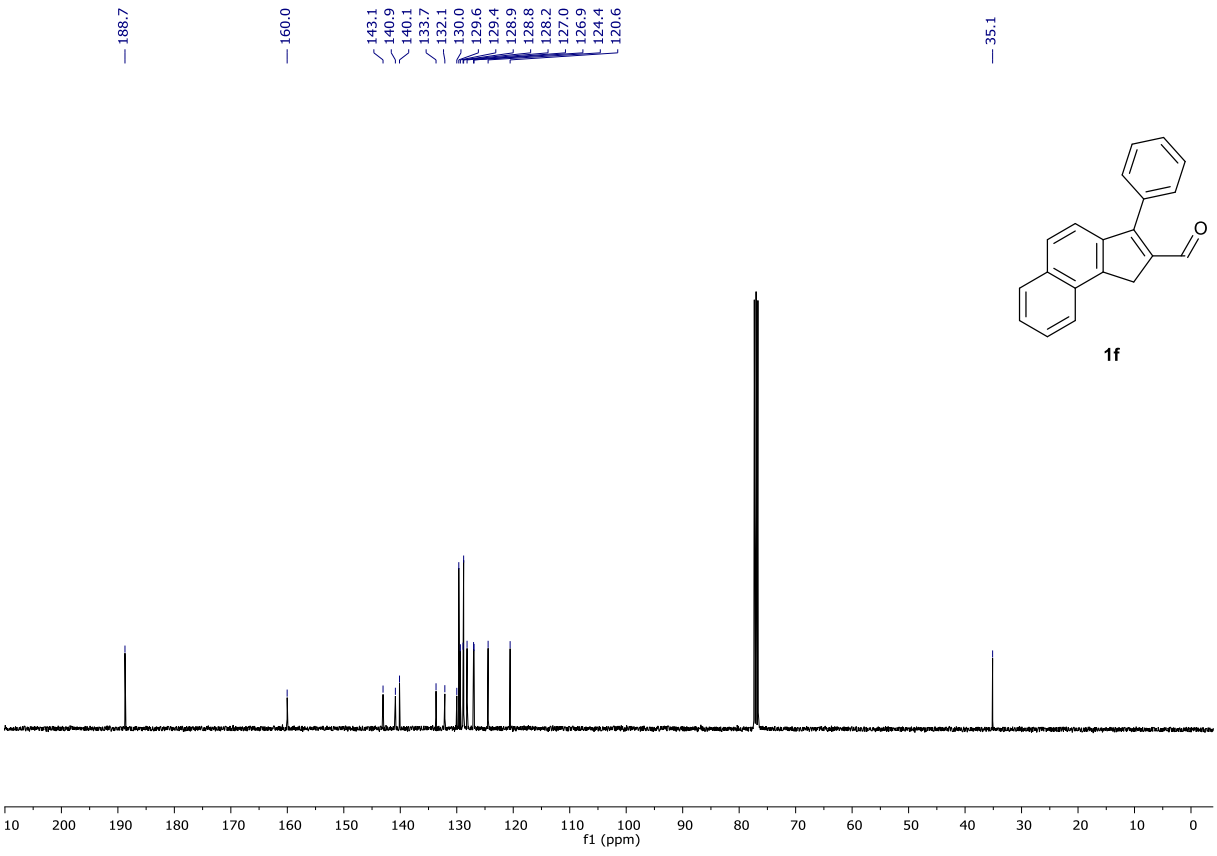


1f

^{1}H NMR

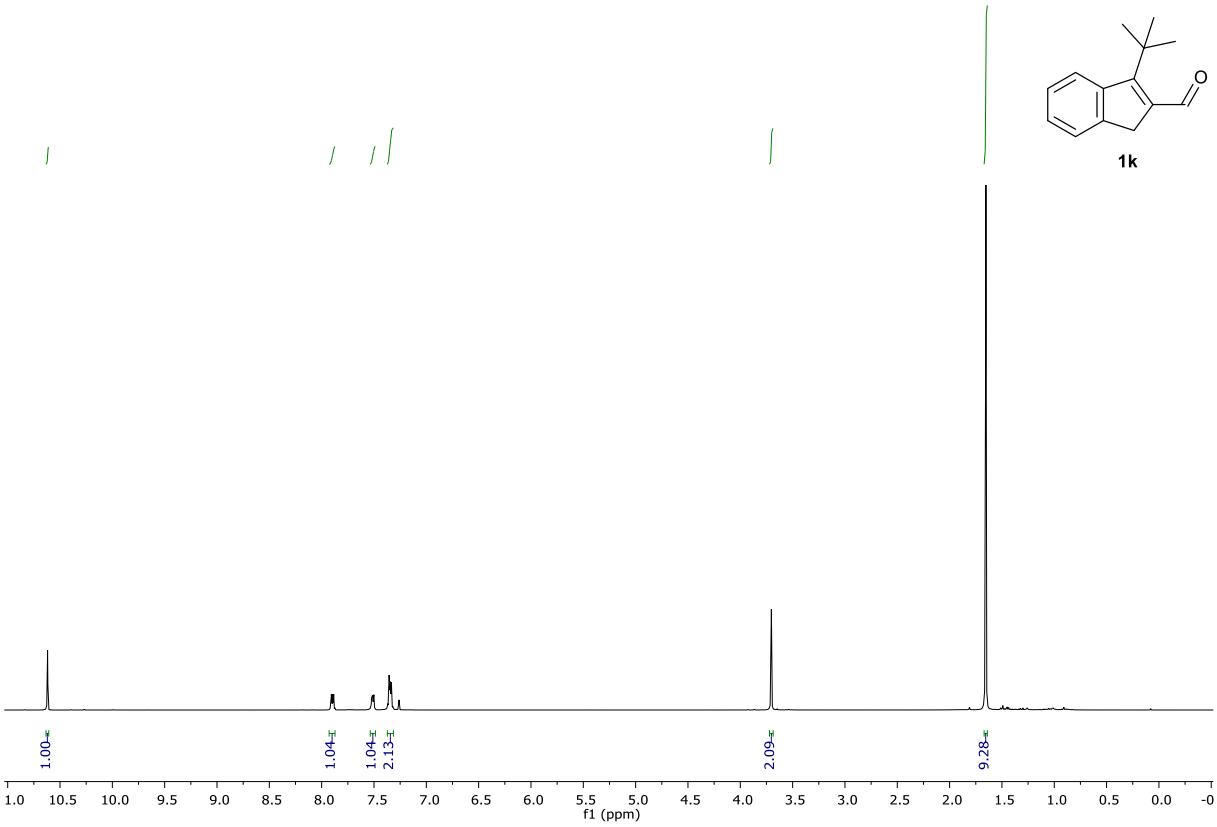


^{13}C NMR

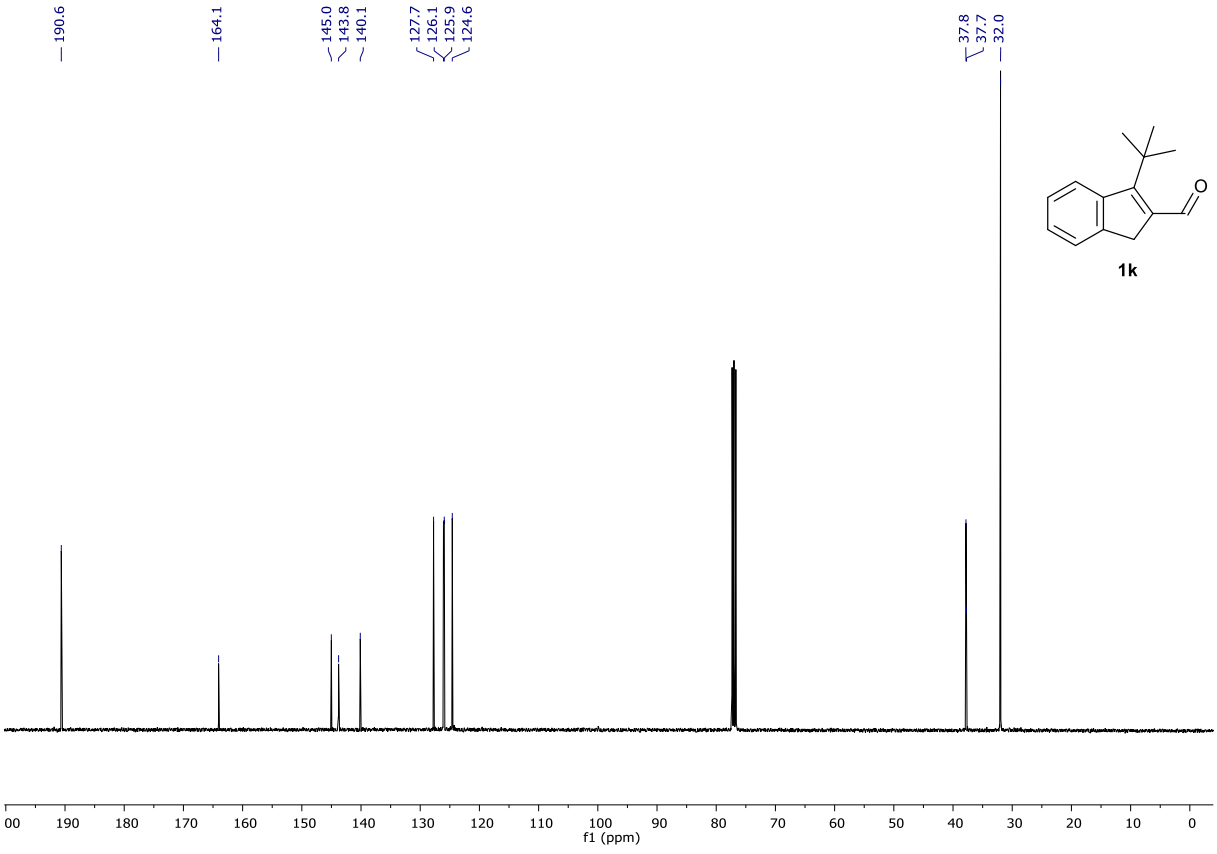


1k

^{1}H NMR

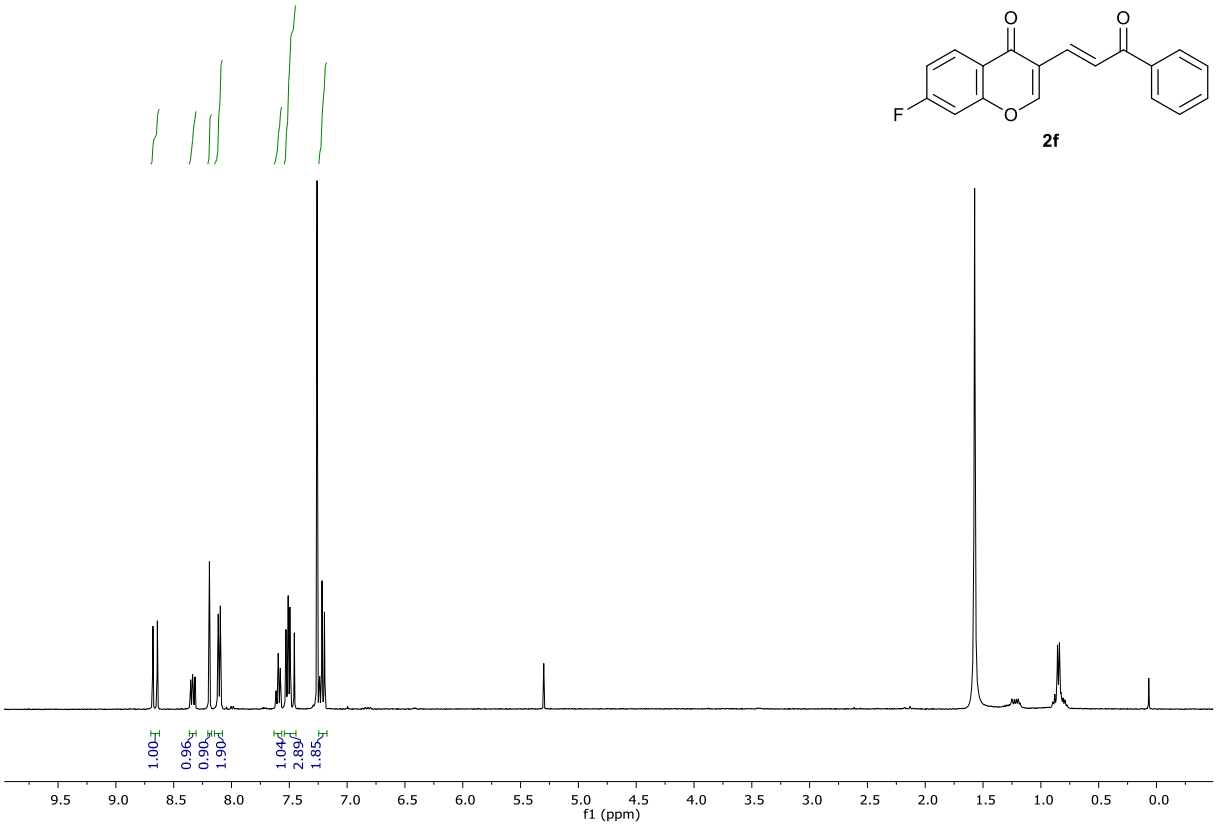


^{13}C NMR

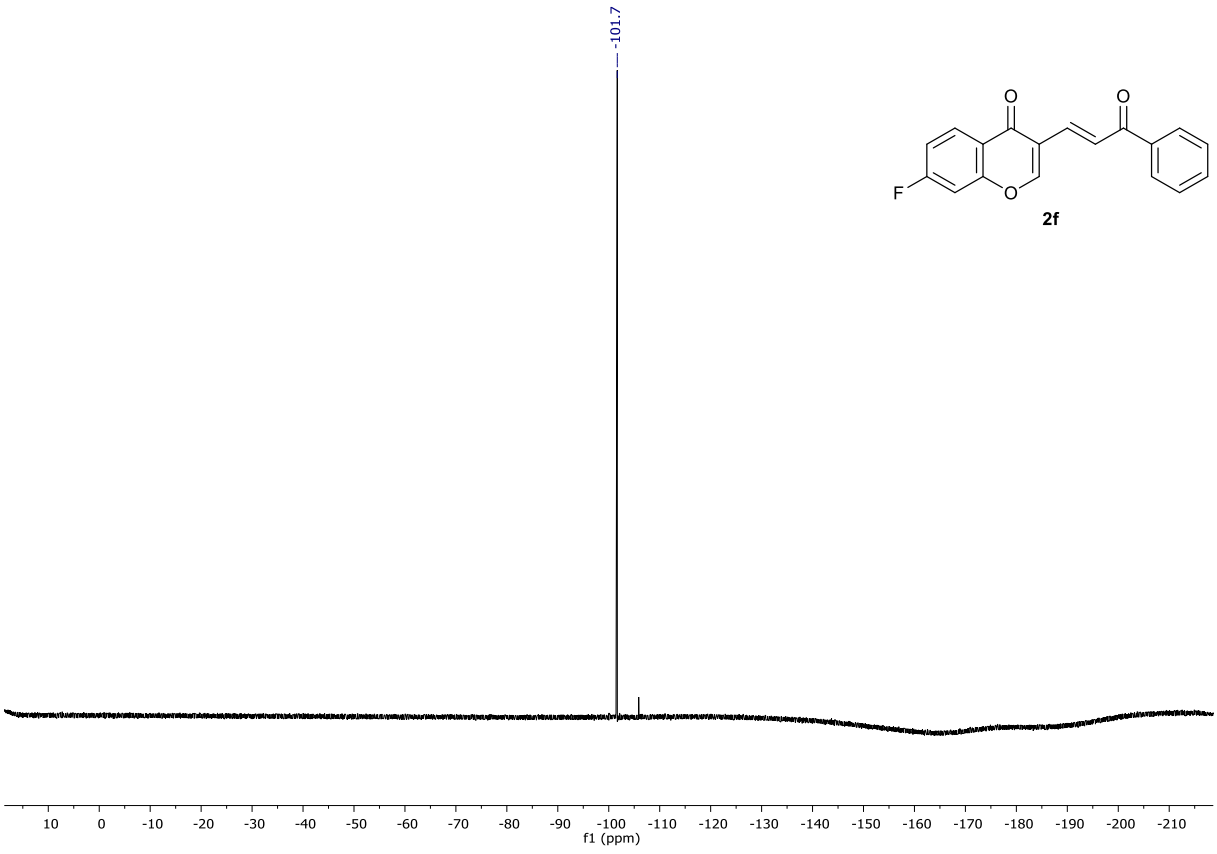


2f

^{1}H NMR

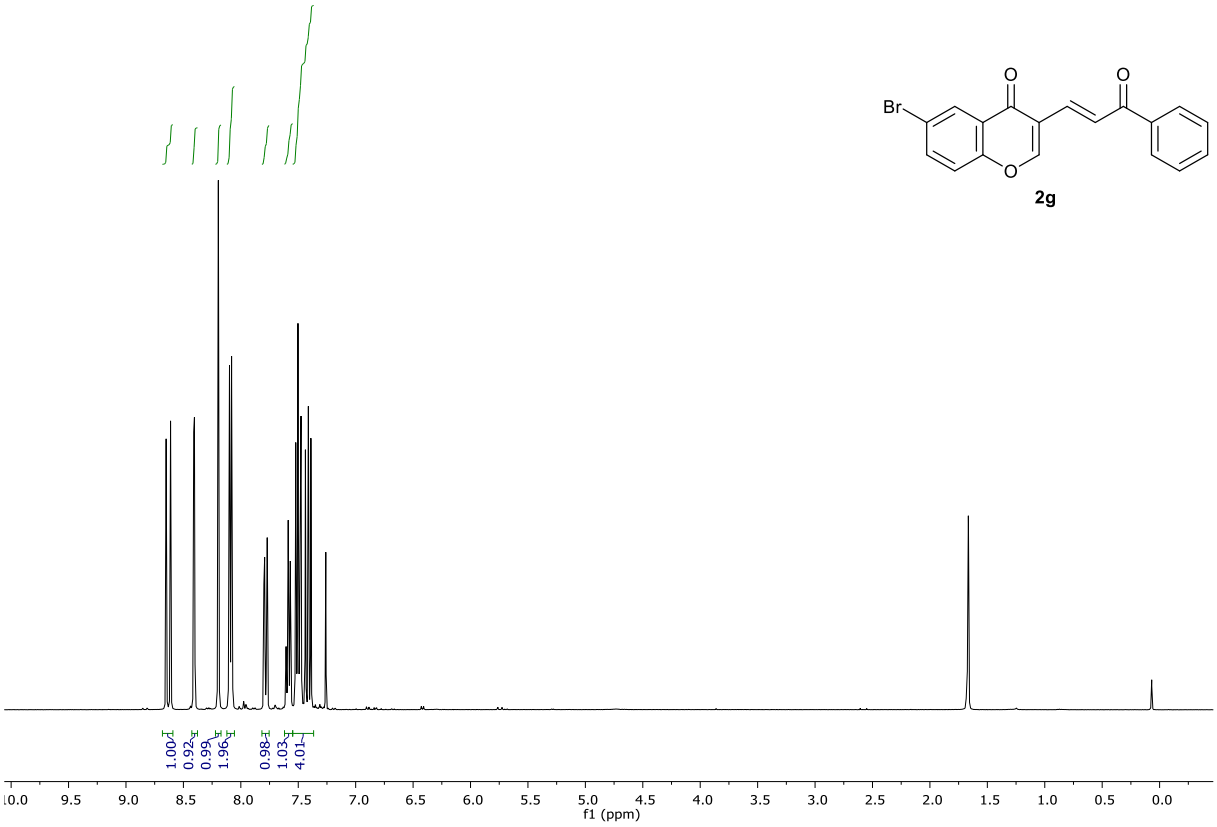


^{19}F NMR

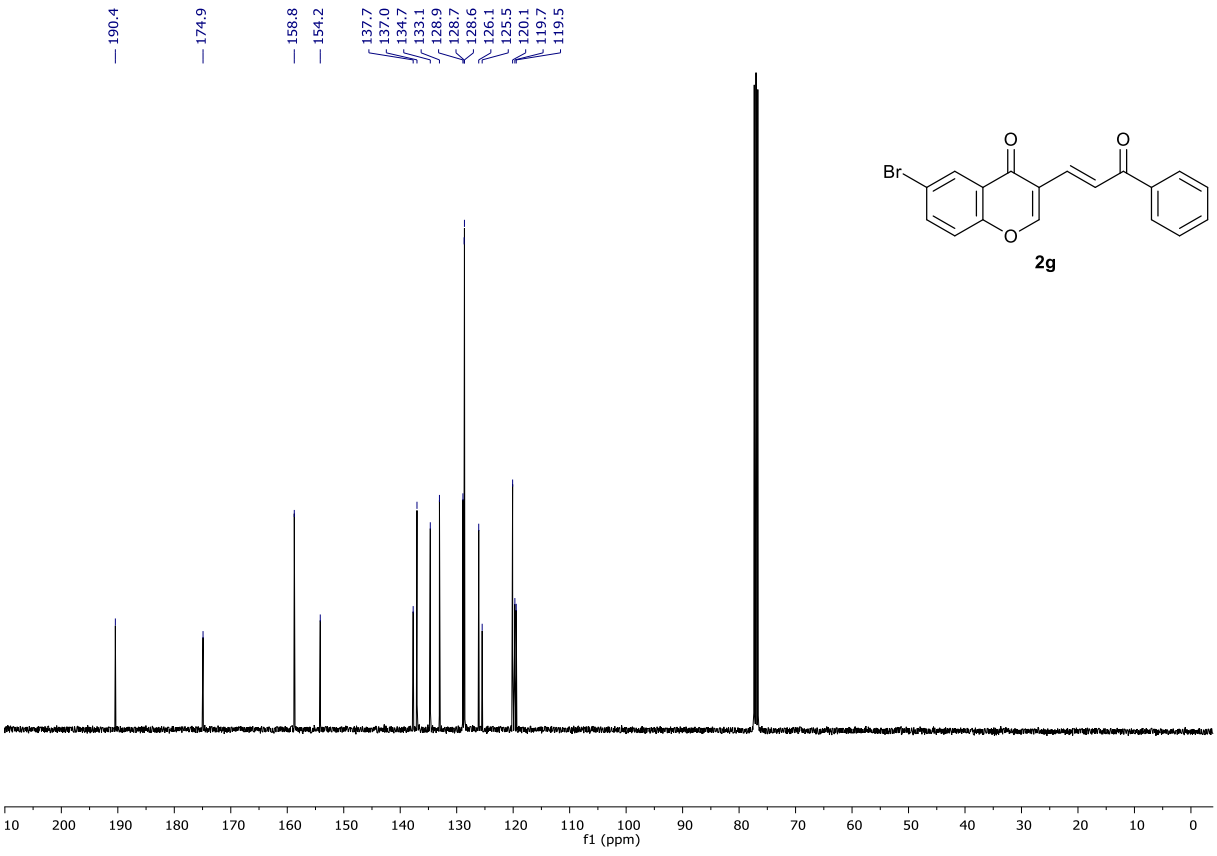


2g

^{1}H NMR

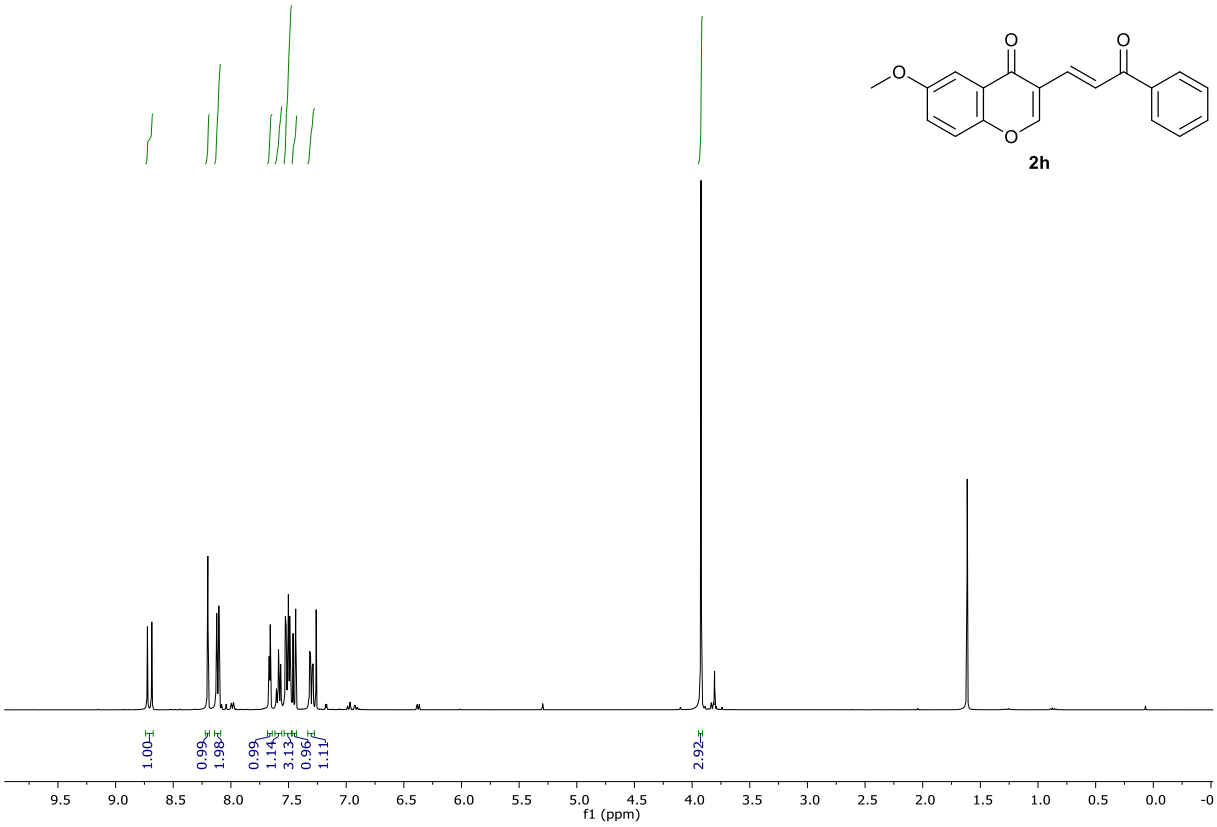


^{13}C NMR

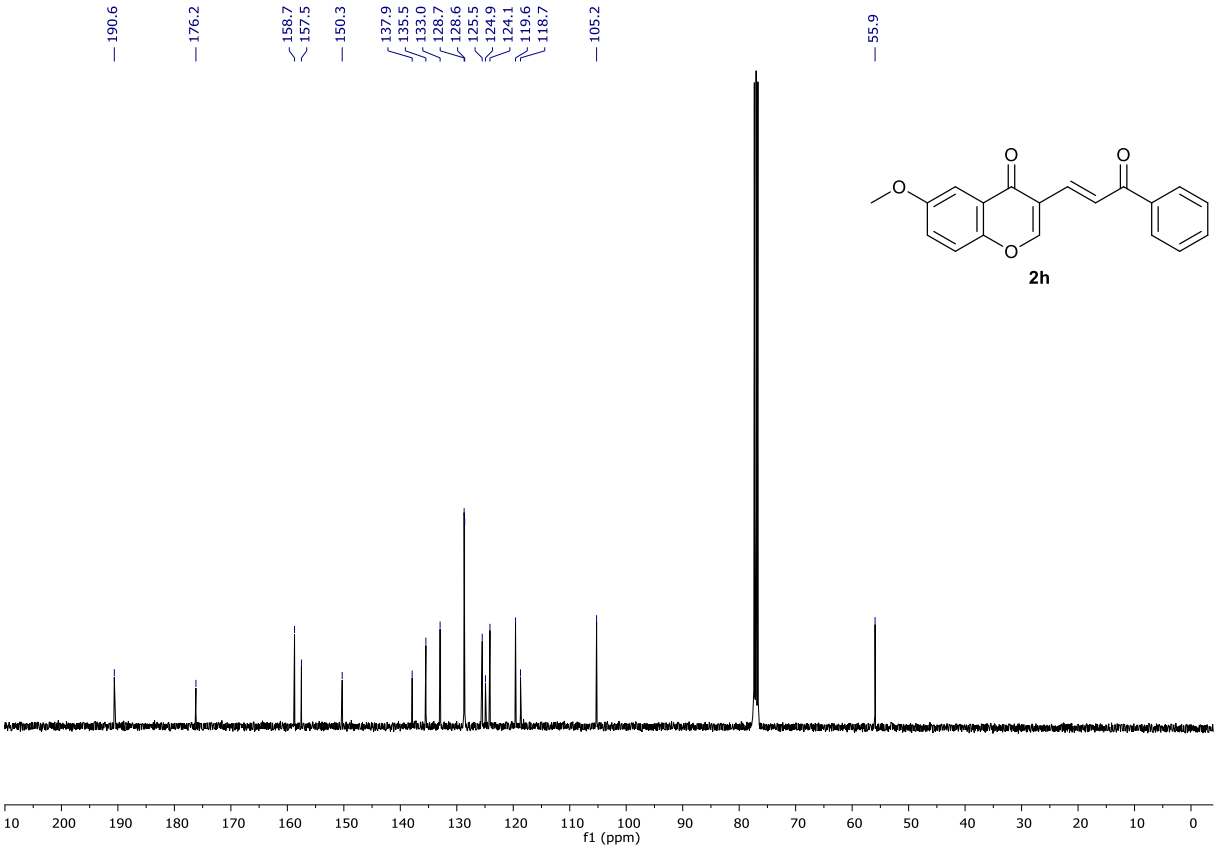


2h

^{1}H NMR

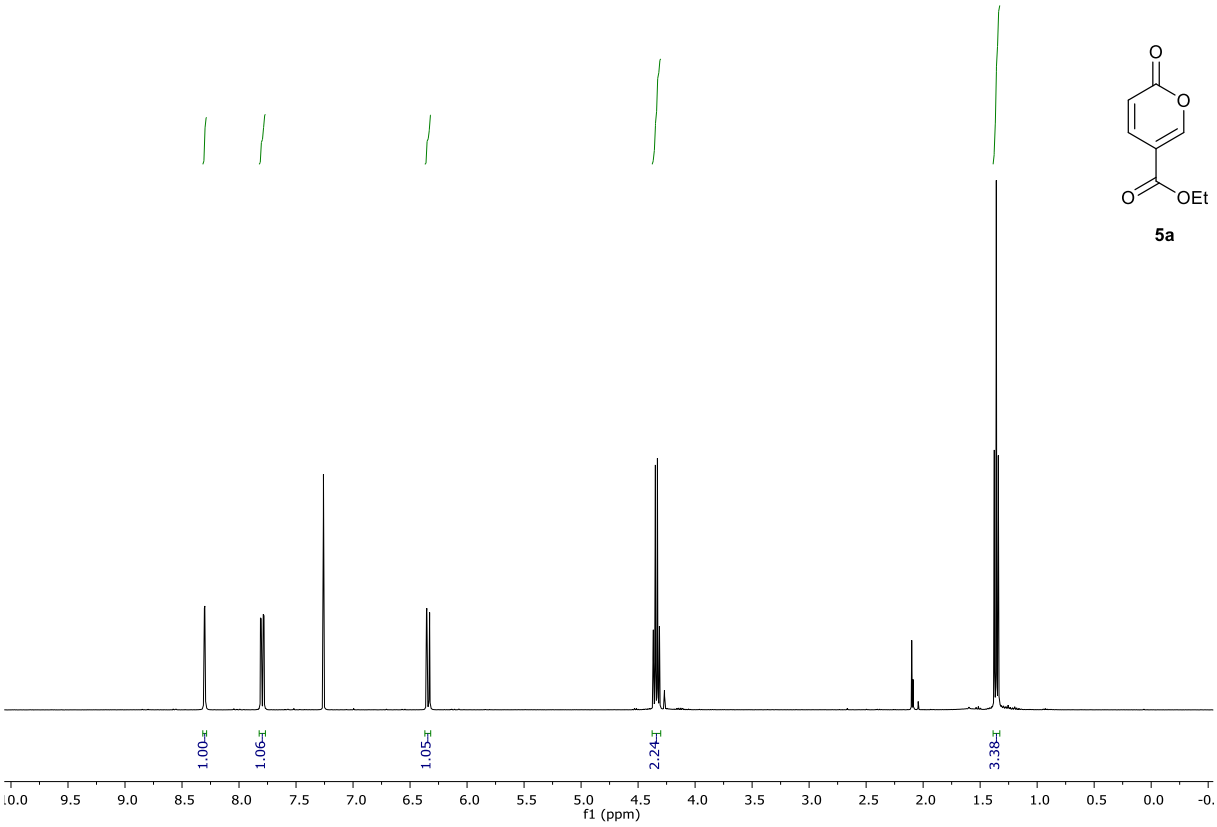


^{13}C NMR

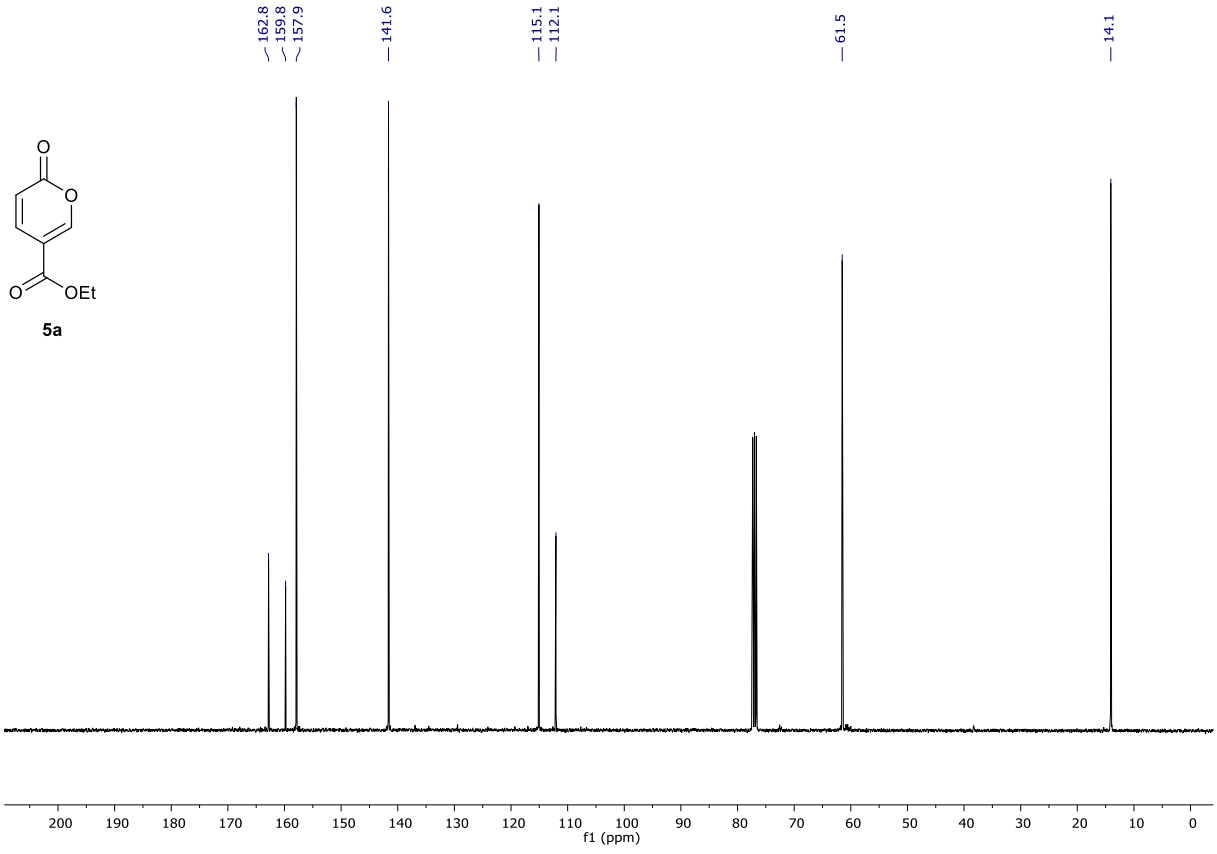


5a

^{1}H NMR

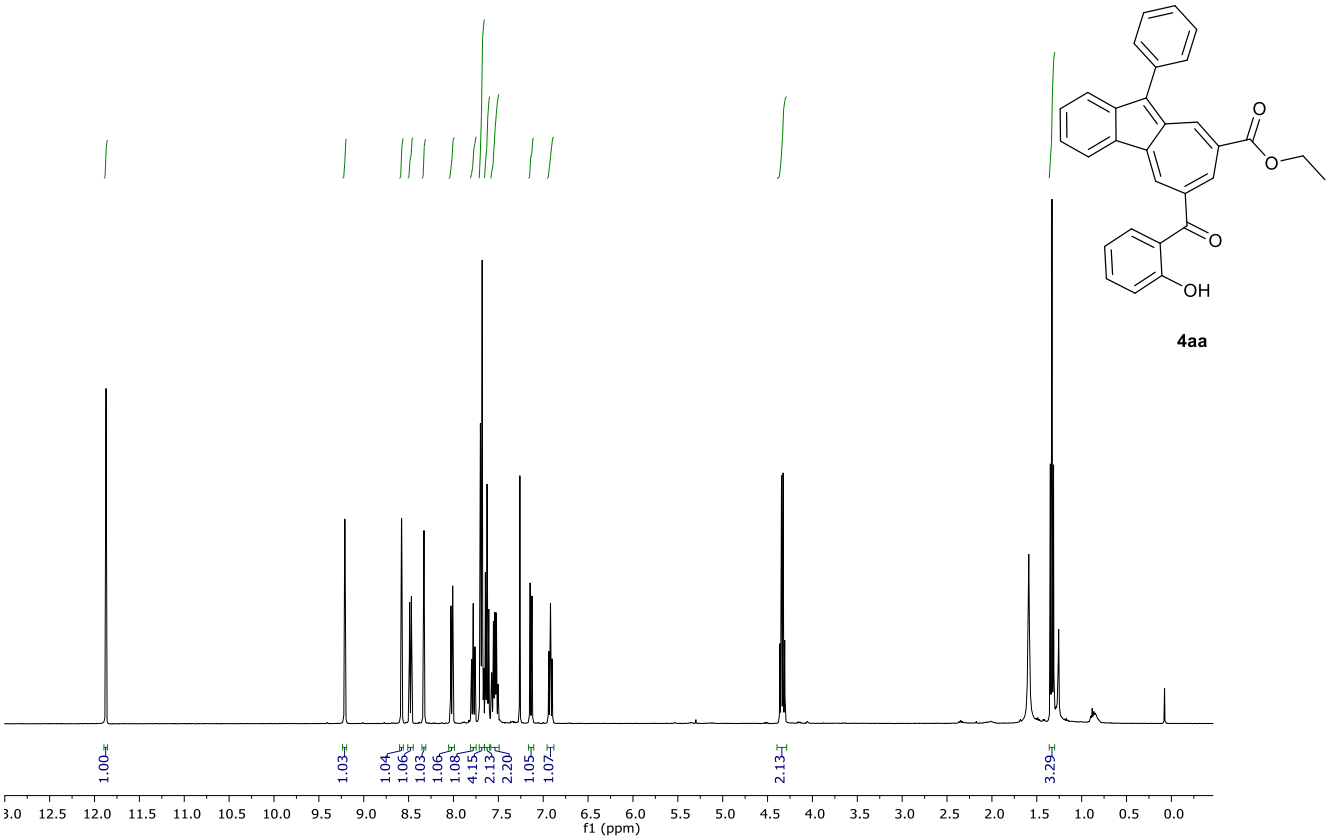


^{13}C NMR

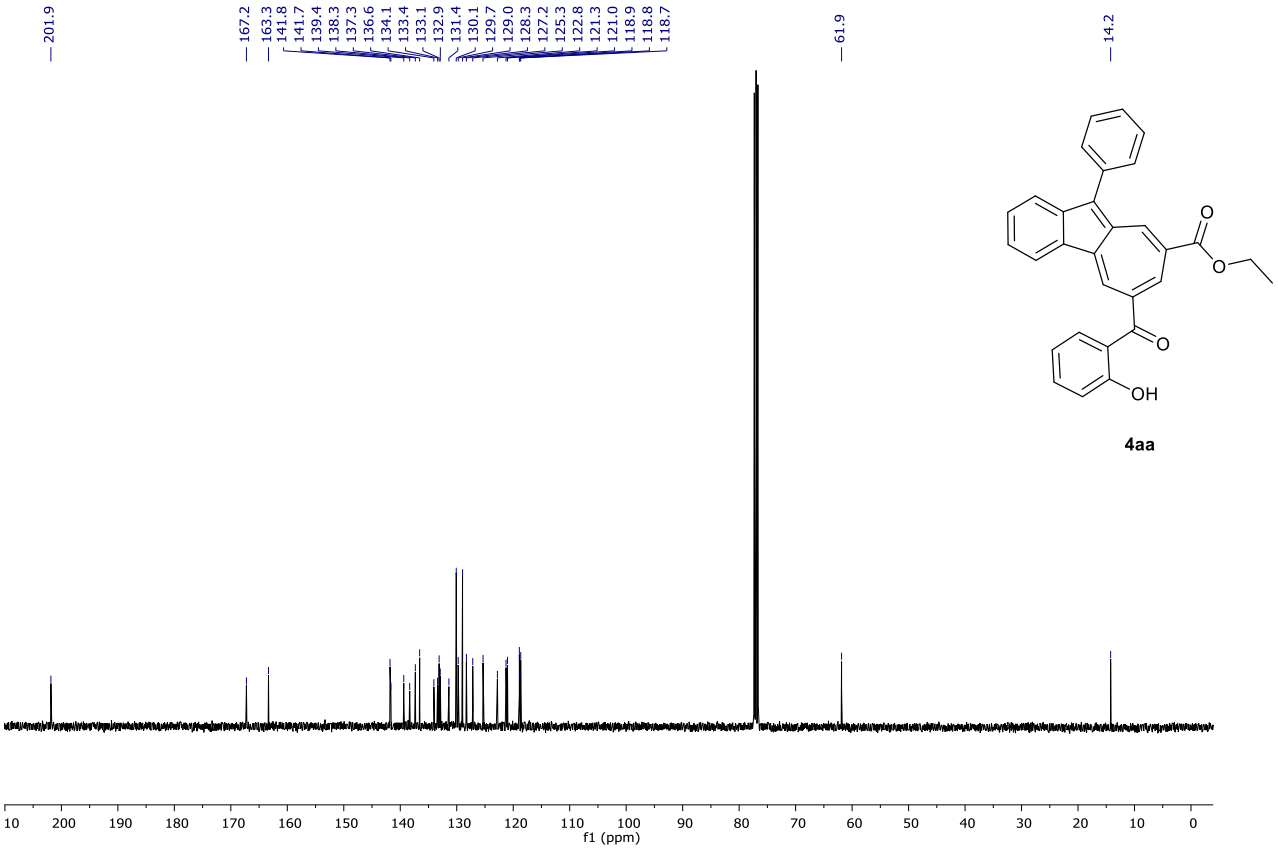


4aa

^{1}H NMR

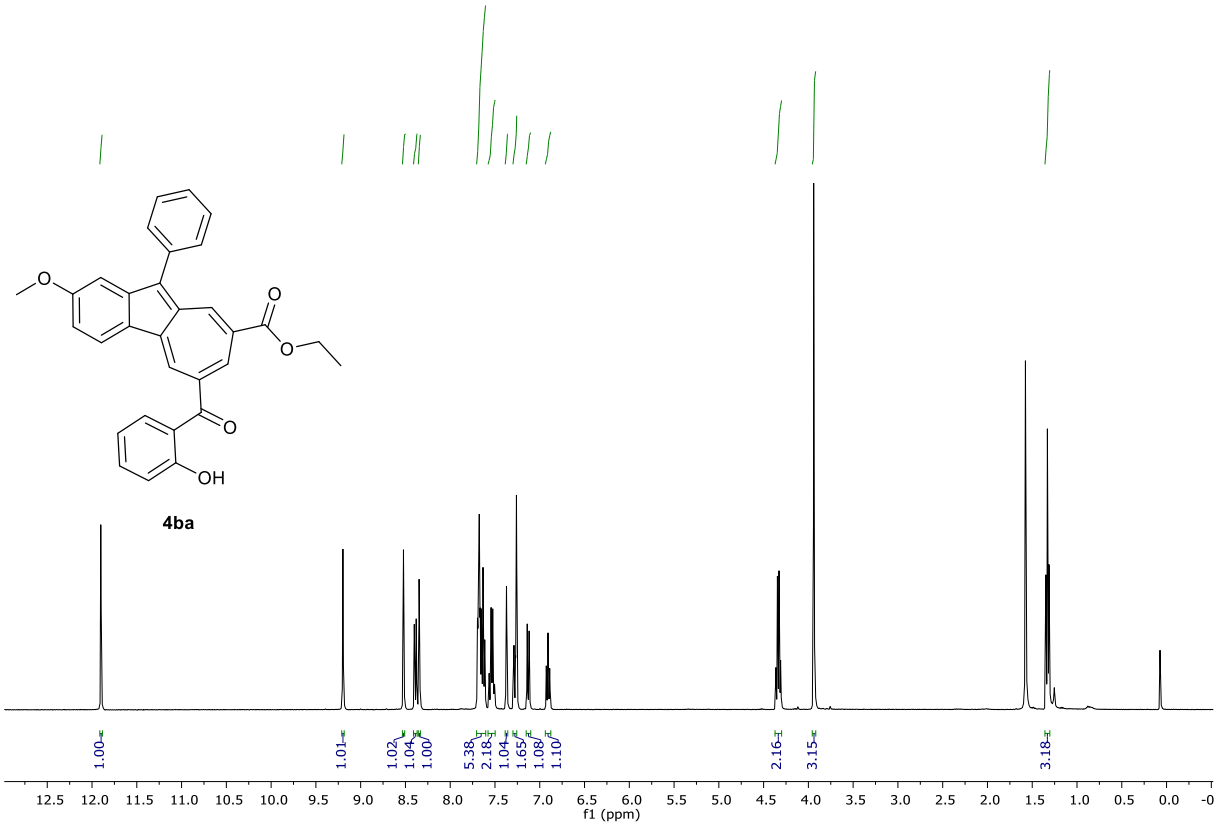


^{13}C NMR

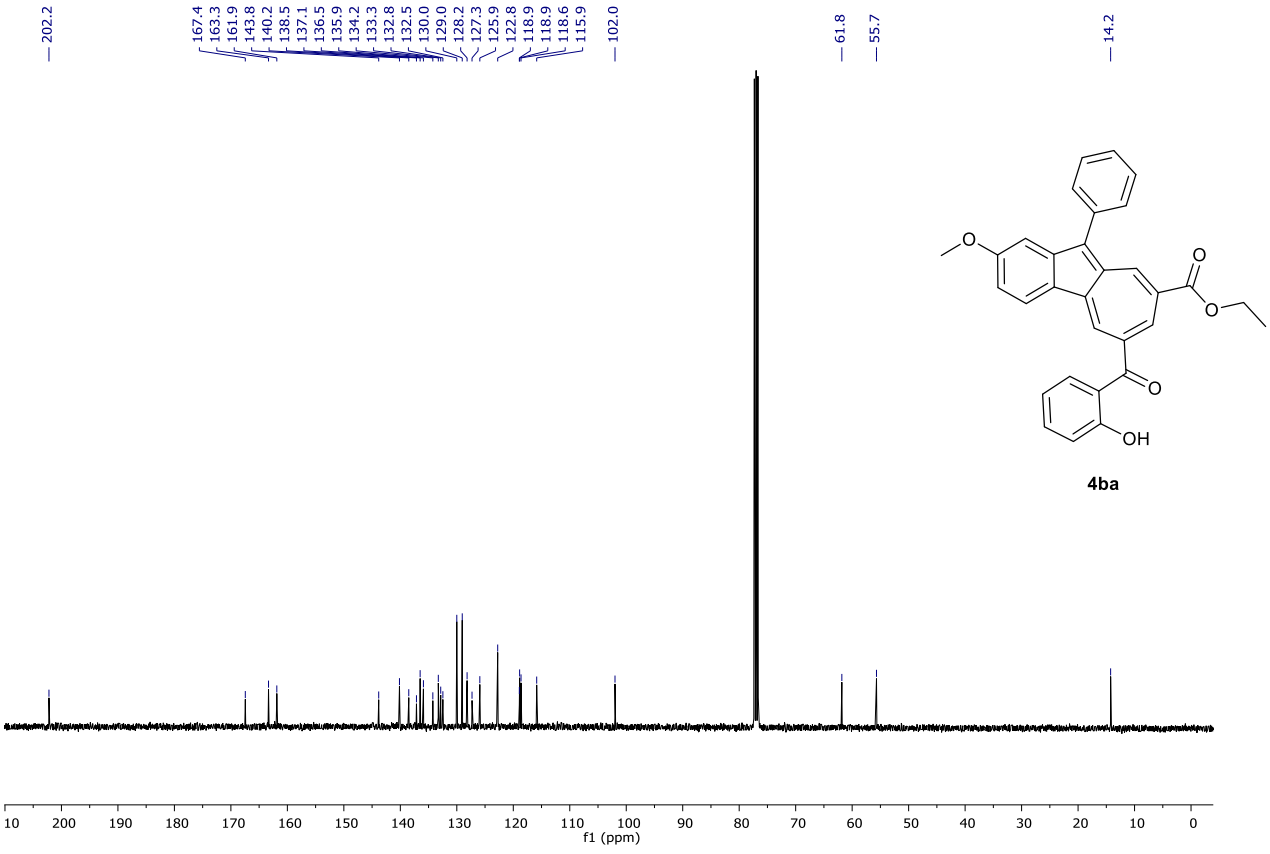


4ba

^{1}H NMR

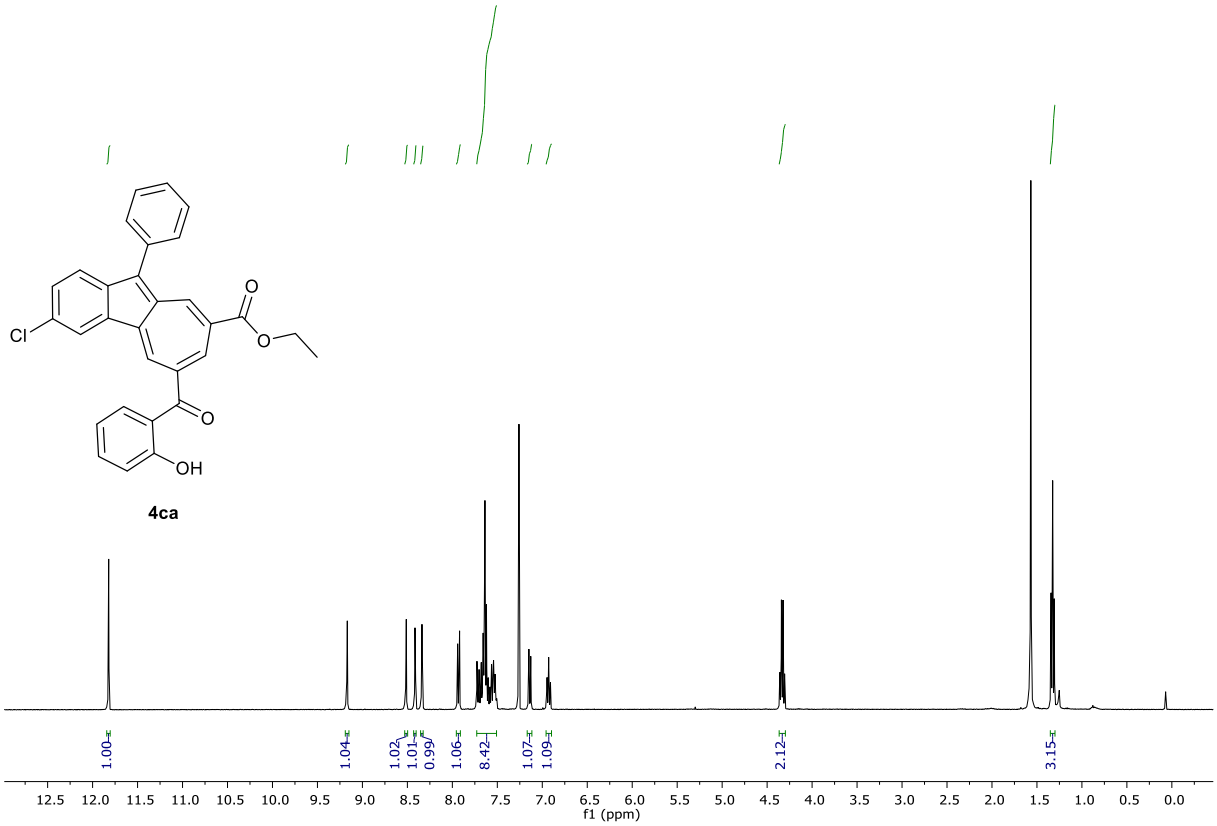


^{13}C NMR

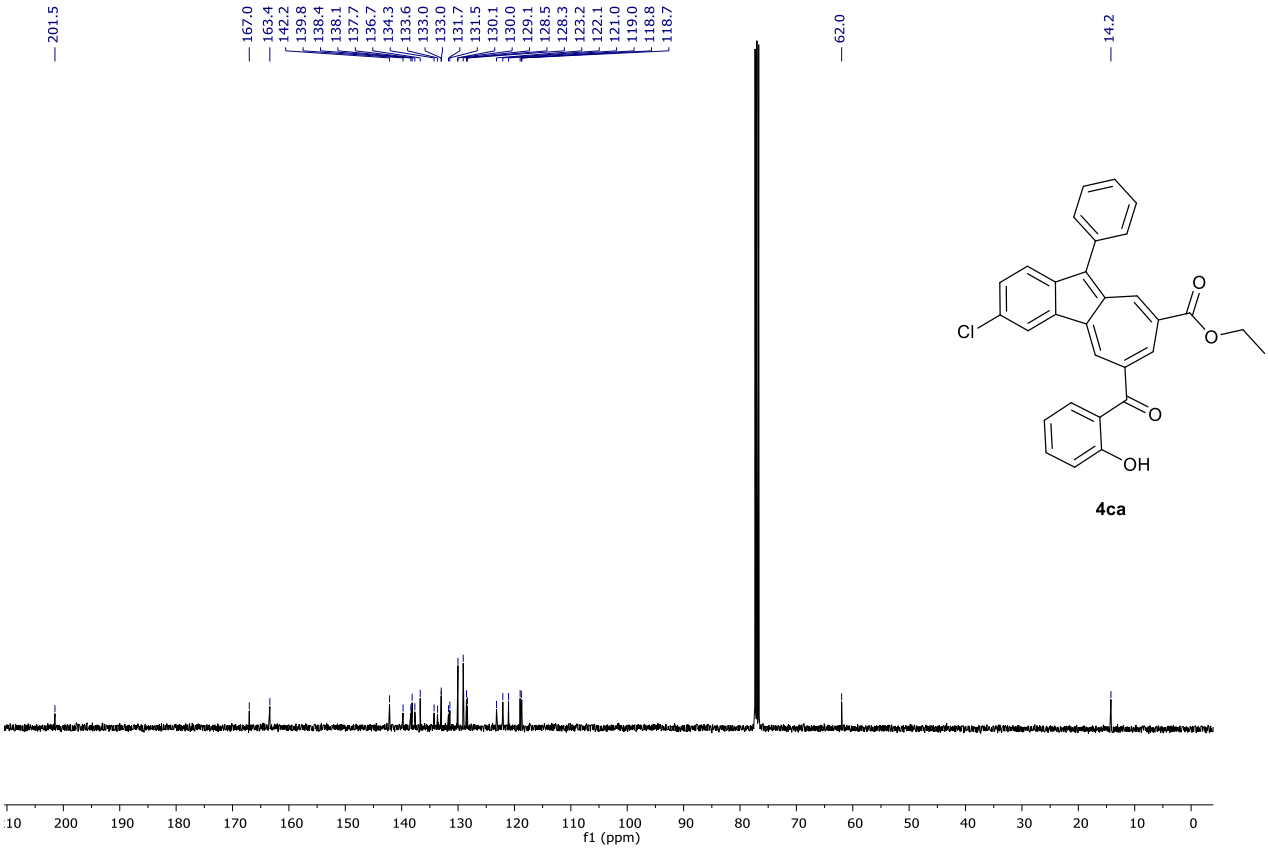


4ca

^{1}H NMR

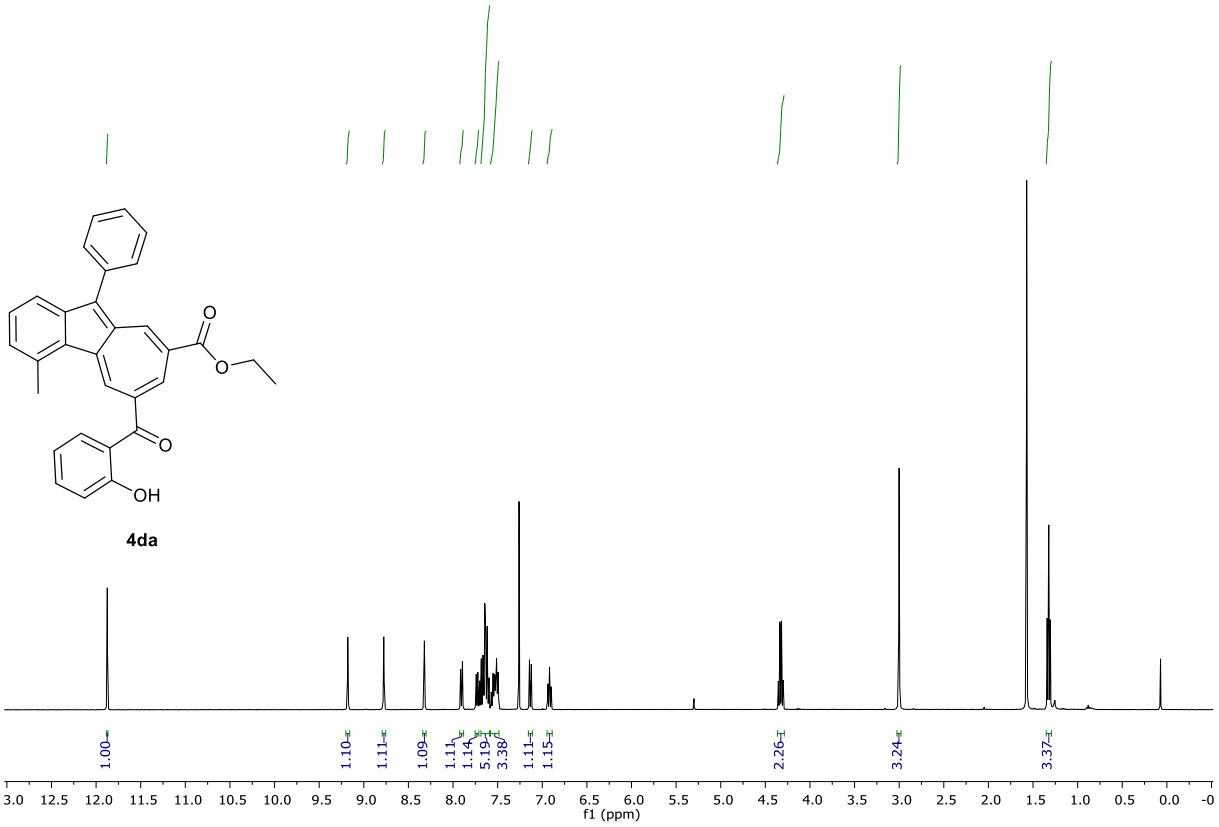


^{13}C NMR

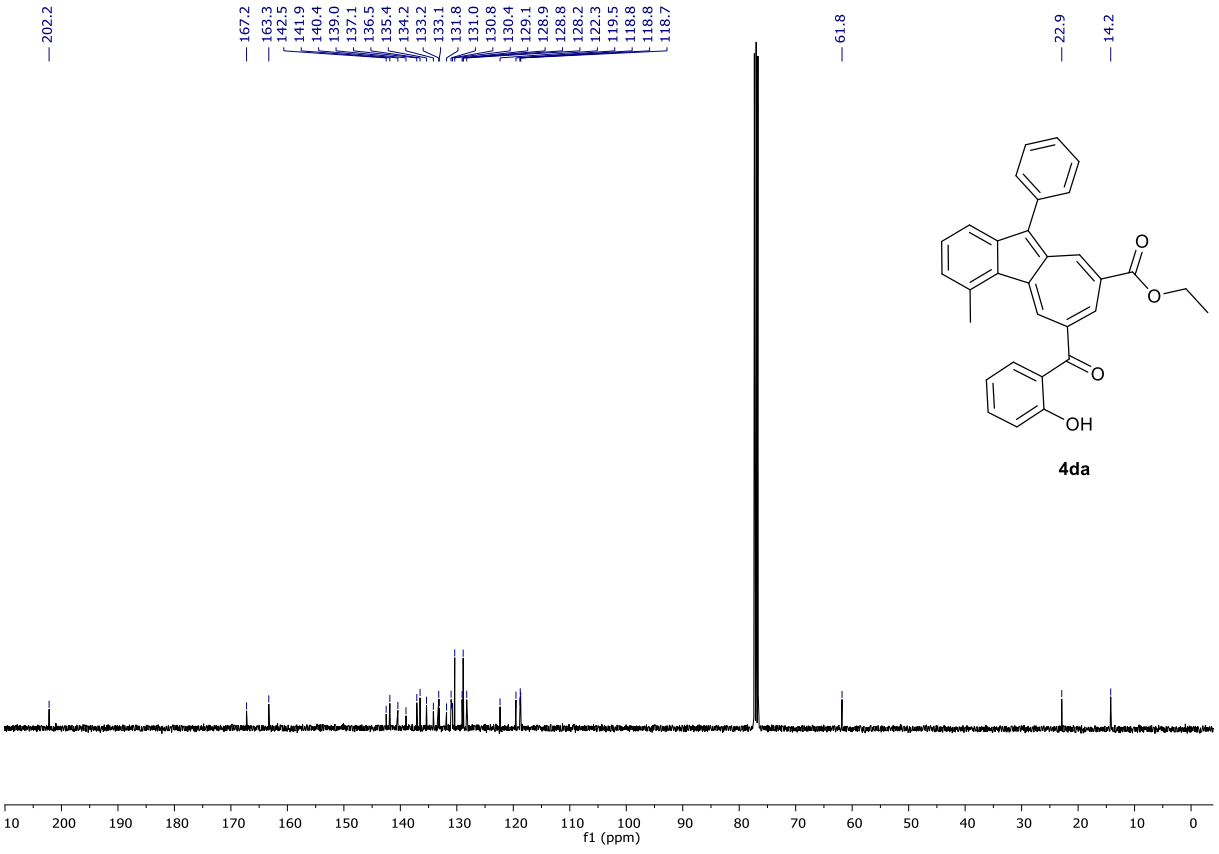


4da

^{1}H NMR

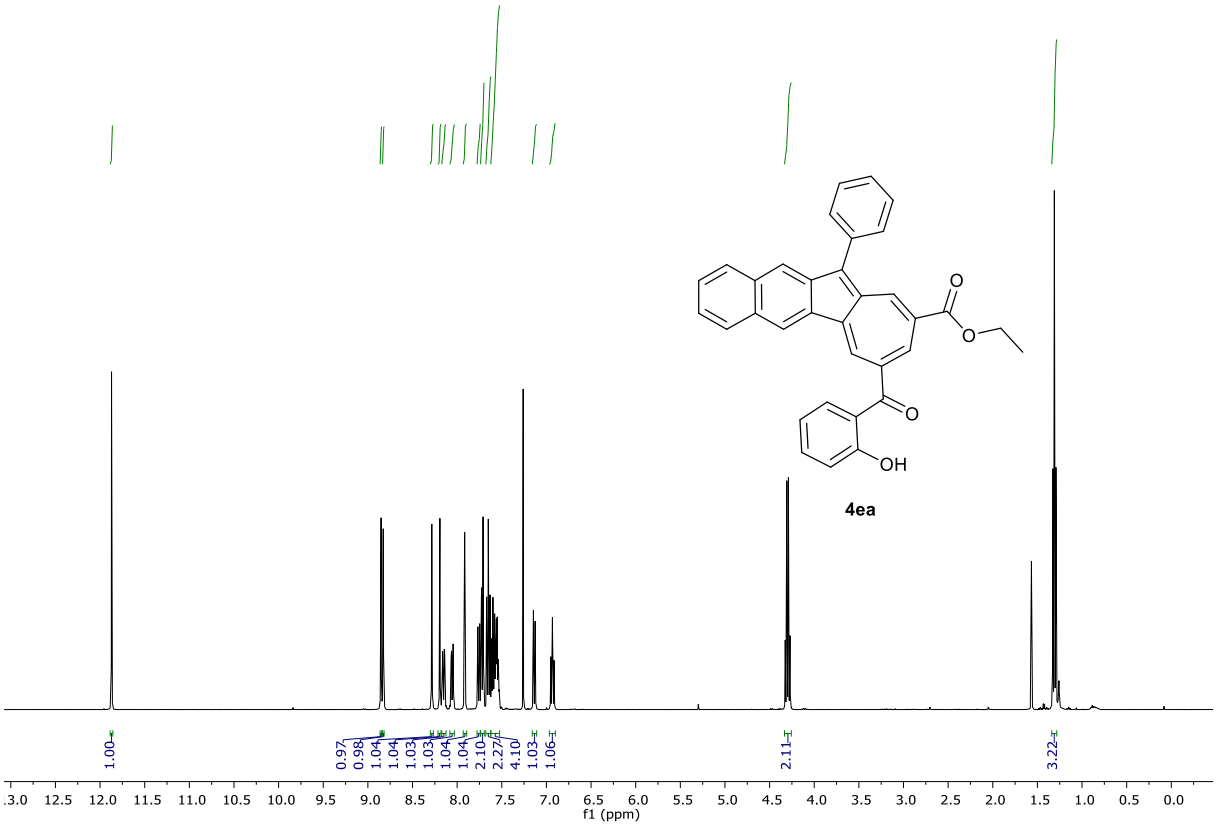


^{13}C NMR

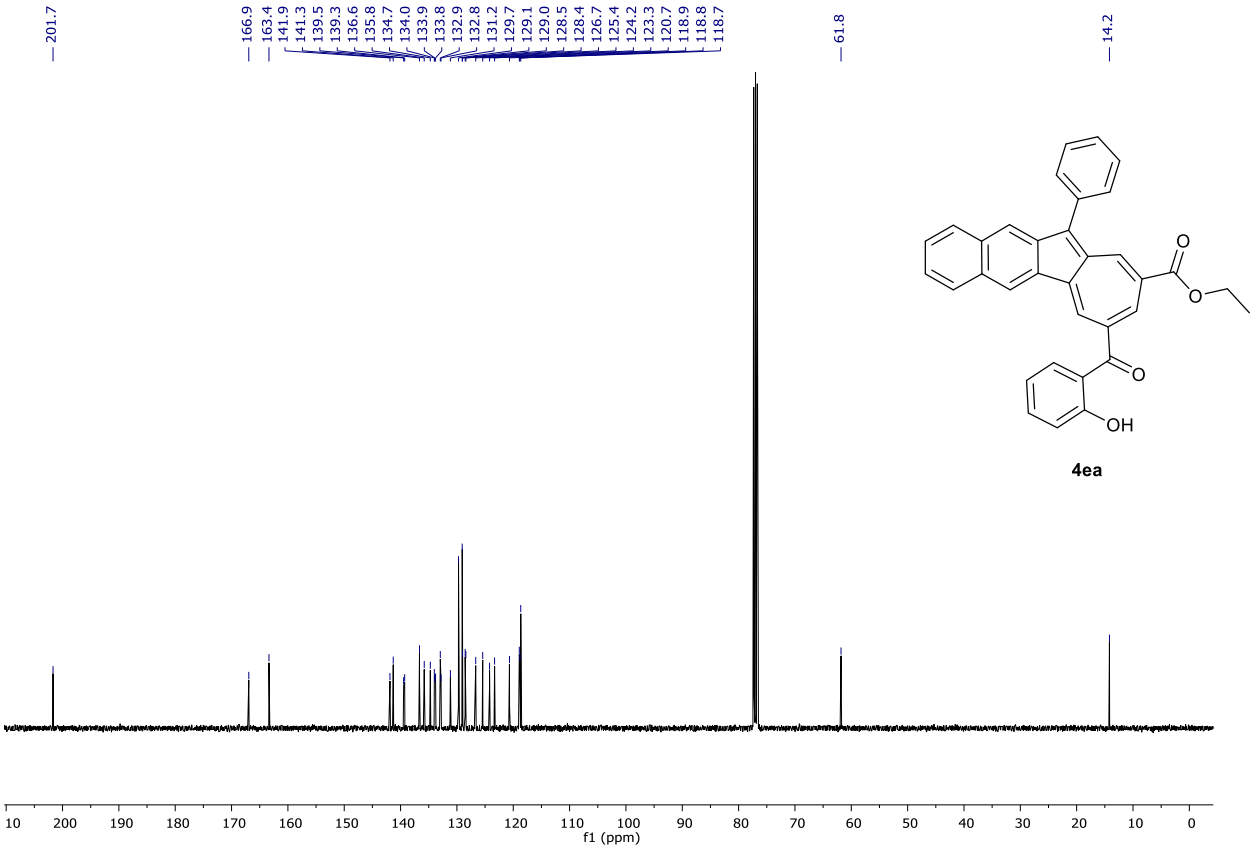


4ea

^{1}H NMR

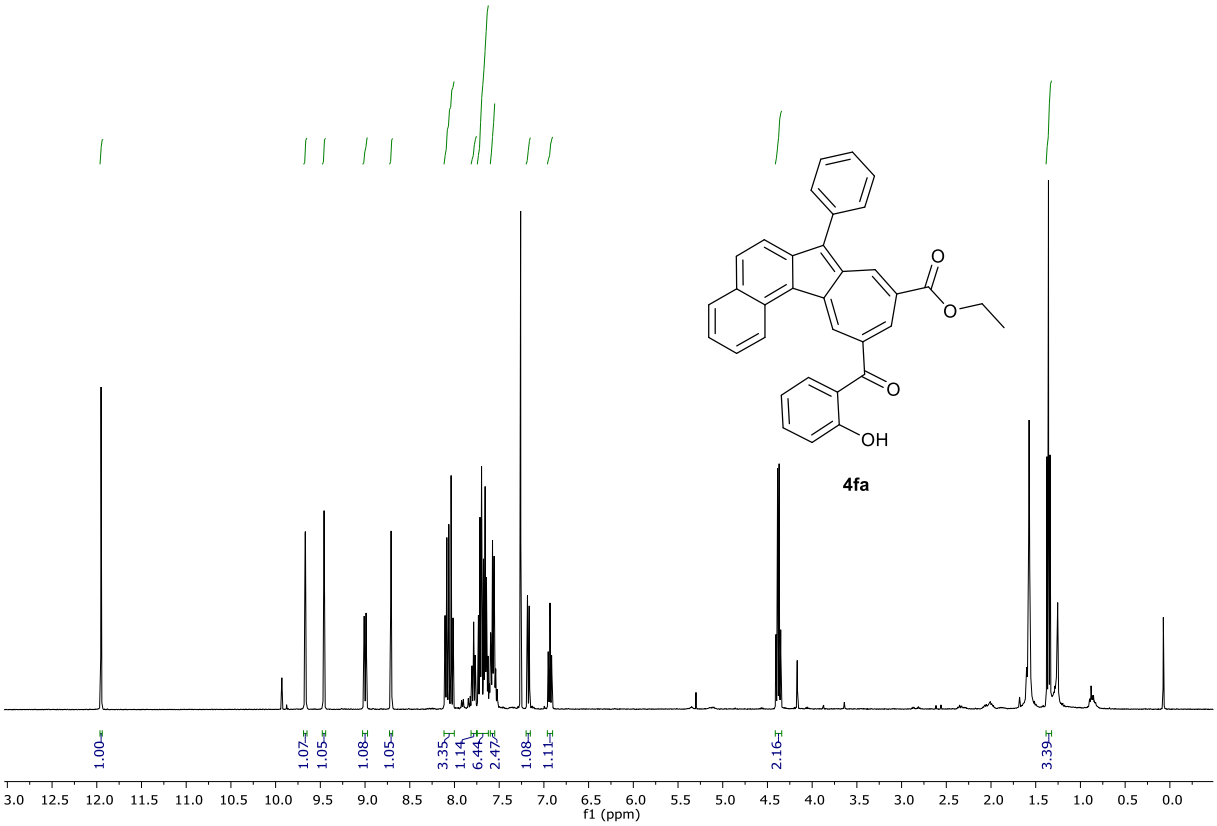


^{13}C NMR

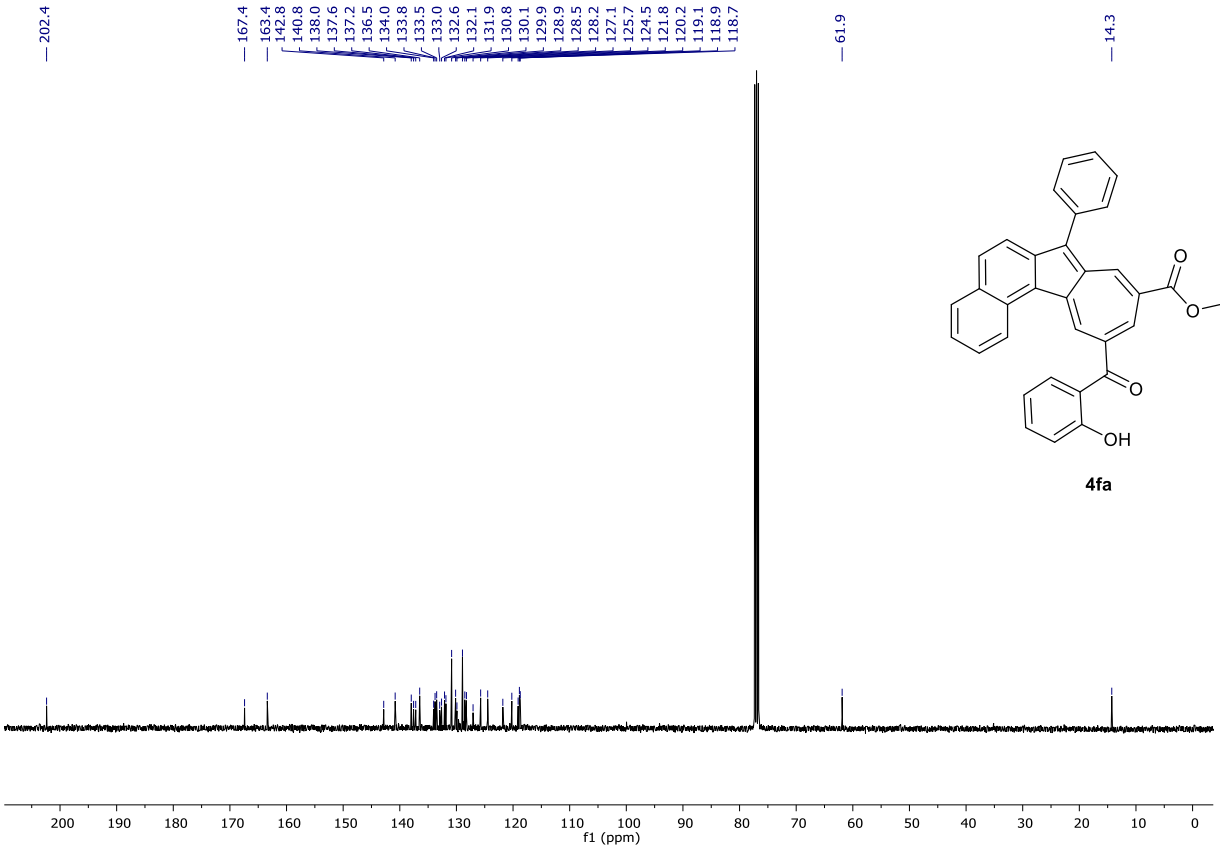


4fa

^{1}H NMR

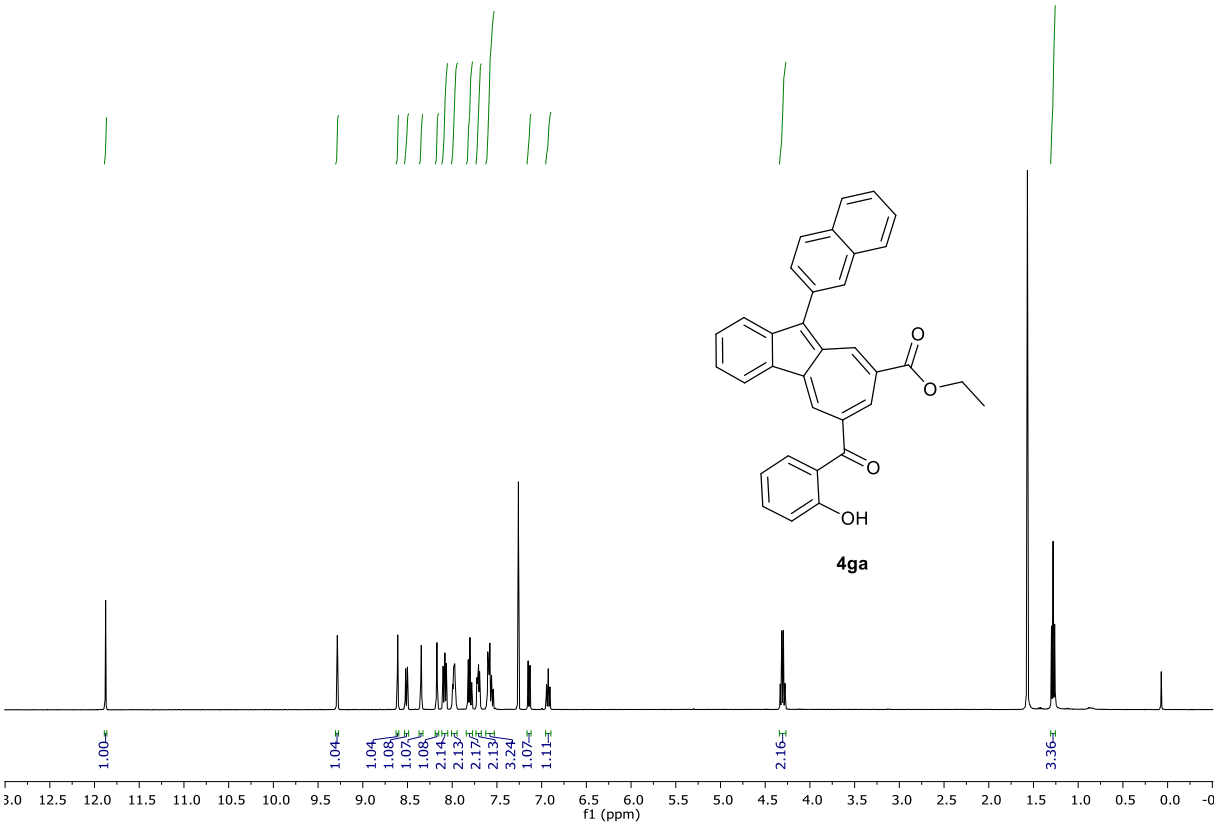


^{13}C NMR

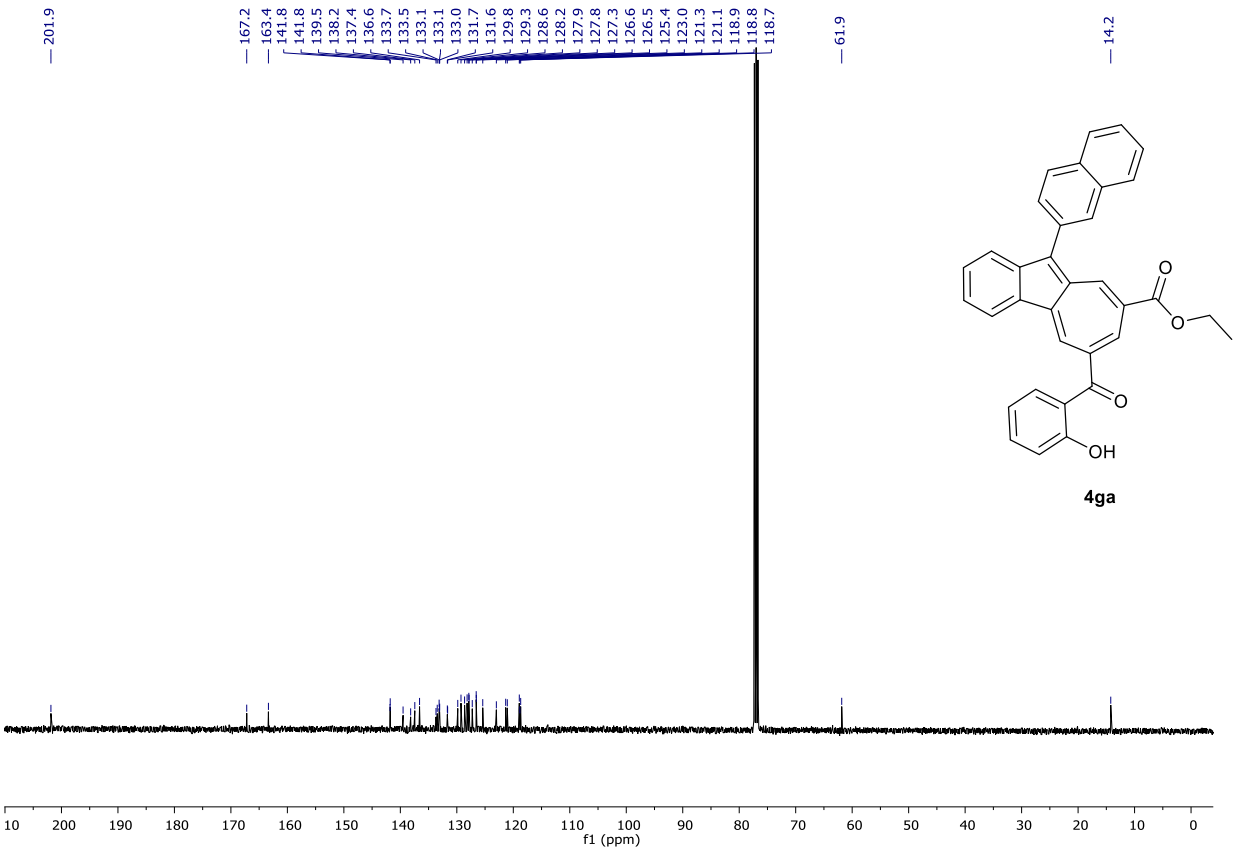


4ga

^{1}H NMR

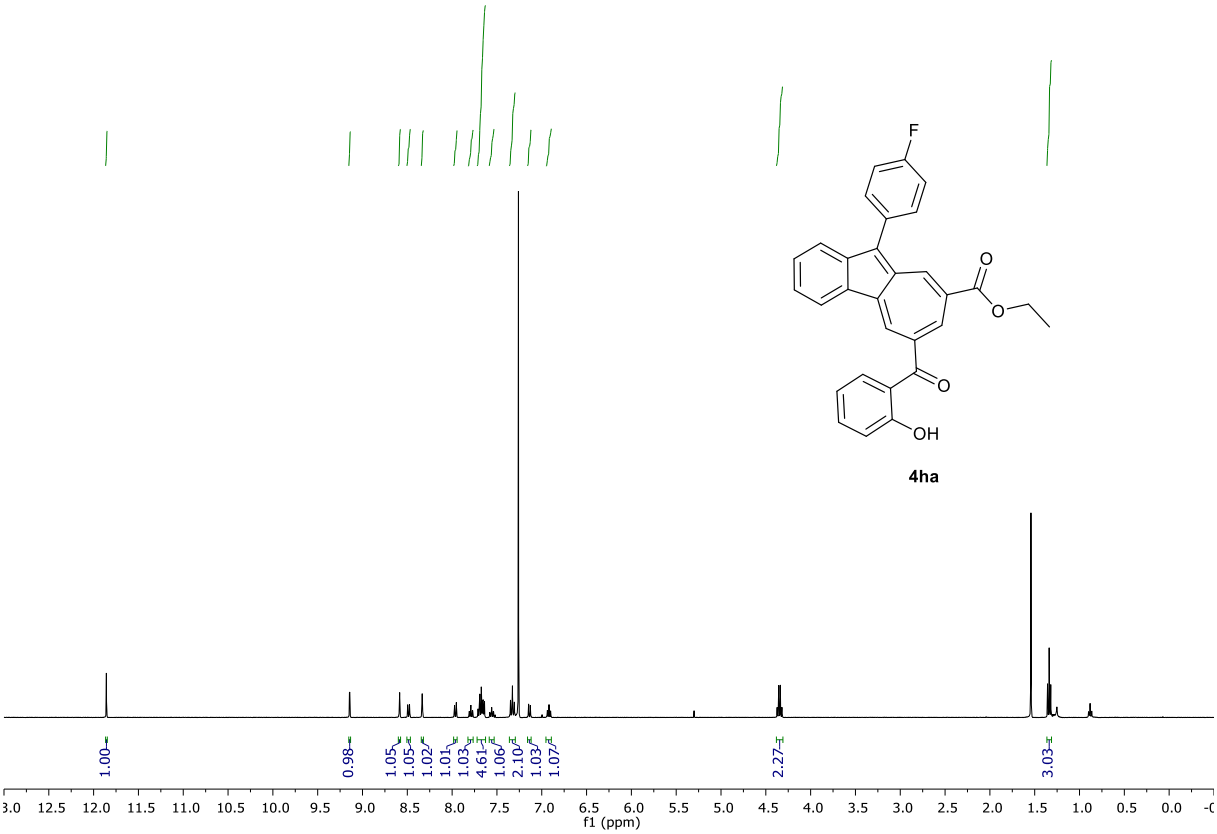


^{13}C NMR

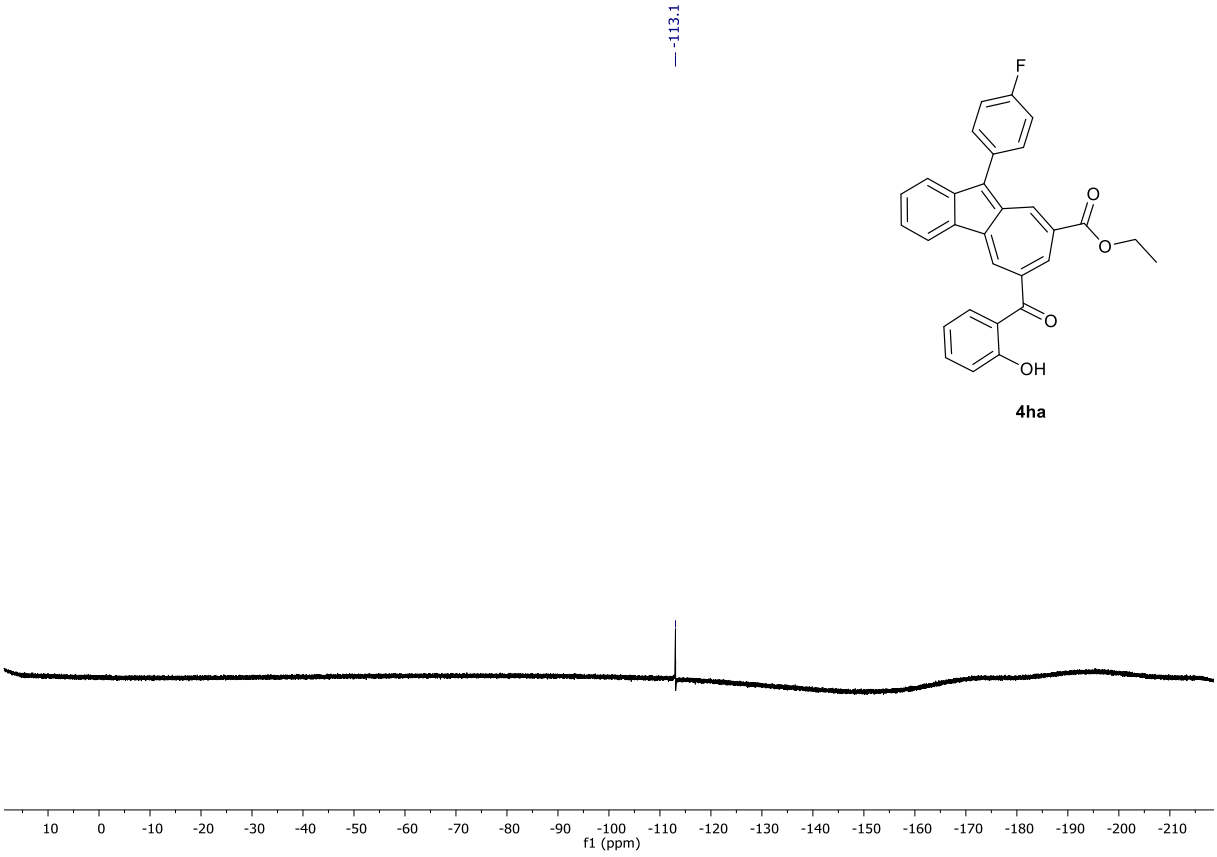


4ha

^{1}H NMR

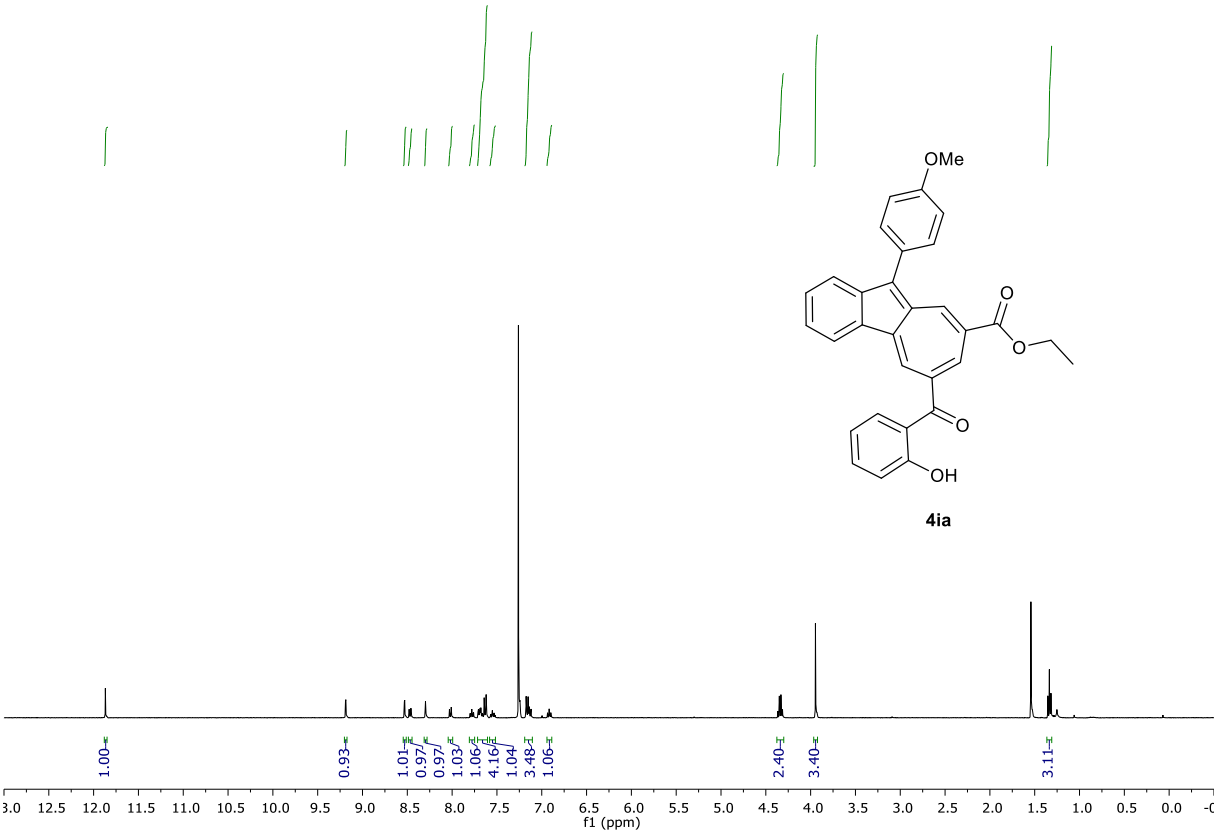


^{19}F NMR

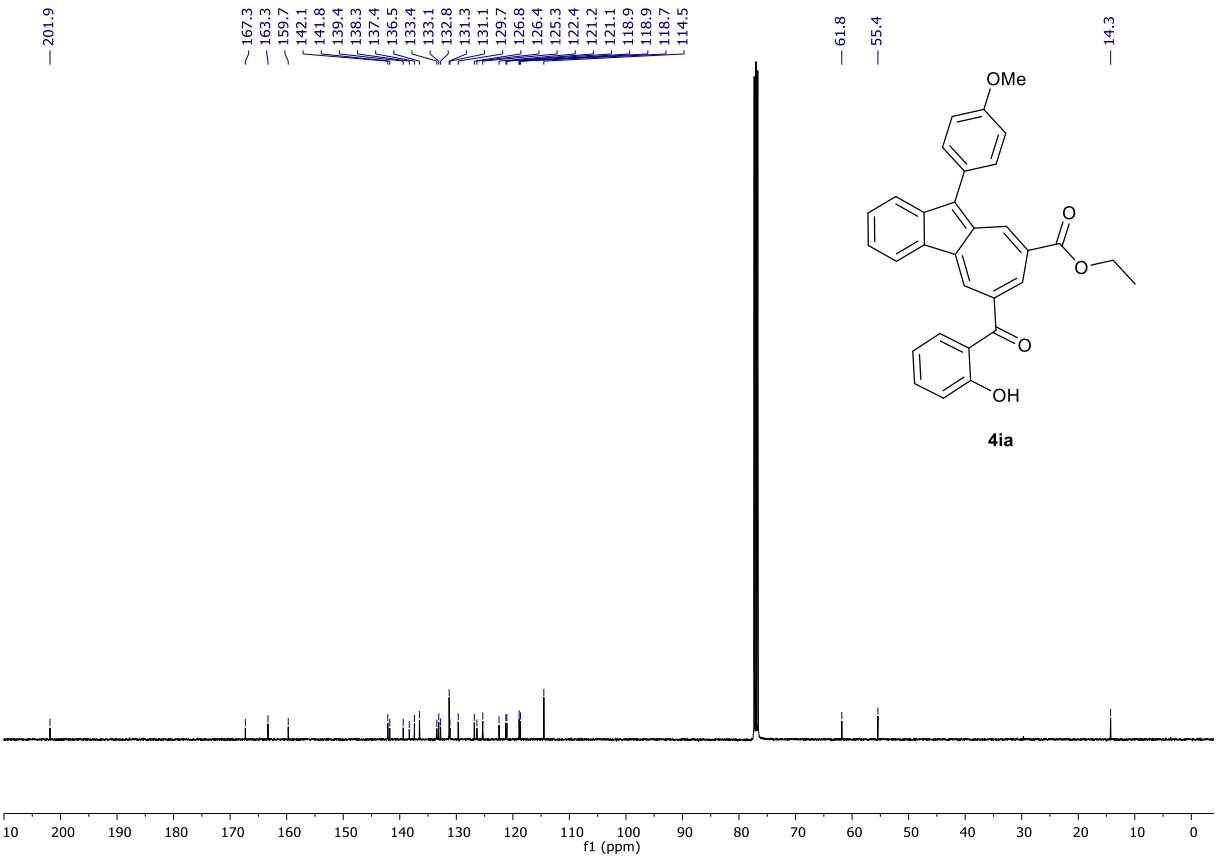


4ia

^{1}H NMR

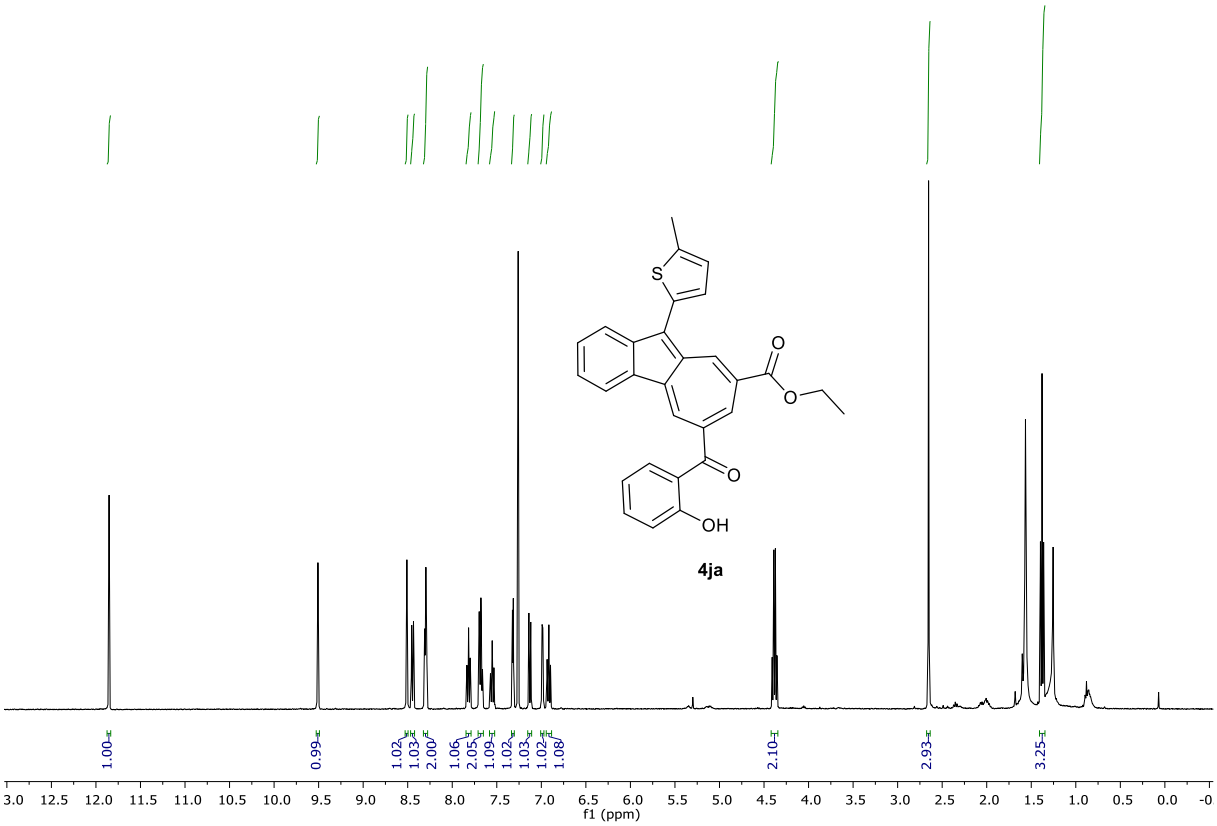


^{13}C NMR

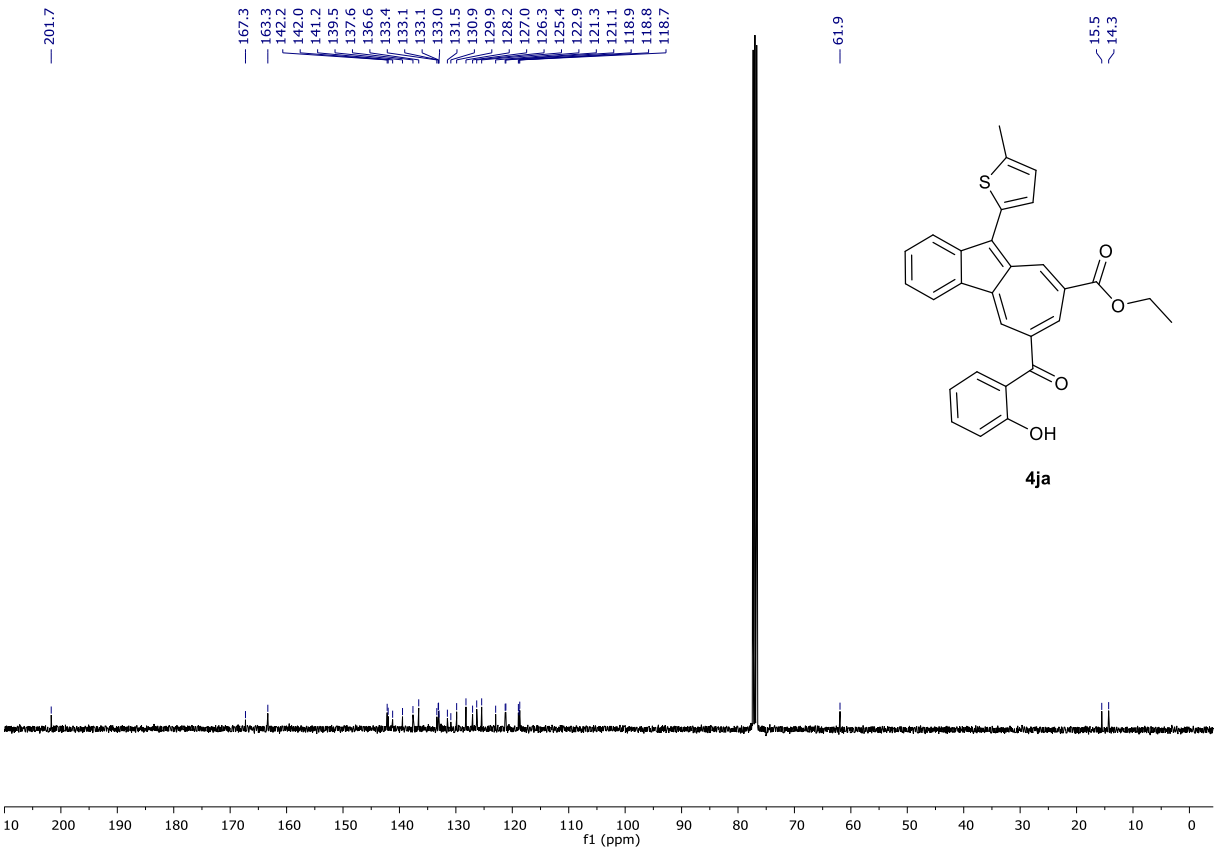


4ja

^{1}H NMR

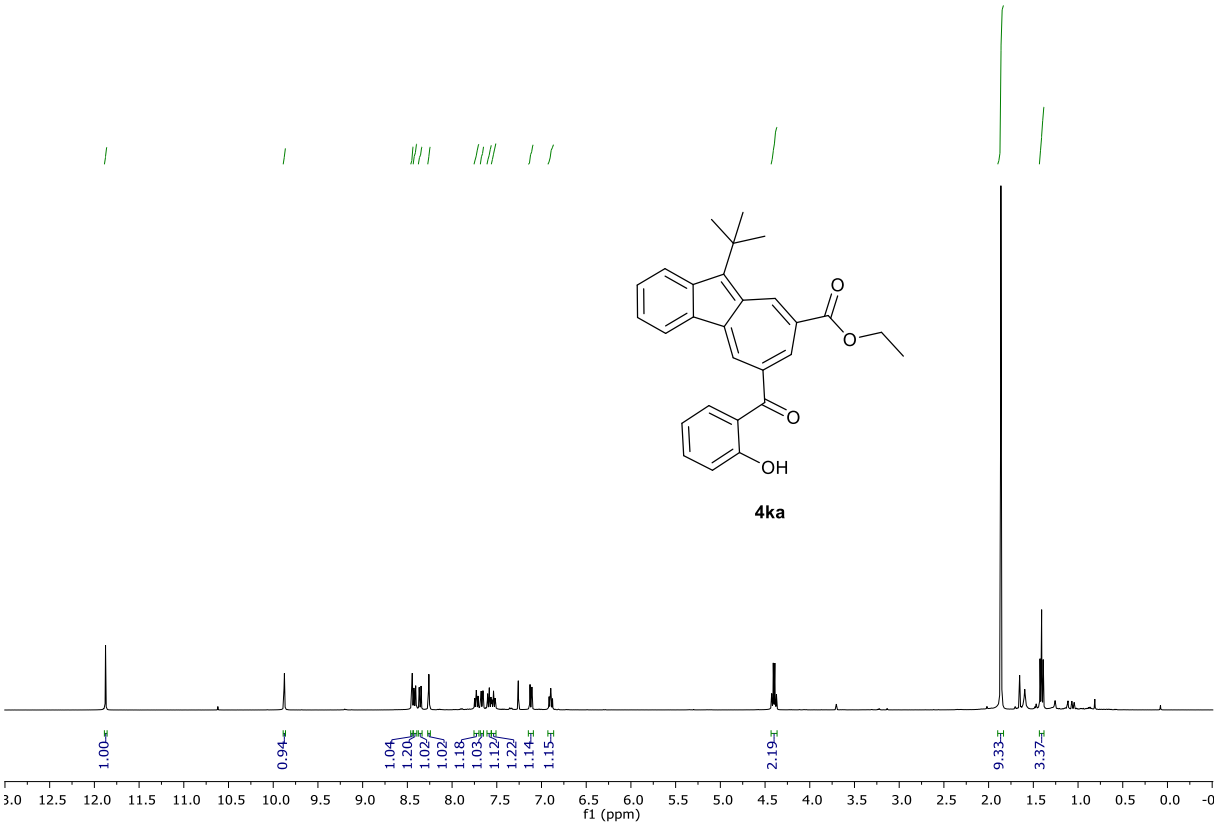


^{13}C NMR

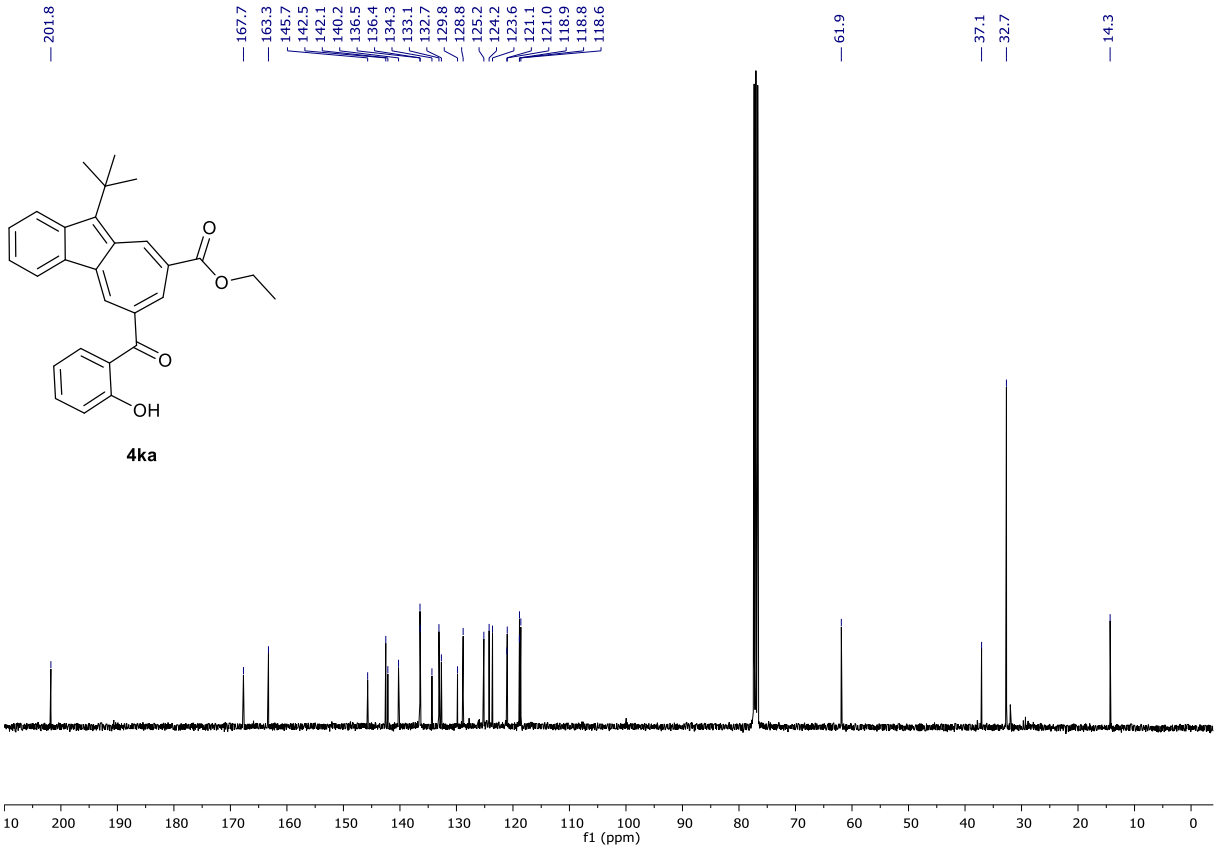


4ka

^{1}H NMR

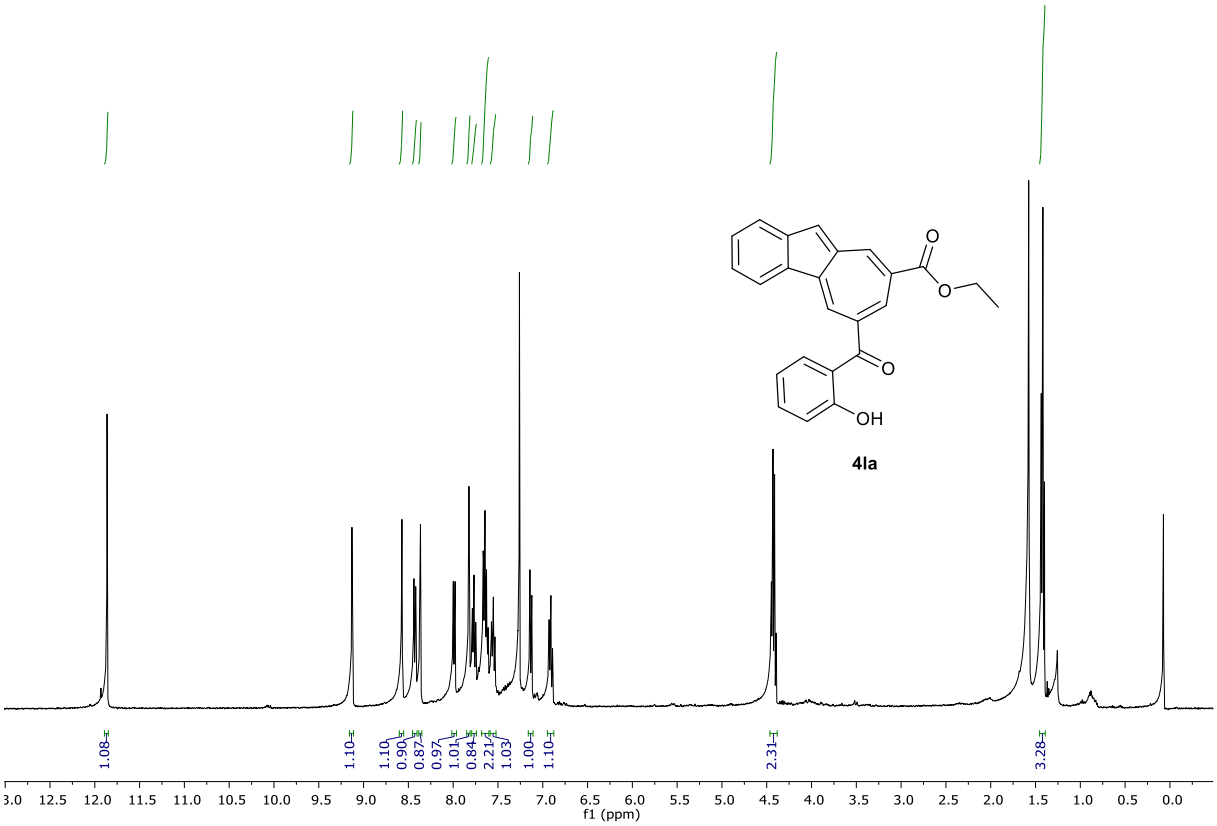


^{13}C NMR

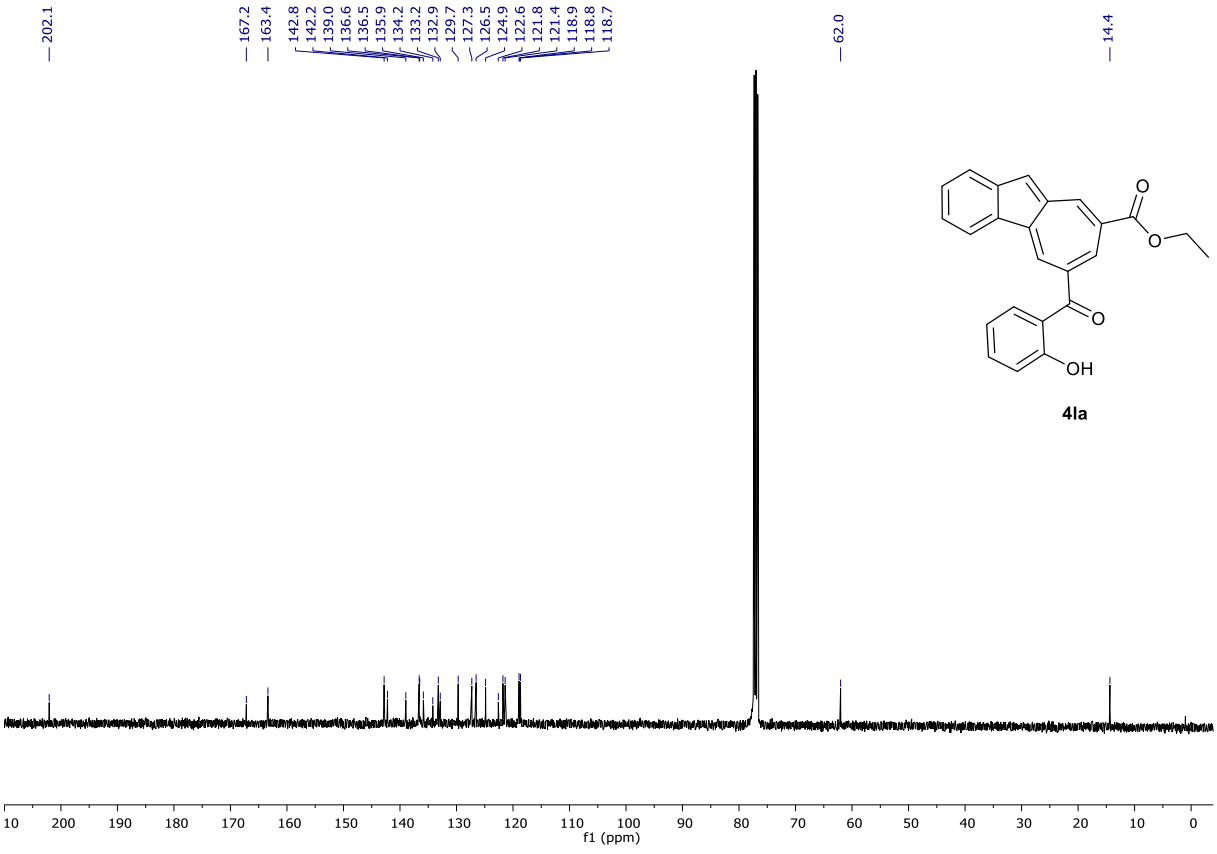


4la

^{1}H NMR

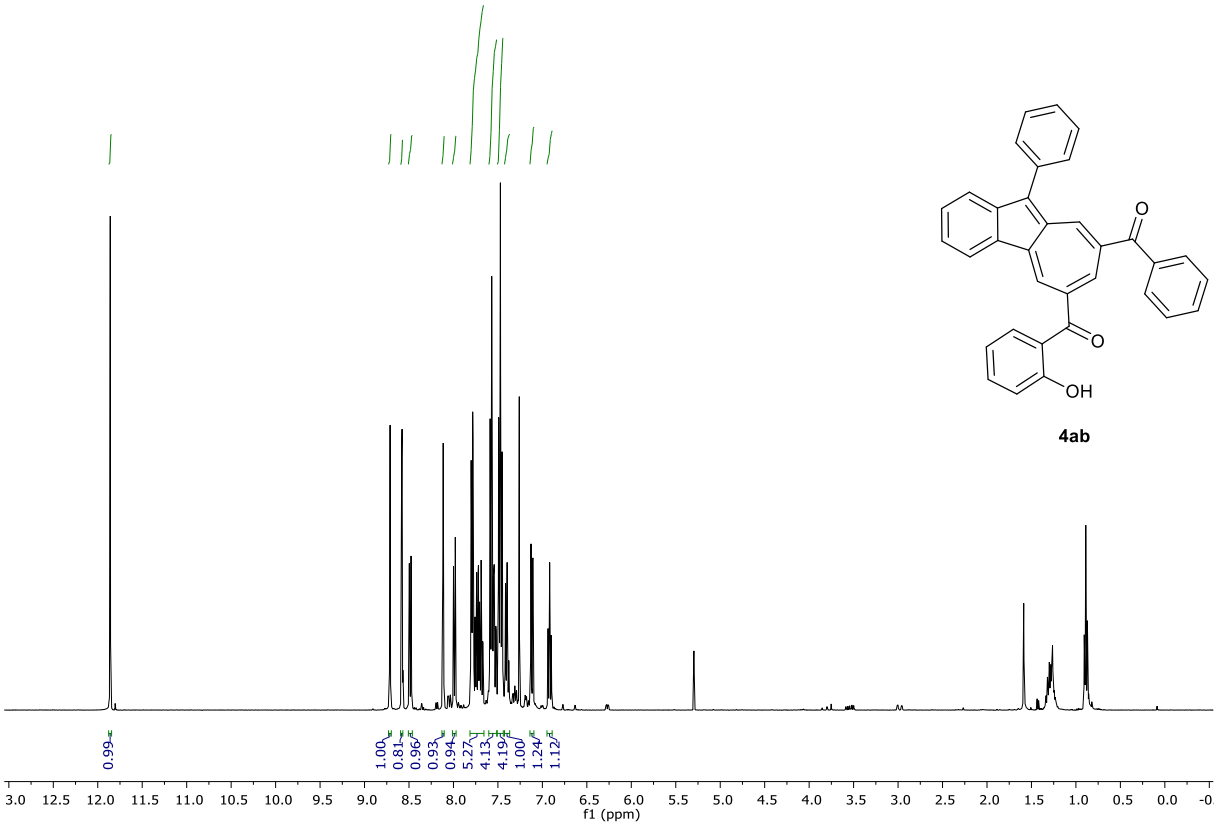


^{13}C NMR



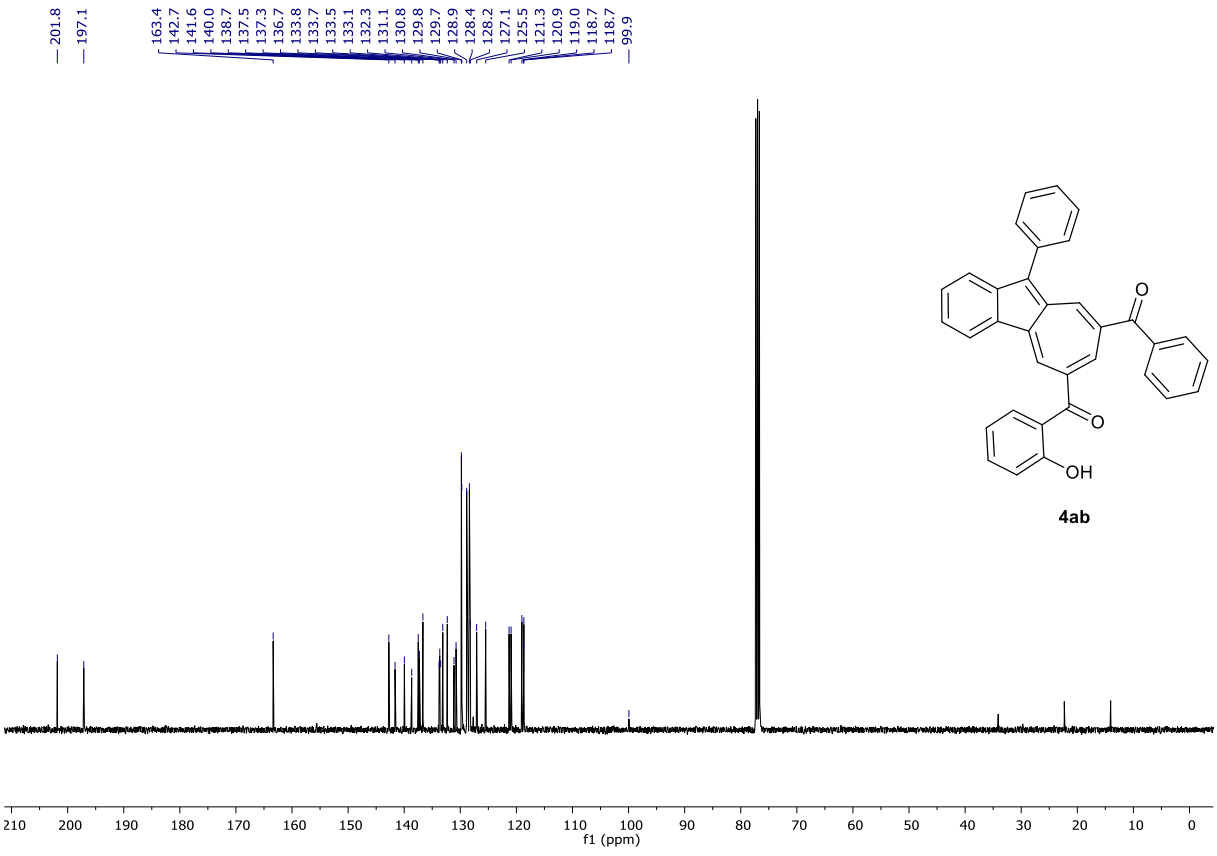
4ab

^{1}H NMR



4ab

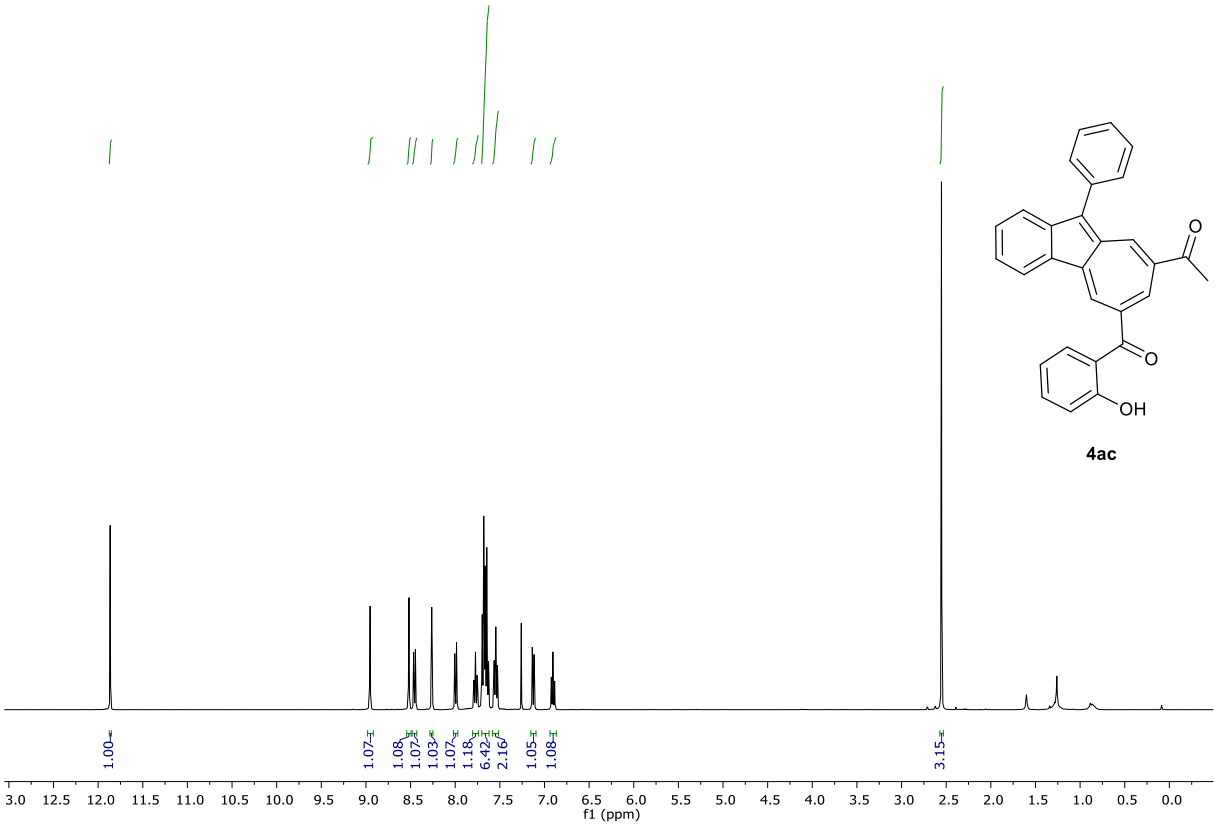
^{13}C NMR



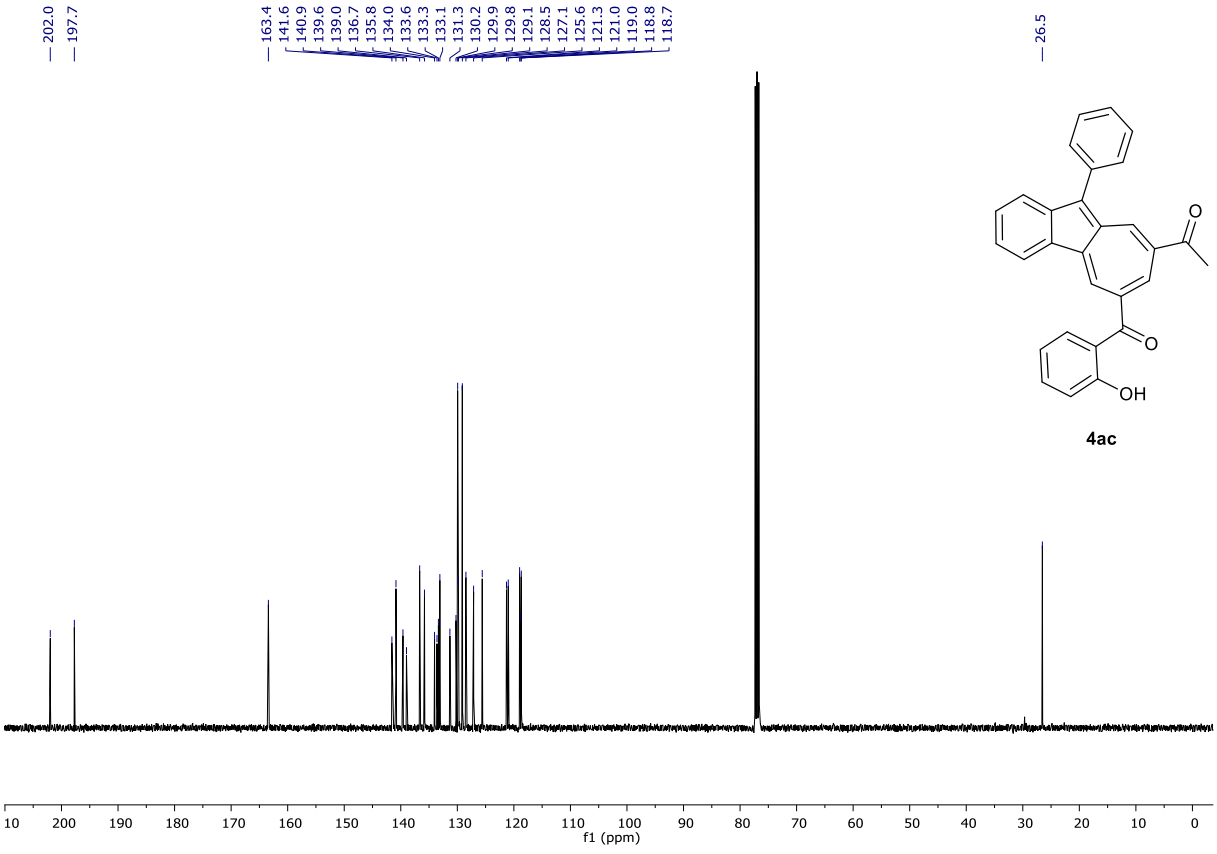
4ab

4ac

^{1}H NMR

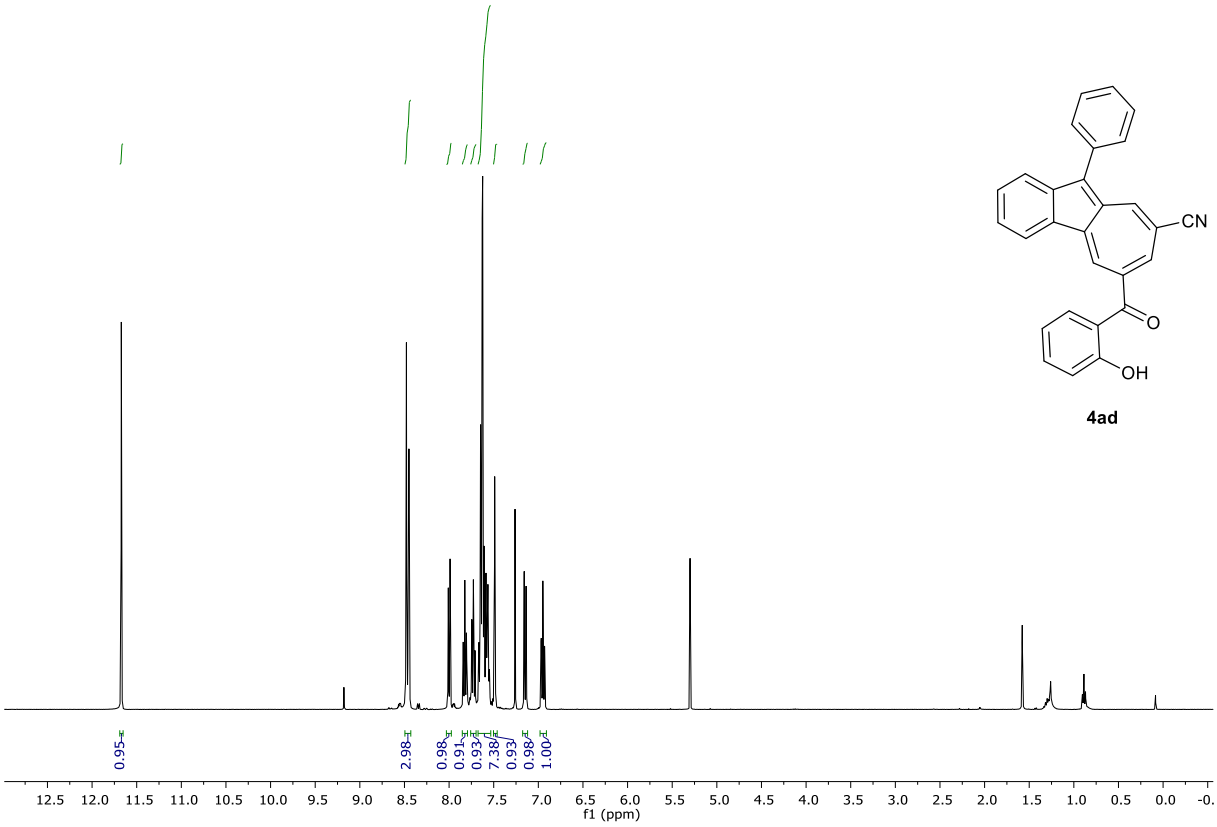


^{13}C NMR

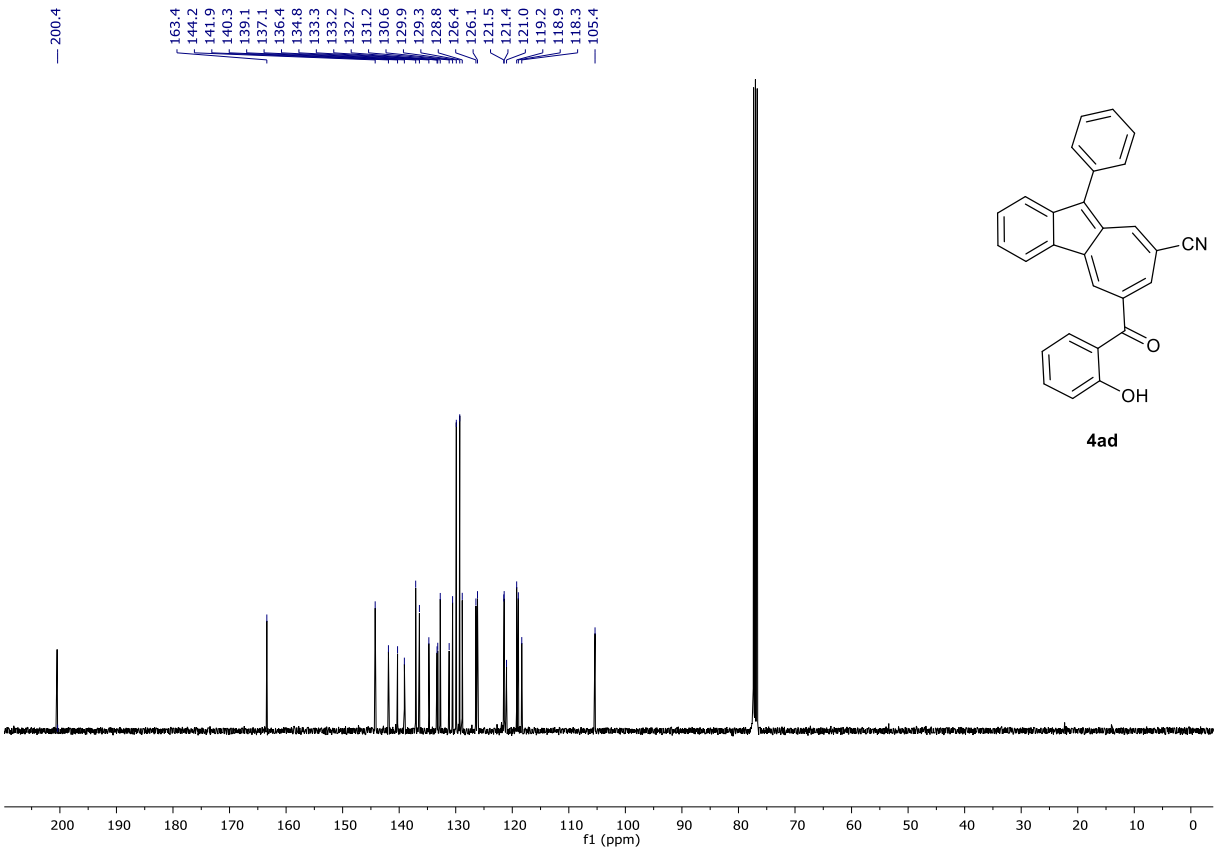


4ad

^{1}H NMR

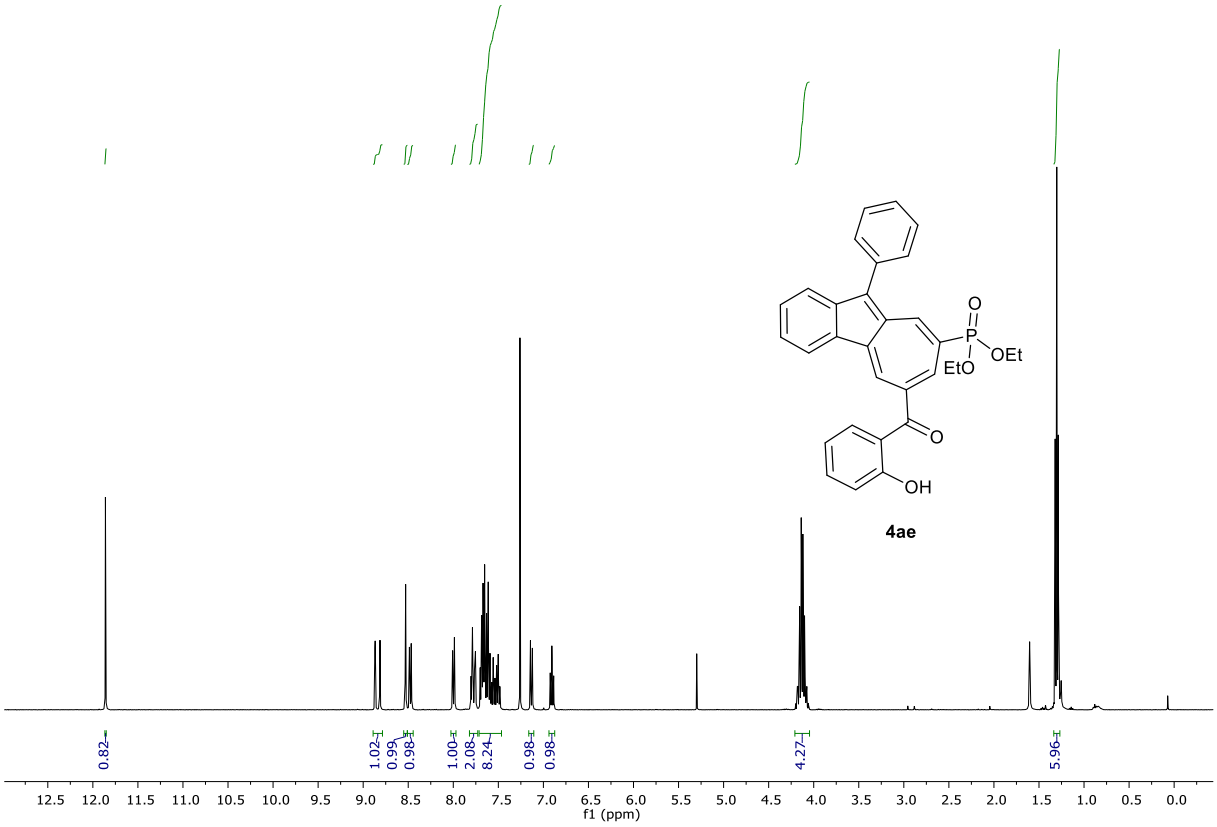


^{13}C NMR

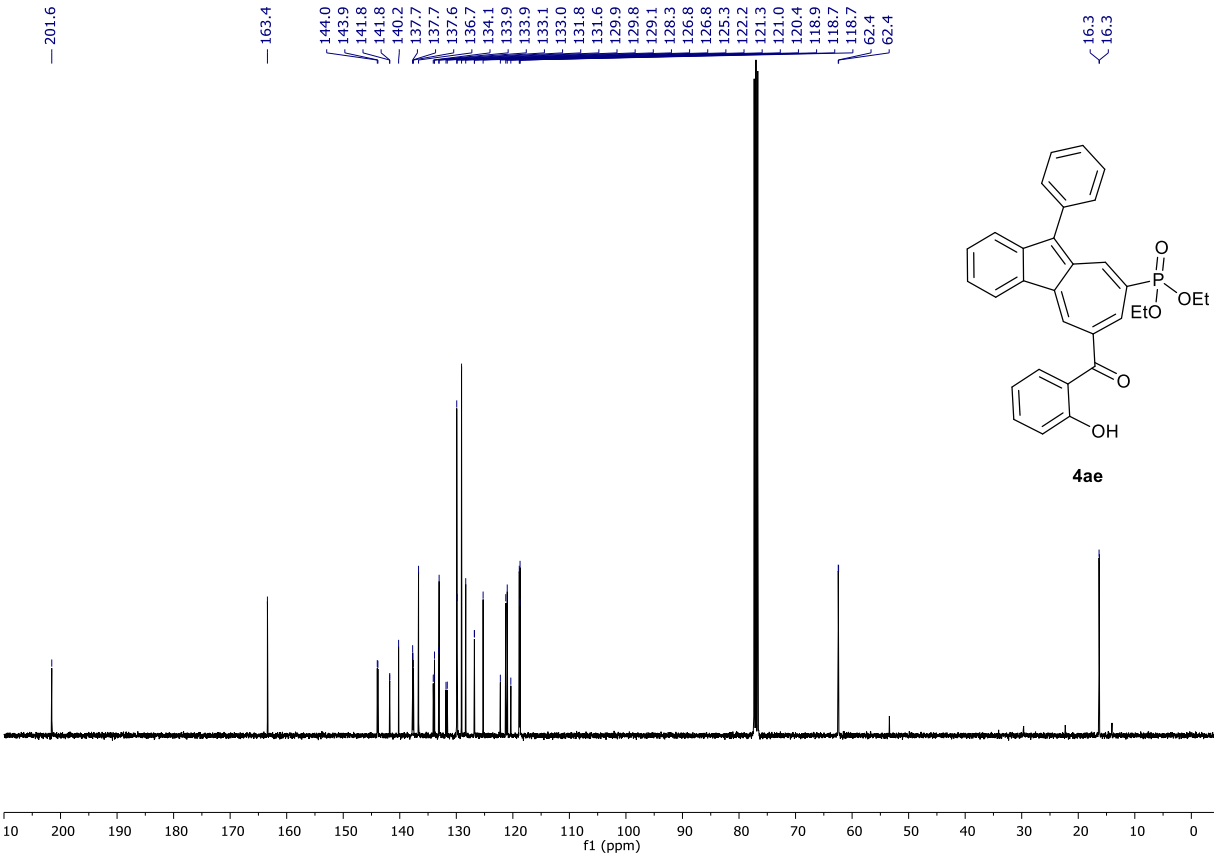


4ae

^{1}H NMR

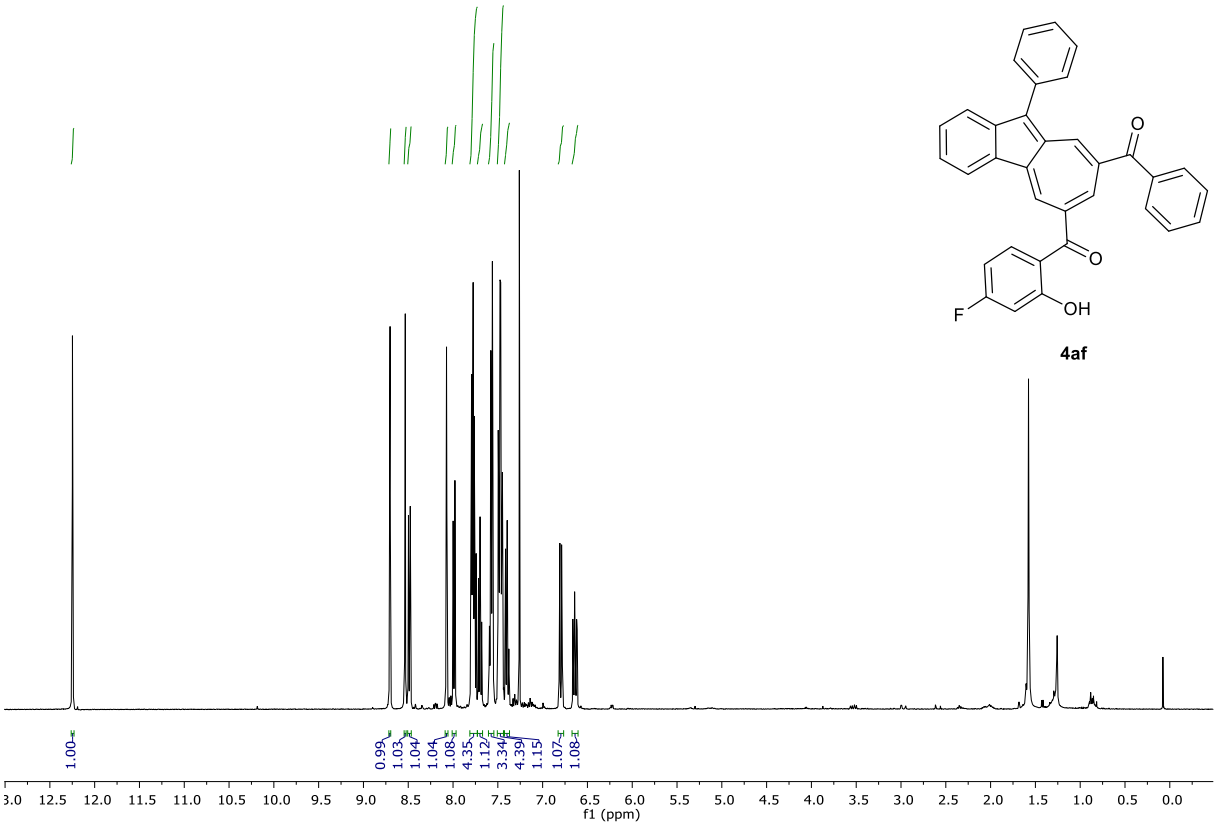


^{13}C NMR

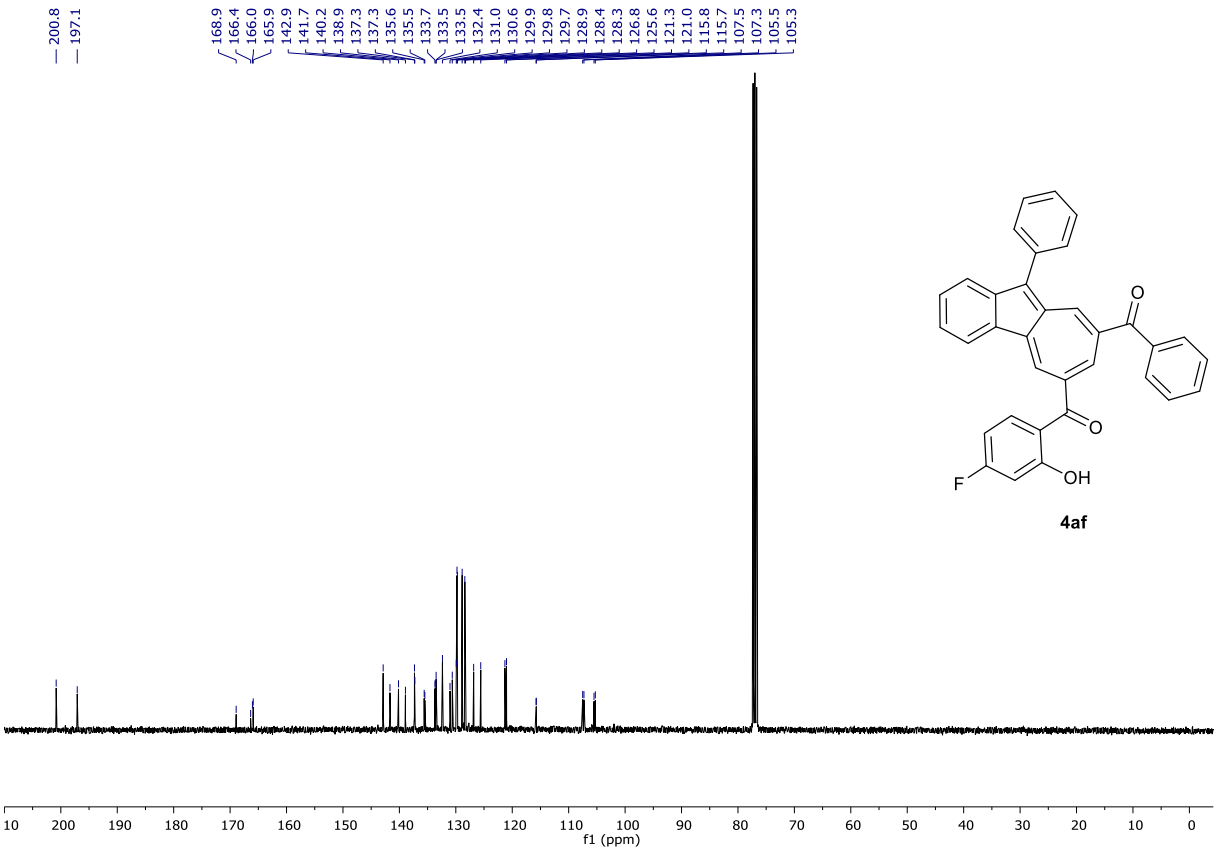


4af

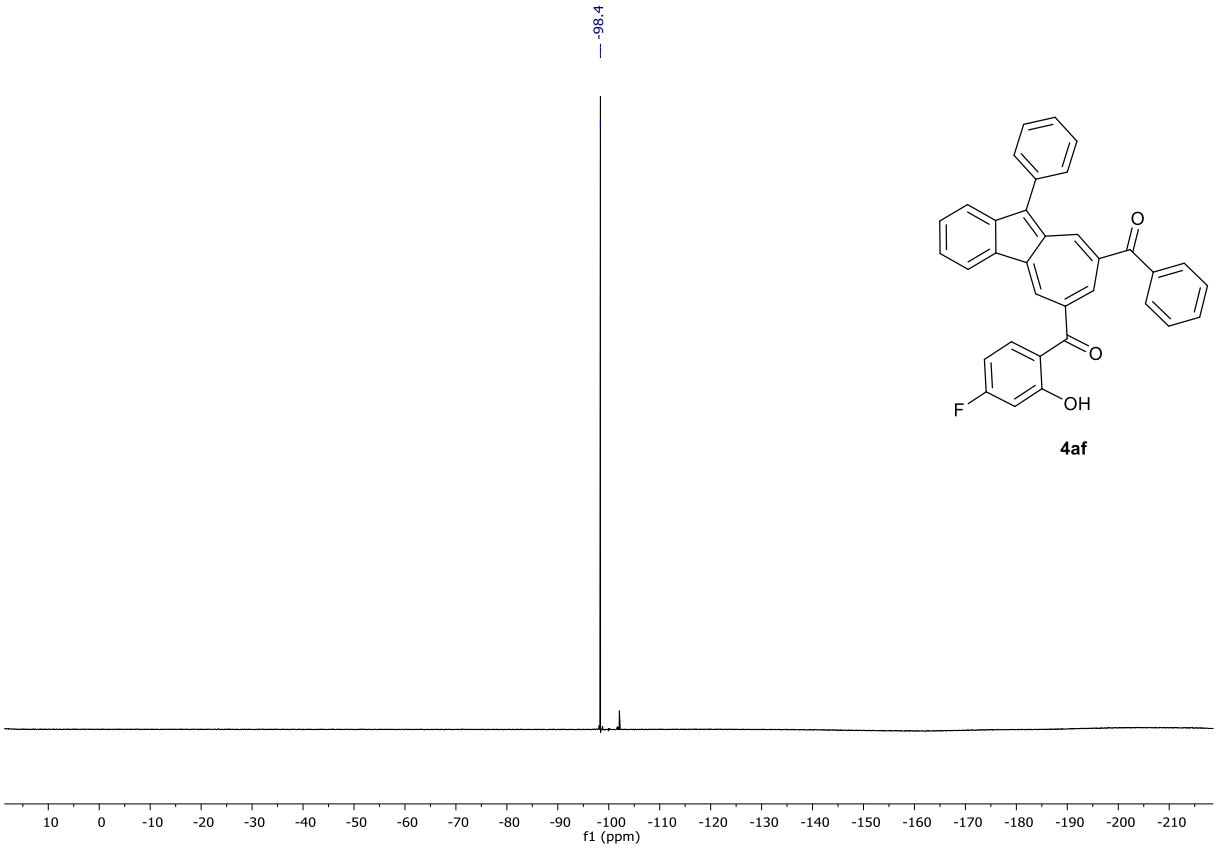
^{1}H NMR



^{13}C NMR



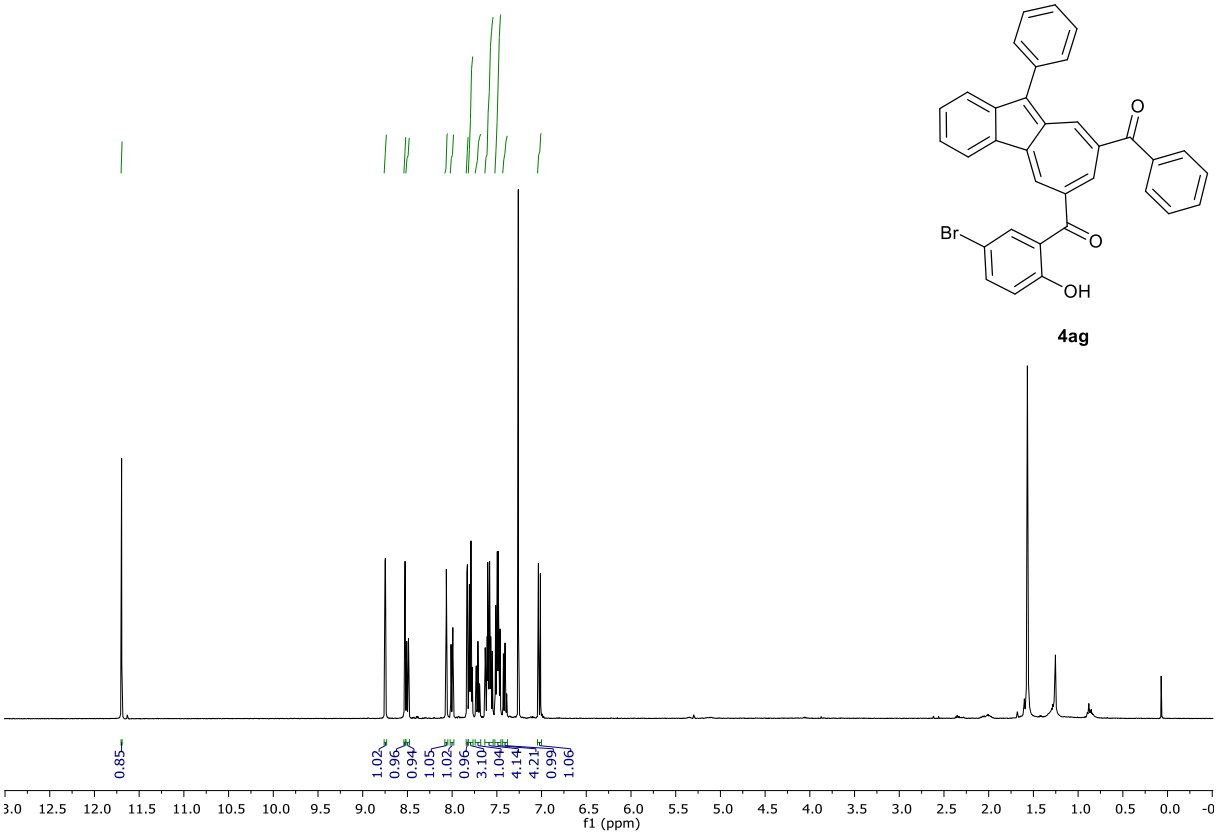
^{19}F NMR


-98.4
O
O
F
OH
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

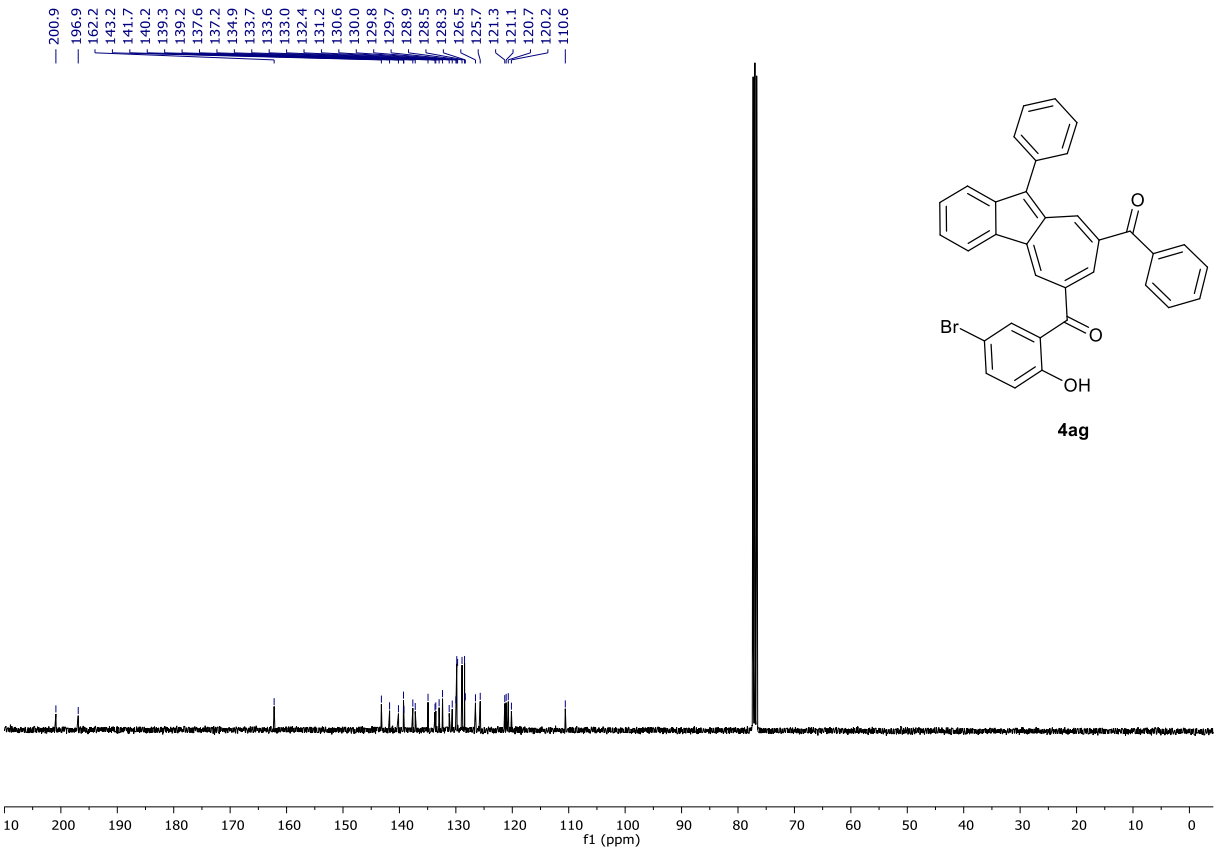
4af

4ag

^{1}H NMR

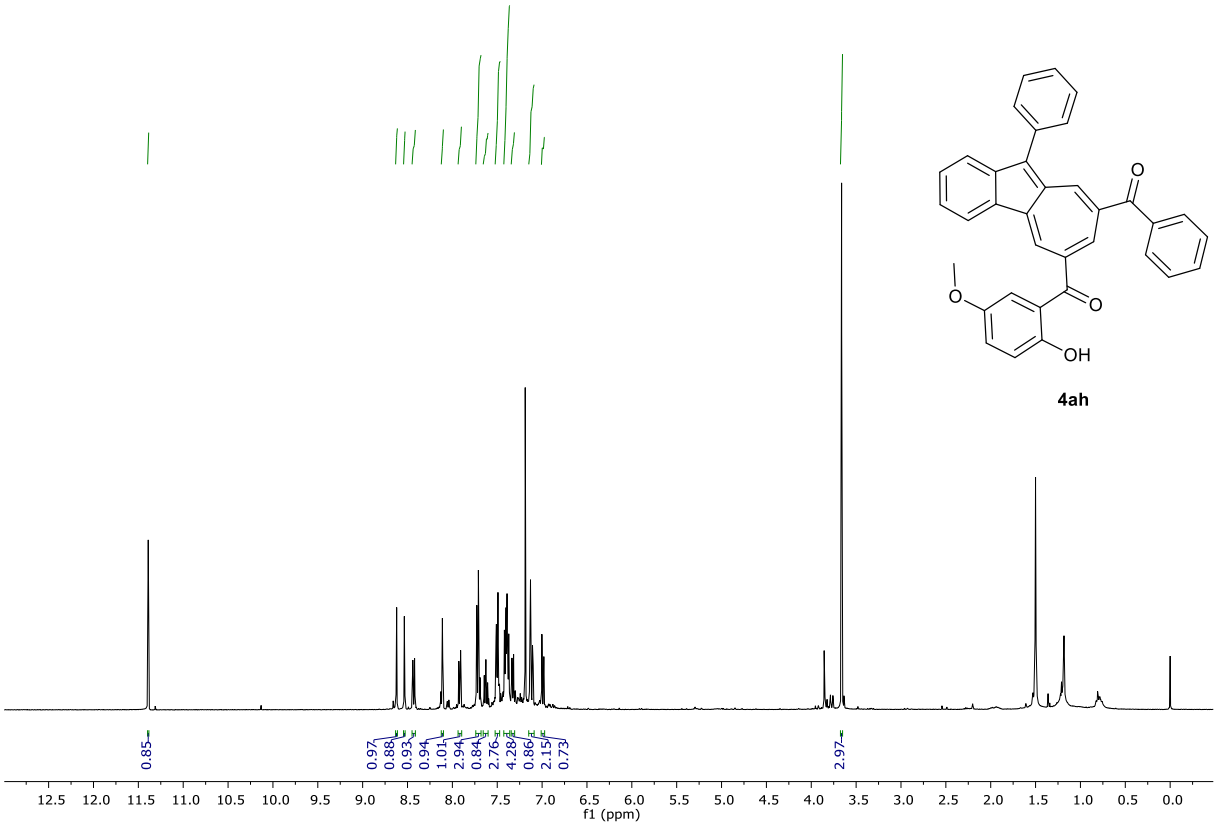


^{13}C NMR



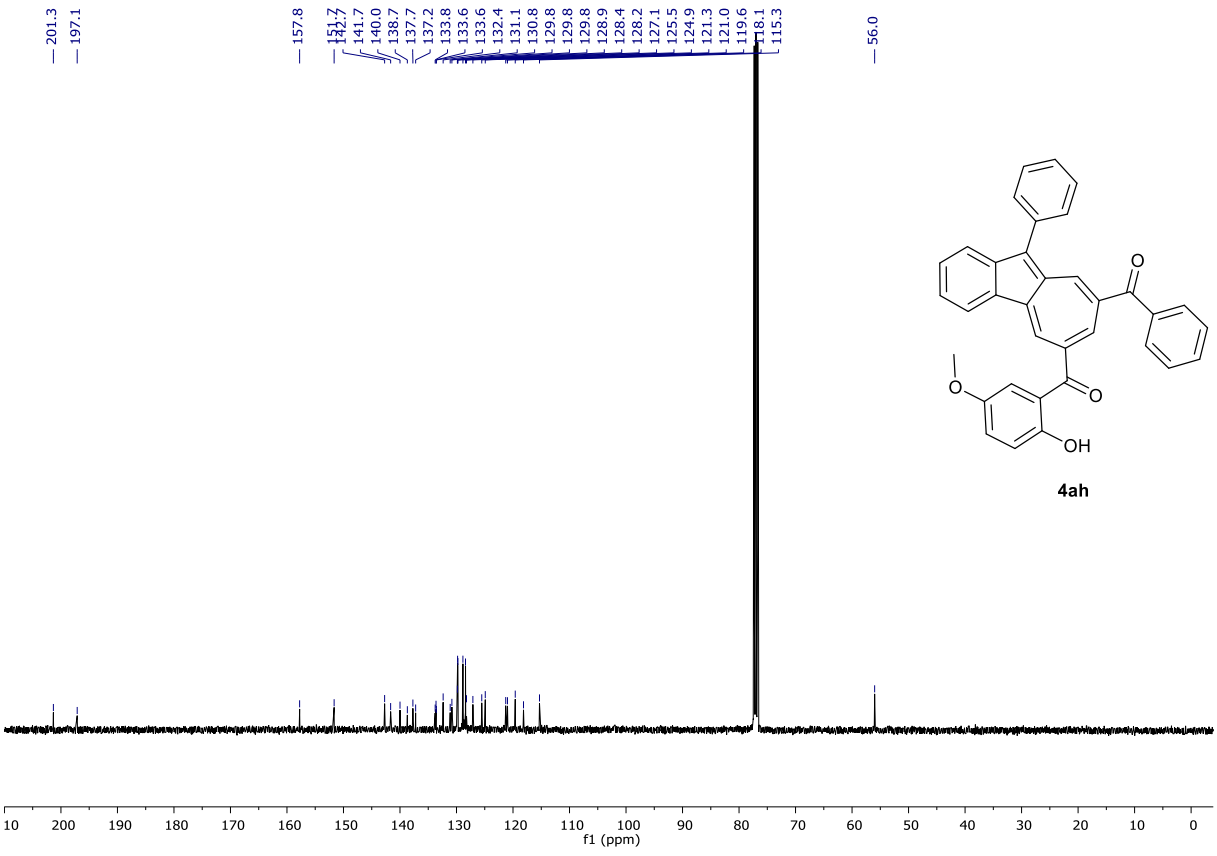
4ah

^{1}H NMR



4ah

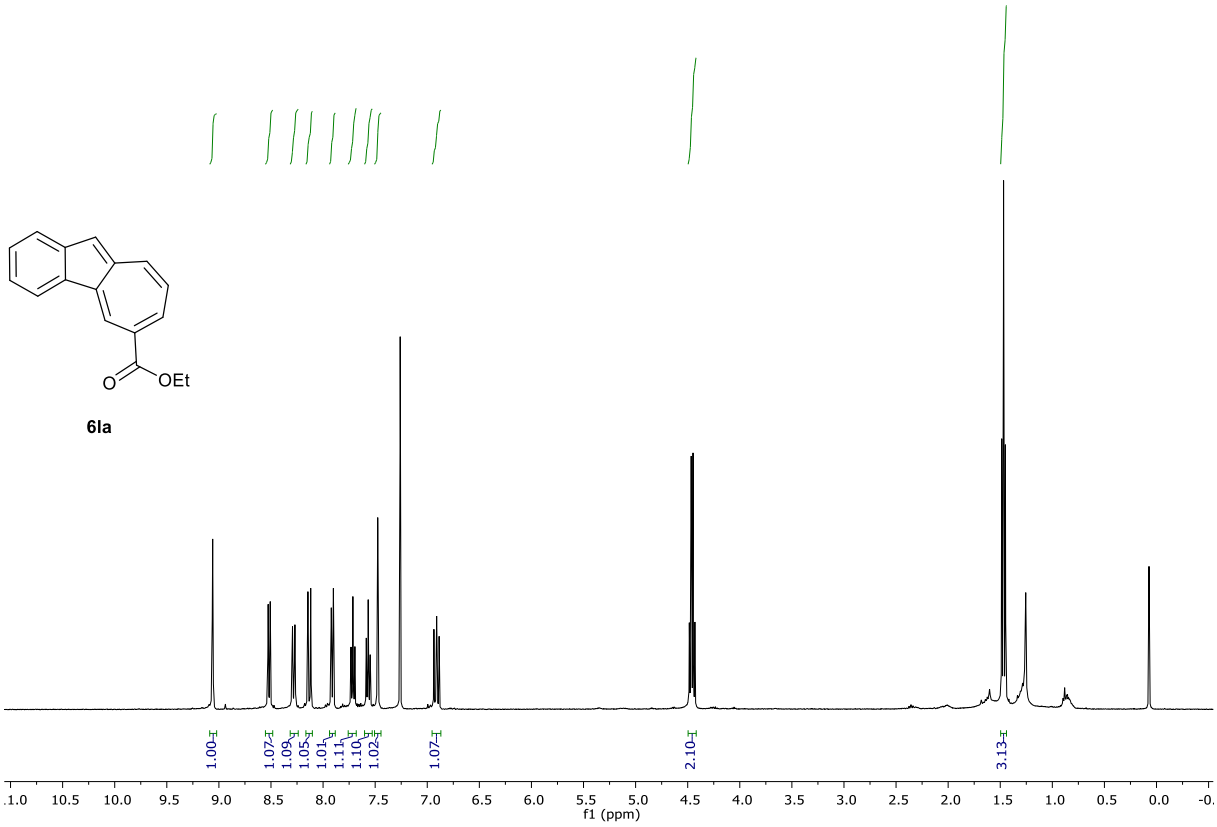
^{13}C NMR



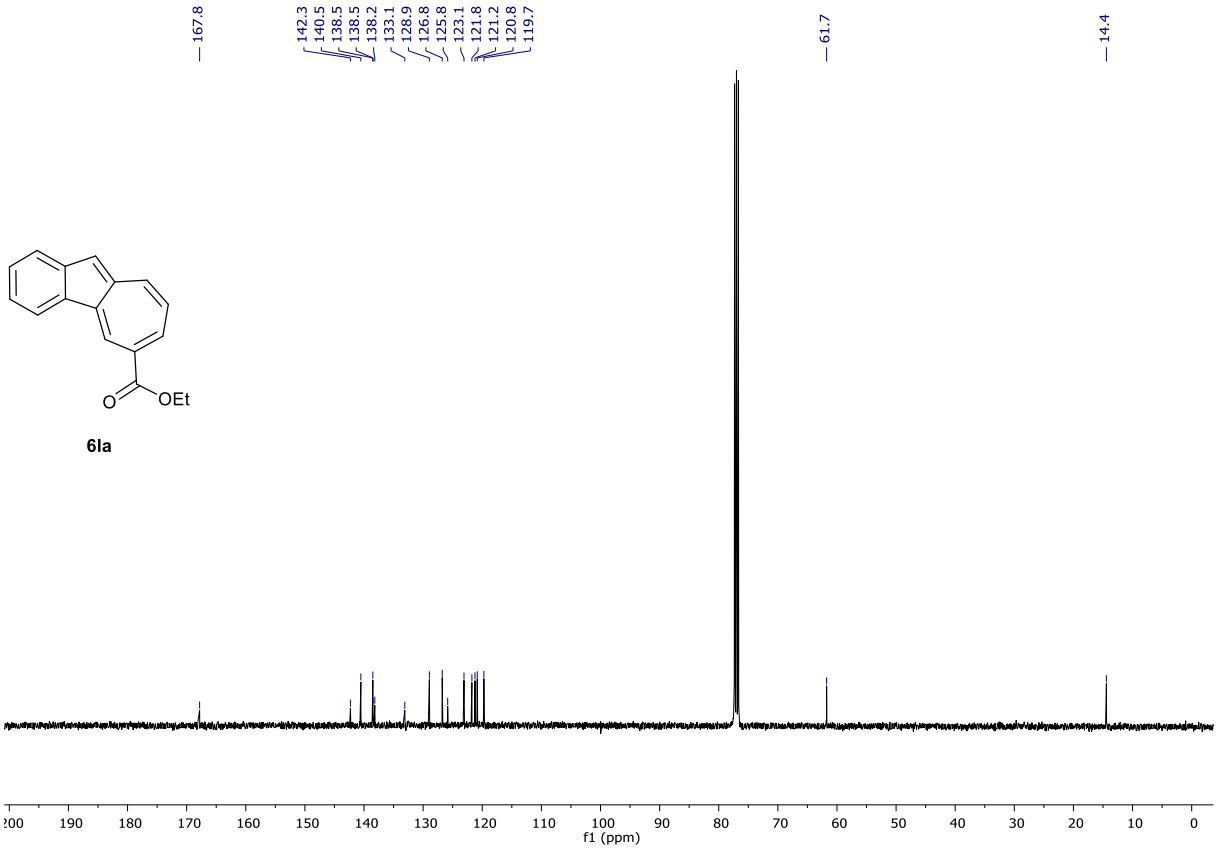
4ah

6la

^{1}H NMR

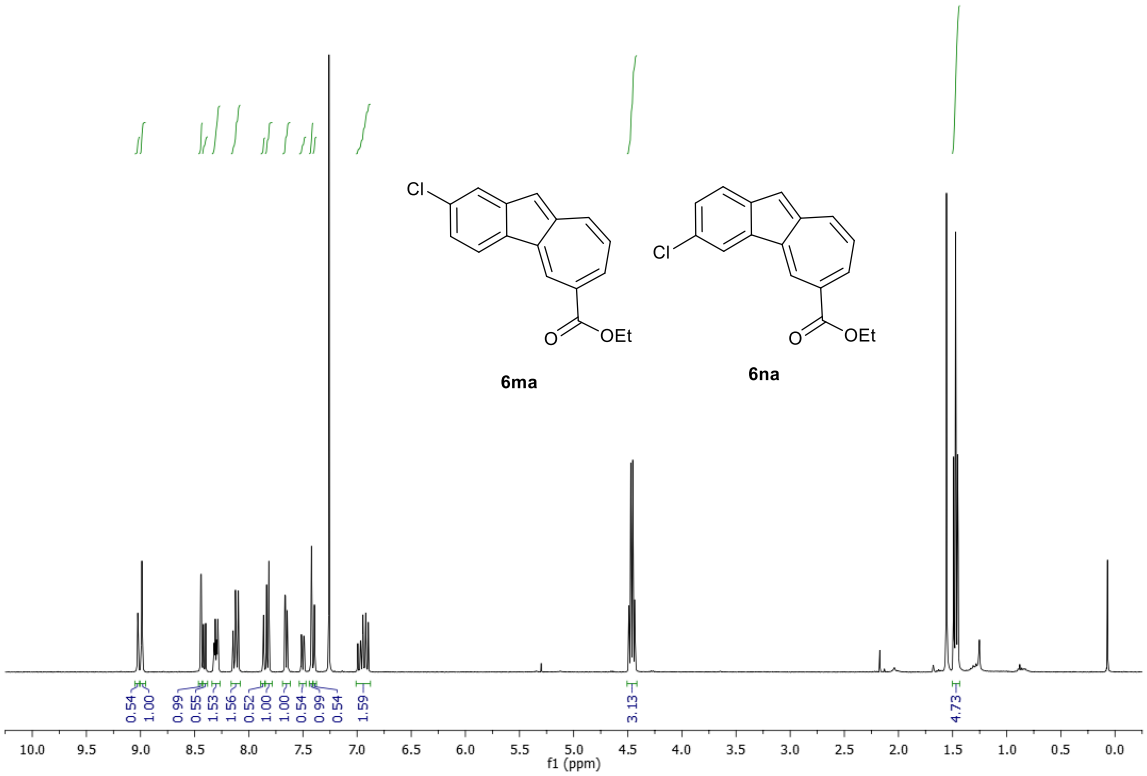


^{13}C NMR

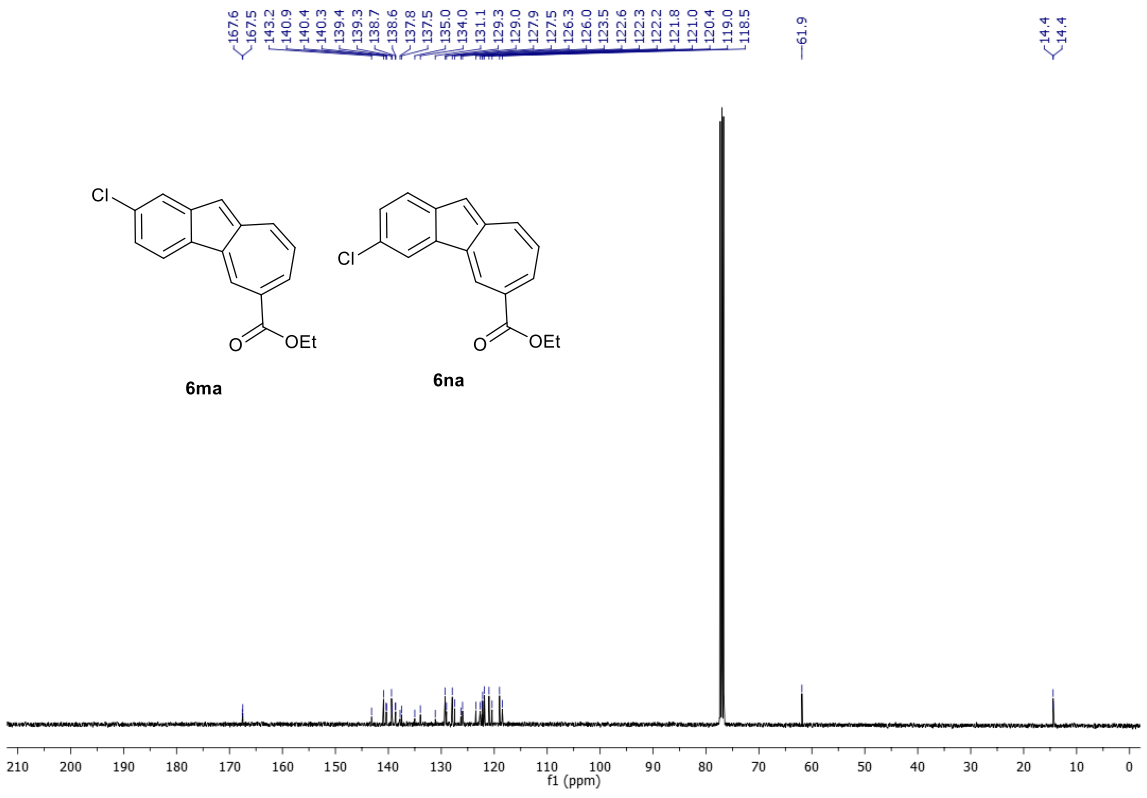


6ma/6na

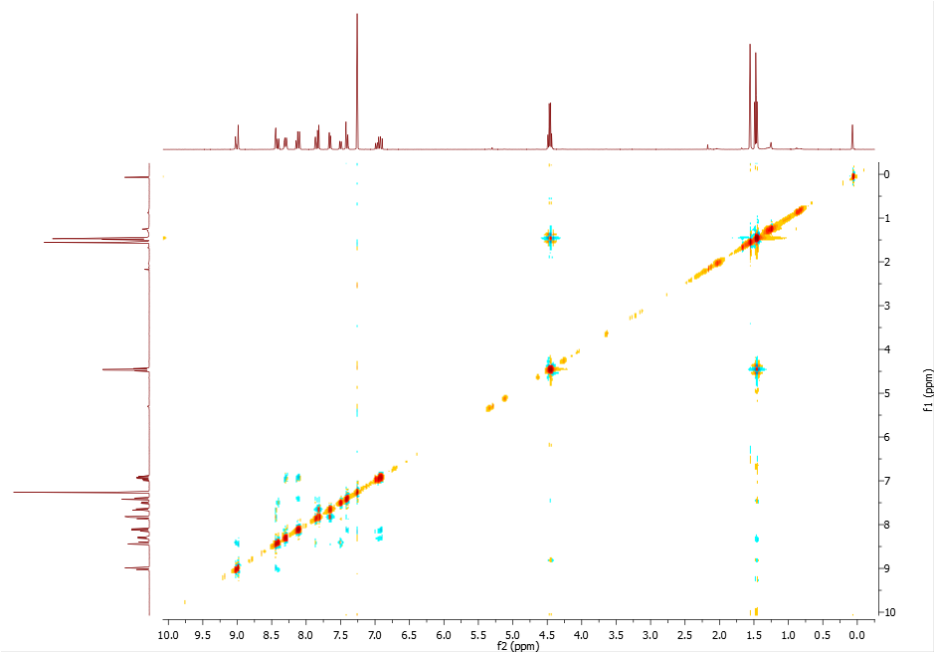
^{1}H NMR



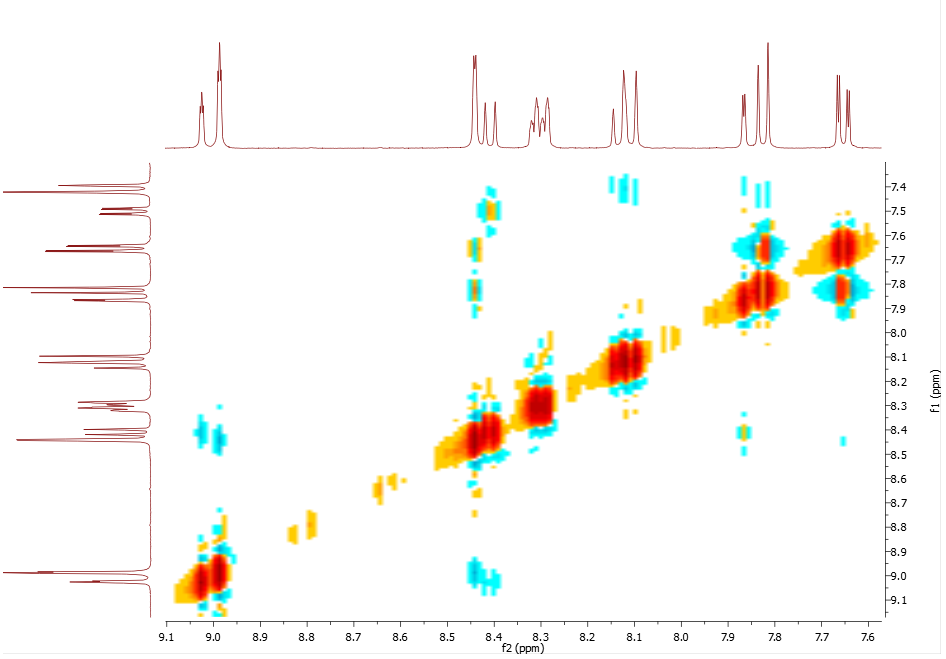
^{13}C NMR



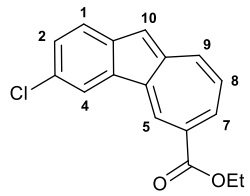
NOESY spectrum of **6ma** / **6na**



NOESY spectrum of **6ma** / **6na** (zoom)



The major product of the regioisomeric mixture of **6ma** and **6na** is assigned to be **6na** based on the following NOESY couplings.

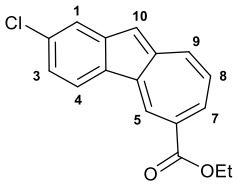


6na

Signal (1) δ	Assignment (1)	NOESY coupling to signal(s) (2) δ	Assignment (2)
8.99 (t, *J* = 1.3 Hz, 1H)	H5	8.44 (d, *J* = 1.8 Hz, 1H)	H4
8.44 (d, *J* = 1.8 Hz, 1H)	H4	8.99 (t, *J* = 1.3 Hz, 1H) 7.65 (dd, *J* = 8.4, 1.9 Hz, 1H) 7.83 (d, *J* = 8.4 Hz, 1H)	H5 H2 H1
7.65 (dd, *J* = 8.4, 1.9 Hz, 1H)	H2	8.44 (d, *J* = 1.8 Hz, 1H) 7.83 (d, *J* = 8.4 Hz, 1H)	H4 H1

Based on the small coupling constant of H4 (d, *J* = 1.8 Hz) relative to H2 (dd, *J* = 8.4, 1.9 Hz) and H1 (7.83 (d, *J* = 8.4 Hz, 1H)), the major product of the regioisomeric mixture is assigned to be the 3-Cl-substituted **6na**.

The minor product of the regioisomeric mixture of **6ma** and **6na** is assigned to be **6ma** based on the highlighted NOESY couplings.



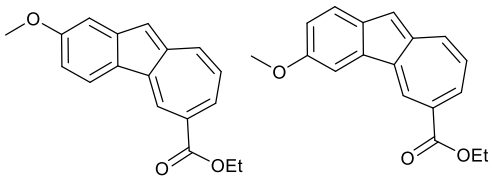
6ma

Signal (1) δ	Assignment (1)	NOESY coupling to signal(s) (2) δ	Assignment (2)
9.03 (t, *J* = 1.3 Hz, 1H)	H5	8.41 (d, *J* = 8.5 Hz, 1H)	H4
8.41 (d, *J* = 8.5 Hz, 1H)	H4	9.03 (t, *J* = 1.3 Hz, 1H) 7.50 (dd, *J* = 8.4, 1.9 Hz, 1H)	H5 H3
7.50 (dd, *J* = 8.4, 1.9 Hz, 1H)	H3	8.41 (d, *J* = 8.5 Hz, 1H) 7.87 (d, *J* = 1.8 Hz, 1H)	H4 H1

Based on the small coupling constant of H1 (d, *J* = 1.8 Hz, 1H) relative to H3 (dd, *J* = 8.4, 1.9 Hz, 1H) and H4 (d, *J* = 8.5 Hz, 1H), the minor product of the regioisomeric mixture is assigned to be the 2-Cl-substituted **6ma**.

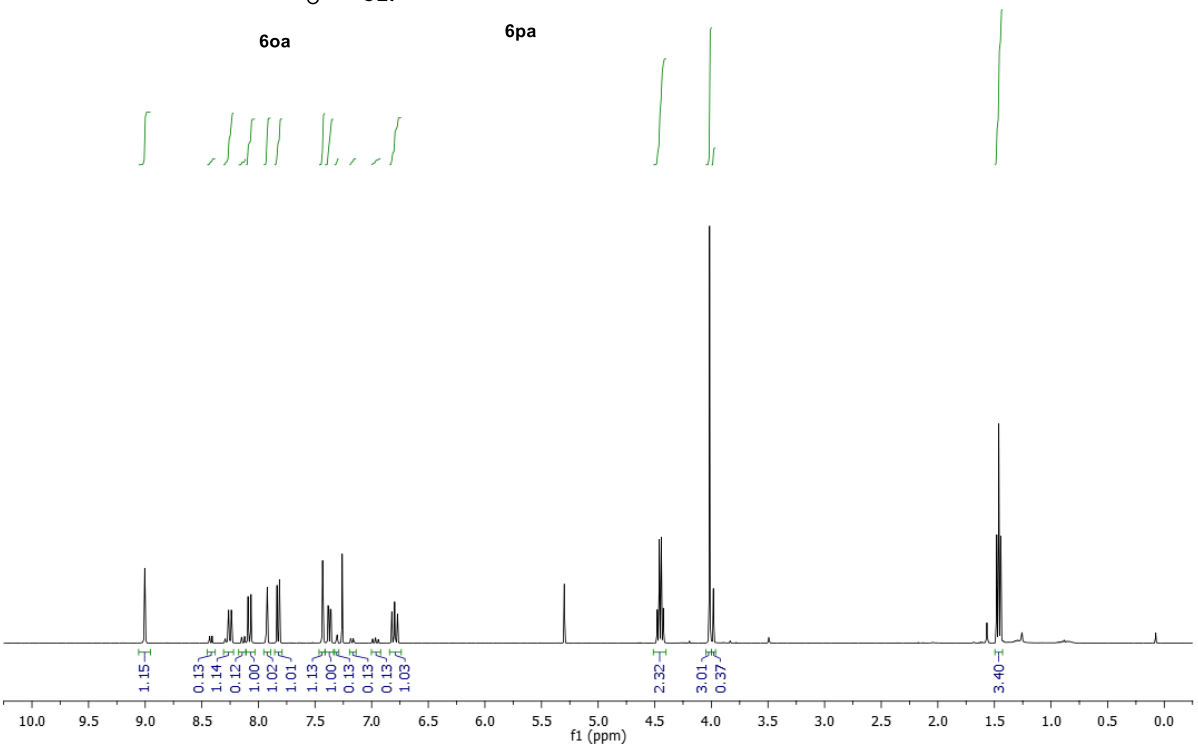
6oa/6pa

^{1}H NMR

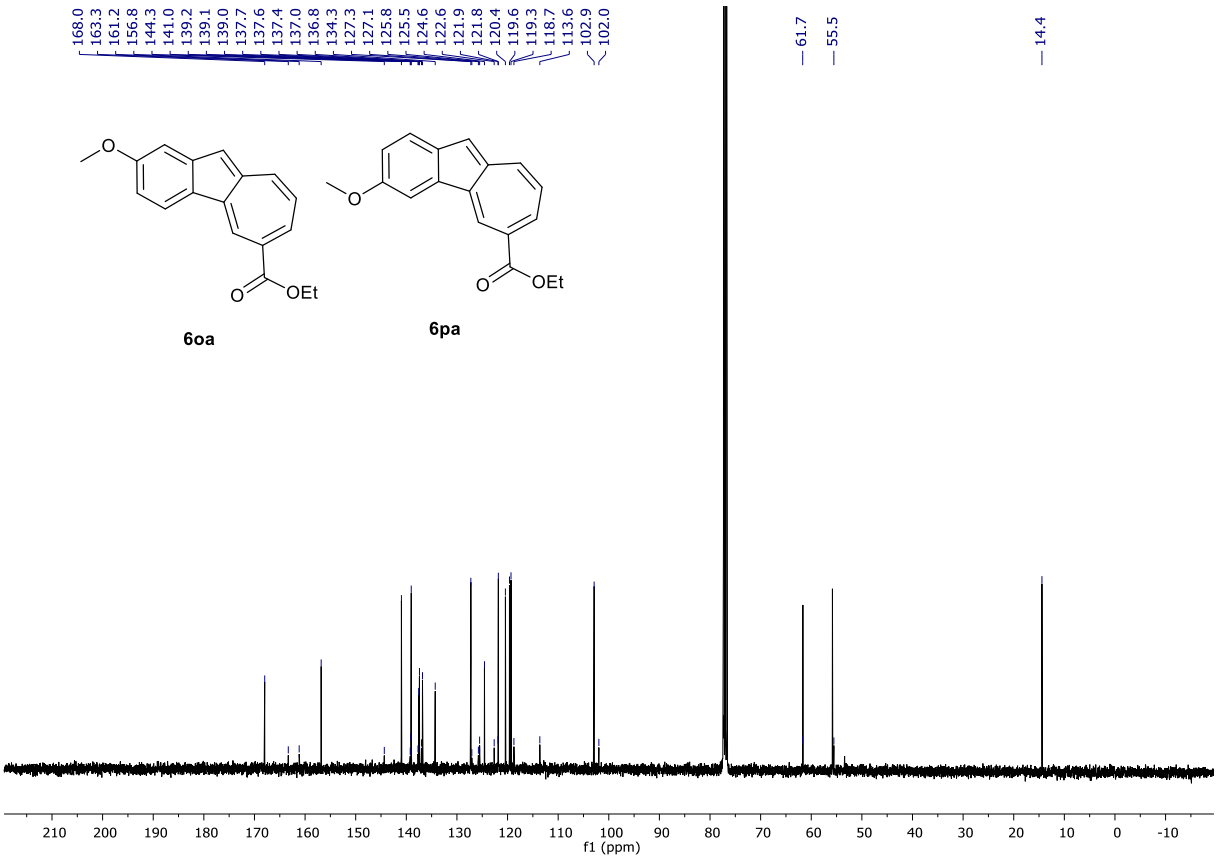


6oa

6pa



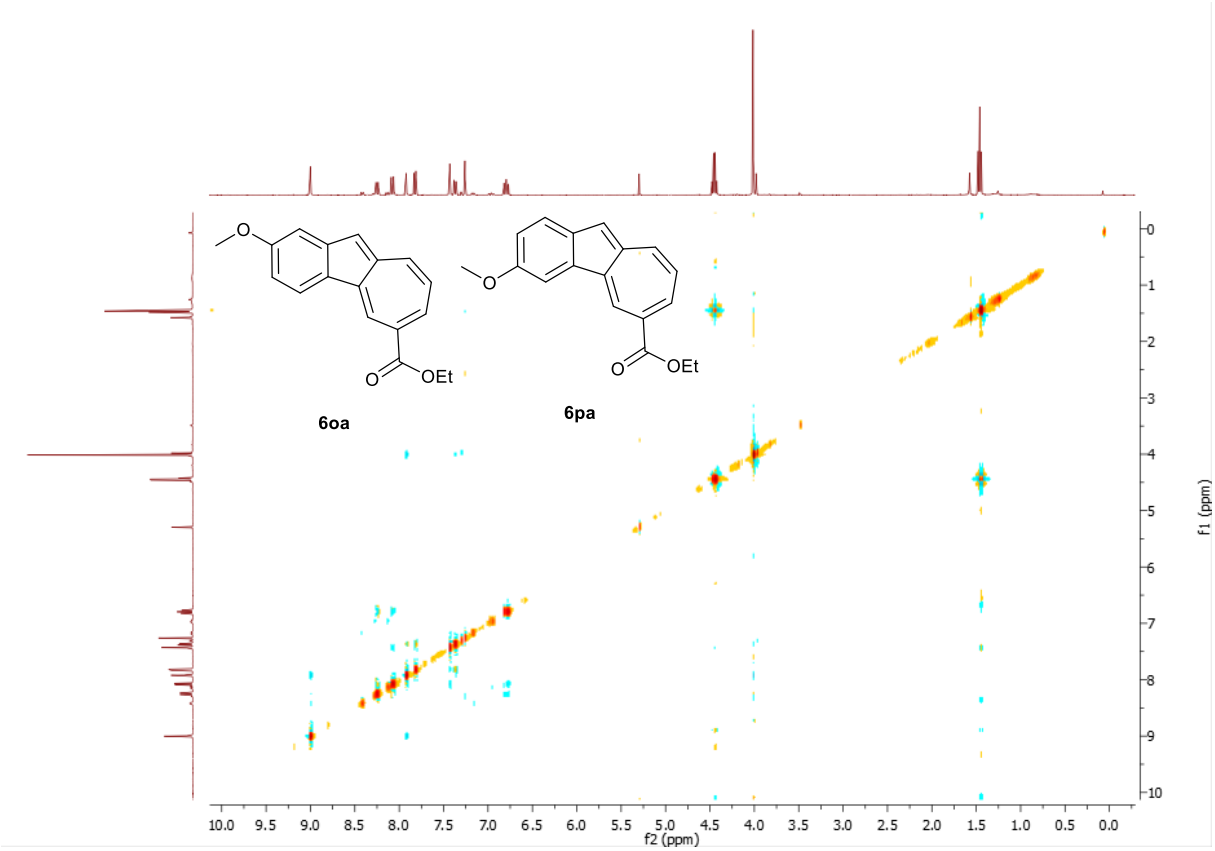
^{13}C NMR



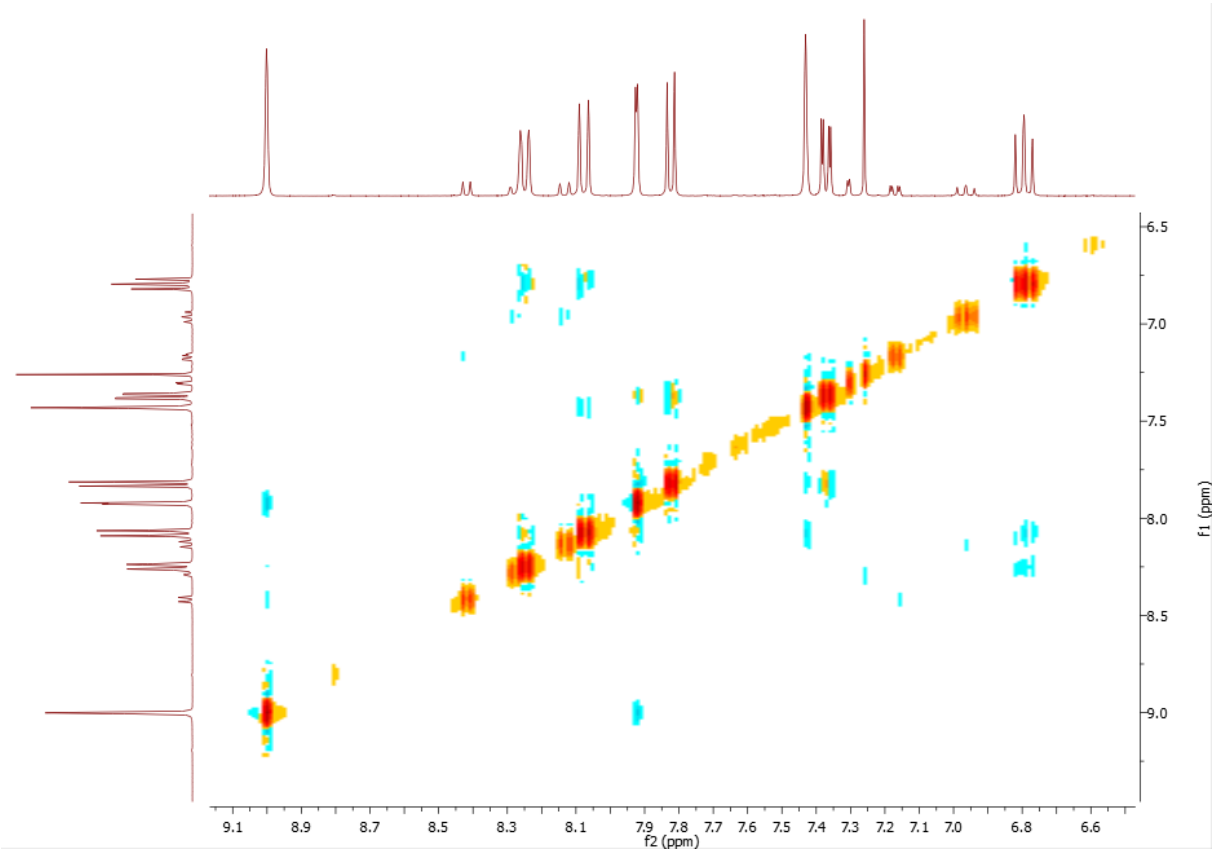
6oa

6pa

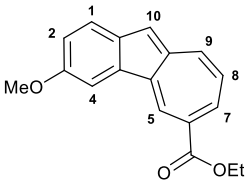
NOESY spectrum of **6oa** / **6pa**



NOESY spectrum of **6oa** / **6pa** (zoom)



The major product of the regioisomeric mixture is assigned to be **6pa** based on the following NOESY couplings.

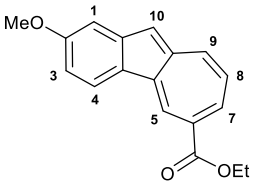


6pa

Signal (1) δ	Assignment (1)	NOESY coupling to signal(s) (2) δ	Assignment (2)
9.03-8.98 (m, 1H)	H5	7.92 (d, *J* = 2.2 Hz, 1H)	H4
7.92 (d, *J* = 2.2 Hz, 1H)	H4	9.03-8.98 (m, 1H) 7.37 (dd, *J* = 8.6, 2.3 Hz, 1H)	H5 H2
7.37 (dd, *J* = 8.6, 2.3 Hz, 1H)	H2	7.92 (d, *J* = 2.2 Hz, 1H) 7.83 (d, *J* = 8.6 Hz, 1H)	H4 H1

Based on the small coupling constant of H4 (d, *J* = 2.2 Hz) relative to H2 (dd, *J* = 8.6, 2.3 Hz) and H1 (d, *J* = 8.6 Hz), the major product of the regioisomeric mixture is assigned to be the 3-MeO-substituted **6pa**.

The minor product of the regioisomeric mixture is assigned to be **6oa** based on the following NOESY couplings.



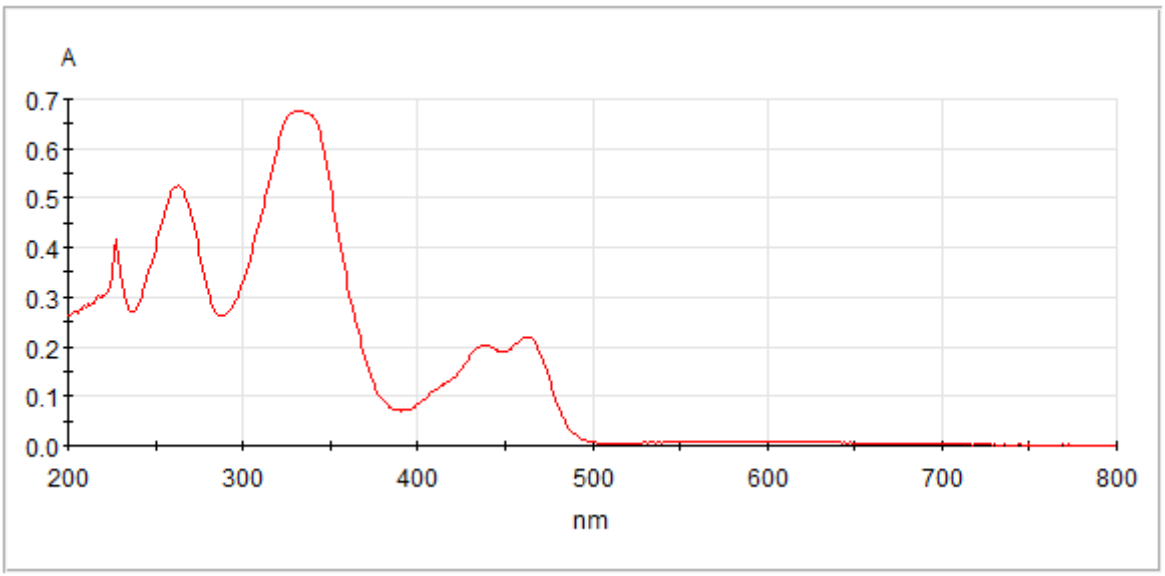
6oa

Signal (1) δ	Assignment (1)	NOESY coupling to signal(s) (2) δ	Assignment (2)
9.03-8.98 (m, 1H)	H5	8.42 (d, *J* = 8.7 Hz, 1H)	H4
8.42 (d, *J* = 8.7 Hz, 1H)	H4	9.03-8.98 (m, 1H) 7.17 (dd, *J* = 8.7, 2.3 Hz, 1H)	H5 H3
7.17 (dd, *J* = 8.7, 2.3 Hz, 1H)	H3	8.42 (d, *J* = 8.7 Hz, 1H)	H4

Based on the coupling constants of H4 (*J* = 8.7 Hz) and H3 (*J* = 8.7, 2.3 Hz) and the absence of additional NOESY couplings to H3, the minor product of the regioisomeric mixture is determined to be the 2-MeO-substituted **6oa**.

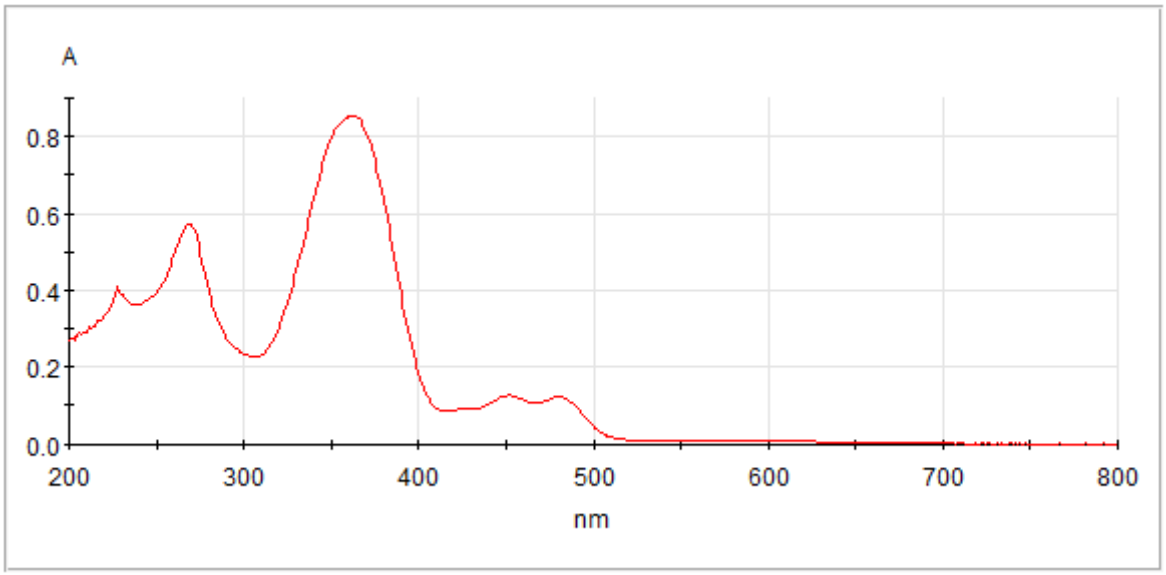
UV/Vis spectra

4aa



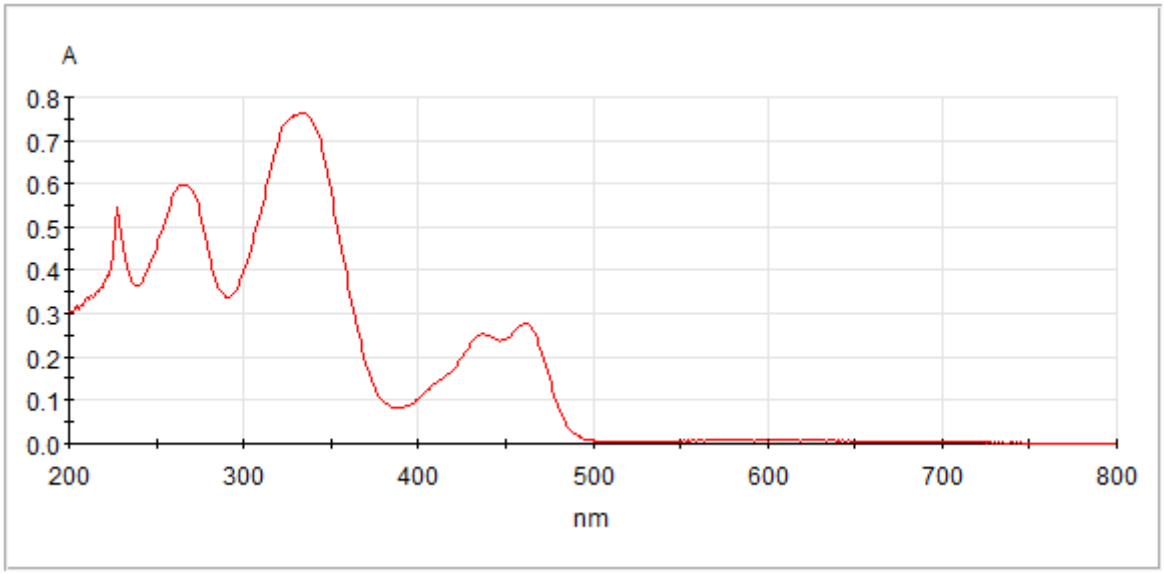
$\lambda_{max}(CH_2Cl_2)$/nm 227 (24800), 263 (31200), 330 (40100), 439 (12100), 463 (13100).

4ba



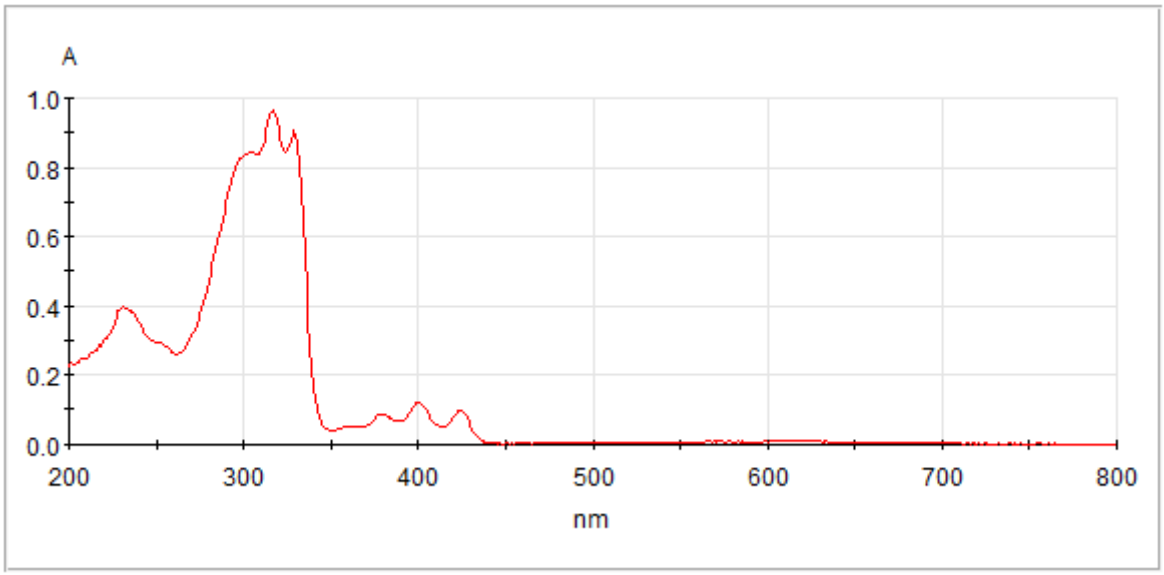
$\lambda_{max}(CH_2Cl_2)$/nm 228 (24300), 269 (34100), 362 (50900), 451 (7500), 481 (7300).

4ca



$\lambda_{max}(CH_2Cl_2)$/nm 227 (32800), 265 (36000), 334 (45800), 438 (15200), 461 (16700).

6la



$\lambda_{max}(CH_2Cl_2)$/nm 231 (14800), 304 (31700), 317 (36200), 329 (33900), 379 (3200), 400 (4500), 424 (3700).