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Intermolecular dearomative [4+2] cycloaddition of naphthalenes via visible-light energy-transfer-catalysis

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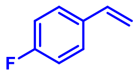
1. General Information

Unless specified otherwise, all the reactions have been performed under an inert atmosphere (Ar) or (N_2) in oven-dried glassware. Reaction temperatures correspond to the temperature of the bath surrounding the vessel. Analytics: ^{1}H, ^{13}C, and ^{19}F NMR spectra have been recorded on Bruker (^{1}H: 500 MHz, ^{13}C {^{1}H}: 126 MHz, ^{19}F {^{1}H}: 470 MHz) and JEOL (^{1}H: 400 MHz, ^{13}C {^{1}H}: 101 MHz, ^{19}F {^{1}H}: 376 MHz) at room temperature and were referenced to the resonances of the solvent used. Multiplicities have been indicated as: br (broad), s (singlet), d (doublet), t (triplet), dd (doublet of doublet), dt (doublet of triplet) or m (multiplet). Coupling constants (J) are reported in Hertz (Hz). FT-IR spectra were recorded by Perkin–Elmer FT–IR Spectrometer. Mass spectra were recorded on Bruker micrOTOF-Q II Spectrometer. UV−vis spectral studies were carried out using an Agilent diode array Cary-8454 spectrophotometer. Photoluminescence emissions were acquired on a spectrofluorometer (Fluoremax X instrument) at room temperature. For thin-layer chromatography (TLC) analysis, Merck pre-coated TLC plates (silica gel 60 F254 0.25 mm) were used, and visualization was accomplished by UV light (254 nm), I_2, $KMnO_4$, and cerium ammonium molybdate.

Chemicals: Commercially available chemicals were bought from Sigma–Aldrich, Alfa–Aesar, Avra Synthesis, BLD Pharma, and used without further purification. Dry solvents were prepared according to the standard procedure and degassed by freeze–pump–thaw cycles prior to use. No attempts were made to optimize yields for substrate and catalyst.

2. Numbering of starting materials

Styrene derivatives



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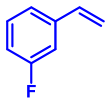

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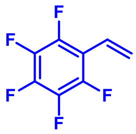

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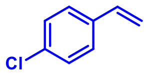

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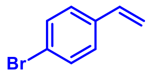

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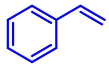

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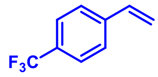

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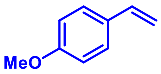

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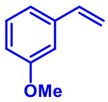

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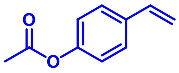

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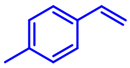

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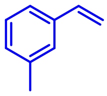

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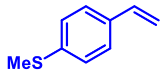

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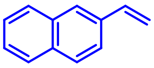

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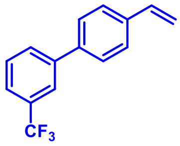

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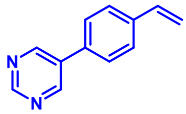

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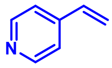

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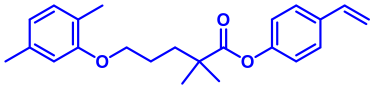

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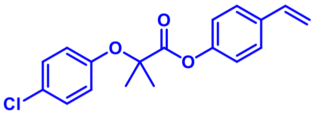

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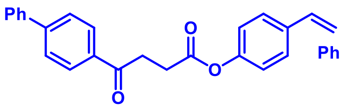

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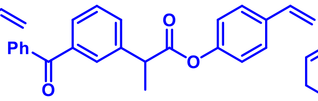

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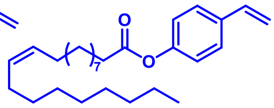

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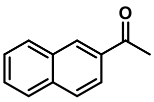
Naphthalene derivatives



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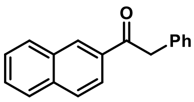

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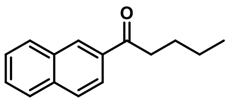

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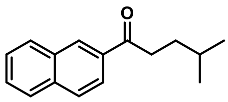

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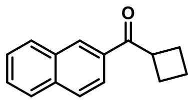

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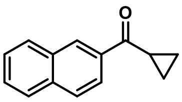

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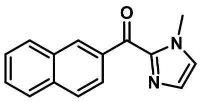

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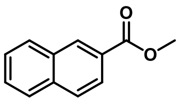

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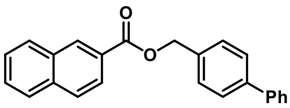

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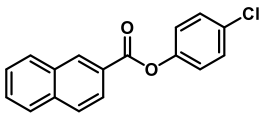

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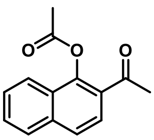

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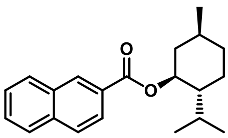

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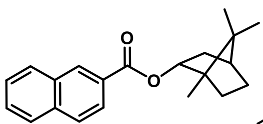

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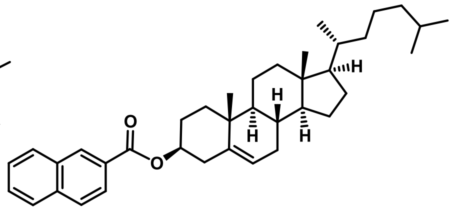


S38

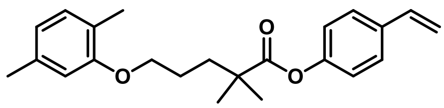
3. Synthesis of starting material and characterization

3.1. General procedure A for the synthesis of styrene derivatives[1]

In a 50 mL round-bottomed flask fitted with a magnetic stir bar, a mixture of 4-hydroxy styrene (3 mmol), corresponding acid (3 mmol), and DMAP (10 mol%) was dissolved in CH_2Cl_2. The mixture was placed in an ice bath and stirred for 10 min before DCC (3 mmol) was added. The mixture was allowed to stir at room temperature for 16 h. The solid precipitate was filtered and washed twice with CH_2Cl_2. The combined organic layers were washed with water, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the corresponding products (EtOAc in hexane=2-20%).

Compounds **S21**, **S22**, **S23**, **S24** and **S25** were synthesized according to this procedure.

4-vinylphenyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate:



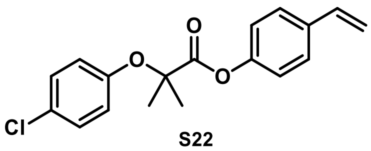
S21

Isolated yield: 814 mg (77%, 2.31 mmol), white solid.

R_f: 0.7, Eluent: Ethyl acetate in Hexane 10% mixture.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 8.4, 1.7 Hz, 2H), 7.05 – 6.99 (m, 3H), 6.77 – 6.64 (m, 3H), 5.72 (d, *J* = 17.6 Hz, 1H), 5.26 (dd, *J* = 10.9, 1.5 Hz, 1H), 4.07 – 3.97 (m, 2H), 2.33 (s, 3H), 2.21 (s, 3H), 1.91 (d, *J* = 1.8 Hz, 4H), 1.40 (s, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 176.4, 157.0, 150.7, 136.6, 136.1, 135.3, 130.5, 127.3, 123.8, 121.7, 120.9, 114.0, 112.1, 67.9, 42.6, 37.3, 25.4, 25.3, 21.5, 15.9.

4-vinylphenyl 2-(4-chlorophenoxy)-2-methylpropanoate:



S22

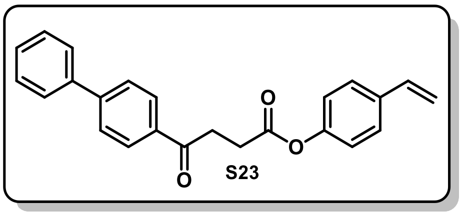
Isolated yield: 513 mg (54%, 1.62 mmol), white solid.

R_f: 0.7, Eluent: Ethyl acetate in Hexane 10% mixture.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 2H), 7.24 – 7.14 (m, 2H), 6.94 – 6.89 (m, 2H), 6.89 – 6.81 (m, 2H), 6.63 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.64 (d, *J* = 17.6 Hz, 1H), 5.19 (d, *J* = 10.8 Hz, 1H), 1.67 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.7, 154.1, 150.1, 135.9, 135.9, 129.4, 127.7, 127.4, 121.4, 120.7, 114.4, 79.7, 25.5.

4-vinylphenyl 4-([1,1'-biphenyl]-4-yl)-4-oxobutanoate:



Isolated yield: 588 mg, (1.65 mmol, 55%), off white solid.

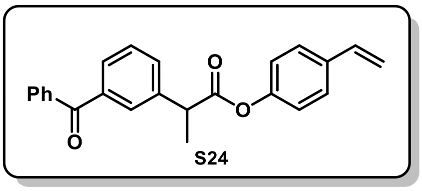
R_f: 0.6, Eluent: Ethyl acetate in Hexane 8% mixture.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 7.0 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.45 – 7.37 (m, 3H), 7.10 (d, *J* = 8.7 Hz, 2H), 6.70 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.71 (d, *J* = 17.5 Hz, 1H), 5.24 (d, *J* = 11.0 Hz, 1H), 3.46 (t, *J* = 6.6 Hz, 2H), 3.04 (t, *J* = 6.6 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 200.1, 174.2, 153.0, 148.7, 142.5, 138.6, 138.0, 137.8, 131.6, 131.3, 130.9, 130.0, 129.9, 129.8, 124.3, 116.6, 36.1, 31.2.

HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{18}H_{17}ClO_3Na$, 339.0758, found 339.0732.

4-vinylphenyl 2-(3-benzoylphenyl)propanoate:



Isolated yield: 481 mg (45%, 1.35 mmol), white solid.

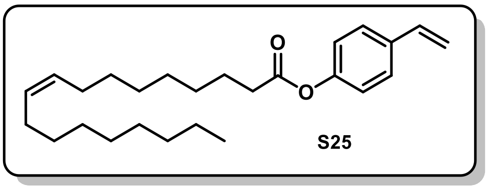
R_f: 0.6, Eluent: Ethyl acetate in Hexane 8% mixture.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (t, *J* = 1.8 Hz, 1H), 7.83 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.77 – 7.72 (m, 1H), 7.69 – 7.63 (m, 1H), 7.63 – 7.57 (m, 1H), 7.55 – 7.44 (m, 3H), 7.42 – 7.35 (m, 2H), 7.05 – 6.95 (m, 2H), 6.69 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.70 (d, *J* = 17.6 Hz, 1H), 5.24 (d, *J* = 10.8 Hz, 1H), 4.06 (q, *J* = 7.1 Hz, 1H), 1.67 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 196.4, 172.5, 150.3, 140.4, 138.2, 137.5, 135.9, 135.5, 132.6, 131.6, 130.1, 129.3, 129.3, 128.8, 128.4, 127.2, 121.4, 114.1, 45.6, 18.5.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{24}H_{21}O_3$, 357.1485, found 357.1474.

4-vinylphenyl oleate:



S25

Isolated yield: 619 mg, (50%, 1.5 mg), colourless liquid.

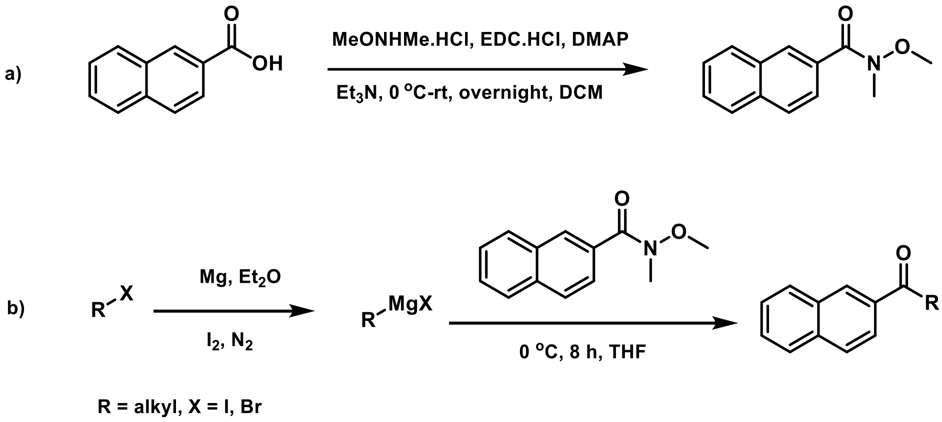
R*f*: 0.5, Eluent: Ethyl acetate in Hexane 4% mixture.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.41 (d, *J* = 8.6 Hz, 2H), 7.09 – 6.99 (m, 2H), 6.70 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.70 (d, *J* = 17.7 Hz, 1H), 5.41 – 5.32 (m, 2H), 5.24 (d, *J* = 11.0 Hz, 1H), 2.55 (t, *J* = 7.5 Hz, 2H), 2.13 – 1.92 (m, 4H), 1.76 (p, *J* = 7.5 Hz, 2H), 1.47 – 1.32 (m, 10H), 1.32 – 1.24 (m, 10H), 0.89 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 172.4, 150.5, 136.1, 135.4, 130.2, 129.9, 127.3, 121.8, 114.1, 34.5, 32.1, 29.9, 29.8, 29.7, 29.5, 29.3, 29.2, 27.4, 27.3, 25.1, 22.8, 14.2.

HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{26}H_{40}O_2Na$, 407.2921, found 407.2914.

3.2. General procedure B for the synthesis of naphthalene derivatives[2]

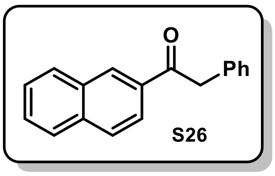


In a 100 mL round-bottomed flask fitted with a magnetic stir bar, a mixture of the naphthoic acid (10 mmol), *N,O*-dimethylhydroxylamine hydrochloride (13 mmol), and DMAP (1 mmol) in CH_2Cl_2 (50 mL) was kept at 0 °C. After 5 min, NEt_3 (13 mmol) and EDC (13 mmol) were added successively. The reaction mixture was stirred at 0 °C for 1 h, then allowed to warm to room temperature, and stirred overnight. The CH_2Cl_2 was evaporated and then diluted with EtOAc (60 mL). The organic layer was washed with 1 *N* HCl (3 x10 mL) and aqueous saturated $NaHCO_3$ (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the Weinreb amide (EtOAc in hexane = 30%). R_f = 0.5.

In an oven-dried two-neck round-bottomed flask fitted with a magnetic stir bar was added magnesium turnings (6 mmol), a small amount of iodine, followed by Et_2O (6 mL) at 0 ºC. Then alkyl halide (3 mmol) was added dropwise to the solution. The solution was allowed to stir at room temperature for 2 h. The Weinreb amide (2.5 mmol) in THF was then added before keeping the reaction mixture at 0 ºC. After 6 h, the reaction mixture was quenched with cold water and diluted with CH_2Cl_2. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the naphthalene derivatives (EtOAc in hexane = 2-5%).

Compounds **S26**, **S27**, **S28**, **S29**, and **S30** were synthesized according to this procedure.

1-(naphthalen-2-yl)-2-phenylethan-1-one:

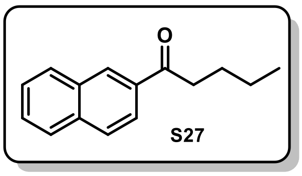


Isolated yield: 467 mg (76%, 1.9 mmol), white solid.

R_f: 0.6, Eluent: Ethyl acetate in Hexane 5% mixture.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61 – 8.55 (m, 1H), 8.14 – 8.06 (m, 1H), 7.99 (t, *J* = 7.5 Hz, 1H), 7.90 (q, *J* = 8.0 Hz, 2H), 7.68 – 7.52 (m, 2H), 7.42 – 7.31 (m, 4H), 7.31 – 7.21 (m, 1H), 4.47 – 4.40 (m, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 197.7, 135.7, 134.8, 134.1, 132.6, 130.5, 129.7, 129.6, 128.8, 128.6, 127.9, 127.0, 126.9, 124.4, 77.4, 77.2, 76.9, 45.7.
HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{18}H_{14}NaO$, 269.0937, found 269.0962.

1-(naphthalen-2-yl)pentan-1-one:



Isolated yield: 312 mg (59%, 1.5 mmol), white solid.

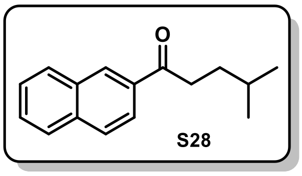
R_f: 0.5, Eluent: Ethyl acetate in Hexane 5% mixture.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 (d, *J* = 2.0 Hz, 1H), 8.04 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.88 (dd, *J* = 9.9, 7.4 Hz, 2H), 7.64 – 7.50 (m, 2H), 3.13 – 3.08 (m, 2H), 1.83 – 1.76 (m, 2H), 1.49 – 1.43 (m, 2H), 0.99 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 200.7, 135.7, 134.6, 132.7, 129.7, 129.7, 128.5, 128.5, 127.9, 126.8, 124.1, 38.6, 26.8, 22.7, 14.1.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{16}NaO$, 235.1093, found 235.1083.

4-methyl-1-(naphthalen-2-yl)pentan-1-one:



Isolated yield: 350 mg (62%, 1.5 mmol), white solid.

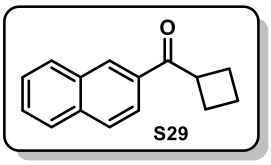
R*f*: 0.5, Eluent: Ethyl acetate in Hexane 5% mixture.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 – 8.44 (m, 1H), 8.04 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.96 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.87 (t, *J* = 8.8 Hz, 2H), 7.63 – 7.51 (m, 2H), 3.11 – 3.07 (m, 2H), 1.75 – 1.68 (m, 3H), 0.99 (d, *J* = 6.3 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 200.7, 135.5, 134.4, 132.6, 129.6, 129.6, 128.4, 128.3, 127.8, 126.7, 124.0, 77.3, 77.1, 76.8, 36.7, 33.4, 27.9, 22.5.

HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{16}H_{18}NaO$, 249.1250, found 249.1279.

cyclobutyl(naphthalen-2-yl)methanone:



Isolated yield: 242 mg (45%, 1.2 mmol), white solid.

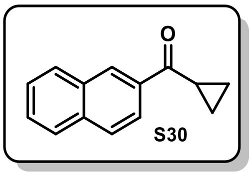
R*f*: 0.6, Eluent: Ethyl acetate in Hexane 5% mixture.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (s, 1H), 8.00 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.94 (dd, *J* = 8.2, 2.5 Hz, 1H), 7.89 – 7.81 (m, 2H), 7.61 – 7.49 (m, 2H), 4.19 – 4.07 (m, 1H), 2.54 – 2.44 (m, 2H), 2.41 – 2.32 (m, 2H), 2.18 – 2.06 (m, 1H), 2.00 – 1.89 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 201.0, 135.6, 133.0, 132.6, 129.9, 129.6, 128.4, 128.3, 127.8, 126.7, 124.3, 42.3, 25.3, 18.3.

HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{15}H_{14}NaO$, 233.0937, found 233.0942.

cyclopropyl(naphthalen-2-yl)methanone:

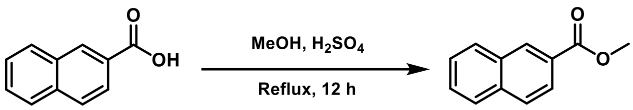


Isolated yield: 342 mg (70%, 1.7 mmol), white solid.

R_f: 0.6, Eluent: Ethyl acetate in Hexane 3% mixture.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (d, J = 1.8 Hz, 1H), 8.11 – 8.02 (m, 1H), 7.98 (d, J = 7.9 Hz, 1H), 7.93 – 7.85 (m, 2H), 7.65 – 7.48 (m, 2H), 2.89 – 2.78 (m, 1H), 1.36 – 1.27 (m, 2H), 1.14 – 1.04 (m, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 200.6, 135.6, 135.5, 132.7, 129.7, 128.5, 128.4, 127.9, 126.8, 124.1, 17.4, 11.8.
HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{14}H_{12}NaO$, 219.0780, found 219.0764.

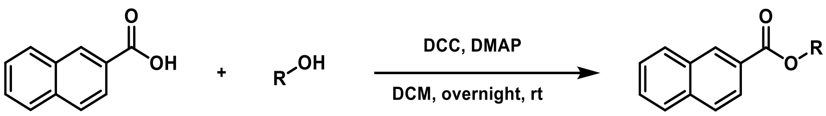
3.3. General procedure C for the synthesis of naphthalene derivatives[3]



In a 50 mL round-bottomed flask fitted with a magnetic stir bar, was added naphthoic acid (2 mmol), and sulphuric acid (0.2 mL), followed by methanol (6 mL). The reaction mixture was refluxed for 12 h. The mixture was diluted with ethyl acetate (25 mL) and water. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the corresponding product and referenced with the reported literature. (EtOAc in hexane = 5%), R_f = 0.6

Isolated yield: 260.4 mg (70%, 1.4 mmol), white solid.

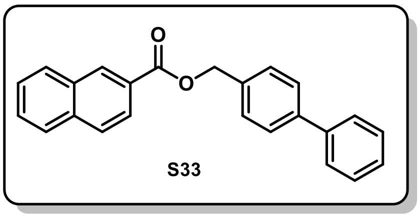
3.4. General procedure D for the synthesis of naphthalene derivatives[1]



In a 50 mL round-bottomed flask fitted with a magnetic stir bar, the mixture of naphthoic acid (3 mmol), corresponding alcohol (3 mmol), and DMAP (10 mol%) were dissolved in DCM and kept at 0 ^{o}C. After 10 min DCC was added to the reaction mixture. The mixture was allowed to stir at room temperature for 8 h. The solid precipitate was filtered out by washing with CH_2Cl_2 two times. The combined organics were washed with distilled water, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the corresponding products (EtOAc in hexane=1-5%).

Compounds **S33**, **S34**, **S35**, **S36**, and **S37** were synthesized according to this procedure

[1,1'-biphenyl]-4-ylmethyl 2-naphthoate:



Isolated yield: 781.7 mg (77%, 2.31 mmol), white solid.

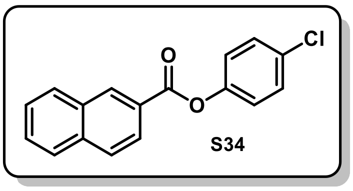
R*f*: 0.6, Eluent: Ethyl acetate in Hexane 5% mixture.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.19 – 8.11 (m, 1H), 7.98 (d, *J* = 8.1 Hz, 1H), 7.90 (dd, *J* = 8.4, 5.7 Hz, 2H), 7.69 – 7.55 (m, 8H), 7.50 – 7.43 (m, 2H), 7.40 (dd, *J* = 7.8, 1.3 Hz, 1H), 5.51 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.7, 141.4, 140.8, 135.7, 135.2, 132.6, 131.4, 129.5, 128.9, 128.9, 128.4, 128.3, 127.9, 127.6, 127.5, 127.5, 127.3, 126.8, 125.4, 66.7.

HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{24}H_{18}NaO_2$ 361.1199, found 361.1183.

4-chlorophenyl 2-naphthoate:



Isolated yield: 678.5 mg (80%, 2.4 mmol), white solid.

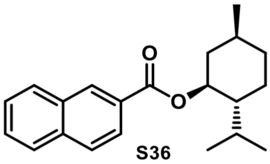
R*f*: 0.4, Eluent: Ethyl acetate in Hexane 5% mixture.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.78 (d, *J* = 1.8 Hz, 1H), 8.18 (d, *J* = 1.8 Hz, 1H), 8.01 (d, *J* = 8.1 Hz, 1H), 7.94 (dd, *J* = 13.1, 8.4 Hz, 2H), 7.65 (s, 1H), 7.59 (s, 1H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 8.7 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.2, 149.7, 136.0, 132.6, 132.2, 131.4, 129.7, 129.6, 128.9, 128.6, 128.0, 127.1, 126.5, 125.5, 123.3.

HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{17}H_{11}ClNaO_2$, 305.0340, found 305.0346.

(1S,2R,5S)-2-isopropyl-5-methylcyclohexyl 2-naphthoate:



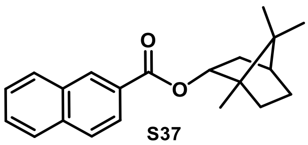
S36

Isolated yield: 736 mg (79%, 2.37 mmol), white solid.

R*f*: 0.5, Eluent: Ethyl acetate in Hexane 5% mixture.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.08 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.91 – 7.84 (m, 2H), 7.63 – 7.50 (m, 2H), 5.06 – 4.98 (m, 1H), 2.19 (d, *J* = 12.0 Hz, 1H), 2.06 – 1.99 (m, 1H), 1.79 – 1.73 (m, 2H), 1.64 – 1.56 (m, 2H), 1.17 (d, *J* = 11.5 Hz, 2H), 0.95 (dd, *J* = 6.8, 2.5 Hz, 7H), 0.83 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 166.4, 135.6, 132.7, 131.0, 129.5, 128.3, 128.2, 128.2, 127.9, 126.7, 125.5, 75.1, 47.5, 41.2, 34.5, 31.6, 26.7, 23.9, 22.2, 20.9, 16.7.
HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{21}H_{26}NaO_2$, 333.1825, found 333.1852.

(1R,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 2-naphthoate:



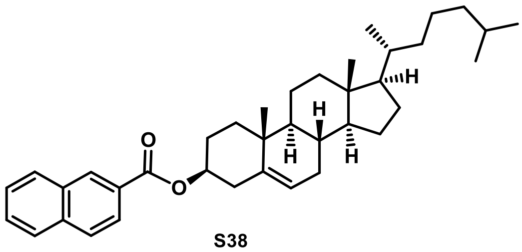
S37

Isolated yield: 749 mg (81%, 2.43 mmol), white solid.

R*f*: 0.7, Eluent: Ethyl acetate in Hexane 2% mixture.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.09 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.89 (dd, *J* = 8.4, 2.1 Hz, 2H), 7.63 – 7.51 (m, 2H), 5.23 – 5.17 (m, 1H), 2.56 – 2.49 (m, 1H), 2.27 – 2.20 (m, 1H), 1.89 – 1.80 (m, 1H), 1.77 (t, *J* = 4.5 Hz, 1H), 1.51 – 1.42 (m, 1H), 1.40 – 1.33 (m, 1H), 1.19 (dd, *J* = 13.9, 3.5 Hz, 1H), 1.00 (s, 3H), 0.95 (d, *J* = 8.7 Hz, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 167.1, 135.6, 132.6, 130.9, 129.5, 128.2, 127.9, 126.7, 125.4, 80.8, 49.3, 48.0, 45.1, 37.1, 28.3, 27.6, 19.9, 19.1, 13.8.
HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{21}H_{24}NaO_2$, 331.1674, found 331.1652.

(3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl2-naphthoate:



S38

Isolated yield: 1233 mg (76%, 2.28 mmol), white solid.

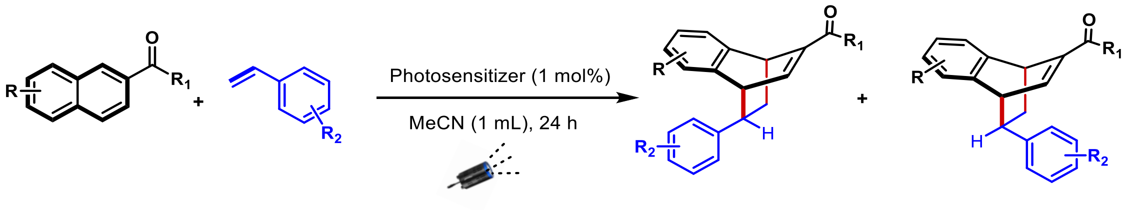
R*f*: 0.6, Eluent: Ethyl acetate in Hexane 5% mixture.

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.61 (s, 1H), 8.07 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.88 (d, *J* = 8.3 Hz, 2H), 7.61 – 7.51 (m, 2H), 5.45 (d, *J* = 5.0 Hz, 1H), 4.94 (dd, *J* = 8.6, 4.5 Hz, 1H), 2.53 (d, *J* = 8.1 Hz, 2H), 2.11 – 1.90 (m, 4H), 1.89 – 1.75 (m, 2H), 1.63 – 1.46 (m, 6H), 1.42 – 1.31 (m, 3H), 1.26 (dd, *J* = 10.4, 3.3 Hz, 2H), 1.10 (s, 9H), 1.06 – 0.97 (m, 3H), 0.93 (d, *J* = 6.5 Hz, 3H), 0.88 (dd, *J* = 6.7, 2.2 Hz, 6H), 0.70 (s, 3H).

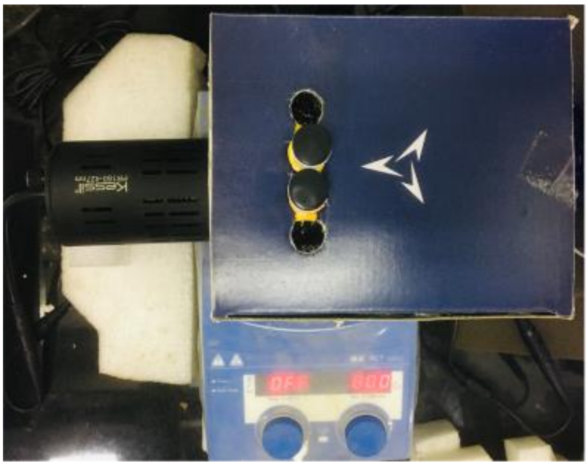
^{13}C NMR (126 MHz, CDCl$_3$) δ 166.3, 139.9, 135.6, 132.7, 131.0, 129.5, 128.3, 128.2, 128.2, 127.9, 126.7, 125.5, 123.0, 74.9, 56.9, 56.3, 50.2, 42.5, 39.9, 39.7, 38.5, 37.2, 36.8, 36.4, 36.0, 32.1, 32.1, 28.4, 28.2, 28.1, 24.5, 24.0, 23.0, 22.7, 21.2, 19.6, 18.9, 12.0.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{38}H_{52}NaO_2$, 541.4040, found 541.0468.

4. General catalytic procedure for the dearomative [4+2] cycloaddition reaction

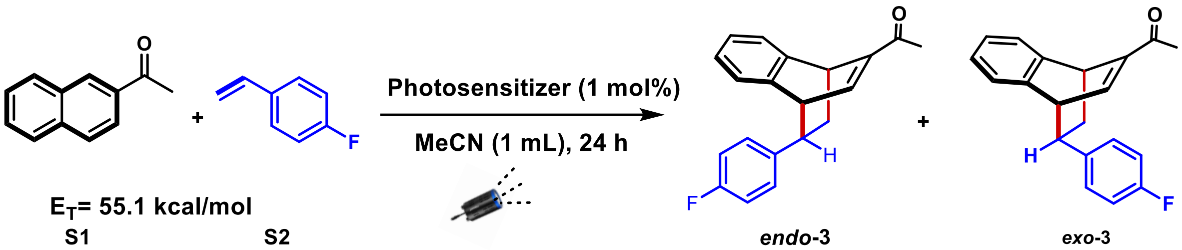


The corresponding naphthalene (0.1 mmol), and photosensitizer [Ir(dF-CF_3ppy)$_2$(dtbbpy)]PF_6 (1 mol%) were placed into a dry 15 mL sealed tube. The tube was evacuated and backfilled with nitrogen three times. Dry and degassed acetonitrile (1-2 mL) followed by alkene (0.12-0.2 mmol) was added under a nitrogen atmosphere. The tube was sealed with a screw cap, and the resulting solution was placed 5 cm away from a 427 nm Blue LED (Kessil lamp model; PR160L-427 nm, see the picture below) and irradiated for 24-48 h. Afterward, the mixture was diluted with CH_2Cl_2 (2 mL), and then 1,3,5-trimethoxy benzene (0.1 mmol) was added. The reaction mixture was filtered through a small pack of silica gel, and then the solvent was evaporated by a rotary evaporator, keeping the water bath temperature below 40 °C. The ^{1}H NMR ($CDCl_3$, 500 MHz) analysis of this crude reaction mixture was carried out to determine yields and the *endo:exo* ratios.



5. Reaction optimization reaction

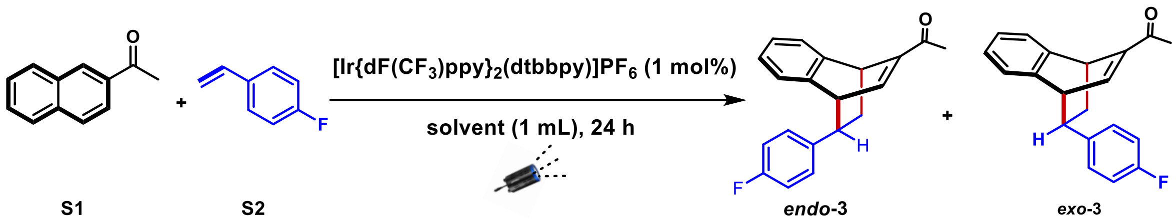
Table S1: optimization of photosensitizer



Entry	photosensitizer	Wavelenght	E_T (kcal/mol)	yields[a] *endo/exo*
1	Xanthone	370 nm	74.0	51% (1.3:1)
2	Benzophenone	370 nm	69.1	42% (1.3:1)
3	Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6	427 nm	61.8	98% (2:1)
4	Michler's Ketone	370 nm	61.0	25 % (4:1)
5	Ir(ppy)$_3$	427 nm	58.1	25% (2:1)
6	Benzil	427 nm	54	ND
7	[Ir(ppy)$_2$bpy]PF_6	427 nm	53.1	30% (2:1)
8	4CzIPN	427 nm	53	50% (1.5:1)
9	TPPT	427 nm	53	ND
10	[Ir(ppy)$_2$(dtbbpy)]PF_6	427 nm	49.2	45% (2:1)
11	Ru(bpy)$_3$(PF_6)$_2$	427 nm	46.5	53% (1.6:1)
12	Eosin Y	427 nm	44	ND
13	Rose Bengal	427 nm	42	ND

Reaction condition; **S1** (0.1 mmol), **S2** (0.12 mmol), photosensitizer (1 mol%) in MeCN (1 mL) under argon under the irradiation of blue LED for 24 h. [a]Yields and *endo:exo* ratio were determined by the ^{1}H NMR analysis of crude reaction mixture using 1,3,5-trimethoxy benzene as an internal standard.

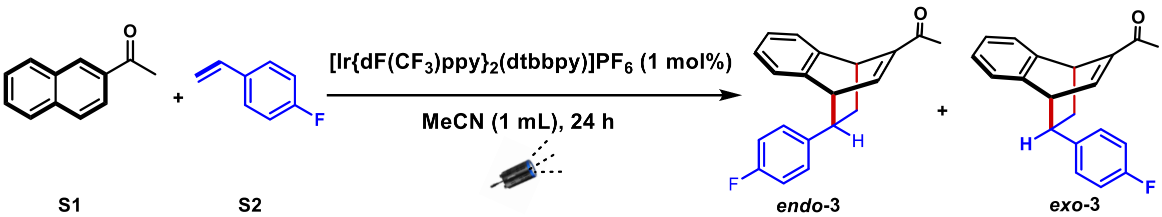
Table S2: optimization of solvents



Entry	Solvent	yields[a] *endo/exo*
1	CH_2Cl_2	97% (1.9:1)
2	Toluene	47% (1.1:1)
3	Dioxane	46% (1.1:1)
4	THF	95% (1.1:1)
5	^{t}BuOH	46% (1:1)
6	DMF	74 (1:1)
7	DMSO	96% (2:1)
8	MeOH	92% (2:1)
9	HFIP	48% (1:1)
10	^{i}PrOH	90% (1:1)

Reaction condition; **S1** (0.1 mmol), **S2** (0.12 mmol), [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6 (1 mol%) in a solvent (1 mL) under argon under the irradiation of 427 nm blue LED for 24 h. [a]Yields and *endo:exo* ratio were determined by the ^{1}H NMR analysis of crude reaction mixture using 1,3,5-trimethoxy benzene as an internal standard.

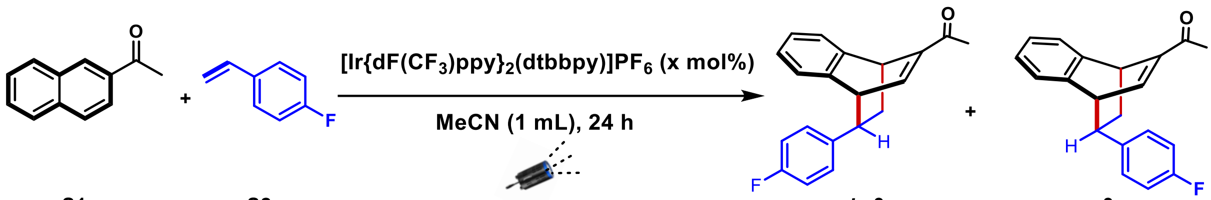
Table S3: optimization of wavelengths



Entry	Wavelength	yields[a] *endo/exo*
1	370 nm	72% (2:1)
2	390 nm	88% (2:1)
3	427 nm	98% (2:1)
4	440 nm	94% (2:1)
5	456 nm	33% 2:1)
6	467 nm	45% (2:1)

Reaction condition; **S1** (0.1 mmol), **S2** (0.12 mmol), [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6 (1 mol%) in MeCN (1 mL) under argon under the irradiation of 370-467 nm blue LED for 24 h. [a]Yields and *endo:exo* ratio were determined by the ^{1}H-NMR analysis of crude reaction mixture using 1,3,5-trimethoxy benzene as an internal standard.

Table S4: optimization of catalyst loading

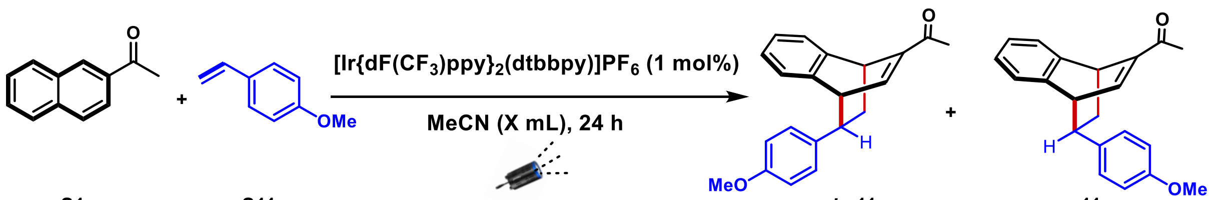


S1 S2 *endo*-3 *exo*-3

Entry	$[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$	yields[a] *endo/exo*
1	1 mol%	98% (2:1)
2	0.5 mol%	86% (2:1)

Reaction condition; **S1** (0.1 mmol), **S2** (0.12 mmol), $[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$ (1 mol%) in MeCN (1 mL) under argon under the irradiation of 427 nm blue LED for 24 h. [a]Yields and *endo:exo* ratio were determined by the ^{1}H-NMR analysis of crude reaction mixture using 1,3,5-trimethoxy benzene as an internal standard.

Table S5: optimization of concentration

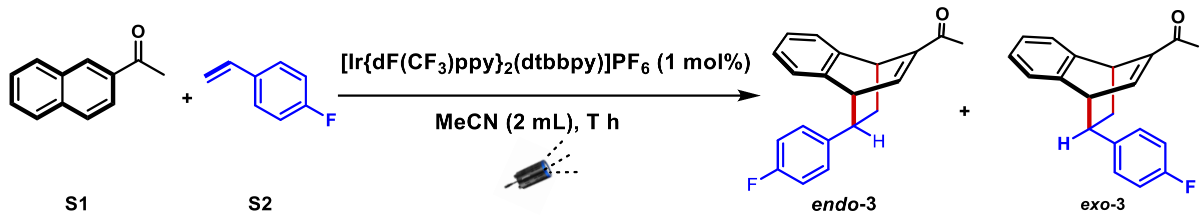


S1 S11 *endo*-11 *exo*-11

Entry	MeCN (X mL)	yields[a] *endo/exo*
1	1 mL	50% (1.9:1)
2	2 mL	67% (1.9:1)

Reaction condition; **S1** (0.1 mmol), **S11** (0.12 mmol), $[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$ (1 mol%) in MeCN (1 mL) under argon under the irradiation of 427 nm blue LED for 24 h. [a]Yields and *endo:exo* ratio were determined by the ^{1}H-NMR analysis of crude reaction mixture using 1,3,5-trimethoxy benzene as an internal standard.

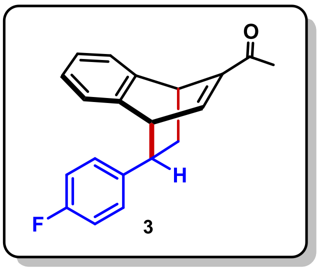
Table S6: optimization of reaction time



Entry	Time (h)	yields[a] *endo/exo*
1	12	67% (2:1)
2	18	76% (2:1)
3	24	98% (2:1)
4[a]	24	98% (2:1)

Reaction condition; **S1** (0.1 mmol), **S2** (0.12 mmol), [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6 (1 mol%) in MeCN (2 mL) under argon under the irradiation of 427 nm blue LED. [a]yields and *endo:exo* ratio were determined by the ^{1}H-NMR analysis of crude reaction mixture using 1,3,5-trimethoxy benzene as an internal standard. [a]Reaction performed in 1 mL solvent.

6. Analytical data of the products



3

Combined NMR yield: 98% (*endo:exo* = 2:1)

Major isomer: 17 mg (58%, 0.058 mmol), *endo*-diastereoisomer
R*f*: 0.5, Eluent: Ethyl acetate in Hexane 5% mixture.

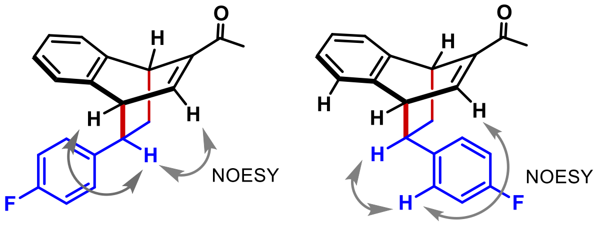
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 6.5, 1.8 Hz, 1H), 7.39 – 7.34 (m, 1H), 7.24 – 7.18 (m, 1H), 7.09 – 7.03 (m, 1H), 6.89 – 6.82 (m, 1H), 6.76 (t, *J* = 8.7 Hz, 2H), 6.43 – 6.34 (m, 2H), 4.79 (q, *J* = 2.4 Hz, 1H), 3.91 (dd, *J* = 6.4, 2.3 Hz, 1H), 3.20 – 3.13 (m, 1H), 2.31 (s, 3H), 2.15 – 2.06 (m, 1H), 1.55 – 1.49 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 195.0, 161.6 (d, ^1J = 244.5 Hz), 148.3, 147.1, 144.1, 139.2 (d, ^4J = 3.3 Hz), 138.6, 129.4 (d, ^3J = 7.8 Hz), 126.5, 126.2, 125.5, 123.2, 114.8 (d, ^2J = 20.9 Hz),49.6, 43.2, 38.3, 34.5, 25.2.
^{19}F NMR (471 MHz, $CDCl_3$) δ -116.83.
IR (ATR / cm^{-1}): 3060, 2972, 2913, 1727, 1659, 1602, 1506, 1477, 1371, 1217, 1158, 1015.

HRMS (ESI) m/z: [M + Na]+ calcd for $C_{20}H_{17}FONa$, 315.1156, found 315.1165.

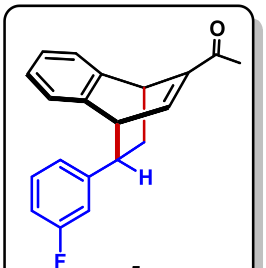
Minor isomer: 9.6 mg (33%, 0.033 mmol). *exo*-diastereoisomer

R*f*: 0.7, Eluent: Ethyl acetate in Hexane 5% mixture.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.23 – 7.15 (m, 3H), 7.10 – 7.03 (m, 2H), 7.03 – 6.95 (m, 2H), 6.93 – 6.85 (m, 2H), 4.71 (t, *J* = 2.4 Hz, 1H), 4.06 (dd, *J* = 6.3, 2.1 Hz, 1H), 3.05 – 2.96 (m, 1H), 2.23 (d, *J* = 1.7 Hz, 3H), 2.09 – 2.01 (m, 1H), 1.64 – 1.60 (m, 1H).
^{13}C NMR (126 MHz, CDCl$_3$) δ 194.8, 161.7 (d, ^1J = 244.9 Hz),149.8, 144.5, 143.2, 142.9, 140.3 (d, ^4J = 3.8 Hz), 129.2 (d, ^3J = 7.6 Hz), 126.2, 125.8, 124.0, 123.0, 115.3 (d, ^2J = 21.3 Hz), 49.3, 44.8, 38.7, 35.0, 25.3.



major minor



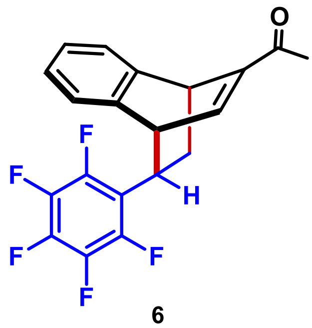
5

Combined NMR yield: 67% (*endo:exo* = 1.9:1)

Major isomer: 12.5 mg (43%, 0.043 mmol), white solid, *endo*-diastereoisomer

R*f*: 0.4, Eluent: Ethyl acetate in Hexane 5% mixture.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.56 (dd, *J* = 6.5, 1.8 Hz, 1H), 7.36 (d, *J* = 7.3 Hz, 1H), 7.22 (d, *J* = 1.1 Hz, 1H), 7.11 – 7.01 (m, 2H), 6.87 (d, *J* = 7.3 Hz, 1H), 6.82 – 6.76 (m, 1H), 6.30 (d, *J* = 7.8 Hz, 1H), 6.11 – 6.03 (m, 1H), 4.79 (d, *J* = 2.4 Hz, 1H), 3.96 (dd, *J* = 6.4, 2.4 Hz, 1H), 3.19 – 3.15 (m, 1H), 2.31 (s, 3H), 2.13 – 2.08 (m, 1H), 1.57 – 1.53 (m, 1H).
^{13}C NMR (126 MHz, CDCl$_3$) δ 195.0, 162.6 (d, ^1J = 245.2 Hz), 148.5, 146.9, 146.3 (d, ^3J = 7.0 Hz),144.0, 138.5, 129.40 (d, ^3J = 8.4 Hz), 126.6, 126.1, 125.6, 123.7(d, ^4J = 2.8 Hz), 123.3, 114.8 (d, *J* = 21.8 Hz), 113.3 (d, ^2J = 21.2 Hz), 49.3, 43.8, 38.3, 34.4, 25.3.
^{19}F NMR (471 MHz, CDCl$_3$) δ -113.65.
IR (ATR / cm^{-1}): 3068, 2951, 2817, 1664, 1610, 1589, 1475, 1365, 1272, 1231, 1155, 1023.
HRMS (ESI) m/z: [M + Na]+ calcd for $C_{20}H_{17}FONa$, 315.1156, found 315.1141.



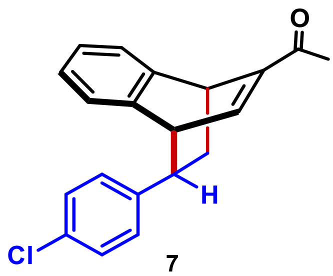
6

Combined NMR yield: 75% (*endo:exo* = 3:1)

Major isomer: 20 mg (55%, 0.055 mmol), *endo*-diastereoisomer, white solid.

R*f*: 0.4, Eluent: Ethyl acetate in Hexane 5% mixture.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 6.4, 1.9 Hz, 1H), 7.35 (s, 1H), 7.23 – 7.18 (m, 1H), 7.10 – 7.04 (m, 1H), 6.92 (d, *J* = 7.3 Hz, 1H), 4.84 (q, *J* = 2.5 Hz, 1H), 3.99 (dd, *J* = 6.5, 2.2 Hz, 1H), 3.55 – 3.48 (m, 1H), 2.31 (s, 3H), 2.10 – 2.04 (m, 1H), 1.97 – 1.89 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 194.93, 148.80, 146.7(m), 145.86, 144.7 (m), 140.77 (m), 139.8 (m),138.13, 136.6 (m) 127.40, 126.96, 125.90, 124.51, 123.89, 116.3 (m), 48.01, 38.09, 34.55, 28.87, 28.84, 28.82, 25.27.
^{19}F NMR (471 MHz, $CDCl_3$) δ -142.08 – -142.19 (m), -156.58 (t, *J* = 21.1 Hz), -162.48 – -162.65 (m).
IR (ATR / cm^{-1}): 2921, 2853, 1666, 1611, 1580, 1519, 1496, 1462, 1366.
HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{20}H_{13}F_5ONa$, 387.0779, found 387.0795.



7

Combined NMR yield: 80% (*endo:exo* = 1.7:1)

Major isomer: 14 mg (42%, 0.042 mmol), *endo*-diastereoisomer, white solid.

R*f*: 0.4, Eluent: Ethyl acetate in Hexane 5% mixture.

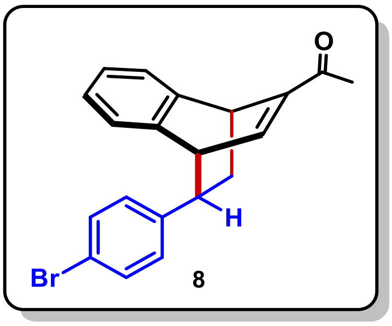
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 6.5, 1.8 Hz, 1H), 7.36 (d, *J* = 7.3 Hz, 1H), 7.23 – 7.19 (m, 1H), 7.10 – 7.00 (m, 3H), 6.85 (d, *J* = 7.3 Hz, 1H), 6.38 – 6.33 (m, 2H), 4.79 (q, *J* =

2.5 Hz, 1H), 3.91 (dd, *J* = 6.5, 2.3 Hz, 1H), 3.17 – 3.13 (m, 1H), 2.30 (s, 3H), 2.12 – 2.07 (m, 1H), 1.54 – 1.50 (m, 1H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 195.0, 148.4, 147.0, 144.0, 142.0, 138.5, 132.2, 129.3, 128.2, 126.6, 126.2, 125.6, 123.3, 49.5, 43.4, 38.3, 34.4, 25.3.

IR (ATR / cm^{-1}): 3063, 2956, 2920, 2884, 1659, 1610, 1488, 1459, 1368, 1275, 1238, 1085, 1015.

HRMS (ESI) m/z: [M + Na]$^+$ calcd for $C_{20}H_{17}OClNa$, 331.0860, found 331.0878.



Combined NMR yield: 80% (*endo:exo* = 1.5:1)

Major isomer: 14 mg (40%, 0.040 mmol), *endo*-diastereoisomer, white solid.

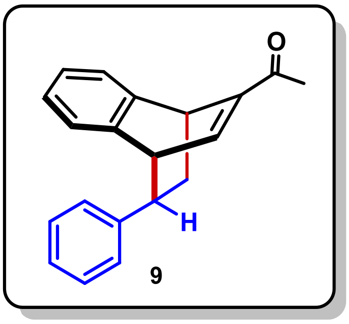
R*f*: 0.4, Eluent: Ethyl acetate in Hexane 5% mixture.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.56 – 7.54 (m, 1H), 7.36 (d, *J* = 7.3 Hz, 1H), 7.24 – 7.17 (m, 3H), 7.11 – 7.03 (m, 1H), 6.85 (d, *J* = 7.3 Hz, 1H), 6.32 – 6.26 (m, 2H), 4.79 (d, *J* = 2.4 Hz, 1H), 3.91 (dd, *J* = 6.5, 2.3 Hz, 1H), 3.15 – 3.12 (m, 1H), 2.30 (s, 3H), 2.12 – 2.06 (m, 1H), 1.53 – 1.49 (m, 1H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 195.0, 148.4, 146.9, 144.0, 142.5, 138.4, 131.1, 129.7, 126.6, 126.2, 125.6, 123.3, 120.3, 49.4, 43.5, 38.3, 34.4, 25.3.

IR (ATR / cm^{-1}): 3066, 2964, 2930, 2876, 1657, 1607, 1490, 1459, 1371, 1280, 1236, 1139, 1077.

HRMS (ESI) m/z: [M + Na]$^+$ calcd for $C_{20}H_{17}OBrNa$, 375.0355, found 375.0385.



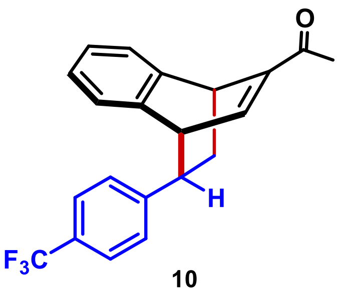
Combined NMR yield: 69% (*endo:exo* = 2:1)

Major isomer: 12.3 mg (45%, 0.045 mmol), *endo*-diastereoisomer, colorless liquid.

R$_f$: 0.6, Eluent: Ethyl acetate in Hexane 5% mixture.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.58 (dd, *J* = 6.5, 1.9 Hz, 1H), 7.37 (d, *J* = 7.3 Hz, 1H), 7.23 – 7.19 (m, 1H), 7.11 – 6.99 (m, 4H), 6.87 (d, *J* = 7.3 Hz, 1H), 6.52 – 6.40 (m, 2H), 4.80 (q, *J* = 2.4 Hz, 1H), 3.96 (dd, *J* = 6.5, 2.3 Hz, 1H), 3.23 – 3.13 (m, 1H), 2.31 (s, 3H), 2.15 – 2.06 (m, 1H), 1.58 (dd, *J* = 5.1, 2.4 Hz, 1H).
^{13}C NMR (126 MHz, CDCl$_3$) δ 195.1, 148.3, 147.4, 144.2, 143.5, 138.8, 128.1, 128.1, 126.5, 126.4, 126.2, 125.5, 123.2, 49.6, 44.0, 38.4, 34.3, 25.3.
IR (ATR / cm^{-1}): 3058, 3021, 2962, 2928, 2871, 2855, 1711, 1664, 1604, 1477, 1371, 1282, 1119, 1020.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{19}O$, 275.1430, found 275.1469.



10

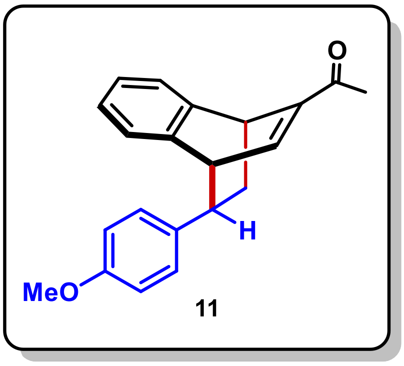
Combined NMR yield: 60%, (*endo:exo* = 1.2:1)

Major isomer: 10 mg (30%, 0.030 mmol), *endo*-diastereoisomer, white solid.

R$_f$: 0.4, Eluent: Ethyl acetate in Hexane 5% mixture.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.57 (dd, *J* = 6.5, 1.9 Hz, 1H), 7.38 (d, *J* = 7.3 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.24 – 7.21 (m, 1H), 7.09 – 7.06 (m, 1H), 6.85 (d, *J* = 7.3 Hz, 1H), 6.54 (d, *J* = 8.1 Hz, 2H), 4.82 (q, *J* = 2.4 Hz, 1H), 3.95 (dd, *J* = 6.5, 2.3 Hz, 1H), 3.25 – 3.25 (m, 1H), 2.32 (s, 3H), 2.16 – 2.10 (m, 1H), 1.59 – 1 55 (m, 1H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 195.0, 148.5, 147.6, 146.8, 144.0, 138.3, 128.76 (q, ^2J = 32.4 Hz), 128.4, 126.7, 126.2, 125.7, 125.0 (q, ^4J = 3.8 Hz), 123.4, 124.3(q, ^1J = 270 Hz). 49.2, 43.9, 38.2, 34.4, 25.3.
^{19}F NMR (471 MHz, CDCl$_3$) δ -62.40.
IR (ATR / cm^{-1}): 3065, 2964, 2885,1662, 1612, 1417, 1326, 1243, 1158, 1067,1020.
HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{21}H_{17}F_3ONa$, 365.1124, found 365.1120.



Combined NMR yield: 67% (*endo:exo* = 1.9:1)

Mixture of major and minor isomer: 20 mg (66%, 0.066 mmol), colorless liquid.

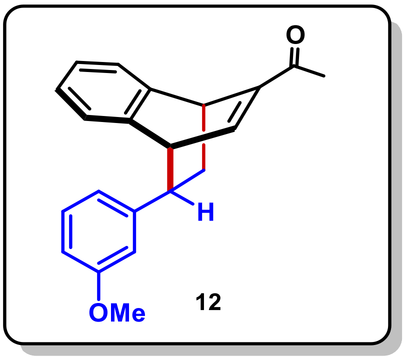
R_f: 0.38, Eluent: Ethyl acetate in Hexane 5% mixture.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 6.5, 1.9 Hz, 0.70H_{maj}), 7.38 (d, *J* = 7.3 Hz, 0.70H_{maj}), 7.34 (d, *J* = 8.2 Hz, 0.6H_{min}), 7.29 (d, *J* = 5.0 Hz, 0.3H_{min}), 7.26 – 7.21 (m, 0.70H_{maj}), 7.20 – 7.15 (m, 0.60H_{min}), 7.11 – 7.04 (m, 1.40H_{maj}), 6.91 (d, *J* = 7.3 Hz, 0.70H_{maj}), 6.86 (d, *J* = 12.1 Hz, 0.60H_{min}), 6.65 (d, *J* = 8.7 Hz, 1.40H_{maj}), 6.39 (d, *J* = 8.7 Hz, 1H + 0.3H_{min}), 4.84 – 4.78 (m, 0.7H_{maj} + 0.3H_{min}), 4.20 – 4.15 (m, 0.30H_{min}), 3.94 (dd, *J* = 6.5, 2.4 Hz, 0.70H_{maj}), 3.82 (s, 0.90H_{min}), 3.74 (s, 2.10H_{maj}), 3.20 – 3.07 (m, 0.7H_{maj} + 0.3H_{min}), 2.34 (d, *J* = 7.2 Hz, 2.10H_{maj} + 0.90H_{min}), 2.16 – 2.09 (m, 0.7H_{maj} + 0.3H_{min}), 1.77 – 1.72 (m, 0.3H_{min}), 1.58 – 1.53 (m, , 0.70H_{maj}).

^{13}C NMR (126 MHz, $CDCl_3$) δ 195.1, 158.4, 158.2, 149.5, 148.1, 147.5, 145.0, 144.2, 143.4, 143.0, 138.9, 136.7, 135.6, 128.9, 128.7, 126.3, 126.2, 126.1, 125.7, 125.4, 124.0, 123.1, 123.0, 114.0, 113.4, 55.4, 55.2, 49.8, 49.5, 44.8, 43.2, 38.8, 38.3, 34.9, 34.5, 25.3, 25.2.

IR (ATR / cm^{-1}): 3045, 3026, 2995, 2949, 2832, 1660, 1600, 1462, 1431, 1371, 1293, 1154, 1043.

HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{21}H_{20}O_2Na$, 327.1356, found 327.1374.



Combined NMR yield: 56% (*endo:exo* = 1.9:1)

Mixture of major and minor isomer: 16.5 mg (54%, 0.054 mmol), colorless liquid.

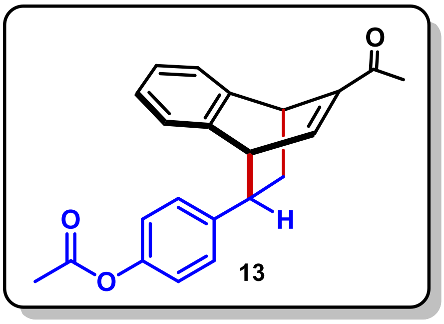
R_f: 0.38, Eluent: Ethyl acetate in Hexane 5% mixture.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 6.5, 1.9 Hz, 0.60H_{maj}), 7.38 (d, *J* = 7.3 Hz, 0.60H_{maj}), 7.36 – 7.31 (m, 0.80H_{min}), 7.28 (dd, *J* = 5.6, 2.9 Hz, 0.40H_{min}), 7.23 – 7.20 (m, 0.6H_{maj} + 0.4H_{min}), 7.18 – 7.15 (m, 0.60H_{maj}), 7.10 – 7.07 (m, 0.60H_{maj}), 7.03 (t, *J* = 7.9 Hz, 0.60H_{maj}), 6.92 (d, *J* = 7.3 Hz, 0.60H_{maj}), 6.78 (d, *J* = 2.6 Hz, 0.40H_{min}), 6.73 (d, *J* = 7.7 Hz, 0.40H_{min}), 6.71 – 6.60 (m, 0.6H_{maj} + 0.4H_{min}), 6.22 (d, *J* = 7.6 Hz, 0.60H_{maj}), 5.93 – 5.75 (m, 0.60H_{maj}), 4.91 – 4.74 (m, 0.6H_{maj} + 0.4H_{min}), 4.21 (dd, *J* = 6.3, 2.2 Hz, 0.40H_{min}), 3.98 (dd, *J* = 6.5, 2.3 Hz, 0.6H_{maj}), 3.80 (s, 1.20H_{min}), 3.54 (s, 1.8H_{maj}), 3.22 – 3.07 (m, 0.6H_{maj} + 0.4H_{min}), 2.32 (d, *J* = 5.6 Hz, 1.8H_{maj} + 1.2H_{min}), 2.19 – 2.08 (m, 0.6H_{maj} + 0.4H_{min}), 1.77 – 1.73 (m, 0.4H_{min}), 1.60 – 1.56 (m, 0.6H_{maj}).

^{13}C NMR (126 MHz, $CDCl_3$) δ 195.1, 194.7, 159.8, 159.3, 149.6, 148.3, 147.3, 146.4, 145.2, 144.9, 144.2, 143.3, 143.0, 138.9, 129.5, 128.9, 126.4, 126.2, 126.1, 125.7, 125.5, 124.0, 123.2, 123.0, 120.6, 120.2, 114.0, 112.9, 112.5, 111.5, 55.3, 54.9, 49.5, 49.1, 45.6, 44.0, 38.7, 38.3, 34.9, 34.5, 25.3, 25.2.

IR (ATR / cm^{-1}): 3045, 3026, 2995, 2949, 2832, 1660, 1600, 1462, 1431, 1371, 1293, 1154, 1043.

HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{21}H_{20}O_2Na$, 327.1356, found 327.1354.



13

Combined NMR yield: 80% (*endo:exo* = 2:1)

Major isomer: 16.3 mg (49%, 0.049 mmol,), *endo*-diastereoisomer, orange solid.

R_f: 0.4, Eluent: Ethyl acetate in Hexane 5% mixture.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 6.5, 1.9 Hz, 1H), 7.36 (dd, *J* = 7.3, 1.1 Hz, 1H), 7.23 – 7.18 (m, 1H), 7.09 – 7.04 (m, 1H), 6.91 – 6.86 (m, 1H), 6.83 – 6.75 (m, 2H), 6.47 – 6.40 (m, 2H), 4.78 (q, *J* = 2.5 Hz, 1H), 3.95 (dd, *J* = 6.4, 2.3 Hz, 1H), 3.20 – 3.14 (m, 1H), 2.30 (s, 3H), 2.24 (s, 3H), 2.14 – 2.08 (m, 1H), 1.55 – 1.50 (m, 1H).

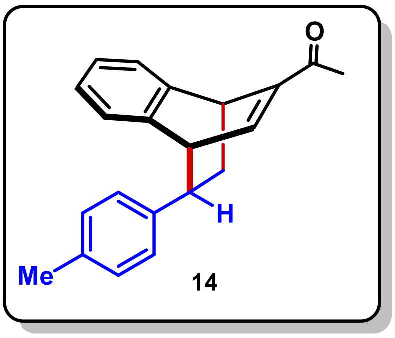
^{13}C NMR (126 MHz, $CDCl_3$) δ 194.9, 169.5, 149.1, 148.1, 147.1, 144.0, 140.9, 138.5, 128.8, 126.3, 126.1, 125.4, 123.1, 120.9, 49.2, 43.3, 38.1, 34.5, 25.1, 21.1.

IR (ATR / cm^{-1}): 3047, 2938, 2850, 1763, 1662, 1607, 1588, 1371, 1259, 1186, 1051.

HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{22}H_{20}O_3Na$, 355.1305, found 355.1305.

Minor isomer: 7.3 mg (22%, 0.033 mmol), *exo*-diastereoisomer, orange solid

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 2H), 7.27 (d, *J* = 5.5 Hz, 1H), 7.17 – 7.14 (m, 2H), 7.12 (d, *J* = 8.6 Hz, 2H), 7.00 (d, *J* = 8.5 Hz, 2H), 4.80 (d, *J* = 2.3 Hz, 1H), 4.18 (dd, *J* = 6.3, 2.2 Hz, 1H), 3.14 – 3.09 (m, 1H), 2.31 (d, *J* = 7.4 Hz, 6H), 2.16 – 2.10 (m, 1H), 1.75 – 1.70 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 194.7, 169.6, 149.6, 149.2, 144.5, 143.1, 142.8, 142.1, 128.6, 126.1, 125.6, 123.9, 122.9, 121.5, 49.0, 44.9, 38.6, 34.8, 25.2, 21.1.

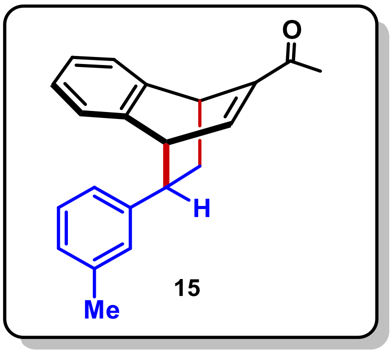


Combined NMR yield: 50% (*endo:exo* = 1.6:1)

Major isomer: 8 mg (28%, 0.028 mmol), *endo*-diastereoisomer, colorless liquid.

R_f: 0.4, Eluent: Ethyl acetate in Hexane 5% mixture.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 6.4, 1.8 Hz, 1H), 7.37 – 7.34 (m, 1H), 7.22 – 7.19 (m, 1H), 7.07 – 7.04 (m, 1H), 6.89 (dd, *J* = 7.5, 5.2 Hz, 3H), 6.37 – 6.32 (m, 2H), 4.78 (q, *J* = 2.5 Hz, 1H), 3.94 (dd, *J* = 6.5, 2.3 Hz, 1H), 3.15 – 3.12 (m, 1H), 2.30 (s, 3H), 2.24 (s, 3H), 2.12 – 2.07 (m, 1H), 1.57 – 1.52 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 195.1, 148.2, 147.5, 144.3, 140.5, 138.9, 136.0, 128.8, 127.9, 126.4, 126.2, 125.4, 123.2, 49.7, 43.6, 38.4, 34.5, 25.3, 21.0.
IR (ATR / cm^{-1}): 3045, 3024, 2954, 2876,1659, 1605, 1584, 1480, 1368, 1275, 1137, 1022.
HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{21}O$, 289.1587, found 289.1564.



Combined NMR yield: 56% (*endo:exo* = 2:1)

Major isomer: 10 mg (35%, 0.035 mmol), *endo*-diastereoisomer, colorless liquid.

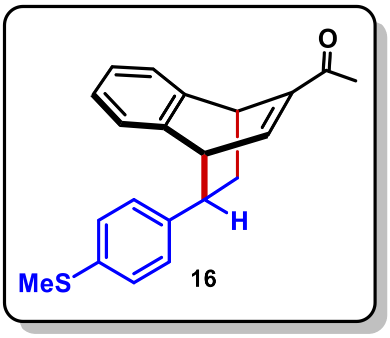
R$_f$: 0.4, Eluent: Ethyl acetate in Hexane 5% mixture.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.58 (dd, *J* = 6.5, 1.8 Hz, 1H), 7.39 – 7.35 (m, 1H), 7.23 – 7.20 (m, 1H), 7.08 – 7.05 (m, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 7.5 Hz, 1H), 6.90 – 6.86 (m, 1H), 6.26 (s, 1H), 6.22 (d, *J* = 7.6 Hz, 1H), 4.79 (d, *J* = 2.3 Hz, 1H), 3.95 (dd, *J* = 6.5, 2.3 Hz, 1H), 3.16 – 3.12 (m, 1H), 2.31 (s, 3H), 2.17 (s, 3H), 2.12 – 2.07 (m, 1H), 1.59 – 1.55 (m, 1H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 195.1, 148.3, 147.4, 144.2, 143.4, 138.9, 137.5, 129.0, 127.9, 127.1, 126.3, 126.2, 125.3, 125.0, 123.2, 49.6, 44.0, 38.4, 34.4, 25.2, 21.4.

IR (ATR / cm^{-1}): 3045, 3024, 2954, 2876,1659, 1605, 1584, 1480, 1368, 1275, 1137, 1022.

HRMS (ESI) m/z: [M + Na]$^+$ calcd for $C_{21}H_{20}ONa$, 311.1406, found 311.1387.



Combined NMR yield: 25% (*endo:exo* = 1.5:1)

Major isomer: 3.8 mg (12%, 0.012 mmol), *endo*-diastereoisomer, white solid.

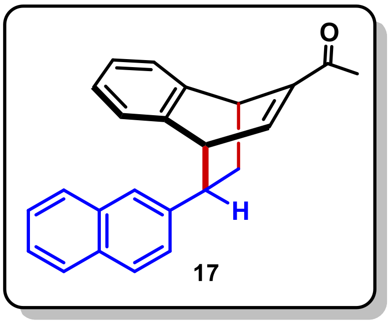
R$_f$: 0.4, Eluent: Ethyl acetate in Hexane 5% mixture.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.57 (dd, *J* = 6.5, 1.8 Hz, 1H), 7.35 (d, *J* = 7.3 Hz, 1H), 7.22 – 7.19 (m, 1H), 7.07 – 7.04 (m, 1H), 7.00 – 6.96 (m, 2H), 6.87 (d, *J* = 7.2 Hz, 1H), 6.36 (d, *J* = 8.3 Hz, 2H), 4.78 (q, *J* = 2.5 Hz, 1H), 3.92 (dd, *J* = 6.5, 2.3 Hz, 1H), 3.15 – 3.11 (m, 1H), 2.40 (s, 3H), 2.30 (s, 3H), 2.12 – 2.06 (m, 1H), 1.54 – 1.50 (m, 1H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 195.1, 148.3, 147.3, 144.1, 140.5, 138.7, 136.2, 128.5, 126.5, 126.5, 126.2, 125.5, 123.2, 49.6, 43.6, 38.3, 34.4, 25.3, 16.1.

IR (ATR / cm^{-1}): 3024, 2959, 2923, 2865, 1659, 1607, 1490, 1365, 1275, 1241, 1012.

HRMS (ESI) m/z: [M + Na]$^+$ calcd for $C_{21}H_{20}OSNa$, 343.1127, found 343.1137.



Combined NMR yield: 39%, (*endo:exo* = 1.4:1)

Major isomer: 7.5 mg (23%, 0.023 mmol), *endo*-diastereoisomer, colorless liquid.

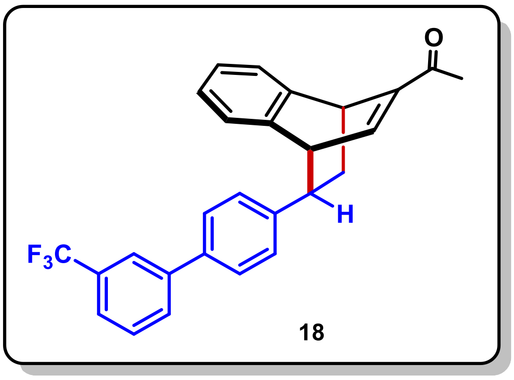
R$_f$: 0.5, Eluent: Ethyl acetate in Hexane 5% mixture.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.73 – 7.70 (m, 1H), 7.61 (dd, *J* = 6.4, 1.8 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.43 (s, 1H), 7.38 (dd, *J* = 6.3, 3.3 Hz, 2H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.04 (t, *J* = 7.4 Hz, 1H), 6.96 (s, 1H), 6.82 (d, *J* = 7.3 Hz, 1H), 6.48 (dd, *J* = 8.6, 1.8 Hz, 1H), 4.85 (d, *J* = 2.5 Hz, 1H), 4.03 (dd, *J* = 6.4, 2.3 Hz, 1H), 3.38 – 3.32 (m, 1H), 2.33 (s, 3H), 2.21 – 2.15 (m, 1H), 1.73 – 1.69 (m, 1H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 195.2, 148.4, 147.3, 144.2, 141.0, 138.9, 133.3, 132.3, 127.7, 127.5, 126.7, 126.5, 126.3, 125.9, 125.5, 123.3, 49.7, 44.2, 38.4, 34.4, 25.3.

IR (ATR / cm^{-1}): 3058, 3029, 2930, 2858, 1662, 1607, 1477, 1456, 1368, 1275, 1241, 1186, 1145, 1025.

HRMS (ESI) m/z: $[M + K]^+$ calcd for $C_{24}H_{20}OK$, 363.1146, found 363.1162.



18

Combined NMR yield: 61% (*endo:exo* = 2:1)

Major isomer: 16.7 mg (40%, 0.040 mmol), *endo*-diastereoisomer, colorless liquid.

R$_f$: 0.4, Eluent: Ethyl acetate in Hexane 5% mixture.

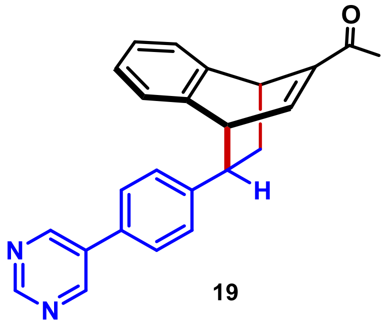
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.75 (s, 1H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.60 (dd, *J* = 6.4, 1.8 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.39 (d, *J* = 7.3 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.25 – 7.21 (m, 1H), 7.10 – 7.06 (m, 1H), 6.91 (d, *J* = 7.3 Hz, 1H), 6.54 (d, *J* = 8.1 Hz, 2H), 4.82 (d, *J* = 2.4 Hz, 1H), 3.99 (dd, *J* = 6.4, 2.3 Hz, 1H), 3.28 – 3.20 (m, 1H), 2.32 (s, 3H), 2.18 – 2.11 (m, 1H), 1.64 – 1.60 (m, 1H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 195.1, 148.4, 147.2, 144.2, 143.6, 141.7, 138.7, 137.9, 131.3 (q, ^2J = 32.5 Hz), 130.3, 129.3, 128.7, 126.8, 126.5, 126.4 (q, ^1J = 239 Hz), 126.2, 125.6, 123.9 (q, ^4J = 3.7 Hz), 123.3, 49.5, 43.8, 38.4, 34.5, 25.3.

^{19}F NMR (471 MHz, CDCl$_3$) δ -62.5.

IR (ATR / cm^{-1}): 3052, 2956, 2933, 2858, 1662, 1610, 1491, 1449, 1329, 1267, 1165, 1124, 1035.

HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{27}H_{21}F_3ONa$, 441.1437, found 441.1412.



19

Combined NMR yield: 48% (*endo:exo* = 1.2:1)

Mixture of major and minor isomer: 15.9 mg (45%, 0.045 mmol), white solid.

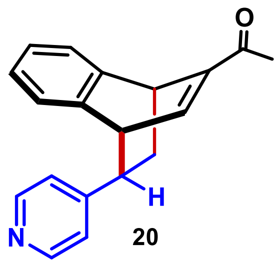
R_f: 0.3, Eluent: Ethyl acetate in Hexane 10% mixture.

^{1}H NMR (500 MHz, CDCl$_3$) δ 9.22 – 9.14 (m, 1H), 8.95 – 8.86 (m, 2H), 7.59 (dd, *J* = 6.5, 1.8 Hz, $0.6H_{maj}$), 7.51 (d, *J* = 8.1 Hz, $0.8H_{min}$), 7.39 (d, *J* = 7.3 Hz, $0.6H_{maj}$), 7.34 – 7.27 (m, 3H), 7.25 – 7.21 (m, $0.6H_{maj}$), 7.20 – 7.12 (m, $0.8H_{min}$), 7.08 (t, *J* = 7.4 Hz, $0.6H_{maj}$), 6.89 (d, *J* = 7.3 Hz, $0.6H_{maj}$), 6.59 (d, *J* = 8.1 Hz, $1H_{maj} + 0.4H_{min}$), 4.83 (q, *J* = 2.6 Hz, 1H), 4.23 (dd, *J* = 6.3, 2.1 Hz, $0.4H_{min}$), 3.99 (dd, *J* = 6.4, 2.3 Hz, $0.6H_{maj}$), 3.27 – 3.22 (m, $0.6H_{maj}$), 3.22 – 3.17 (m, $0.4H_{min}$), 2.33 (d, *J* = 8.1 Hz, 3H), 2.21 – 2.14 (m, 1H), 1.81 – 1.76 (m, $0.4H_{min}$), 1.62 – 1.58 (m, $0.6H_{maj}$).

^{13}C NMR (126 MHz, CDCl$_3$) δ 195.0, 194.8, 157.5, 157.4, 154.9, 154.8, 150.0, 148.5, 147.0, 145.9, 144.8, 144.4, 144.1, 138.5, 134.1, 132.3, 129.2, 129.0, 127.2, 126.6, 126.6, 126.3, 126.2, 125.9, 125.6, 124.1, 123.3, 123.1, 49.4, 49.1, 45.4, 43.8, 38.8, 38.3, 34.9, 34.5, 25.4, 25.3.

IR (ATR / cm^{-1}): 3034, 2954, 2923, 2855, 1659, 1610, 1462, 1410, 1376, 1256, 1187, 1020.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{24}H_{21}N_2O$, 353.1648, found 353.1643.



20

Combined NMR yield: 55% (*endo:exo* = 1:1)

Mixture of major and minor isomer: 13.8 mg (50%, 0.050 mmol), yellow solid.

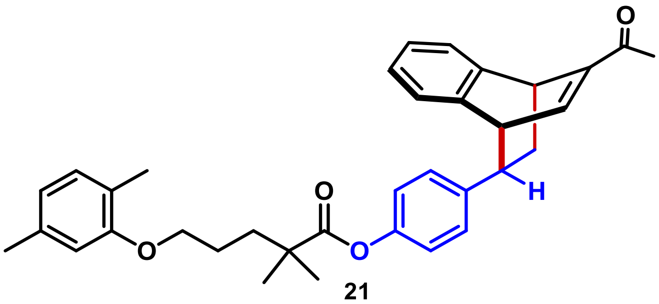
R$_f$: 0.1, Eluent: Ethyl acetate in Hexane 30% mixture.

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.43 (d, *J* = 5.1 Hz, 1H), 8.30 – 8.17 (m, 1H), 7.48 (dd, *J* = 6.5, 1.9 Hz, 0.52H$_{maj}$), 7.30 (d, *J* = 7.3 Hz, 0.48H$_{min}$), 7.24 (dd, *J* = 5.9, 2.6 Hz, 0.48H$_{min}$), 7.21 – 7.18 (m, 1H), 7.17 – 7.13 (m, 0.52H$_{maj}$), 7.12 – 7.06 (m, 1H), 7.04 – 6.94 (m, 1H$_{maj}$ + 0.48H$_{min}$), 6.76 (d, *J* = 7.3 Hz, 0.52H$_{maj}$), 6.35 – 6.27 (m, 1H), 4.75 (q, *J* = 2.6 Hz, 1H), 4.13 (dd, *J* = 6.3, 2.3 Hz, 0.48H$_{min}$), 3.89 (dd, *J* = 6.5, 2.4 Hz, 0.52H$_{maj}$), 3.11 – 3.06 (m, 0.48H$_{min}$), 3.05 – 2.97 (m, 0.52H$_{maj}$), 2.24 (s, 3H), 2.12 – 2.01 (m, 1H), 1.73 – 1.59 (m, 0.48H$_{min}$), 1.53 – 1.45 (m, 0.52H$_{maj}$).

^{13}C NMR (126 MHz, CDCl$_3$) δ 194.9, 194.6, 153.9, 153.0, 150.1, 149.7, 149.1, 148.7, 146.3, 143.8, 143.7, 142.8, 142.5, 137.9, 126.8, 126.4, 126.1, 125.9, 125.7, 124.1, 123.4, 123.4, 123.2, 123.1, 48.7, 48.1, 45.0, 43.4, 38.5, 38.0, 34.4, 33.9, 25.3, 25.2.

IR (ATR / cm^{-1}): 2951, 2930, 2858, 1761, 1662, 1607, 1500, 1365, 1212, 1191, 1165, 1020.

HRMS (ESI) m/z: [M + Na]$^+$ calcd for $C_{19}H_{17}NONa$, 298.1202, found 298.1206.



21

Combined NMR yield: 74% (*endo:exo* = 2:1)

Major isomer: 23.5 mg (45%, 0.045 mmol), *endo*-diastereoisomer, white solid. **Minor isomer:**15 mg (29%, 0.029 mmol), *exo*-diastereoisomer, white solid.

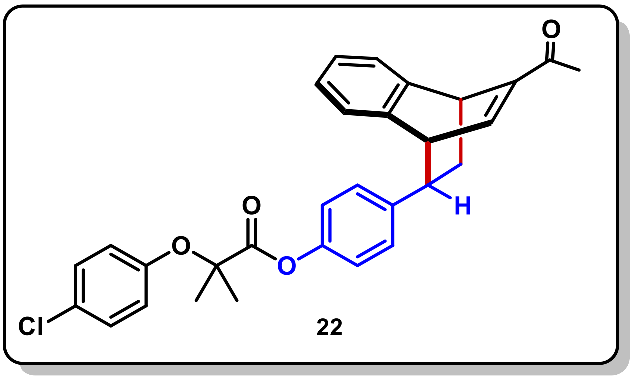
R$_f$: 0.3, Eluent: Ethyl acetate in Hexane 10% mixture.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.58 (dd, *J* = 6.5, 1.7 Hz, 1H), 7.37 (d, *J* = 7.3 Hz, 1H), 7.24 – 7.19 (m, 1H),7.09 – 7.05 (m, 1H), 7.01 (d, *J* = 7.4 Hz, 1H), 6.89 (d, *J* = 7.3 Hz, 1H), 6.79 – 6.74 (m, 2H), 6.67 (d, *J* = 7.5 Hz, 1H), 6.62 (s, 1H), 6.43 (d, *J* = 8.2 Hz, 2H), 4.80 (t, *J* = 2.3 Hz, 1H), 3.98 – 3.93 (m, 3H), 3.20 – 3.17 (m, 1H), 2.31 (d, *J* = 3.1 Hz, 6H), 2.17 (s, 3H), 2.14 – 2.09 (m, 1H), 1.85 (d, *J* = 3.0 Hz, 4H), 1.57 – 1.57 (m, 1H), 1.34 (s, 6H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 195.1, 176.5, 157.0, 149.5, 148.3, 147.2, 144.1, 140.9, 138.6, 136.6, 130.5, 130.4, 128.9, 126.5, 126.3, 125.6, 123.7, 123.2, 121.0, 120.9, 120.8, 112.1, 67.9, 49.5, 43.5, 42.5, 38.3, 37.3, 37.1, 34.6, 25.3, 25.2, 21.5, 15.9.

IR (ATR / cm^{-1}): 2954, 2925, 2868, 1748, 1670, 1612, 1587, 1503, 1469, 1374, 1262, 1199, 1160, 1043.

HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{35}H_{38}O_4Na$, 545.2668, found 545.2632.



22

Combined NMR yield: 64% (*endo:exo* = 1.3:1)

Major isomer: 17.5 mg (36%, 0.036 mmol), *endo*-diastereoisomer, white solid.

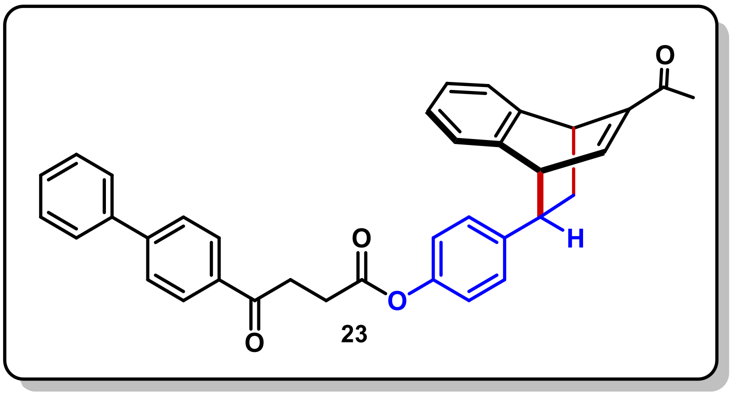
R*f*: 0.3, Eluent: Ethyl acetate in Hexane 10% mixture.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 6.5, 1.7 Hz, 1H), 7.36 (d, *J* = 7.4 Hz, 1H), 7.25 – 7.16 (m, 3H), 7.08 – 7.02 (m, 1H), 6.90 – 6.81 (m, 3H), 6.77 – 6.68 (m, 2H), 6.43 (d, *J* = 8.3 Hz, 2H), 4.78 (t, *J* = 2.4 Hz, 1H), 3.93 (dd, *J* = 6.4, 2.4 Hz, 1H), 3.22 – 3.13 (m, 1H), 2.30 (s, 3H), 2.14 – 2.07 (m, 1H), 1.69 (s, 6H), 1.56 – 1.49 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 195.0, 172.8, 154.1, 149.0, 148.4, 147.1, 144.1, 141.5, 138.5, 129.4, 129.0, 127.6, 126.5, 126.2, 125.6, 123.2, 120.7, 120.6, 79.7, 49.4, 43.5, 38.3, 34.6, 25.4, 25.3.

IR (ATR / cm^{-1}): 3042, 2990, 2941, 2876, 1750, 1664, 1607, 1498, 1485, 1374, 1280, 1233, 1160, 1103, 1015.

HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{30}H_{27}ClO_4Na$, 509.1490, found 509.1496.



23

Combined NMR yield: 70% (*endo:exo* = 1.3:1)

Mixture of major and minor isomer:34 mg (65%, 0.065 mmol), colorless liquid.

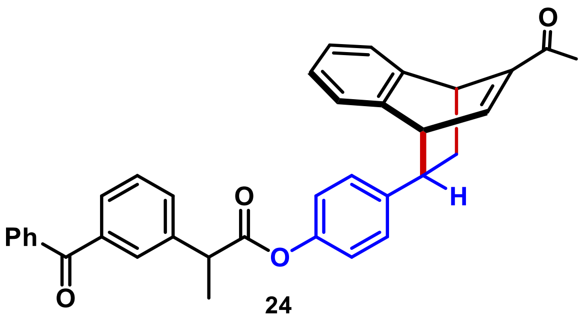
R*f*: 0.5, Eluent: Ethyl acetate in Hexane 10% mixture.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 – 8.06 (m, 2H), 7.70 (dd, *J* = 5.2, 3.4 Hz, 2H), 7.67 – 7.61 (m, 3H), 7.48 (t, *J* = 7.4 Hz, 3H), 7.43 – 7.41 (m, 1H), 7.22 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.15 – 7.11 (m, 1H), 7.09 – 7.03 (m, 2H), 6.87 (dd, *J* = 11.7, 7.7 Hz, 2H), 6.44 (d, *J* = 8.2 Hz, 1H), 4.84 – 4.75 (m, 1H), 4.18 (dd, *J* = 6.3, 2.1 Hz, 0.4H_{min}), 3.95 (dd, *J* = 6.5, 2.3 Hz, 0.6H_{maj}), 3.47 – 3.45 (m, 1H), 3.43 (d, *J* = 6.8 Hz, 1H), 3.22 – 3.09 (m, 1H), 3.05 – 3.03 (m, 1H), 2.98 (d, *J* = 8.1 Hz, 1H), 2.31 (t, *J* = 2.2 Hz, 3H), 2.15 – 2.09 (m, 1H), 1.76 – 1.72 (m, 0.6H_{maj}), 1.59 – 1.50 (m, 0.4H_{min}).

^{13}C NMR (126 MHz, $CDCl_3$) δ 197.5, 195.1, 171.8, 171.6, 149.7, 149.3, 148.2, 147.3, 146.1, 144.7, 144.1, 143.2, 142.9, 142.1, 142.0, 141.0, 139.9, 138.6, 135.2, 129.1, 128.9, 128.9, 128.8, 128.7, 128.7, 128.4, 127.6, 127.4, 127.4, 126.4, 126.2, 126.1, 125.7, 125.5, 124.0, 123.1, 123.0, 121.6, 121.4, 121.0, 120.8, 49.4, 49.1, 45.0, 43.4, 38.6, 38.2, 34.9, 34.5, 33.6, 33.5, 28.6, 28.6, 25.3, 25.2.

IR (ATR / cm^{-1}): 3063, 2962, 2925, 2855, 1756, 1683, 1664, 1605, 1511, 1407, 1360, 1190, 1168, 1129, 1017.

HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{36}H_{30}O_4Na$, 549.2018, found 549.2036.



24

Combined NMR yield: 80% (*endo:exo* = 2:1)

Major isomer: 23 mg (44%, 0.044 mmol), *endo*-diastereoisomer, colorless liquid. **Minor isomer:** 10 mg (19%, 0.019 mmol,), *exo*-diastereoisomer, colorless liquid.

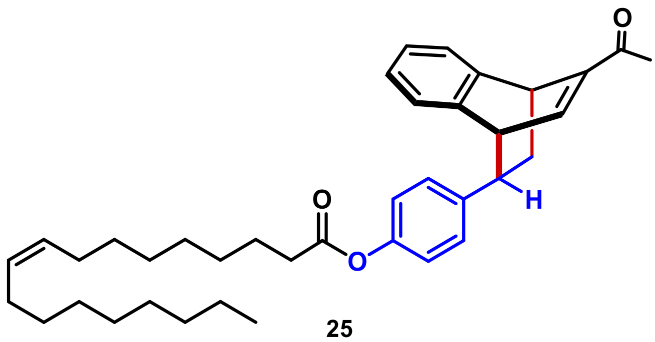
R_f: 0.3, Eluent: Ethyl acetate in Hexane 20% mixture.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 9.4, 5.0 Hz, 3H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.61 – 7.55 (m, 3H), 7.50 – 7.45 (m, 3H), 7.35 (d, *J* = 7.3 Hz, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.04 (t, *J* = 7.4 Hz, 1H), 6.86 (d, *J* = 7.3 Hz, 1H), 6.73 (dd, *J* = 8.7, 2.4 Hz, 2H), 6.40 (d, *J* = 8.2 Hz, 2H), 4.78 (d, *J* = 3.1 Hz, 1H), 4.01 – 3.97 (m, 1H), 3.92 (dd, *J* = 6.5, 2.2 Hz, 1H), 3.18 – 3.14 (m, 1H), 2.30 (s, 3H), 2.15 – 2.05 (m, 1H), 1.63 – 1.58 (m, 3H), 1.54 – 1.50 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 196.54, 195.06, 172.66, 149.23, 148.29, 147.16, 144.09, 141.18, 140.45, 138.56, 138.24, 137.57, 132.67, 131.61, 130.19, 129.36, 129.32, 128.89, 128.46, 126.47, 126.21, 125.55, 123.21, 120.82, 120.80, 49.43, 45.60, 43.43, 38.26, 34.55, 25.24, 18.59.

IR (ATR / cm^{-1}): 3061, 2972, 2936, 2855, 1755, 1657, 1599, 1506, 1454, 1324, 1285, 1202, 1171, 1074.

HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{36}H_{30}O_4Na$, 549.2036, found 549.2018.



25

Combined NMR yield: 75%, (*endo:exo* = 1.7:1)

Major isomer: 23 mg (41%, 0.041 mmol), *endo*-diastereoisomer, white solid.

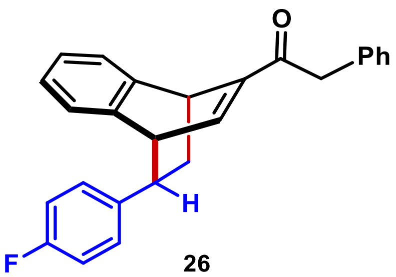
R_f: 0.4, Eluent: Ethyl acetate in Hexane 5% mixture.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 6.5, 1.8 Hz, 1H), 7.36 (d, *J* = 7.3 Hz, 1H), 7.23 – 7.19 (m, 1H), 7.07 – 7.04 (m, 1H), 6.89 (d, *J* = 7.3 Hz, 1H), 6.82 – 6.74 (m, 2H), 6.43 (d, *J* = 8.6 Hz, 2H), 5.36 – 5.34 (m, 2H), 4.78 (d, *J* = 2.4 Hz, 1H), 3.94 (dd, *J* = 6.5, 2.3 Hz, 1H), 3.19 – 3.15 (m, 1H), 2.49 (t, *J* = 7.5 Hz, 2H), 2.30 (s, 3H), 2.14 – 2.06 (m, 1H), 2.05 – 1.99 (m, 4H), 1.74 – 1.68 (m, 2H), 1.56 – 1.51 (m, 1H), 1.37 – 1.31 (m, 10H), 1.27 (d, *J* = 5.4 Hz, 10H), 0.88 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 197.6, 174.9, 151.8, 150.8, 149.7, 146.7, 143.4, 141.1, 132.7, 132.4, 131.4, 129.0, 128.8, 128.1, 125.7, 124.2, 123.6, 79.9, 79.9, 79.7, 79.4, 51.9, 46.0, 40.8, 37.1, 37.0, 34.6, 32.4, 32.3, 32.2, 32.0, 31.8, 31.7, 31.7, 29.9, 29.8, 27.8, 27.6, 25.3, 16.8.

IR (ATR / cm^{-1}): 3011, 2920, 2855, 1756, 1667, 1610, 1506, 1467, 1374, 1202, 1168, 1137, 1015.

HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{38}H_{50}O_3Na$, 577.3652, found 577.3629.



26

Combined NMR yield: 70% (*endo:exo* = 1.5:1)

Major isomer: 15 mg (41%, 0.041 mmol), *endo*-diastereoisomer, white solid.

R*f*: 0.4, Eluent: Ethyl acetate in Hexane 5% mixture.

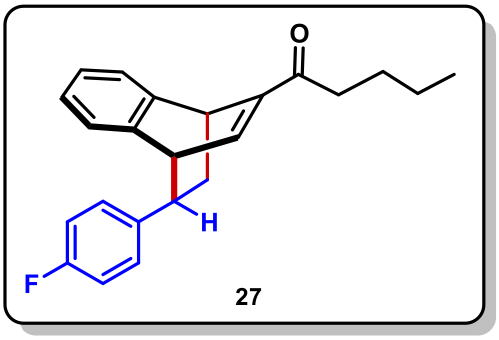
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 6.5, 1.9 Hz, 1H), 7.39 – 7.32 (m, 3H), 7.30 – 7.27 (m, 1H), 7.26 – 7.20 (m, 3H), 7.11 – 7.07 (m, 1H), 6.88 (d, *J* = 7.3 Hz, 1H), 6.79 (t, *J* = 8.7 Hz, 2H), 6.43 – 6.36 (m, 2H), 4.82 (t, *J* = 2.5 Hz, 1H), 4.06 (d, *J* = 15.4 Hz, 1H), 3.99 – 3.89 (m, 2H), 3.20 – 3.11 (m, 1H), 2.15 – 2.08 (m, 1H), 1.57 – 1.51 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 194.5, 161.6 (d, ^1J = 245.1 Hz), 147.7, 147.1, 144.0, 139.1, 138.5, 135.0, 129.5, 129.4 (d, ^3J = 7.9 Hz), 128.7, 126.9, 126.5, 126.2, 125.6, 123.3, 114.81 (d, ^2J = 21.0 Hz).49.7, 44.3, 43.2, 38.7, 34.5.

^{19}F NMR (471 MHz, $CDCl_3$) δ -116.81.

IR (ATR / cm^{-1}): 3060, 3012, 2920, 1659, 1605, 1508, 1454, 1355, 1233, 1160.

HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{26}H_{21}FONa$, 391.1469, found 391.1454.



27

Combined NMR yield: 72% (*endo:exo* = 1.8:1)

Major isomer: 14 mg (42%, 0.042 mmol), *endo*-diastereoisomer, white solid.

R*f*: 0.4, Eluent: Ethyl acetate in Hexane 3% mixture.

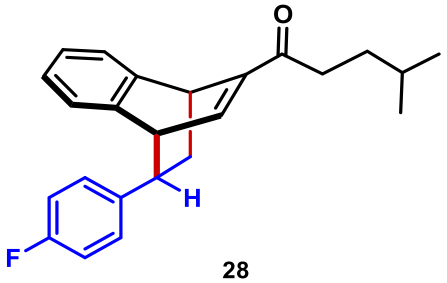
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 6.4, 1.8 Hz, 1H), 7.36 (d, *J* = 7.3 Hz, 1H), 7.23 – 7.19 (m, 1H), 7.08 – 7.03 (m, 1H), 6.84 (d, *J* = 7.3 Hz, 1H), 6.76 (t, *J* = 8.5 Hz, 2H), 6.38 (dd, *J* = 8.5, 5.5 Hz, 2H), 4.78 (q, *J* = 2.4 Hz, 1H), 3.90 (dd, *J* = 6.5, 2.3 Hz, 1H), 3.18 – 3.13 (m, 1H), 2.73 – 2.65 (m, 1H), 2.63 – 2.55 (m, 1H), 2.12 – 2.06 (m, 1H), 1.64 – 1.58 (m, 2H), 1.53 – 1.49 (m, 1H), 1.33 (q, *J* = 7.5 Hz, 2H), 0.91 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 197.7, 161.6 (d, ^1J = 244.8 Hz), 148.0, 145.8, 144.2, 139.3 (d, ^4J = 3.3 Hz), 138.7, 129.4 (d, ^3J = 8.0 Hz), 126.5, 126.1, 125.5, 123.3, 114.8 (d, ^2J = 21.0 Hz), 49.6, 43.3, 38.5, 37.2, 34.6, 26.9, 22.7, 14.0.

^{19}F NMR (471 MHz, $CDCl_3$) δ -116.89.

IR (ATR / cm^{-1}): 3003, 2962, 2871, 1662, 1602, 1506, 1472, 1454, 1428, 1207, 1150, 1067.

HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{23}H_{23}FONa$, 357.1625 found 357.1607.



28

Combined NMR yield: 67% (*endo:exo* = 1.8:1)

Major isomer: 13.2 mg (38%, 0.038 mmol), *endo*-diastereoisomer, white solid.

R$_f$: 0.5, Eluent: Ethyl acetate in Hexane 5% mixture.

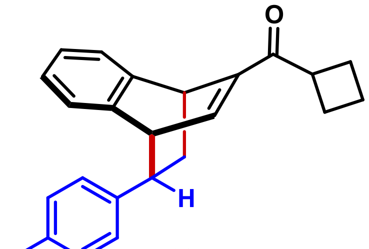
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.56 (dd, *J* = 6.4, 1.8 Hz, 1H), 7.36 (dd, *J* = 7.3, 1.2 Hz, 1H), 7.22 – 7.18 (m, 1H), 7.07 – 7.03 (m, 1H), 6.84 (dd, *J* = 7.3, 1.1 Hz, 1H), 6.77 (d, *J* = 8.7 Hz, 2H), 6.39 – 6.35 (m, 2H), 4.78 (d, *J* = 2.3 Hz, 1H), 3.90 (dd, *J* = 6.4, 2.4 Hz, 1H), 3.18 – 3.13 (m, 1H), 2.72 – 2.65 (m, 1H), 2.62 – 2.56 (m, 1H), 2.13 – 2.06 (m, 1H), 1.57 – 1.47 (m, 4H), 0.90 (dd, *J* = 6.4, 1.5 Hz, 6H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 197.9, 161.6 (d, ^{1}J = 244.5 Hz), 147.9, 145.7, 144.2, 139.3 (d, ^{4}J = 3.2 Hz), 138.7, 129.4 (d, ^{3}J = 7.8 Hz), 126.5, 126.1, 125.5, 123.3, 114.8 (d, ^{2}J = 21.2 Hz),49.6, 43.3, 38.5, 35.5, 34.6, 33.7, 28.0, 22.6, 22.5.

^{19}F NMR (471 MHz, CDCl$_3$) δ -116.90.

IR (ATR / cm^{-1}): 3003, 2951, 2839, 1667, 1589, 1586, 1451, 1430, 1202, 1142, 1067.

HRMS (ESI) m/z: [M + Na]$^+$ calcd for $C_{24}H_{25}FONa$, 371.1782, found 371.1765.



29

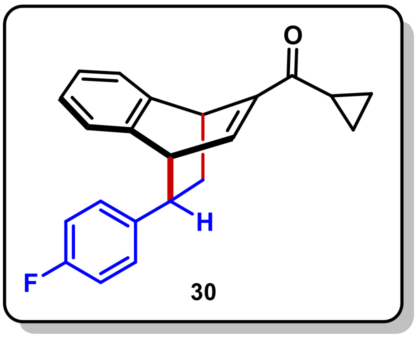
Combined NMR yield: 84% (*endo:exo* = 1.8:1)

Major isomer: 16.2 mg (49%, 0.049 mmol), *endo*-diastereoisomer, white solid.

R$_f$: 0.4, Eluent: Ethyl acetate in Hexane 5% mixture.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.43 (dd, *J* = 6.4, 1.8 Hz, 1H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.22 – 7.18 (m, 1H), 7.06 – 7.03 (m, 1H), 6.83 (d, *J* = 7.3 Hz, 1H), 6.76 (t, *J* = 8.7 Hz, 2H), 6.37 (dd,

J = 8.6, 5.5 Hz, 2H), 4.77 (d, *J* = 2.4 Hz, 1H), 3.87 (dd, *J* = 6.4, 2.4 Hz, 1H), 3.69 (p, *J* = 8.3 Hz, 1H), 3.16 – 3.11 (m, 1H), 2.38 – 2.32 (m, 1H), 2.26 (dd, *J* = 11.0, 8.8 Hz, 1H), 2.22 – 2.17 (m, 1H), 2.12 – 2.05 (m, 2H), 2.03 – 1.96 (m, 1H), 1.88 – 1.83 (m, 1H), 1.53 – 1.48 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 198.3, 161.6 (d, ^1J = 244.5 Hz), 146.4, 145.8, 144.1, 139.3 (d, ^4J = 3.1 Hz), 138.7, 129.4 (d, ^3J = 7.8 Hz), 126.4, 126.1, 125.5, 123.2, 114.8 (d, ^2J = 21.2 Hz), 49.6, 48.5, 47.7, 45.6, 43.3, 41.3, 38.6, 34.6, 25.7, 25.2, 18.4.
^{19}F NMR (471 MHz, $CDCl_3$) δ -116.93.
IR (ATR / cm^{-1}): 3052, 2949, 2873, 1651, 1602, 1506, 1477, 1459, 1371, 1204, 1150.
HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{23}H_{21}FONa$, 355.1469, found 355.1452.



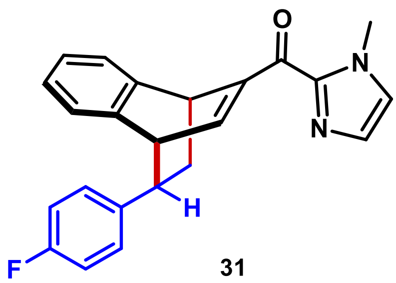
30

Combined NMR yield: 89% (*endo:exo* = 1.7:1)

Major isomer: 17 mg (53%, 0.058 mmol), *endo*-diastereoisomer, white solid.

R*f*: 0.6, Eluent: Ethyl acetate in Hexane 3% mixture.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 6.4, 1.9 Hz, 1H), 7.36 (d, *J* = 7.3 Hz, 1H), 7.23 – 7.20 (m, 1H), 7.09 – 7.03 (m, 1H), 6.87 (d, *J* = 7.3 Hz, 1H), 6.80 – 6.72 (m, 2H), 6.43 – 6.37 (m, 2H), 4.87 – 4.72 (m, 1H), 3.95 (dd, *J* = 6.5, 2.4 Hz, 1H), 3.26 – 3.17 (m, 1H), 2.39 – 2.32 (m, 1H), 2.17 – 2.10 (m, 1H), 1.56 – 1.50 (m, 1H), 1.16 – 1.11 (m, 1H), 1.08 – 1.02 (m, 1H), 0.93 – 0.89 (m, 1H), 0.88 – 0.82 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 197.1, 161.6 (d, ^1J = 244.5 Hz), 148.7, 145.8, 144.2, 139.3 (d, ^4J = 3.0 Hz), 138.8, 129.4 (d, ^3J = 7.6 Hz), 126.5, 126.1, 125.5, 123.3, 114.8 (d, ^2J = 21.3 Hz), 54.3, 49.7, 43.3, 38.8, 34.6, 16.0, 11.1.
^{19}F NMR (471 MHz, $CDCl_3$) δ -117.04.
IR (ATR / cm^{-1}): 3034, 3003, 2949, 1655, 1607, 1506, 1394, 1228, 1163, 1103, 1028.
HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{22}H_{19}FONa$, 341.1312, found 341.1294.



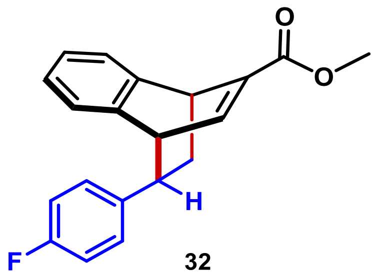
31

Combined yield: 87% (*endo:exo* = 2:1)

Major isomer: 20.8 mg (58%, 0.058 mmol), *endo*-diastereoisomer, white solid.

R*f*: 0.55, Eluent: Ethyl acetate in Hexane 10% mixture.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.45 (dd, *J* = 6.7, 1.8 Hz, 1H), 7.38 (d, *J* = 7.3 Hz, 1H), 7.22 – 7.17 (m, 1H), 7.12 (s, 1H), 7.06 – 7.00 (m, 2H), 6.85 (d, *J* = 7.3 Hz, 1H), 6.79 – 6.72 (m, 2H), 6.40 (dd, *J* = 8.5, 5.4 Hz, 2H), 4.90 (q, *J* = 2.5 Hz, 1H), 4.01 – 3.95 (m, 4H), 3.33 – 3.28 (m, 1H), 2.28 – 2.22 (m, 1H), 1.59 – 1.55 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 180.2, 161.6 (d, ^1J = 244.4 Hz), 146.0, 144.3, 143.1, 139.5, 139.5, 138.6, 129.4 (d, ^3J = 7.7 Hz), 128.8, 126.4, 126.3 (d, ^3J = 4.1 Hz), 125.5, 123.0, 114.8 (d, ^2J = 20.9 Hz), 50.1, 43.0, 39.3, 36.3, 34.8, 14.2.
^{19}F NMR (471 MHz, $CDCl_3$) δ -117.05.
Minor isomer: 10.4 mg (29%, 0.029 mmol,), *exo*-diastereoisomer, white solid.
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 6.2, 1.8 Hz, 1H), 7.24 (dd, *J* = 5.7, 2.9 Hz, 1H), 7.19 – 7.17 (m, 1H), 7.14 – 7.09 (m, 2H), 7.08 – 7.04 (m, 2H), 7.03 (s, 1H), 6.95 (s, 1H), 6.90 – 6.84 (m, 2H), 4.82 (q, *J* = 2.5 Hz, 1H), 4.17 (dd, *J* = 6.4, 2.1 Hz, 1H), 3.94 (s, 3H), 3.05 – 3.00 (m, 1H), 2.18 – 2.13 (m, 1H), 1.79 – 1.73 (m, 1H).
IR (ATR / cm^{-1}): 2954, 2881, 1623, 1605, 1511, 1477, 1407, 1223, 1160, 1134, 1103.
HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{23}H_{19}FN_2ONa$, 381.1374, found 381.1353.



32

Combined NMR yield: 83% (*endo:exo* = 2:1)

Major isomer: 13.9 mg (45%, 0.045 mmol), *endo*-diastereoisomer, white solid.

R$_f$: 0.4, Eluent: Ethyl acetate in Hexane 2% mixture.

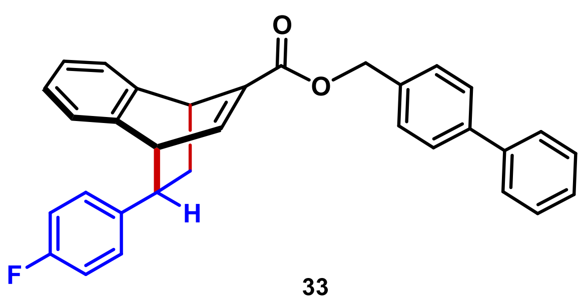
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.62 (dd, J = 6.5, 1.8 Hz, 1H), 7.36 (d, J = 7.3 Hz, 1H), 7.23 – 7.18 (m, 1H), 7.07 – 7.03 (m, 1H), 6.83 (d, J = 7.3 Hz, 1H), 6.78 – 6.73 (m, 2H), 6.40 – 6.34 (m, 2H), 4.63 (d, J = 2.3 Hz, 1H), 3.89 (dd, J = 6.5, 2.3 Hz, 1H), 3.78 (s, 3H), 3.16 – 3.10 (m, 1H), 2.23 – 2.17 (m, 1H), 1.55 – 1.51 (m, 1H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 165.5, 161.6 (d, ^1J = 244.4 Hz), 146.8, 144.0, 139.6, 139.2 (d, ^4J = 3.0 Hz), 138.5, 129.4 (d, ^3J = 7.8 Hz), 126.4, 126.3, 125.6, 123.0, 114.8 (d, ^2J = 21.2 Hz) 51.9, 49.6, 43.5, 43.1, 40.4, 34.8.

^{19}F NMR (471 MHz, CDCl$_3$) δ -116.97.

IR (ATR / cm^{-1}): 3042, 2954, 2917, 2855, 1701, 1625, 1602, 1508, 1462, 1438, 1360, 1230, 1160, 1074.

HRMS (ESI) m/z: [M + Na]$^+$ calcd for $C_{20}H_{17}FO_2Na$, 331.1105, found 331.1093.



33

Combined NMR yield: 85% (*endo:exo* = 1.6:1)

Mixture of major and minor isomer: 36.4 mg (79%, 0.079 mmol), colorless liquid.

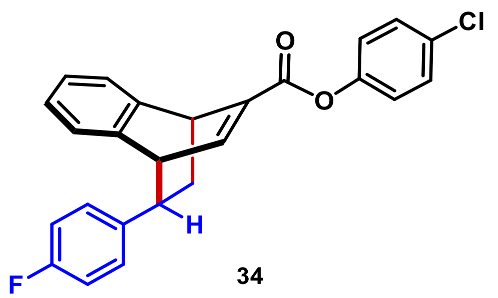
R$_f$: 0.45, Eluent: Ethyl acetate in Hexane 5% mixture.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.71 (d, J = 6.6 Hz, 0.6H$_{maj}$), 7.60 (dd, J = 7.3, 2.9 Hz, 4.40H), 7.46 (q, J = 7.0 Hz, 4H), 7.41 – 7.29 (m, 2H), 7.28 – 7.15 (m, 2H), 7.13 – 7.02 (m, 1.4H), 6.96 (t, J = 8.5 Hz, 0.6H$_{maj}$), 6.84 (d, J = 7.4 Hz, 0.6H$_{maj}$), 6.77 (t, J = 8.5 Hz, 1.4H), 6.42 – 6.36 (m, 1H), 5.44 – 5.25 (m, 2H), 4.69 (s, 1H), 4.15 (d, J = 6.5 Hz, 0.4H$_{min}$), 3.90 (d, J = 6.5 Hz, 0.6H$_{maj}$), 3.20 – 3.04 (m, 0.6H$_{maj}$ + 0.4H$_{min}$), 2.29 – 2.15 (m, 1H), 1.86 – 1.75 (m, 0.4H$_{min}$), 1.57 – 1.52 (m, 0.6H$_{maj}$).

^{13}C NMR (126 MHz, CDCl$_3$) δ 164.7(major), 164.5(minor), 161.5 (d, ^1J = 244.5 Hz), 147.1, 144.4, 143.9, 143.1, 142.6, 141.2, 141.0, 140.7, 140.7, 140.3, 139.4, 139.1, 138.4, 135.1 (d, ^4J = 3.4 Hz), 129.3, 129.2, 129.2, 129.1, 128.8, 128.7, 128.5, 127.5, 127.2 (d, ^2J = 24.3 Hz), 126.3, 126.1, 125.9 (d, ^2J = 23.5 Hz), 125.5, 123.8, 122.9, 115.2 (d, ^2J = 21.0 Hz, minor), 114.7 (d, ^2J = 20.9 Hz, major), 66.1, 49.5, 49.0, 44.6, 42.9, 40.7, 40.2, 35.6, 34.7.

^{19}F NMR (471 MHz, CDCl$_3$) δ -116.71 (minor), -116.90 (major).

IR (ATR / cm^{-1}): 3035, 2956, 2888, 1706, 1618, 1599, 1514, 1275, 1246, 1217, 1158, 1067.
HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{32}H_{25}FO_2Na$, 483.1731, found 483.1709.



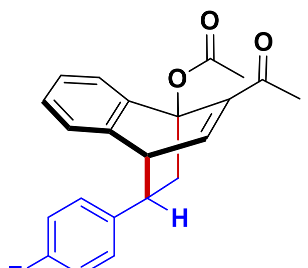
34

Combined NMR yield: 80% (*endo:exo* = 1:1)

Major isomer: 14.5 mg (36%, 0.036 mmol), *endo*-diastereoisomer, white solid.

R*f*: 0.7, Eluent: Ethyl acetate in Hexane 5% mixture.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 6.5, 1.8 Hz, 1H), 7.41 (d, *J* = 7.3 Hz, 1H), 7.37 – 7.34 (m, 2H), 7.25 (d, *J* = 1.2 Hz, 1H), 7.08 (dd, *J* = 9.2, 7.1 Hz, 3H), 6.88 (d, *J* = 7.3 Hz, 1H), 6.78 (t, *J* = 8.7 Hz, 2H), 6.43 – 6.38 (m, 2H), 4.72 (q, *J* = 2.5 Hz, 1H), 3.98 (dd, *J* = 6.5, 2.3 Hz, 1H), 3.27 – 3.19 (m, 1H), 2.32 – 2.25 (m, 1H), 1.63 – 1.59 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 163.1, 161.6 (d, ^1J = 244.9 Hz), 149.5, 149.3, 143.8, 139.0 (d, ^4J = 3.3 Hz), 138.9, 138.2, 131.2, 129.6, 129.4 (d, ^3J = 7.7 Hz), 126.5 (d, ^2J = 24.3 Hz),125.8, 123.3, 123.2, 123.1, 114.9 (d, ^2J = 20.9 Hz), 49.8, 43.0, 40.3, 34.8.
^{19}F NMR (471 MHz, $CDCl_3$) δ -116.70.
IR (ATR / cm^{-1}): 3068, 2956, 2925, 2852, 1712, 1618, 1514, 1480, 1360, 1197, 1155, 1085.
HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{25}H_{18}ClFO_2Na$, 427.0872, found 427.0846.



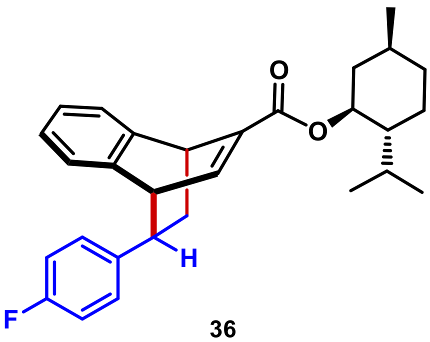
35

NMR yield: 80%, (*endo:exo* = 3.7:1)

Isolated yield: 21 mg (60%, 0.06 mmol, major isomer), white solid.

R*f*: 0.35, Eluent: Ethyl acetate in Hexane 5% mixture.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.30 (dd, *J* = 12.1, 5.0 Hz, 2H), 7.24 (d, *J* = 6.5 Hz, 1H), 7.15 – 7.10 (m, 1H), 6.85 (d, *J* = 7.2 Hz, 1H), 6.78 (t, *J* = 8.6 Hz, 2H), 6.34 (dd, *J* = 8.5, 5.3 Hz, 2H), 3.84 (dd, *J* = 6.6, 2.5 Hz, 1H), 3.28 – 3.17 (m, 1H), 2.36 (s, 3H), 2.30 (s, 3H), 1.80 – 1.66 (m, 2H).
^{13}C NMR (126 MHz, CDCl$_3$) δ 170.9, 161.71 (d, ^1J = 245.1 Hz), 147.1, 138.0, 135.6, 129.23 (d, ^3J = 8.0 Hz), 126.4, 126.2, 125.7, 119.9, 114.95 (d, ^2J = 21.3 Hz), 82.1, 48.1, 42.5, 27.4, 21.8.
IR (ATR / cm^{-1}): 3042, 2954, 2917, 2855, 1701, 1660, 1602, 1508, 1462, 1438, 1360, 1230, 1160, 1074.
HRMS (ESI) m/z: [M + Na]$^+$ calcd for $C_{22}H_{19}FO_3Na$, 373.1210, found 373.1191.



36

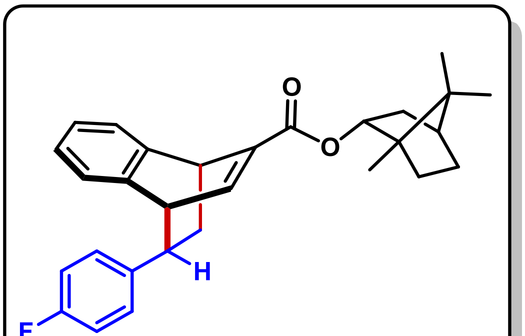
Combined NMR yield: 50% (*endo:exo* = 1.6:1)

Mixture of major and minor isomer: 19.9 mg (46%, 0.046 mmol) colorless liquid.

R$_f$: 0.45, Eluent: Ethyl acetate in Hexane 5% mixture.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.59 (dd, *J* = 6.5, 1.8 Hz, 0.6H), 7.50 – 7.26 (m, 1Hmaj + 0.4Hmin), 7.25 – 7.17 (m, 1H), 7.15 (q, *J* = 3.5 Hz, 0.6Hmaj), 7.12 – 6.97 (m, 1Hmaj + 0.4Hmin), 6.97 – 6.90 (m, 0.6Hmaj), 6.83 (d, *J* = 7.3 Hz, 0.6Hmaj), 6.76 (t, *J* = 8.5 Hz, 1Hmaj + 0.4Hmin), 6.47 – 6.31 (m, 1Hmaj + 0.4Hmin), 4.85 – 4.72 (m, 1H), 4.65 (d, *J* = 13.9 Hz, 1H), 4.18 – 4.03 (m, 0.4Hmin), 3.88 (dd, *J* = 6.5, 2.2 Hz, 0.6Hmaj), 3.20 – 3.02 (m, 1H), 2.27 – 2.14 (m, 1H), 2.12 – 2.01 (m, 1H), 1.98 – 1.82 (m, 1H), 1.73 – 1.67 (m, 2H), 1.58 – 1.41 (m, 3H), 1.09 (dd, *J* = 12.9, 7.5 Hz, 1H), 0.97 – 0.91 (m, 4H), 0.90 – 0.85 (m, 4H), 0.84 – 0.69 (m, 3H).
^{13}C NMR (126 MHz, CDCl$_3$) δ 164.5, 164.4, 164.3, 164.2, 162.4, 160.4, 145.9, 145.8, 144.1, 144.1, 143.5, 143.3, 140.4, 140.1, 139.9, 138.6, 129.3, 129.2, 129.2, 126.2, 126.1, 126.0, 125.9, 125.7, 125.4, 123.8, 123.7, 122.9, 122.8, 115.2, 115.1, 115.1, 115.0, 114.7, 114.6, 77.3, 77.0, 76.8, 74.5, 74.4, 74.4, 49.4, 49.2, 49.0, 47.3, 47.2, 47.2, 47.1, 44.6, 43.0, 41.1, 41.0, 40.6, 40.2, 40.1, 35.7, 35.6, 34.8, 34.8, 34.3, 31.4, 31.4, 27.0, 26.7, 26.3, 26.2, 24.0, 23.8, 23.5, 22.7, 22.1, 22.0, 20.8, 20.8, 20.7, 17.0, 16.8, 16.5.
^{19}F NMR (471 MHz, CDCl$_3$) δ -116.77, -116.85, -117.00, -117.01.
IR (ATR / cm^{-1}): 2925, 2864, 1710, 1601, 1513, 1510, 1479, 1468.

HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{29}H_{33}FO_2Na$, 455.2340, found 455.2357.



37

Combined NMR yield: 80% (*endo:exo* = 1.6:1)

Mixture of major and minor isomer: 32.7 mg (76%, 0.076 mmol) colorless liquid.

R_f: 0.45, Eluent: Ethyl acetate in Hexane 5% mixture.

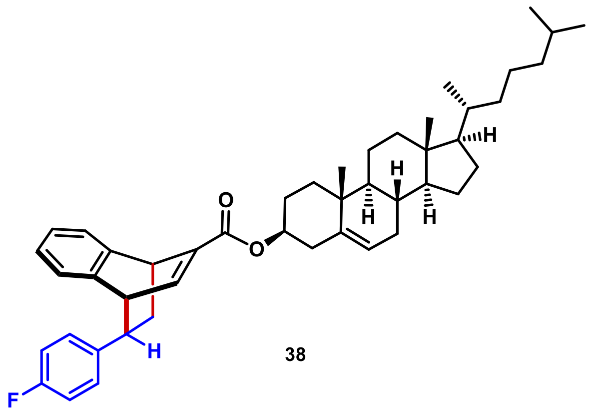
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.65 (d, *J* = 6.5 Hz, 0.7H_{maj}), 7.40 (d, *J* = 7.1 Hz, 0.7H_{maj}), 7.35 (t, *J* = 4.3 Hz, 0.3H_{min}), 7.31 – 7.05 (m, 3H), 6.99 (t, *J* = 7.9 Hz, 0.6H_{min}), 6.93 – 6.64 (m, 2H_{maj} + 0.6H_{min}), 6.42 (q, *J* = 8.9 Hz, 1.4H_{maj}), 5.21 – 4.88 (m, 1H), 4.67 (s, 1H), 4.15 (d, *J* = 6.5 Hz, 0.3H_{min}), 3.92 (d, *J* = 6.5 Hz, 0.7H_{maj}), 3.27 – 3.05 (m, 1H), 2.53 – 2.36 (m, 1H), 2.29 – 2.15 (m, 1H), 2.11 – 1.98 (m, 1H), 1.86 – 1.71 (m, 2H_{maj} + 0.3H_{min}), 1.57 (s, 0.7H_{maj}), 1.45 – 1.15 (m, 2.1H_{maj} + 0.6H_{min}), 1.10 (d, *J* = 11.1 Hz, 0.3H_{min}), 0.97 (d, *J* = 2.9 Hz, 3H), 0.95 – 0.85 (m, 6H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 165.3, 165.3, 165.0, 161.6 (d, ^1J = 245.1 Hz), 146.0, 144.2 (d, ^4J = 3.5 Hz), 143.4, 142.9, 141.6, 140.2, 139.3, 138.7, 129.4 (d, ^3J = 7.5 Hz),126.4, 126.2, 126.1, 125.9, 125.6, 123.8, 123.0, 115.3 (d, ^2J = 20.8 Hz, minor), 114.8 (d, ^2J = 20.8 Hz, major).80.3, 80.2, 49.6, 49.1, 47.9, 45.1, 43.1, 40.4, 37.0, 36.9, 34.9, 28.2, 28.1, 27.4, 19.9, 19.0, 13.8, 13.7.

^{19}F NMR (471 MHz, CDCl$_3$) δ -116.77 (minor), -116.97 (major).

IR (ATR / cm^{-1}): 3071, 2957, 2878, 1698, 1620, 1503, 1456, 1303, 1275, 1228, 1158, 1113, 1069, 1025.

HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{29}H_{31}FO_2Na$, 453.2200, found 453.2181.



38

Combined NMR yield: 58% (*endo:exo* = 1.6:1)

Mixture of major and minor isomer: 37.1 mg (56%, 0.056 mmol), white solid.

R*f*: 0.5, Eluent: Ethyl acetate in Hexane 3% mixture.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.63 – 7.48 (m, 0.70Hmin), 7.39 – 7.28 (m, 1.30Hmaj), 7.25 – 7.18 (m, 1H), 7.17 – 7.12 (m, 0.70Hmin), 7.11 – 7.03 (m, 1.30Hmaj), 6.97 (t, *J* = 8.5 Hz, 0.70Hmin), 6.92 – 6.80 (m, 0.70Hmin), 6.76 (t, *J* = 8.7 Hz, 1.30Hmaj), 6.44 – 6.31 (m, 1.30Hmaj), 5.39 (dd, *J* = 16.4, 5.0 Hz, 1H), 4.81 – 4.66 (m, 1H), 4.63 (p, *J* = 2.3 Hz, 1H), 4.12 (dd, *J* = 6.3, 2.2 Hz, 0.35Hmin), 3.88 (dd, *J* = 6.5, 2.3 Hz, 0.65Hmaj), 3.21 – 3.01 (m, 1H), 2.44 – 2.29 (m, 2H), 2.24 – 2.13 (m, 1H), 2.07 – 1.93 (m, 3H), 1.90 – 1.73 (m, 3H), 1.65 – 1.46 (m, 8H), 1.38 – 1.32 (m, 3H), 1.20 – 1.07 (m, 8H), 1.04 (d, *J* = 1.3 Hz, 3H), 1.00 (dd, *J* = 10.6, 7.1 Hz, 2H), 0.92 (d, *J* = 6.4 Hz, 3H), 0.87 (dd, *J* = 6.6, 2.3 Hz, 6H), 0.69 (s, 3H).

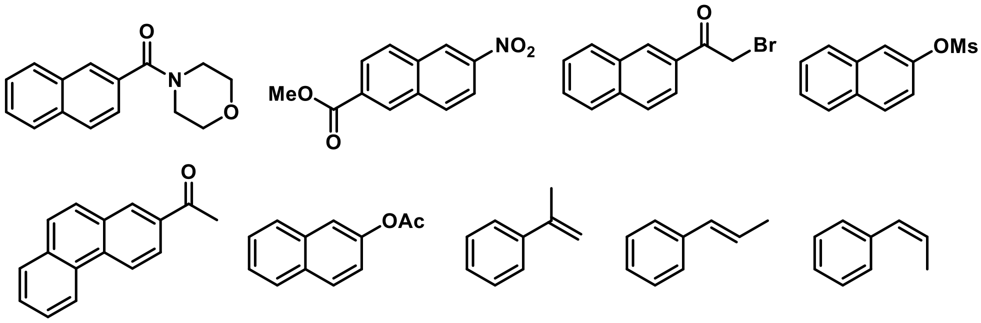
^{13}C NMR (126 MHz, CDCl$_3$) δ 164.5, 164.2, 161.7(d, ^1J = 243.5.0 Hz), 161.5(d, ^1J = 243.5 Hz),, 146.2, 144.2, 143.5, 143.4, 142.9, 141.7, 140.5, 140.1, 139.9, 139.8, 139.4, 138.7, 129.4, 129.3, 129.3, 126.3, 126.2, 126.0, 125.8, 125.5, 123.9, 123.0, 123.0, 122.8, 122.8, 115.30 (d, ^2J = 21.0 Hz), 114.78 (d, ^2J = 21.1 Hz).74.4, 74.3, 56.8, 56.3, 50.2, 49.6, 49.0, 44.8, 43.1, 42.5, 40.7, 40.3, 39.9, 39.7, 38.4, 38.4, 37.2, 37.1, 36.8, 36.3, 35.9, 35.8, 34.9, 32.1, 32.0, 29.8, 28.4, 28.2, 28.1, 28.0, 24.4, 24.0, 23.0, 22.7, 21.2, 19.5, 18.9, 14.3, 12.0.

^{19}F NMR (471 MHz, CDCl$_3$) δ -116.85, -116.99.

IR (ATR / cm^{-1}): 2933, 2871, 2850, 1707, 1626, 1512, 1467, 1374, 1275, 1223, 1158.

HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{46}H_{60}FO_2$, 663.4572, found 663.4502.

Unsuccessful substrate



6.1. Single crystal X-ray diffraction studies

Single crystals of pure compounds ***endo*-3**, ***endo*-7**, ***endo*-31**, and ***exo*-31** were obtained by slow diffusion from the hexane solution at room temperature. Intensity data were collected on an XtaLAB Synergy, Dualflex, HyPix3000 diffractometer. The crystal was kept at 99.99 K during the data collection. The software Olex2 was used for space group, structure determination, and refinements. The least-squares refinement techniques on F2 were performed until the model converged. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were fixed at calculated positions, and their positions were refined by a riding model.

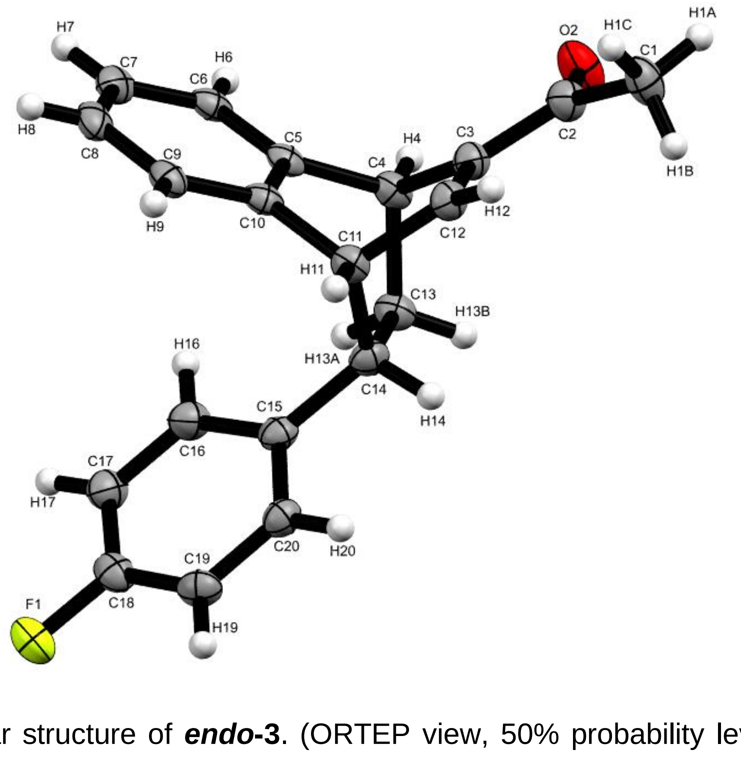


Figure S1: Molecular structure of ***endo*-3**. (ORTEP view, 50% probability level). **(CCDC = 2173728).**

Crystal data and structure refinement for *endo*-3.

Identification code	PRAPD208_2
Empirical formula	$C_{20}H_{17}FO$
Formula weight	292.33
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	Fdd2
a/Å	38.8063(6)
b/Å	15.6732(3)
c/Å	9.8717(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	6004.15(19)
Z	16
ρ_{calc}g/cm^3	1.294
μ/mm^{-1}	0.696
F(000)	2464.0
Crystal size/mm^3	0.05 × 0.05 × 0.025
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.116 to 136.324
Index ranges	-11 ≤ h ≤ 46, -18 ≤ k ≤ 18, -11 ≤ l ≤ 11
Reflections collected	5410
Independent reflections	2167 [R_{int} = 0.0317, R_{sigma} = 0.0260]
Data/restraints/parameters	2167/1/200
Goodness-of-fit on F^2	1.053
Final R indexes [I>=2σ (I)]	R_1 = 0.0385, wR_2 = 0.0993
Final R indexes [all data]	R_1 = 0.0394, wR_2 = 0.1014
Largest diff. peak/hole / e Å^{-3}	0.14/-0.26
Flack parameter	-0.08(13)

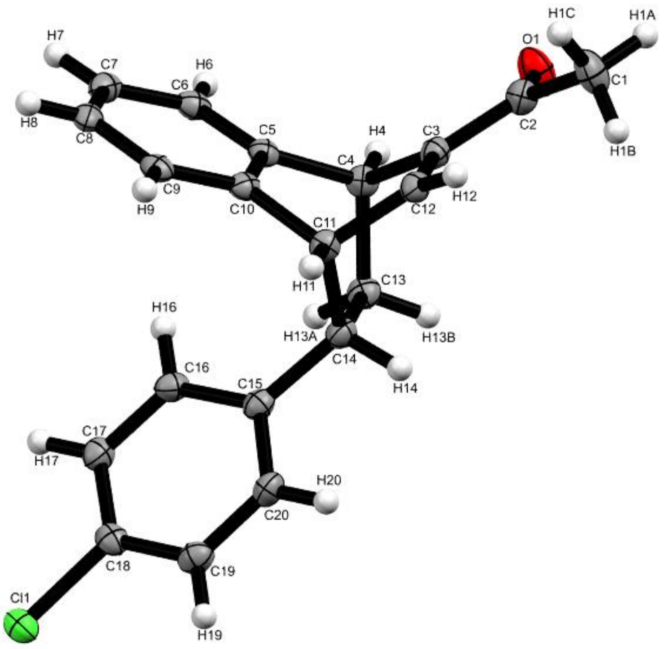


Figure S2: Molecular structure of ***endo*-7** (ORTEP view, 50% probability level). **(CCDC = 2173729).**

Crystal data and structure refinement for *endo*-7.

Identification code	kmcke212_2
Empirical formula	$C_{20}H_{17}ClO$
Formula weight	308.79
Temperature/K	100.00
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.4028(2)
b/Å	19.5701(2)
c/Å	9.3681(2)
α/°	90
β/°	115.798(2)
γ/°	90
Volume/Å^3	1552.05(5)
Z	4
ρ_{calc}g/cm^3	1.321
μ/mm^{-1}	2.153
F(000)	648.0

Crystal size/mm^3	0.1 × 0.1 × 0.05
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.038 to 136.206
Index ranges	$-9 \le h \le 11$, $-22 \le k \le 23$, $-10 \le l \le 11$
Reflections collected	8978
Independent reflections	2500 [R_{int} = 0.0504, R_{sigma} = 0.0331]
Data/restraints/parameters	2500/0/200
Goodness-of-fit on F^2	1.087
Final R indexes [I>=2σ (I)]	R_1 = 0.0429, wR_2 = 0.1047
Final R indexes [all data]	R_1 = 0.0436, wR_2 = 0.1053
Largest diff. peak/hole / e $Å^{-3}$	0.28/-0.22

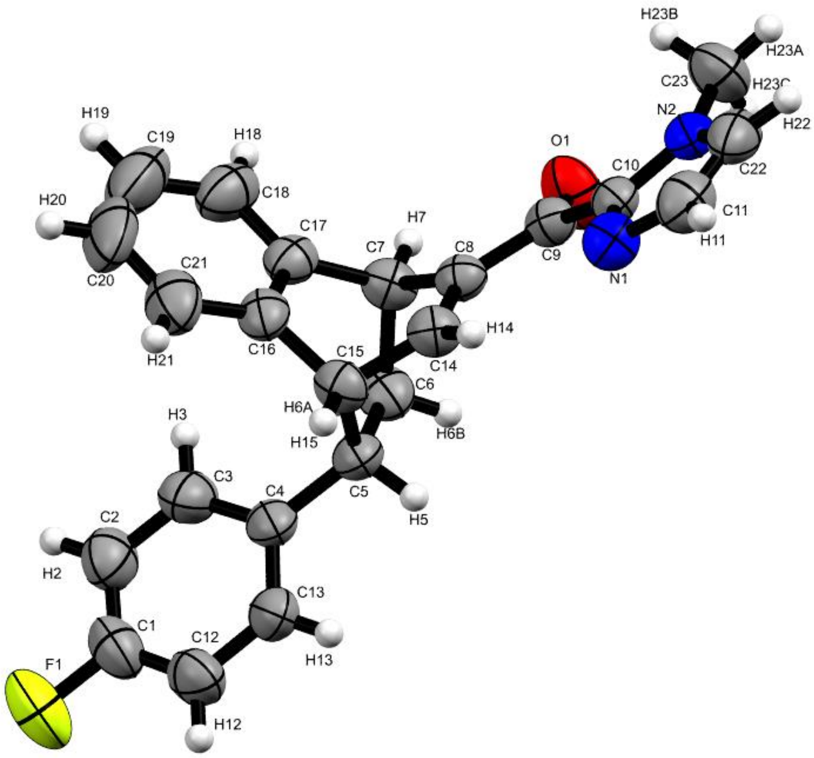


Figure S3: Molecular structure of ***endo*-31**(ORTEP view, 50% probability level). **(CCDC = 2173850).**

Crystal data and structure refinement for *endo*-31.

Identification code	PRAPD205B_0m_a (2)
Empirical formula	$C_{23}H_{19}FN_2O$
Formula weight	358.40
Temperature/K	298
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.6548(4)
b/Å	7.2987(2)
c/Å	20.6049(6)
α/°	90
β/°	98.6430(10)
γ/°	90
Volume/Å^3	1881.53(10)
Z	4
ρ_{calc}g/cm^3	1.265
μ/mm^{-1}	0.085
F(000)	752.0
Crystal size/mm^3	0.25 × 0.21 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.998 to 49.998
Index ranges	-15 ≤ h ≤ 15, -8 ≤ k ≤ 8, -24 ≤ l ≤ 24
Reflections collected	47061
Independent reflections	3308 [R_{int} = 0.1081, R_{sigma} = 0.0373]
Data/restraints/parameters	3308/0/245
Goodness-of-fit on F^2	1.108
Final R indexes [I>=2σ (I)]	R_1 = 0.0400, wR_2 = 0.1107
Final R indexes [all data]	R_1 = 0.0640, wR_2 = 0.1179
Largest diff. peak/hole / e Å^{-3}	0.14/-0.15

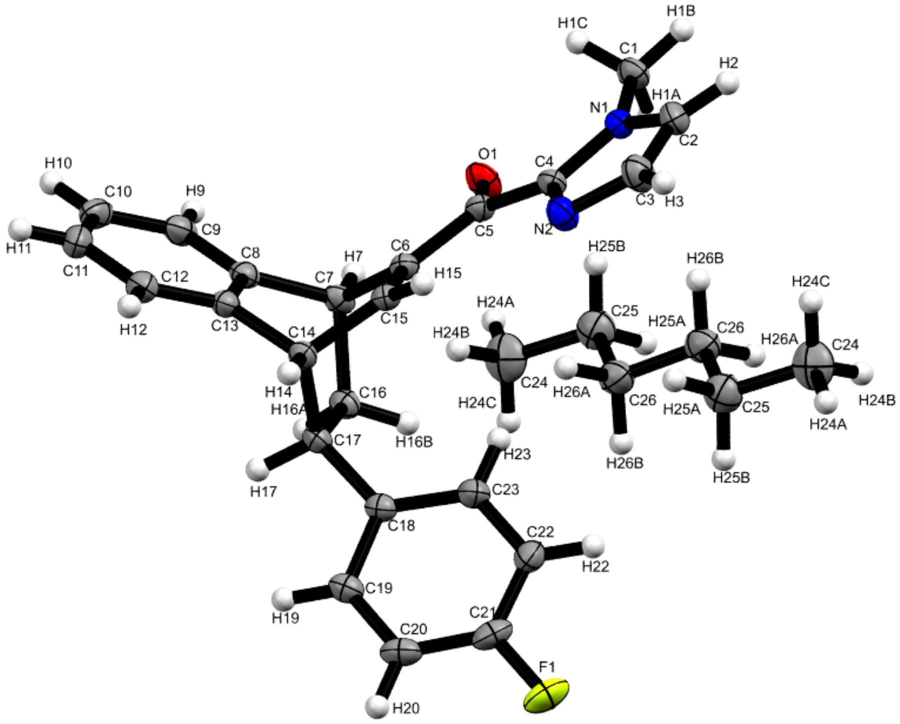


Figure S4 Molecular structure of ***exo*-31•*n*-hexane** (ORTEP view, 50% probability level). **(CCDC = 2173723).**

Crystal data and structure refinement for *exo-31•n-hexane*

Identification code	PRAPD203A_2
Empirical formula	$C_{26}H_{26}FN_2O$
Formula weight	401.49
Temperature/K	100.00
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.1117(2)
b/Å	20.3860(3)
c/Å	9.62050(10)
α/°	90
β/°	107.152(2)
γ/°	90
Volume/Å^3	2082.34(6)
Z	4
ρ_{calc}g/cm^3	1.281

μ/mm^{-1}	0.673
F(000)	852.0
Crystal size/mm^3	0.1 × 0.05 × 0.02
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.328 to 136.556
Index ranges	-13 ≤ h ≤ 13, -14 ≤ k ≤ 24, -11 ≤ l ≤ 10
Reflections collected	15565
Independent reflections	3735 [R_{int} = 0.0948, R_{sigma} = 0.0521]
Data/restraints/parameters	3735/0/273
Goodness-of-fit on F^2	1.056
Final R indexes [I>=2σ (I)]	R_1 = 0.0477, wR_2 = 0.1235
Final R indexes [all data]	R_1 = 0.0516, wR_2 = 0.1278
Largest diff. peak/hole / e Å^{-3}	0.64/-0.26

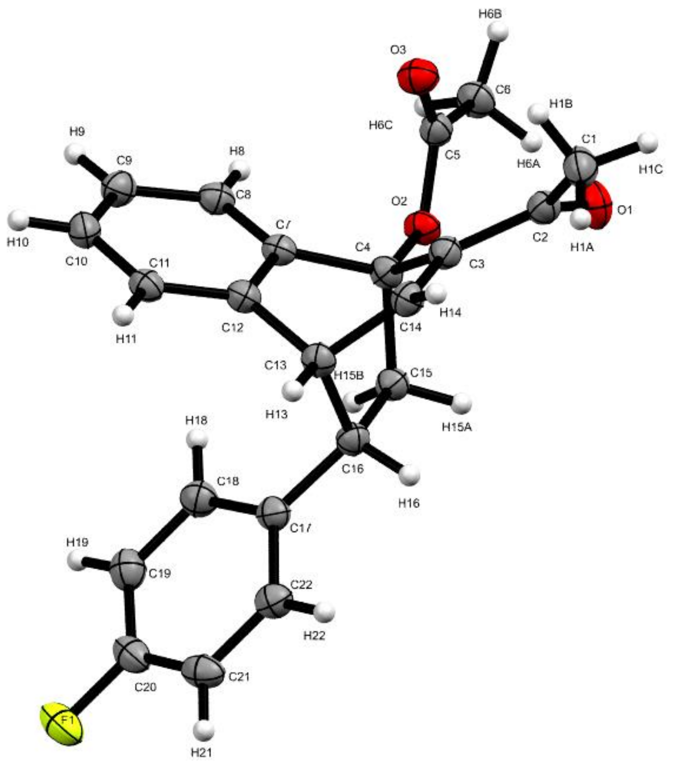
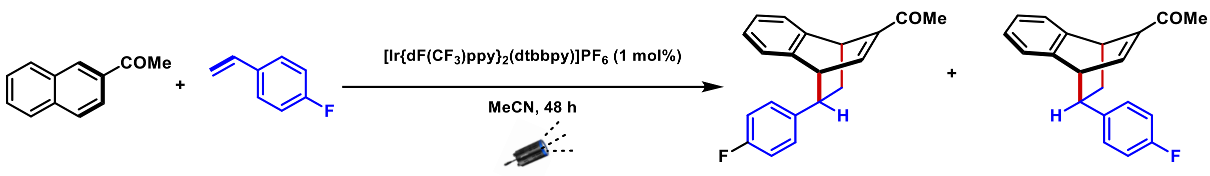


Figure S5 Molecular structure of ***endo*-35** (ORTEP view, 50% probability level). **(CCDC = 2190337).**

Crystal data and structure refinement for *endo*-35.

Identification code	KMC-KE 257_2_auto_2
Empirical formula	$C_{22}H_{19}FO_3$
Formula weight	350.37
Temperature/K	100.01(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	13.8641(2)
b/Å	10.52260(10)
c/Å	12.11710(10)
α/°	90
β/°	103.0290(10)
γ/°	90
Volume/Å^3	1722.21(3)
Z	4
ρ_{calc}g/cm^3	1.351
μ/mm^{-1}	0.790
F(000)	736.0
Crystal size/mm^3	0.1 × 0.05 × 0.03
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.544 to 136.478
Index ranges	-16 ≤ h ≤ 16, -12 ≤ k ≤ 12, -14 ≤ l ≤ 12
Reflections collected	18992
Independent reflections	3149 [R_{int} = 0.0839, R_{sigma} = 0.0338]
Data/restraints/parameters	3149/0/237
Goodness-of-fit on F^2	1.065
Final R indexes [I>=2σ (I)]	R_1 = 0.0402, wR_2 = 0.1059
Final R indexes [all data]	R_1 = 0.0433, wR_2 = 0.1086
Largest diff. peak/hole / e Å^{-3}	0.38/-0.26

7. Scale-up reaction

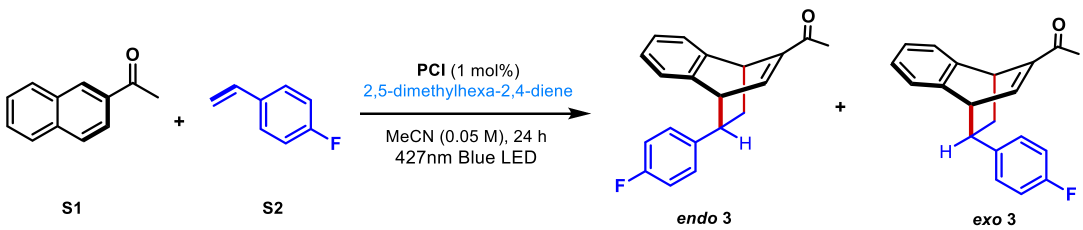


General procedure

2-Acetyl naphthalene **1** (1 mmol), and photosensitizer [Ir(dFCF$_3$ppy)$_2$(dtbbpy)]PF$_6$ (1 mol%) were placed into a dry 100 mL Schlenk tube. The tube was evacuated and backfilled with nitrogen three times. Dry and degassed acetonitrile (20 mL) followed by **2** (1.2 mmol) were added under nitrogen. The tube was sealed, and the resulting solution was placed 5 cm away from a 427 nm Blue LED (Kessil lamp model; PR160L-427 nm) and irradiated for 48 h. The reaction mixture was diluted with CH_2Cl_2. The residue was purified by flash chromatography on silica gel to afford the corresponding product **3** in 84% (0.25 gm, 0.86 mmol). (EtOAc in hexane = 5%).

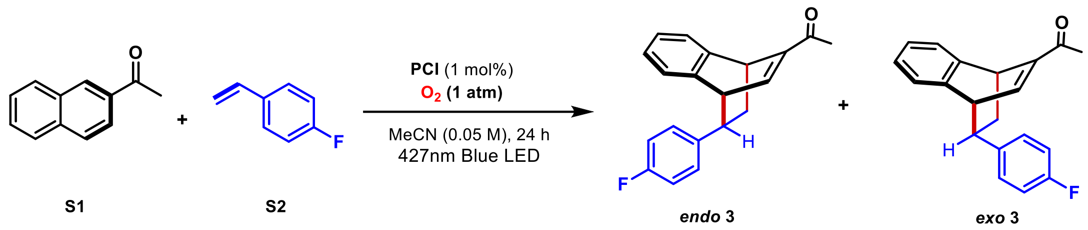
Before reaction During reaction After reaction

8. Reaction in presence of triplet energy quencher



In presence of 2,5-dimethylhexa-2,4-diene; The corresponding naphthalene (0.1 mmol), and photosensitizer [Ir(dF-CF$_3$ppy)$_2$(dtbbpy)]PF$_6$ (1 mol%) were placed into a dry 15 mL sealed tube. The tube was evacuated and backfilled with nitrogen three times. Dry and degassed acetonitrile (2 mL) followed by alkene (0.12-0.2 mmol) and the triplet energy quencher 2,5-dimethylhexa-2,4-diene (0.1 mmol) was added under a nitrogen atmosphere. The tube was sealed with a screw cap, and the resulting solution was placed 5 cm away from a 427 nm Blue LED (Kessil lamp model; PR160L-427 nm, see the picture below) and irradiated for 24 h. Afterward, the mixture was diluted with CH_2Cl_2 (2 mL), and then 1,3,5-trimethoxy benzene (0.1

mmol) was added. The reaction mixture was filtered through a small pack of silica gel, and then the solvent was evaporated by a rotary evaporator, keeping the water bath temperature below 40 °C. The ^{1}H NMR ($CDCl_3$, 500 MHz) analysis of this crude reaction mixture was carried out to determine yields and the *endo:exo* ratios.



In presence of oxygen atmosphere; The corresponding naphthalene (0.1 mmol), and photosensitizer [Ir(dF-CF_3ppy)$_2$(dtbbpy)]PF_6 (1 mol%) were placed into a dry 15 mL sealed tube. The tube was evacuated and purged with oxygen. Dry and degassed acetonitrile (2 mL) followed by alkene (0.12-0.2 mmol) was added under oxygen atmosphere. The tube was sealed with a rubber screw cap having oxygen balloon at the top, and the resulting solution was placed 5 cm away from a 427 nm Blue LED (Kessil lamp model; PR160L-427 nm, see the picture below) and irradiated for 24 h. Afterward, the mixture was diluted with CH_2Cl_2 (2 mL), and then 1,3,5-trimethoxy benzene (0.1 mmol) was added. The reaction mixture was filtered through a small pack of silica gel, and then the solvent was evaporated by a rotary evaporator, keeping the water bath temperature below 40 °C. The ^{1}H NMR ($CDCl_3$, 500 MHz) analysis of this crude reaction mixture was carried out to determine yields and the *endo:exo* ratios.

9. Stern-Volmer quenching studies[4]

Rates of quenching (k_q) were determined using Stern–Volmer kinetics (eq 1).

$I_o/I = k_q \tau_0 [\text{Quencher}] + 1$ ……. (1)

Where I_0 is the luminescence intensity without the quencher, I is the intensity with the quencher, and τ_0 is the lifetime of the photocatalyst (2300 ns for [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6 in acetonitrile).

Stern-Volmer fluorescence quenching studies were carried out using a 10^{-6} M solution of [Ir{dF(CF_3)ppy}$_2$(dtbbpy)PF_6] (**PC1**) in acetonitrile and variable concentrations of both 2-acetyl naphthalene (**1**) and 1-fluoro-4-vinyl benzene (**2**) from 0 to 3.8 mM. The samples were prepared in 3.5 mL quartz cuvettes, equipped with PTFE stoppers, and sealed with Parafilm inside an argon-filled glove bag. The solutions were irradiated at 427 nm, and the luminescence was measured at 473 nm. Both excitation and emission bandwidth were set to 3 nm for each sample.

A linear Stern-Volmer plot was obtained at the variable concentration of **1**. From the plot k_q = 1.6×10^4 $M^{-1}s^{-1}$ was obtained.

A similar experiment was repeated with variable concentrations of **2** that show a lower quenching of the luminescence of [Ir{dF(CF_3)ppy}$_2$(dtbbpy)PF_6]. From the plot k_q = 0.41 × 10^4 $M^{-1}s^{-1}$ was obtained.

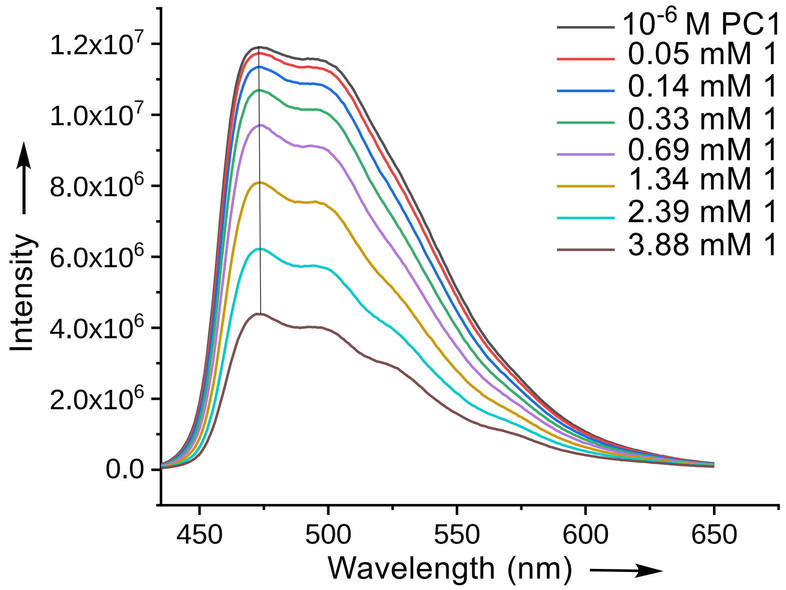


Figure S6: Photoluminescence quenching of **PC1** with **1**.

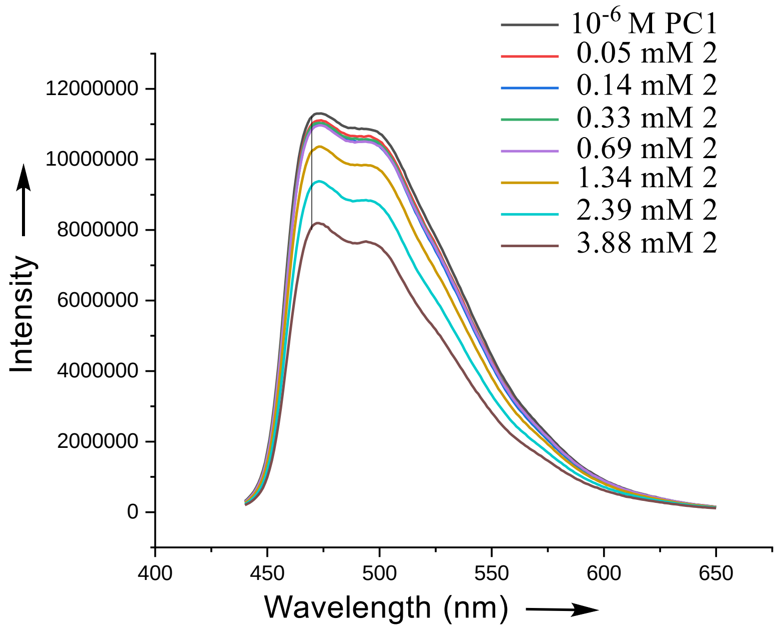


Figure S7: Photoluminescence quenching of **PC1** with **2**.

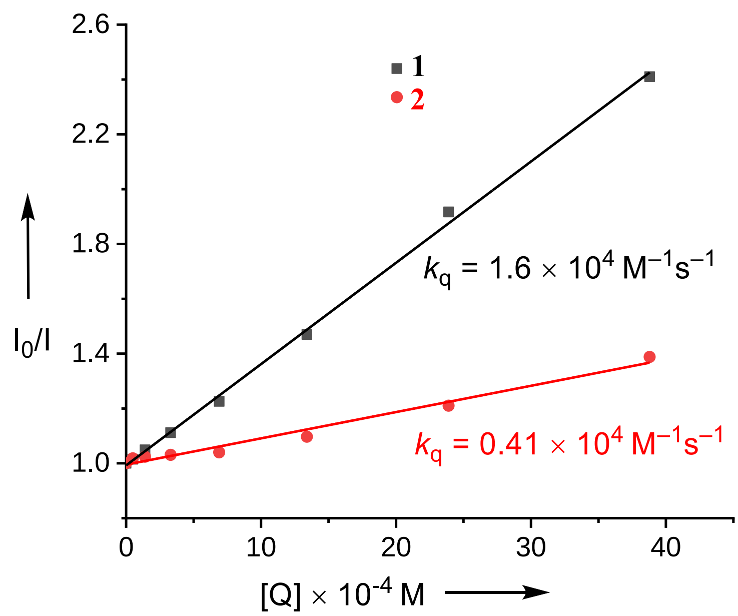


Figure S8: Stern Volmer plot for photoluminescence quenching of **PC1** with **1** and **2**

Then Stern-Vollmer fluorescence quenching studies were carried out using a 10^{-6} M solution of 4CzIPN (**PC5**) in acetonitrile and variable concentrations of both 2-acetyl naphthalene (**1**) and 1-fluoro-4-vinyl benzene (**2**) from 0 to 3.8 mM. The samples were prepared in 3.5 mL quartz cuvettes, equipped with PTFE stoppers, and sealed with Parafilm inside an argon-filled glove bag. The solutions were irradiated at 427 nm, and the luminescence was measured at

540 nm. Both excitation and emission bandwidth were set to 3 nm for each sample. A linear Stern-Volmer plot was obtained at the variable concentration of **1**. From the plot k_q = 0.3×10^4 $M^{-1}s^{-1}$ was obtained. A similar experiment was repeated with variable concentrations of **2** that showed a lower quenching of the luminescence of 4CzIPN (**PC5**). From the plot k_q = 0.08 × 10^4 $M^{-1}s^{-1}$ was obtained.

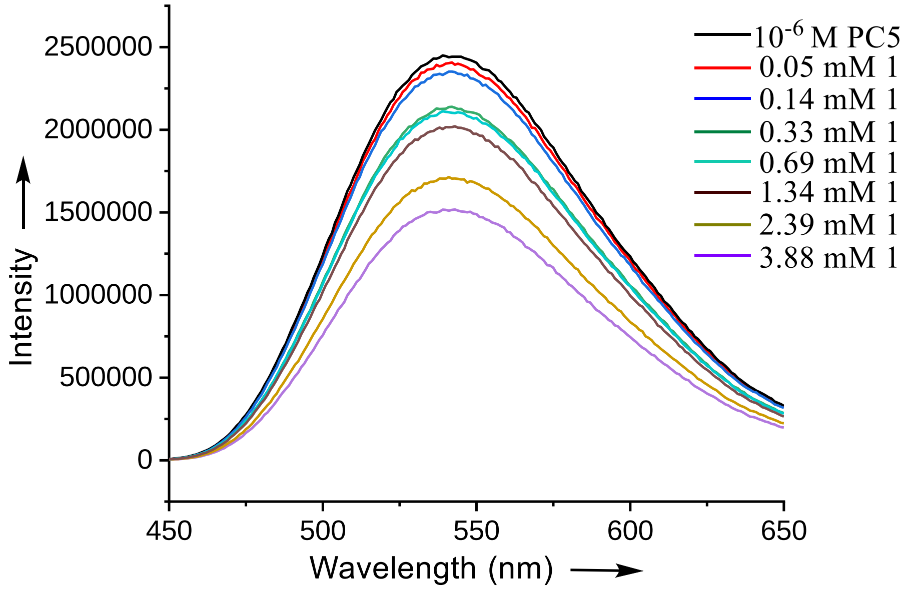


Figure S9: Photoluminescence quenching of **PC5** with **1**.

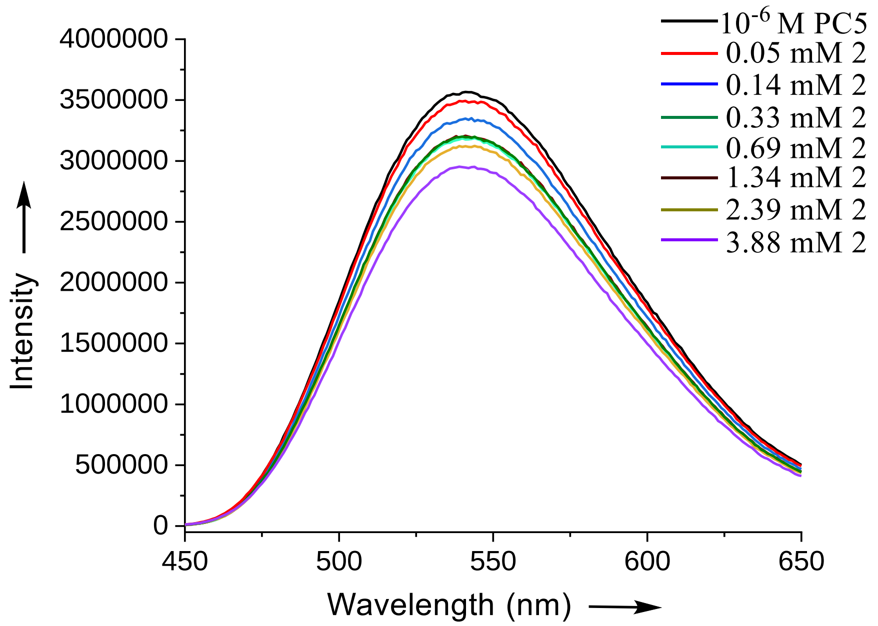


Figure S10: Photoluminescence quenching of **PC5** with **2**.

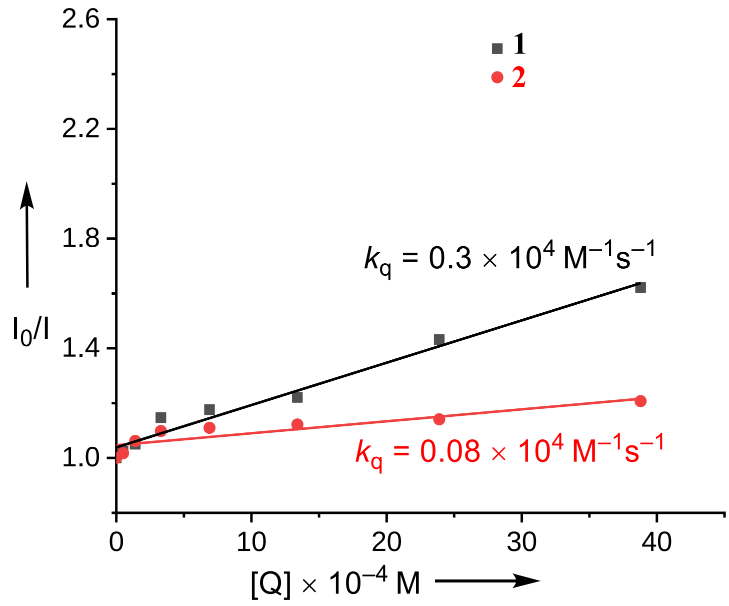


Fig S11: Stern Volmer plot for photoluminescence quenching of **PC5** with **1** and **2**

Then Stern-Vollmer fluorescence quenching studies were carried out using a 10^{-6} M solution of [Ir(ppy)$_3$] (**PC3**) in acetonitrile and variable concentrations of both 2-acetyl naphthalene (**1**) and 1-fluoro-4-vinyl benzene (**2**) from 0 to 3.8 mM. The samples were prepared in 3.5 mL quartz cuvettes, equipped with PTFE stoppers, and sealed with Parafilm inside an argon-filled glove bag. The solutions were irradiated at 427 nm, and the luminescence was measured at 509 nm. Both excitation and emission bandwidth were set to 3 nm for each sample.

A linear Stern-Volmer plot was obtained at the variable concentration of **1**. From the plot $k_q = 0.048 \times 10^4\ M^{-1}s^{-1}$ was obtained.

A similar experiment was repeated with variable concentrations of **2** that show a lower quenching of the luminescence of [Ir(ppy)$_3$]. From the plot $k_q = 0.042 \times 10^4\ M^{-1}s^{-1}$ was obtained.

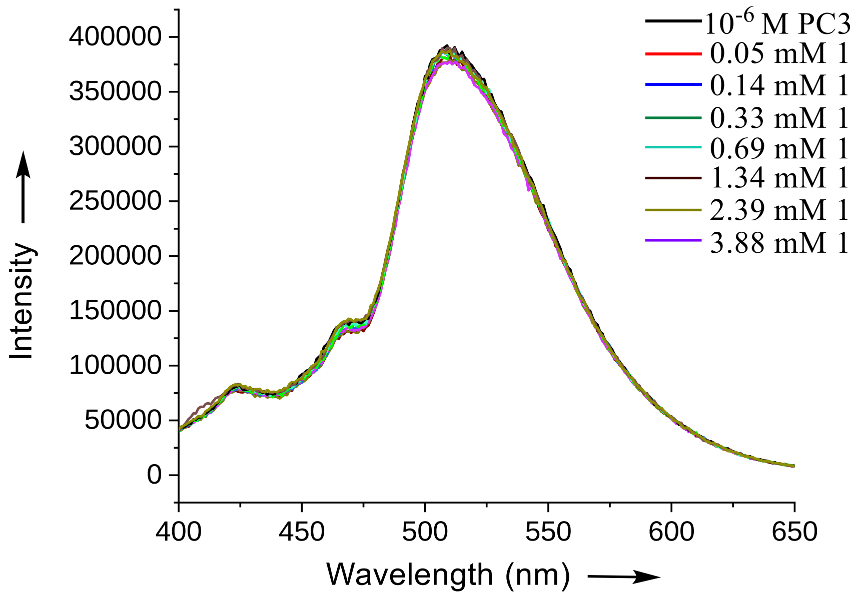


Figure S12: Photoluminescence quenching of **PC3** with **1**

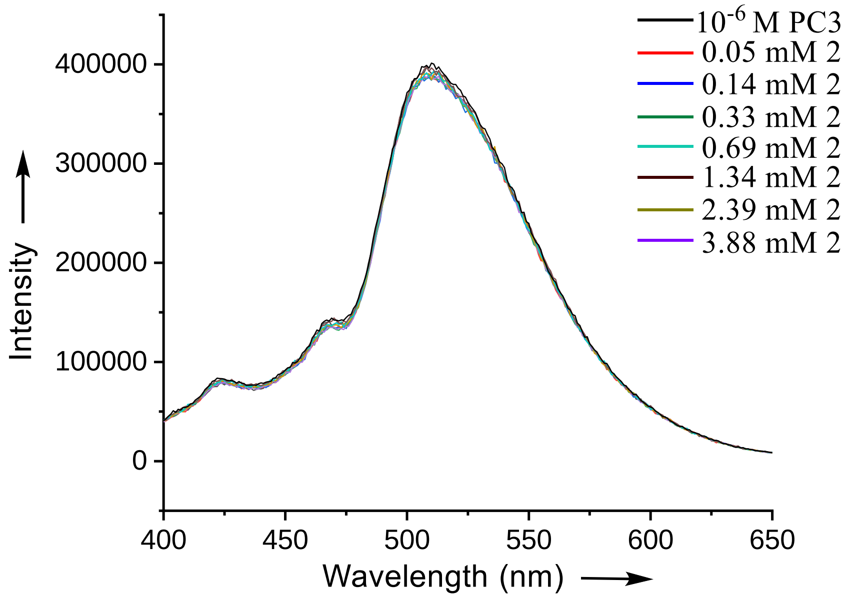
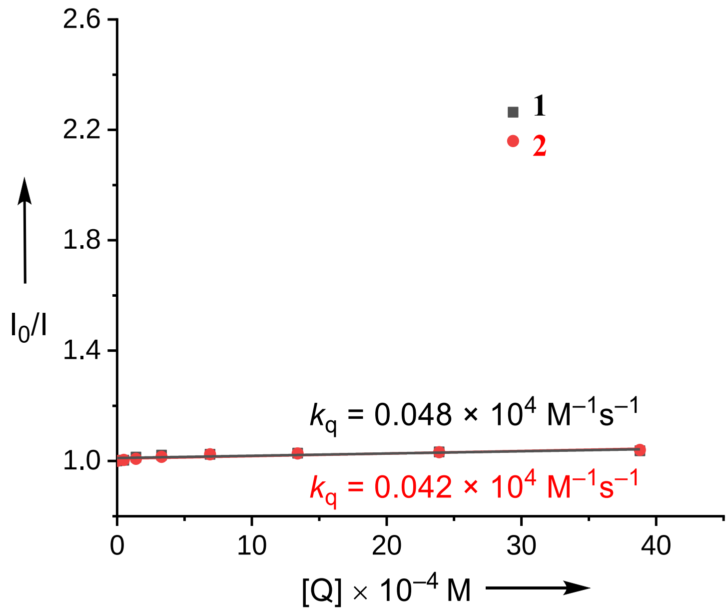


Figure S13: Photoluminescence quenching of **PC3** with **2**



PC	k_q (× 10^4) M^{-1}s^{-1} with respect to **1**	k_q (× 10^4) M^{-1}s^{-1} with respect to **2**	% yield of **3**
PC1	1.60	0.40	98
PC5	0.30	0.08	50
PC3	0.048	0.042	25

Fig S14: Stern Volmer plot for Photoluminescence quenching of **PC3** with **1** and **2**.

9.1 Stern-Volmer plot of other photocatalysts:

Stern-Volmer quenching by acetyl naphthalene (1)

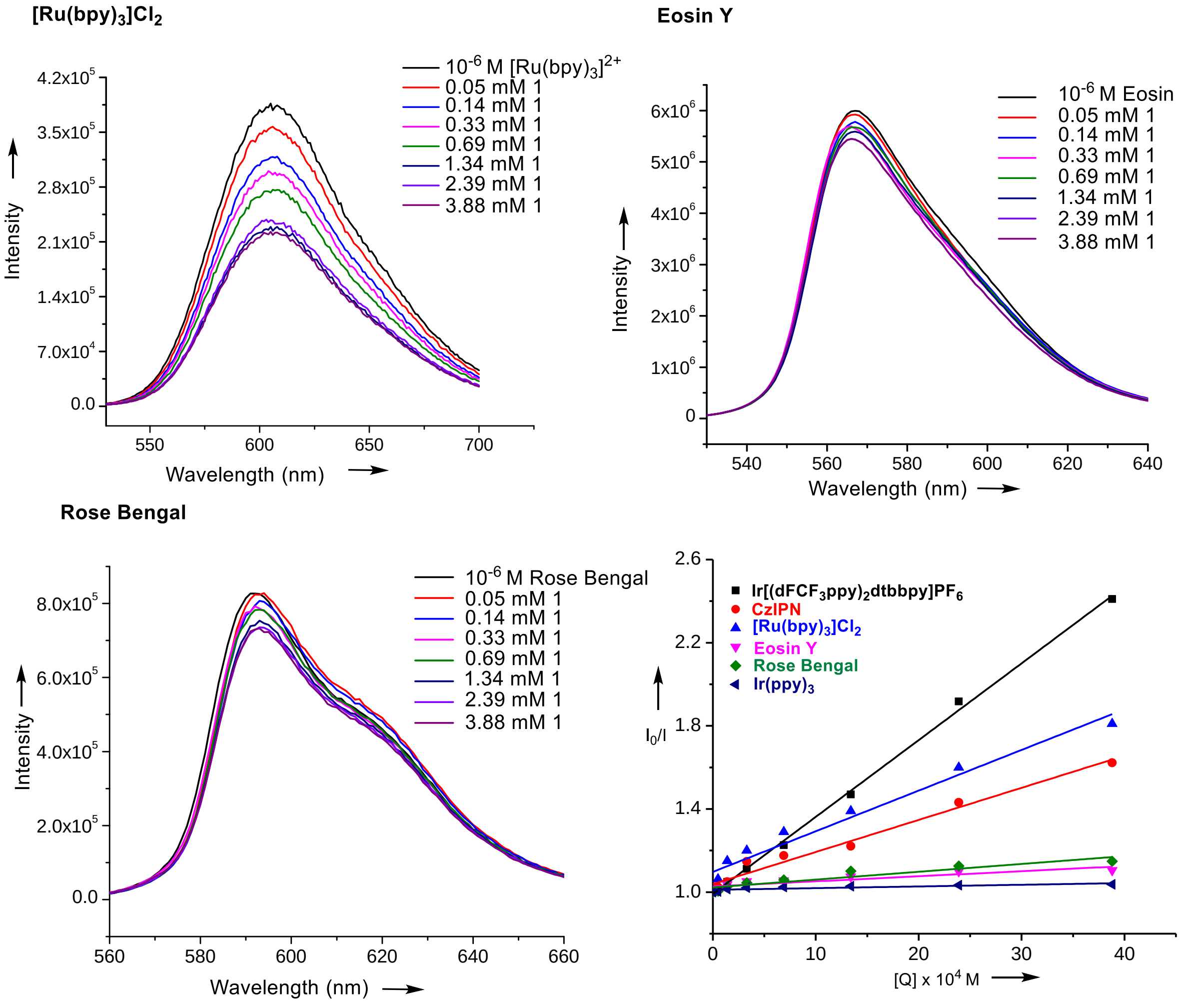


Fig S15: Stern Volmer plot for Photoluminescence quenching of **photosensitizer** with **1**.

Stern-Volmer quenching by 4-fluoro styrene (2)

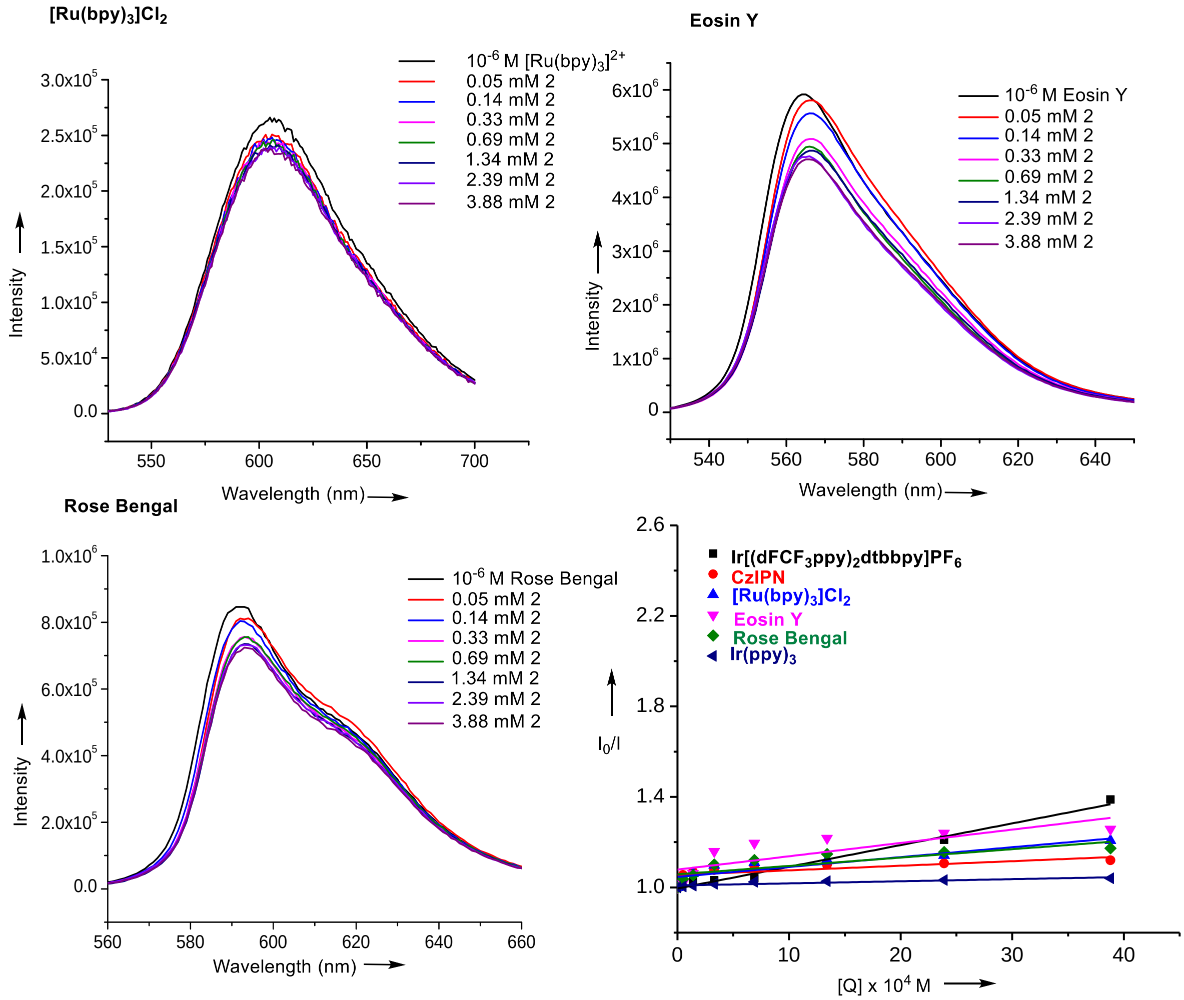


Fig S16: Stern Volmer plot for Photoluminescence quenching of **photosensitizer** with **2**.

Entry	Photocatalyst	E_T (kcal/mol)	*Ksv* (×10^{-3}) wrt **1**	*Ksv* (×10^{-3}) wrt **2**	Yield (%) of **3**
1.	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$	61.8	36.9	9.5	98
2.	$Ir(ppy)_3$	58.1	1.0	0.9	25
3.	CzIPN	53	15.4	4.4	50
4.	$[Ru(bpy)_3]Cl_2$	46.5	19.4	2.0	53
5.	Rose Bengal	44	3.7	3.7	ND
6.	Eosin Y	42	2.4	5.8	ND

10. Cyclic Voltammetry

Cyclic Voltammetry was performed using a CHI 660 potentiostat instrument at a rate of 0.1 V/s in acetonitrile with 0.1 M tetrabutylammonium tetrafluoroborate as a supporting electrolyte. Polished glassy carbon, platinum wire, and Ag/$AgNO_3$ (non-aqueous) were used as the working, counter, and reference electrodes, respectively. To convert the potentials from Ag/$AgNO_3$ (non-aqueous) to saturated calomel electrode SCE, the potential for ferrocene was measured under the above conditions in CH_3CN, and 32 mV was added from the measured values.

Potentials are measured using 10^{-2} M solution of **1** and **2** in MeCN. The reduction potential ($E_{1/2}$) of **1** and **2** was measured as –1.81V and –1.42V *vs*. SCE, respectively. And the oxidation potential (E_{pa}) of **1** and **2** was measured as 1.99V and 2.14V *vs.* SCE, respectively.

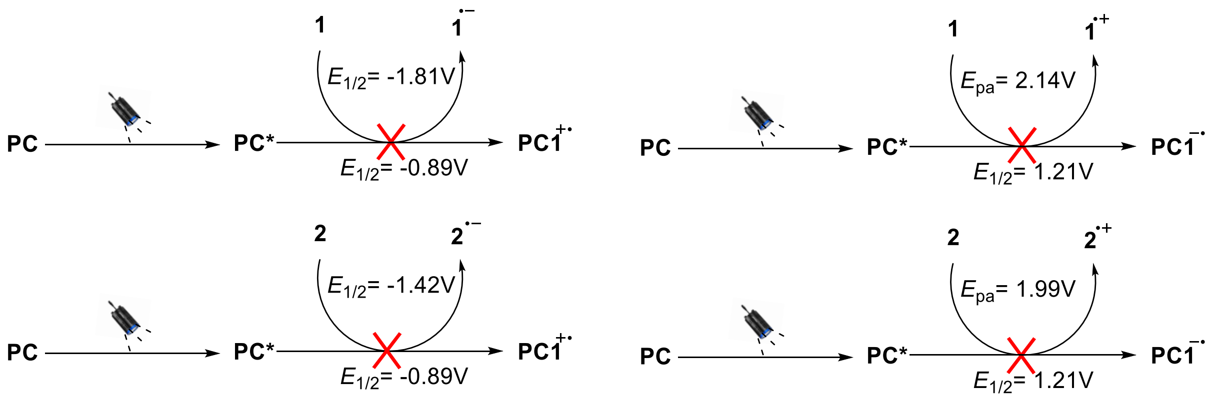


Fig S17: Comparison of oxidation and reduction potential of **1** and **2** with the potential of exited state **PC1**. The comparison shows that both excited state reduction and oxidation of **PC1** are thermodynamically not feasible by either **1** or **2**.

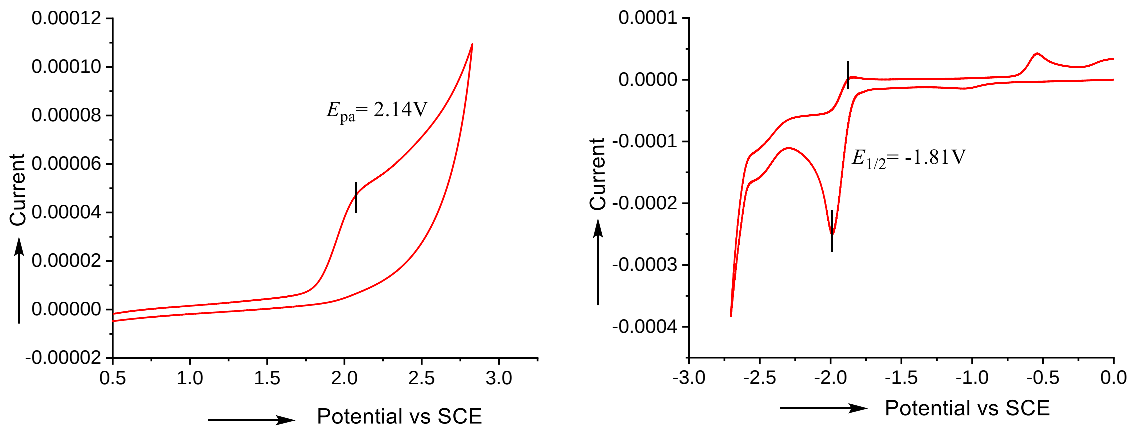


Fig S18: Cyclic Voltammetry of Oxidation and Reduction of **1**

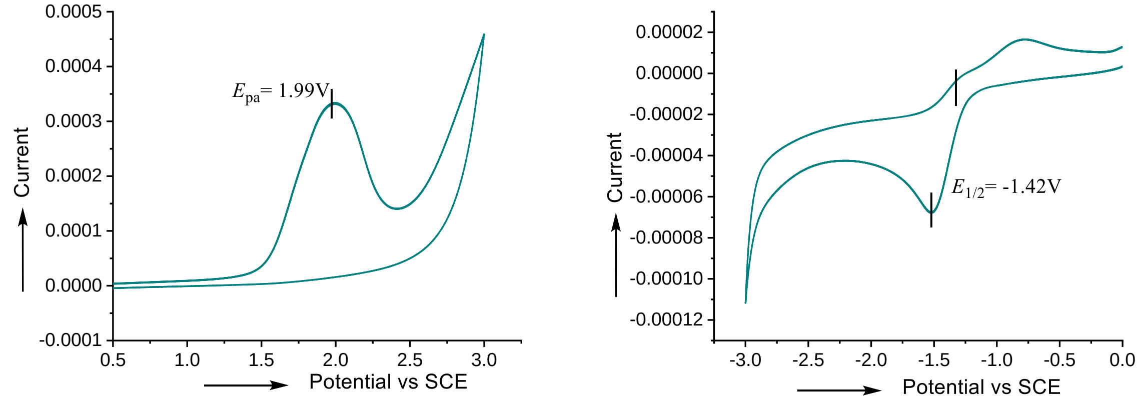


Fig S19: Cyclic Voltammetry of Oxidation and Reduction of **2**

11. UV-Visible studies

UV−vis spectral studies were carried out using an Agilent diode array Cary-8454 spectrophotometer with an attached electrically controlled thermostat. 10^{-2}M solution of both **1** and **2** in acetonitrile is prepared, and its absorbance is measured from 250 to 450nm.

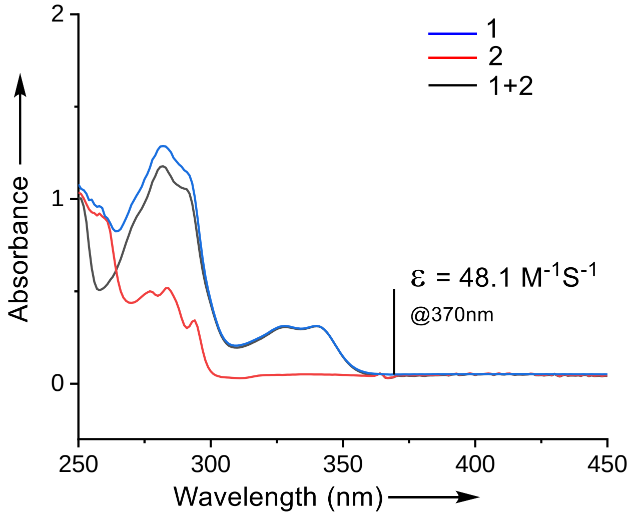


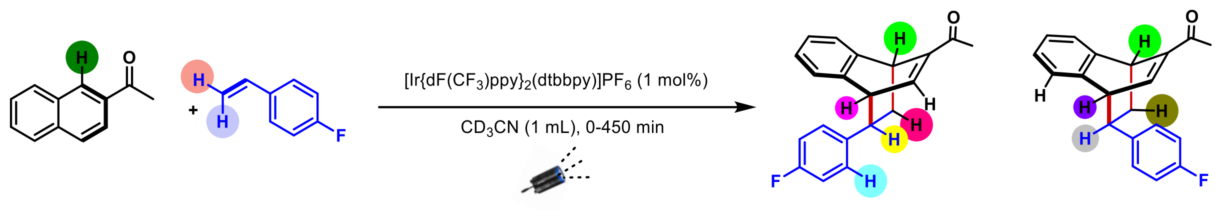
Fig S20: UV-Vis studies using 10^{-2} M solution of **1** and **2** in MeCN (blue and red curve). UV studies by mixing both **1** and **2** in a cuvette (black curve).

Compound	λ_{max} (nm)
1	281, 328, 334
2	277, 283, 293
1+**2**	281, 328, 334

Since there is no new peak in the absorption spectra of the mixture **1** + **2**, the formation of any donor-acceptor complex is being ruled out.

12. Kinetics monitoring via ¹H NMR studies

Experimental procedure: 2-Acetyl naphthalene **1** (0.1 mmol) and photosensitizer $[Ir(dFCF_3ppy)_2(dtbbpy)]PF_6$ (1 mol%) were placed into a dry 2 mL NMR tube inside glove box. CD_3CN (1 mL) was added followed by 1-fluoro-4-vinyl benzene **2** (0.12 mmol). Trimethoxybenzene (0.1mmol, 16.8mg) was added as an internal standard. The tube was sealed, and the resulting solution was irradiated with a 427 nm blue LED light. The progress of the reaction was monitored via ¹H NMR spectroscopy.



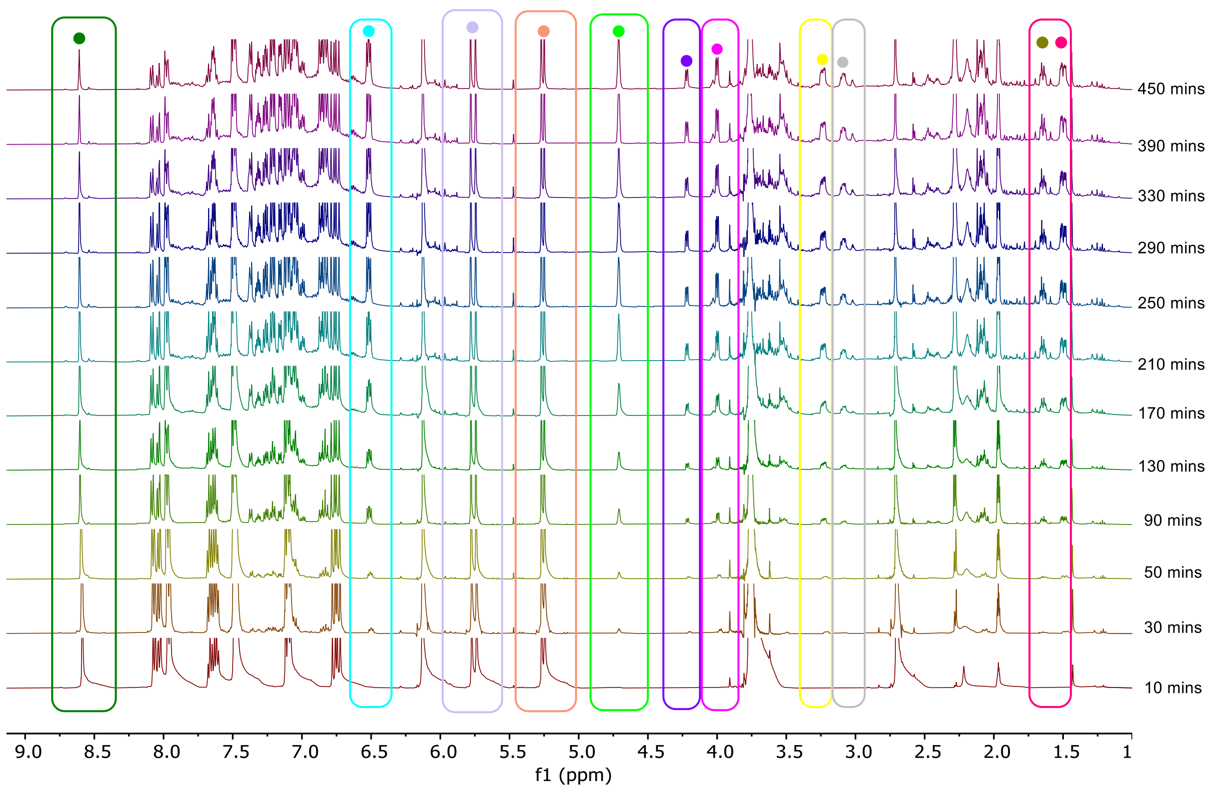


Fig S21: ¹H NMR monitoring of the visible-light E_NT mediated intermolecular [4+2] cycloaddition reaction.

Time (min)	[**1**] mmol	[***endo*-3** + ***exo*-3**] mmol
0	0.1	0
10	0.098	0
30	0.093	0.004
50	0.086	0.01

90	0.069	0.032
130	0.058	0.039
170	0.048	0.051
210	0.036	0.065
250	0.033	0.070
290	0.025	0.079
330	0.017	0.086
390	0.014	0.09
450	0.01	0.92

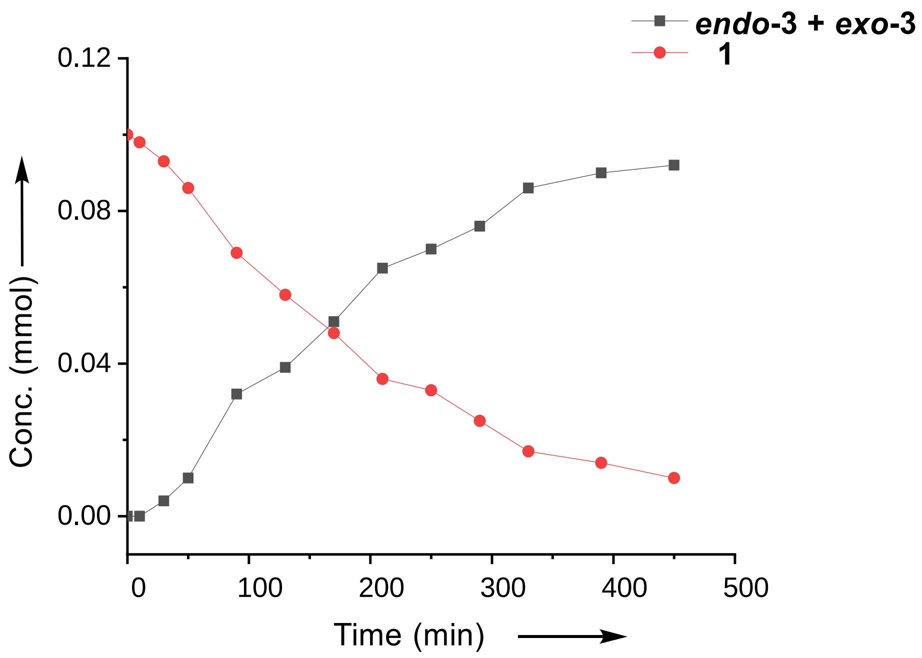
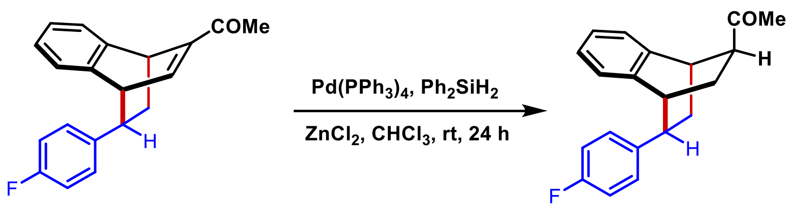


Fig S22: Kinetic monitoring of 4+2 cycloaddition of **1** and **2**.

12. Synthetic application

12.1 Palladium-catalyzed reduction of the α,β-unsaturated double bond

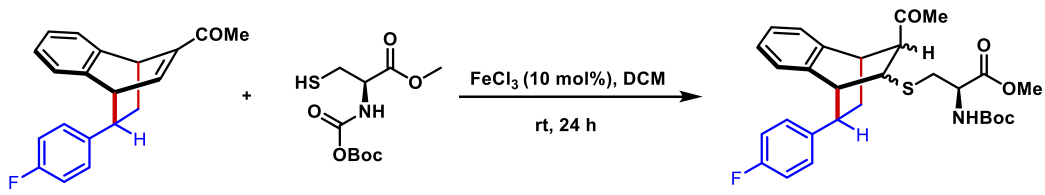


In an oven-dried sealed tube fitted with a magnetic stir bar, was added *endo*-**3** (0.16 mmol), chloroform (2.5 mL), diphenyl silane (0.41 mmol), and zinc chloride (0.08 mmol). $Pd(PPh_3)_4$ (2 mol%) was then added to the reaction mixture and was stirred at room temperature for 24 h.

The reaction mixture was passed through a filter paper and washed with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the corresponding product **39** in 52% yield. (EtOAc in hexane = 10%). (R_f = 0.4 in 10% EtOAc in hexane). Configuration is confirmed by NOE experiments.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.17 (m, 2H), 7.14 (dd, *J* = 8.2, 6.3 Hz, 1H), 6.88 (d, *J* = 7.3 Hz, 1H), 6.77 (t, *J* = 8.5 Hz, 2H), 6.51 (dd, *J* = 8.3, 5.5 Hz, 2H), 3.50 (d, *J* = 3.2 Hz, 1H), 3.19 (dd, *J* = 10.5, 6.1 Hz, 1H), 3.00 (d, *J* = 3.0 Hz, 1H), 2.98 – 2.92 (m, 1H), 2.46 – 2.38 (m, 1H), 2.08 (s, 4H), 1.93 – 1.87 (m, 1H), 1.58 – 1.53 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 208.8, 161.4 (d, ^1J = 243.9 Hz), 142.2, 140.2 (d, ^4J = 2.4 Hz), 128.99 (d, ^3J = 7.9 Hz), 126.7, 126.1, 124.6, 114.8 (d, ^2J = 20.9 Hz), 50.5, 42.7, 41.9, 37.4, 36.9, 30.1, 28.2.
^{19}F NMR (471 MHz, $CDCl_3$) δ -117.55.
IR (ATR / cm^{-1}): 2924, 1863, 1710, 1601, 1512, 1505, 1478, 1458.
HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{20}H_{19}FONa$, 317.1312, found 317.1320.

12.2 Michael addition of *N*-Boc-L-cysteine methyl ester



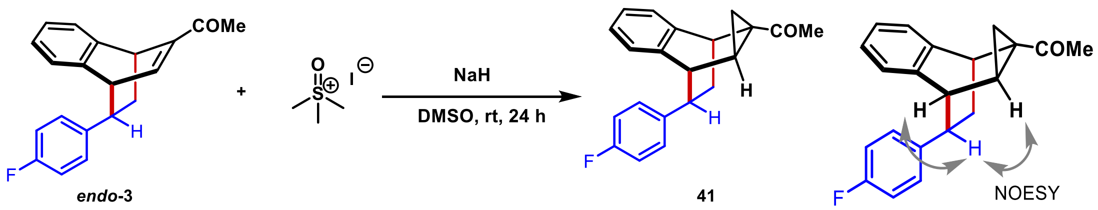
endo-**3** **40**

To a stirred solution of *endo*-**3** (0.15 mmol) in CH_2Cl_2 (1 mL) in an oven-dried sealed tube fitted with a magnetic stir bar, was added *N*-(*tert*-Butoxycarbonyl)-L-cysteine methyl ester (0.2 mmol) followed by $FeCl_3$ (10 mol%). The reaction mixture was stirred for 24 h, filtered through a filter paper, and then washed with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the corresponding product **40** in 56% yield and 2:1 d.r. (EtOAc in hexane = 15-20%). (R_f = 0.5 in 15% EtOAc in hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 2H), 7.23 – 7.17 (m, 1H), 6.99 – 6.91 (m, 1H), 6.75 (t, *J* = 8.7 Hz, 2H), 6.49 – 6.42 (m, 2H), 5.29 (s, 1H), 4.65 – 4.41 (m, 1H), 3.86 – 3.81 (m, 1H), 3.75 (d, *J* = 11.5 Hz, 3H), 3.50 – 3.43 (m, 1H), 3.21 – 3.13 (m, 1H), 3.04 (q, *J* = 2.1 Hz, 1H), 2.99 (dd, *J* = 13.7, 4.7 Hz, 1H), 2.92 – 2.82 (m, 1H), 2.57 – 2.53 (m, 0.66H_{maj}), 2.47 (s, 0.33H_{min}), 2.36 (d, *J* = 6.5 Hz, 3H), 2.14 – 2.08 (m, 1H), 1.43 (d, *J* = 16.8 Hz, 9H), 1.38 – 1.34 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 207.5, 207.2, 171.5, 161.4 (d, ^{1}J = 244.1 Hz), 155.3, 141.7, 141.1, 137.1, 129.1 (d, ^{3}J = 7.8 Hz), 128.7, 128.6, 127.5, 126.9, 126.9, 123.3, 114.8 (d, ^{2}J = 21.0 Hz).
80.3, 60.2, 59.6, 53.6, 53.2, 52.8, 52.7, 47.9, 47.7, 45.0, 44.6, 42.6, 38.0, 34.2, 34.2, 30.8, 29.8, 29.3, 29.2, 28.4, 28.4.
^{19}F NMR (471 MHz, $CDCl_3$) δ -117.13 (major), -117.22 (minor).
IR (ATR / cm^{-1}): 2982, 2928, 2850, 1727, 1710, 1604, 1505, 1458, 1431, 1363, 1223, 1162.
HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{20}H_{19}FONa$, 550.2034, found 550.2119.

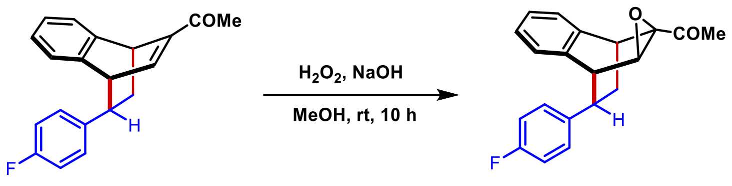
12.3 Corey-Chaykovsky cyclopropanation of *endo*-3



In an oven-dried sealed tube fitted with a magnetic stir bar, was charged with solid NaH (60% in mineral oil, 0.12 mmol), trimethylsulfoxonium iodide (0.12 mmol) under N_2 atmosphere. DMSO (0.3 mL) was added dropwise with stirring. The reaction mixture was stirred for 10 min, during which the solution became clear. A solution of *endo*-**3** (0.09 mmol) in DMSO (0.5 mL) was then added dropwise. The reaction was allowed to stir at room temperature for 24 h. The reaction was quenched with water, and the mixture was extracted with Et_2O (3 × 5 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the corresponding products **41** in 63% yield. (EtOAc in hexane = 4-5%). (R_f = 0.5 in 5% EtOAc in hexane). Configuration is confirmed by NOESY experiments.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, J = 7.5 Hz, 1H), 7.16 (t, J = 7.3 Hz, 2H), 6.81 – 6.71 (m, 3H), 6.47 – 6.39 (m, 2H), 3.94 (s, 1H), 3.27 (dd, J = 4.4, 2.2 Hz, 1H), 3.20 – 3.13 (m, 1H), 2.56 – 2.48 (m, 1H), 2.16 – 2.11 (m, 1H), 2.08 (s, 3H), 1.40 – 1.35 (m, 1H), 0.98 (dd, J = 8.2, 5.9 Hz, 1H), 0.06 (q, J = 5.0 Hz, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 207.6, 161.4 (d, ^{1}J = 243.9 Hz), 141.4, 141.2, 135.7, 129.3 (d, ^{3}J = 7.9 Hz), 127.4, 127.0, 126.8, 124.1, 114.7 (d, ^{2}J = 20.9 Hz), 43.8, 42.9, 35.8, 34.6, 33.5, 27.1, 25.5, 16.0.
^{19}F NMR (471 MHz, $CDCl_3$) δ -117.45.
IR (ATR / cm^{-1}): 2955, 2924, 2850, 1676, 1631, 1509, 1458, 1356, 1298, 1223, 1162.
HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{21}H_{19}FONa$, 329.1312, found 329.1313.

12.4 Epoxidation of *endo*-3



endo-3 42

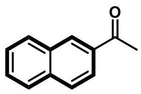
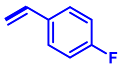
In an oven-dried sealed tube fitted with a magnetic stir bar, was added *endo*-**3** (0.1 mmol), 30% aqueous hydrogen peroxide (0.41 mmol), and 0.5 mL of methanol. The reaction mixture was kept in an ice bath before the addition of 0.02 mmol of 6N aqueous sodium hydroxide. Then the reaction mixture was stirred at room temperature for 10 h. The reaction mixture was poured into water and was extracted with diethyl ether. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the corresponding product **42** in 70% yield. (EtOAc in hexane = 5-8%). (R_f = 0.5 in 8% EtOAc in hexane). Configuration is confirmed by NOE experiments.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 1H), 7.21 (t, *J* = 6.9 Hz, 2H), 6.86 (d, *J* = 7.5 Hz, 1H), 6.80 – 6.72 (m, 2H), 6.48 – 6.38 (m, 2H), 3.98 (s, 1H), 3.91 – 3.85 (m, 1H), 3.53 – 3.48 (m, 1H), 3.19 – 3.10 (m, 1H), 2.65 – 2.56 (m, 1H), 2.11 (s, 3H), 1.53 – 1.49 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 205.8, 161.6 (d, ^1J = 244.8 Hz), 139.8 (d, ^4J = 3.4 Hz), 139.5, 133.9, 129.37 (d, ^3J = 7.7 Hz), 127.7, 127.1, 124.0, 115.0 (d, ^2J = 21.0 Hz)60.8, 57.5, 46.0, 39.4, 37.4, 33.8, 24.5.
^{19}F NMR (471 MHz, $CDCl_3$) δ -116.75.
IR (ATR / cm^{-1}): 2955, 2921, 2850, 1700, 1605, 1509, 1461, 1393, 1356.
HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{20}H_{17}FO_2Na$, 331.1105, found 331.1128.

13. Computational studies

Quantum mechanical calculations were performed on the singlet (S) and triplet (T) states of **1** and **2** to obtain the S–T gap between the two states. Both the singlet and triplet states of **1** and **2** were optimized using B3LYP/6-311+G(2d,p) with the CPCM CH_3CN model in Gaussian 09. Frequency analysis using a simple harmonic oscillation model was performed on the optimized structures to confirm that both structures were stationary on the potential energy surface

13.1 Triplet energy calculation:[5]

	Gas Phase G (Hartree) [b3lyp/6-311+G(2d,p)]		MeCN G (Hartree) [b3lyp/6-311+G(2d,p)]		Gas Phase G (Hartree) [b3lyp/6-311++G(d,p)]		MeCN G (Hartree) [b3lyp/6-311++G(d,p)]	
 **1**	S_0 -538.547421	T_1 -538.458340	S_0 -538.556127	T_1 -538.468349	S_0 -538.532849	T_1 -538.444013	S_0 -538.541958	T_1 -538.454396
	T_1-S_0 (E_T) 0.089081 = 55.9 kcal/mol		T_1-S_0 (E_T) 0.087778 = 55.1 kcal/mol		T_1-S_0 (E_T) 0.088836 = 55.7 kcal/mol		T_1-S_0 (E_T) 0.087562 = 54.9 kcal/mol	
 **2**	S_0 -408.918807	T_1 -408.826590	S_0 -408.922717	T_1 -408.830412	S_0 -408.907840	T_1 -408.815874	S_0 -408.912022	T_1 -408.819995
	T_1-S_0 (E_T) 0.092217 = 57.9 kcal/mol		T_1-S_0 (E_T) 0.092305 = 57.9 kcal/mol		T_1-S_0 (E_T) 0.091966 = 57.7 kcal/mol		T_1-S_0 (E_T) 0.092025 = 57.7 kcal/mol	

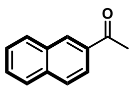
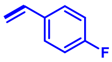
	Gas Phase G (Hartree) [b3lyp/6-31++g(d,p)]		MeCN G (Hartree) [b3lyp/6-31++g(d,p)]		Gas Phase G (Hartree) [b3lyp/3-21+g*]		MeCN G (Hartree) [b3lyp/3-21+g*]		MeCN G (Hartree) [M06/6-31++g(d,p)]	
 **1**	S_0 -538.427708	T_1 -538.339376	S_0 -538.436888	T_1 -538.349977	S_0 -535.489517	T_1 -535.399898	S_0 -535.501171	T_1 -535.413665	S_0 -538.142663	T_1 -538.055341
	T_1-S_0 (E_T) **0.088332 = 55.4 kcal/mol**		T_1-S_0 (E_T) **0.086911 = 54.5 kcal/mol**		T_1-S_0 (E_T) **0.089619 = 56.2 kcal/mol**		T_1-S_0 (E_T) **0.087506 = 54.9 kcal/mol**		T_1-S_0 (E_T) **0.087322 = 54.8 kcal/mol**	
 **2**	S_0 -408.822176	T_1 -408.730757	S_0 -408.826345	T_1 -408.734811	S_0 -406.618353	T_1 -406.524259	S_0 -406.624747	T_1 -406.530404	S_0 -408.629128	T_1 -408.536911
	T_1-S_0 (E_T) **0.091419 = 57.4 kcal/mol**		T_1-S_0 (E_T) **0.091534 = 57.4 kcal/mol**		T_1-S_0 (E_T) **0.094094 = 59.0 kcal/mol**		T_1-S_0 (E_T) **0.094343 = 59.2 kcal/mol**		T_1-S_0 (E_T) **0.092217 = 57.8 kcal/mol**	

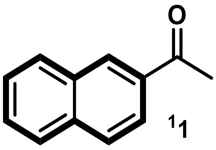
Fig S23: Triplet energy calculation.

Change in the energy of the reaction:

	Gas Phase G (Hartree)[b3lyp/6-311+G(2d,p)]	MeCN G (Hartree) [b3lyp/6-311+G(2d,p)]	Gas Phase G (Hartree)[b3lyp/6-311++G(d,p)]	MeCN G (Hartree) [b3lyp/6-311++G(d,p)]
1	-538.547421	-538.556127	-538.532849	-538.541958
2	-408.918807	-408.922717	-408.907840	-408.912022
3	-947.424434	-947.436034	-947.401296	-947.413401
Change in energy =	26.2 kcal/mol	26.8 kcal/mol	24.7 kcal/mol	25.5 kcal/mol

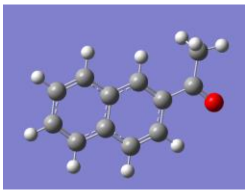
Fig S24: Energy change of a reaction.

Calculated energies:



^{1}**1**

S_0 in Gas phase



b3lyp/6-311+G(2d,p)

Zero-point correction= 0.183790 (Hartree/Particle)

Thermal correction to Energy= 0.194255

Thermal correction to Enthalpy= 0.195199

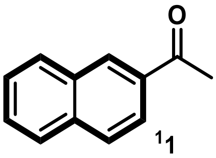
Thermal correction to Gibbs Free Energy= 0.147279

Sum of electronic and zero-point Energies= -538.510910

Sum of electronic and thermal Energies= -538.500446

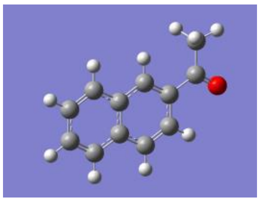
Sum of electronic and thermal Enthalpies= -538.499501

Sum of electronic and thermal Free Energies= -538.547421



^{1}**1**

S_0 in MeCN



Zero-point correction= 0.183704 (Hartree/Particle)

Thermal correction to Energy= 0.194194

Thermal correction to Enthalpy= 0.195138

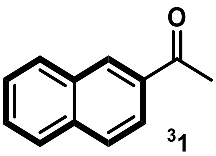
Thermal correction to Gibbs Free Energy= 0.147039

Sum of electronic and zero-point Energies= -538.519462

Sum of electronic and thermal Energies= -538.508972

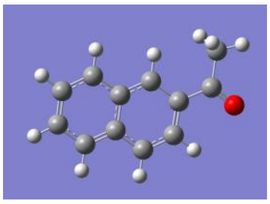
Sum of electronic and thermal Enthalpies= -538.508028

Sum of electronic and thermal Free Energies= -538.556127



^{3}**1**

T_1 in Gas phase



Zero-point correction= 0.179041 (Hartree/Particle)

Thermal correction to Energy= 0.190050

Thermal correction to Enthalpy= 0.190995

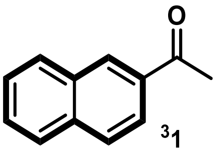
Thermal correction to Gibbs Free Energy= 0.141209

Sum of electronic and zero-point Energies= -538.420508

Sum of electronic and thermal Energies= -538.409499

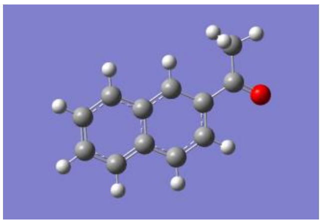
Sum of electronic and thermal Enthalpies= -538.408555

Sum of electronic and thermal Free Energies= -538.458340



^{3}**1**

T_1 in MeCN



Zero-point correction= 0.179333 (Hartree/Particle)

Thermal correction to Energy= 0.190290

Thermal correction to Enthalpy= 0.191234

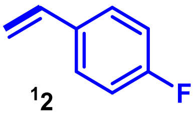
Thermal correction to Gibbs Free Energy= 0.141555

Sum of electronic and zero-point Energies= -538.430571

Sum of electronic and thermal Energies= -538.419615

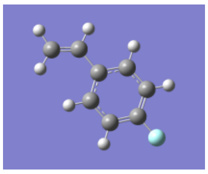
Sum of electronic and thermal Enthalpies= -538.418670

Sum of electronic and thermal Free Energies= -538.468349



^{1}**2**

S_0 in Gas phase



Zero-point correction= 0.124536 (Hartree/Particle)

Thermal correction to Energy= 0.132145

Thermal correction to Enthalpy= 0.133090

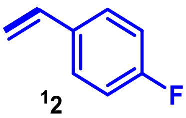
Thermal correction to Gibbs Free Energy= 0.091712

Sum of electronic and zero-point Energies= -408.885983

Sum of electronic and thermal Energies= -408.878374

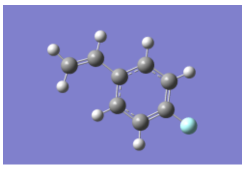
Sum of electronic and thermal Enthalpies= -408.877430

Sum of electronic and thermal Free Energies= -408.918807



^{1}**2**

S_0 in MeCN



Zero-point correction= 0.124413 (Hartree/Particle)

Thermal correction to Energy= 0.131999

Thermal correction to Enthalpy= 0.132944

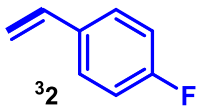
Thermal correction to Gibbs Free Energy= 0.091840

Sum of electronic and zero-point Energies= -408.879449

Sum of electronic and thermal Energies= -408.871863

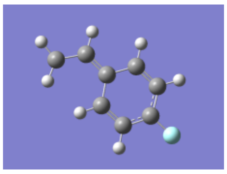
Sum of electronic and thermal Enthalpies= -408.870918

Sum of electronic and thermal Free Energies= -408.912022

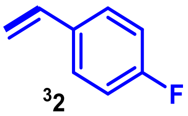


^{3}**2**

T_1 in Gas phase

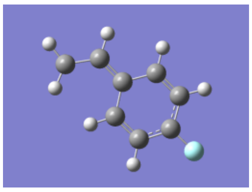


Zero-point correction= 0.119172 (Hartree/Particle)
Thermal correction to Energy= 0.126957
Thermal correction to Enthalpy= 0.127901
Thermal correction to Gibbs Free Energy= 0.085918
Sum of electronic and zero-point Energies= -408.793337
Sum of electronic and thermal Energies= -408.785552
Sum of electronic and thermal Enthalpies= -408.784608
Sum of electronic and thermal Free Energies= -408.826590



^{3}**2**

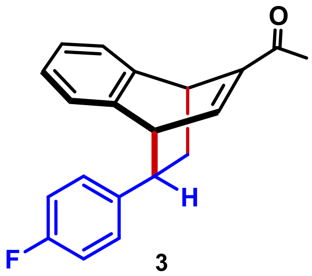
T_1 in MeCN



Zero-point correction= 0.119074 (Hartree/Particle)
Thermal correction to Energy= 0.126856
Thermal correction to Enthalpy= 0.127801
Thermal correction to Gibbs Free Energy= 0.085827
Sum of electronic and zero-point Energies= -408.797165
Sum of electronic and thermal Energies= -408.789383

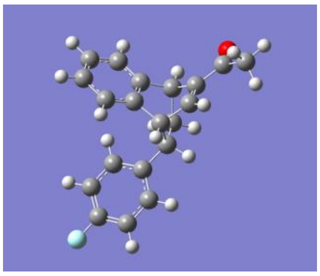
Sum of electronic and thermal Enthalpies= -408.788439

Sum of electronic and thermal Free Energies= -408.830412



3

Gas phase



Zero-point correction= 0.314692 (Hartree/Particle)

Thermal correction to Energy= 0.332314

Thermal correction to Enthalpy= 0.333258

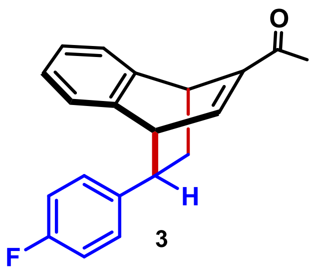
Thermal correction to Gibbs Free Energy= 0.268009

Sum of electronic and zero-point Energies= -947.377752

Sum of electronic and thermal Energies= -947.360130

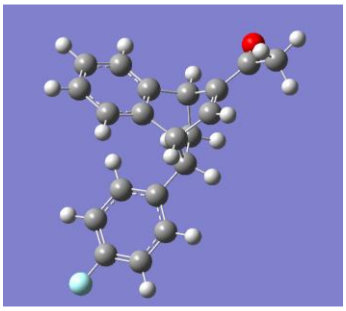
Sum of electronic and thermal Enthalpies= -947.359186

Sum of electronic and thermal Free Energies= -947.424434



3

In MeCN



Zero-point correction= 0.314430 (Hartree/Particle)

Thermal correction to Energy= 0.332092

Thermal correction to Enthalpy= 0.333036

Thermal correction to Gibbs Free Energy= 0.267532

Sum of electronic and zero-point Energies= -947.389136

Sum of electronic and thermal Energies= -947.371474

Sum of electronic and thermal Enthalpies= -947.370530

Sum of electronic and thermal Free Energies= -947.436034

Cartesian coordinates of computed structures:

^{1}1

0 1

C	-6.80505664	-3.77144249	0.00026300
C	-5.43225564	-3.77144249	0.00026300
C	-4.71031764	-2.54632149	0.00026300
C	-5.42818764	-1.32245549	0.00063300
C	-6.84960364	-1.35182849	0.00078700
C	-7.52110864	-2.54980349	0.00049700
H	-2.74124464	-3.47128649	0.00002000
H	-7.36578764	-4.71778849	0.00018300
H	-4.86746664	-4.71576449	0.00003500
C	-3.28859064	-2.51677849	0.00000000
C	-4.70543764	-0.09772949	0.00074800
H	-7.39684464	-0.39737249	0.00086900
H	-8.62074564	-2.57617049	0.00059900
C	-3.33257664	-0.09766149	0.00047500
C	-2.61656464	-1.31955349	0.00001600
H	-5.26989364	0.84681151	0.00100800
H	-1.51693664	-1.29308849	-0.00016600
C	-2.54758121	1.22724686	0.00022579
O	-1.90875589	1.60964023	0.97592274
C	-2.61741636	2.04041151	-1.30571689
H	-3.53156471	2.59589863	-1.33154038
H	-1.78846065	2.71550154	-1.35028015
H	-2.58074552	1.37482512	-2.14270554

^{3}1

0 3

C	-6.80505664	-3.77144249	0.00026300
C	-5.43225564	-3.77144249	0.00026300
C	-4.71031764	-2.54632149	0.00026300
C	-5.42818764	-1.32245549	0.00063300
C	-6.84960364	-1.35182849	0.00078700
C	-7.52110864	-2.54980349	0.00049700
H	-2.74124464	-3.47128649	0.00002000
H	-7.36578764	-4.71778849	0.00018300
H	-4.86746664	-4.71576449	0.00003500
C	-3.28859064	-2.51677849	0.00000000
C	-4.70543764	-0.09772949	0.00074800
H	-7.39684464	-0.39737249	0.00086900
H	-8.62074564	-2.57617049	0.00059900
C	-3.33257664	-0.09766149	0.00047500
C	-2.61656464	-1.31955349	0.00001600
H	-5.26989364	0.84681151	0.00100800
H	-1.51693664	-1.29308849	-0.00016600
C	-2.54758121	1.22724686	0.00022579
O	-1.90875589	1.60964023	0.97592274
C	-2.61741636	2.04041151	-1.30571689
H	-3.53156471	2.59589863	-1.33154038
H	-1.78846065	2.71550154	-1.35028015
H	-2.58074552	1.37482512	-2.14270554

^{1}2

0 1

C	-1.40165886	-3.04909379	0.28941420
C	-0.02523397	-3.04027066	0.02616789
C	0.62896087	-1.83050141	-0.24292215
C	-0.09326872	-0.62955501	-0.24876345
C	-1.46969343	-0.63837803	0.01448382
C	-2.12388888	-1.84814765	0.28357070
H	-1.90115117	-3.97277948	0.49487024
H	0.52620504	-3.95721946	0.03063143
H	0.40622411	0.29413100	-0.45421675
H	-2.02113174	0.27857120	0.01002393
C	2.14151591	-1.82080553	-0.53220272
C	2.77414408	-0.65091867	-0.79242065
H	2.69295448	-2.73775460	-0.52774143
H	3.82507442	-0.64418239	-0.99341824
H	2.22270604	0.26603074	-0.79687911
F	-3.44982980	-1.85664718	0.53716173

^{3}2

0 3

C	-1.40165886	-3.04909379	0.28941420
C	-0.02523397	-3.04027066	0.02616789
C	0.62896087	-1.83050141	-0.24292215
C	-0.09326872	-0.62955501	-0.24876345
C	-1.46969343	-0.63837803	0.01448382
C	-2.12388888	-1.84814765	0.28357070
H	-1.90115117	-3.97277948	0.49487024
H	0.52620504	-3.95721946	0.03063143
H	0.40622411	0.29413100	-0.45421675
H	-2.02113174	0.27857120	0.01002393
C	2.14151591	-1.82080553	-0.53220272
C	2.77414408	-0.65091867	-0.79242065
H	2.69295448	-2.73775460	-0.52774143
H	3.82507442	-0.64418239	-0.99341824
H	2.22270604	0.26603074	-0.79687911
F	-3.44982980	-1.85664718	0.53716173

3

0 1

C	-0.59483300	-0.59735100	-1.08612800
C	-2.00697400	0.44595300	0.79643900
C	0.07802400	-0.91905200	0.30193300
H	-0.14320400	-1.97770300	0.47042700
C	-0.68789300	-0.11636900	1.38586300
H	-0.89557200	-0.75160800	2.24969400
H	-0.10565500	0.73152800	1.74986200
H	-2.64681800	0.84447300	1.58363000
H	-0.03076500	-1.05975700	-1.89823000
C	-2.72440400	-0.63462700	0.02040500
C	-1.99078300	-1.15192900	-0.98208100
C	1.60152600	-0.83596800	0.30275400

C	2.31125500	-1.80025600	-0.42931100
C	2.34522200	0.11141400	1.01170600
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C	3.74000900	0.11199300	0.98663300
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C	4.39353400	-0.85016900	0.23804900
H	4.24467000	-2.56378000	-1.04064700
H	4.31359300	0.84715500	1.53761800
H	-2.34523800	-1.91952500	-1.66173100
C	-4.12223900	-1.01483800	0.34939900
O	-4.71635800	-0.46139200	1.25979400
C	-4.79839500	-2.10404000	-0.46596200
H	-4.84728300	-1.82781200	-1.52298900
H	-4.24530600	-3.04483800	-0.39621100
H	-5.80811200	-2.25037500	-0.08543100
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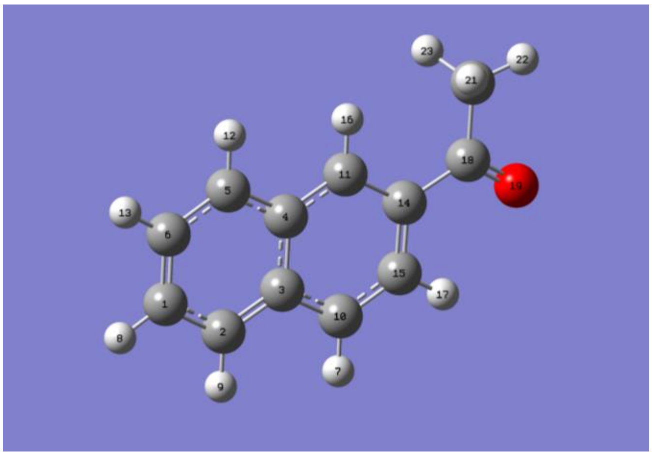
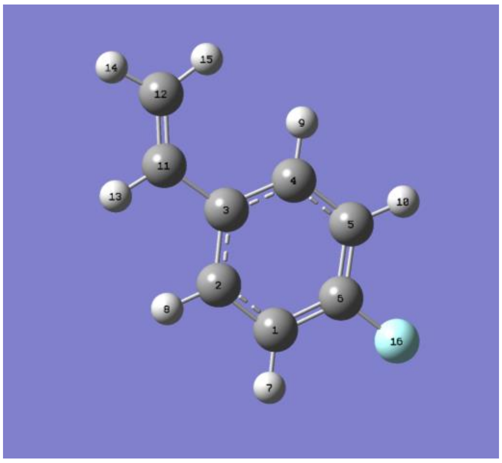




The LUMO of dienophile 2 in 33 number molecular orbital. From the molecular coefficients of dienophile LUMO, atom 12 has the larger contribution to the LUMO.

Molecular Orbital Coefficients in LUMO of **2**

			31	32	33	34	35
			O	O	V	V	V
	Eigenvalues --		-0.27311	-0.23747	-0.05162	-0.03124	0.00797
	11 C	1S	0.00000	0.00000	0.00000	0.00000	-0.00505
191		2PZ	-0.00410	0.09309	-0.11011	-0.01816	-0.00000
195		3PZ	-0.00643	0.14047	-0.16496	-0.02767	-0.00000
199		4PZ	-0.01072	0.12273	-0.24547	-0.02959	-0.00000
203		5PZ	-0.00274	0.03430	-0.19204	0.03282	-0.00000
	12 C	1S	0.00000	-0.00000	-0.00000	0.00000	-0.01565
218		2PZ	0.00218	0.13539	0.13044	0.04141	0.00000
222		3PZ	0.00329	0.20360	0.19106	0.06541	0.00000
226		4PZ	0.00906	0.20090	0.30263	0.07580	0.00000
230		5PZ	0.00068	0.04039	0.29324	0.08811	0.00000

SOMO of diene 1 in 46 number molecular orbital. From the molecular coefficients of diene SOMO, atom 11 has the larger contribution to the SOMO.

Molecular Orbital Coefficients in SOMO of **1**

			46	47	48	49	50
			O	V	V	V	V
	Eigenvalues --		-0.12110	-0.04422	-0.03010	-0.01954	-0.00447
181	**10** C	1S	-0.00083	0.00464	0.00409	0.00333	-0.00687
185		2PZ	-0.11996	-0.01004	0.03142	-0.09839	0.00969
189		3PZ	-0.18287	-0.01678	0.04602	-0.14959	0.01429
193		4PZ	-0.23487	-0.03079	0.08909	-0.23992	0.02476
197		5PZ	-0.16726	0.09429	0.19769	-0.38001	0.22280
208	**11** C	1S	-0.00235	0.00964	0.00780	0.00564	-0.01149
212		2PZ	-0.12152	0.01551	0.04013	-0.08819	-0.00205
216		3PZ	-0.18597	0.02382	0.06023	-0.13265	-0.00383
220		4PZ	-0.23728	0.05356	0.09473	-0.22432	0.02412
224		5PZ	-0.19405	0.05696	0.21296	-0.45699	0.02228

14. References

[1] P. Rai, K. Maji, B. Maji, *Org. Lett.* **2019**, *21*, 3755-3759.

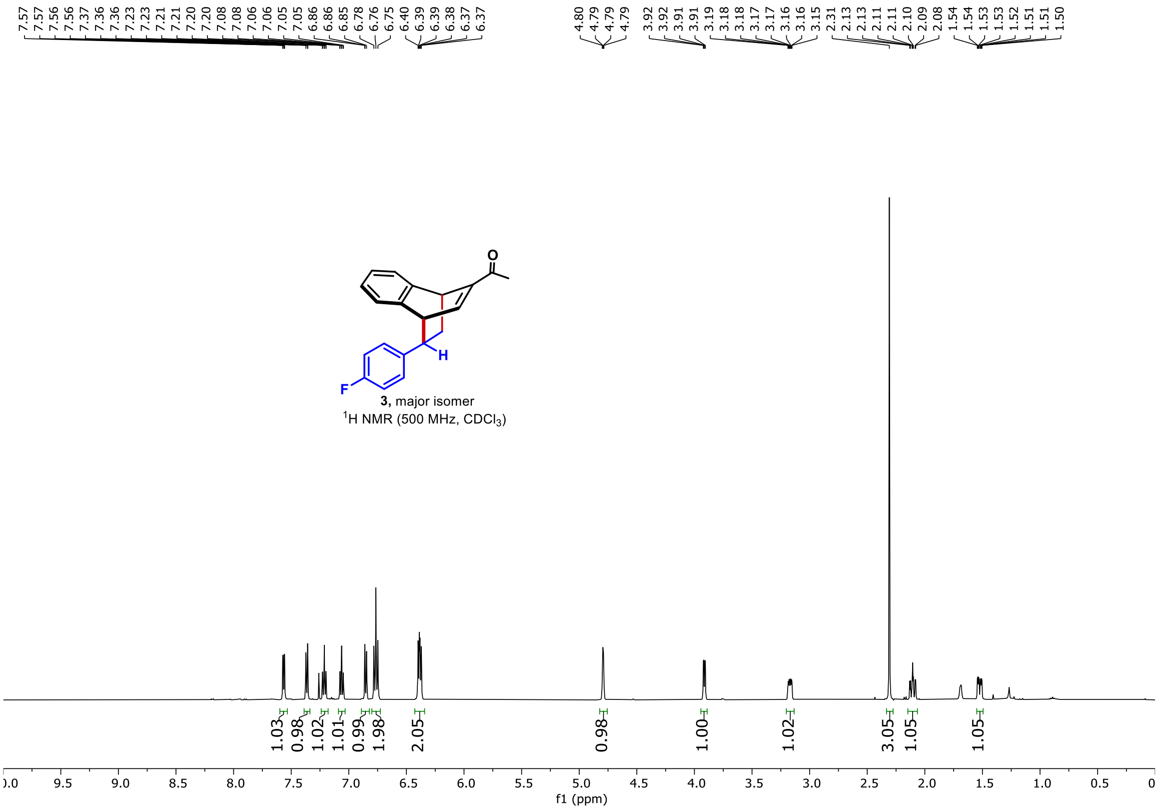
[2] a) H. Huo, X. Shen, C. Wang, L. Zhang, P. Röse, L.-A. Chen, K. Harms, M. Marsch, G. Hilt, E. Meggers, *Nature* **2014**, *515*, 100-103; b) Q. Li, C. Moussallem, F. Castet, L. Muccioli, M.-A. Dourges, T. Toupance, Y. Nicolas, *Org. Lett.* **2022**, *24*, 344-348.

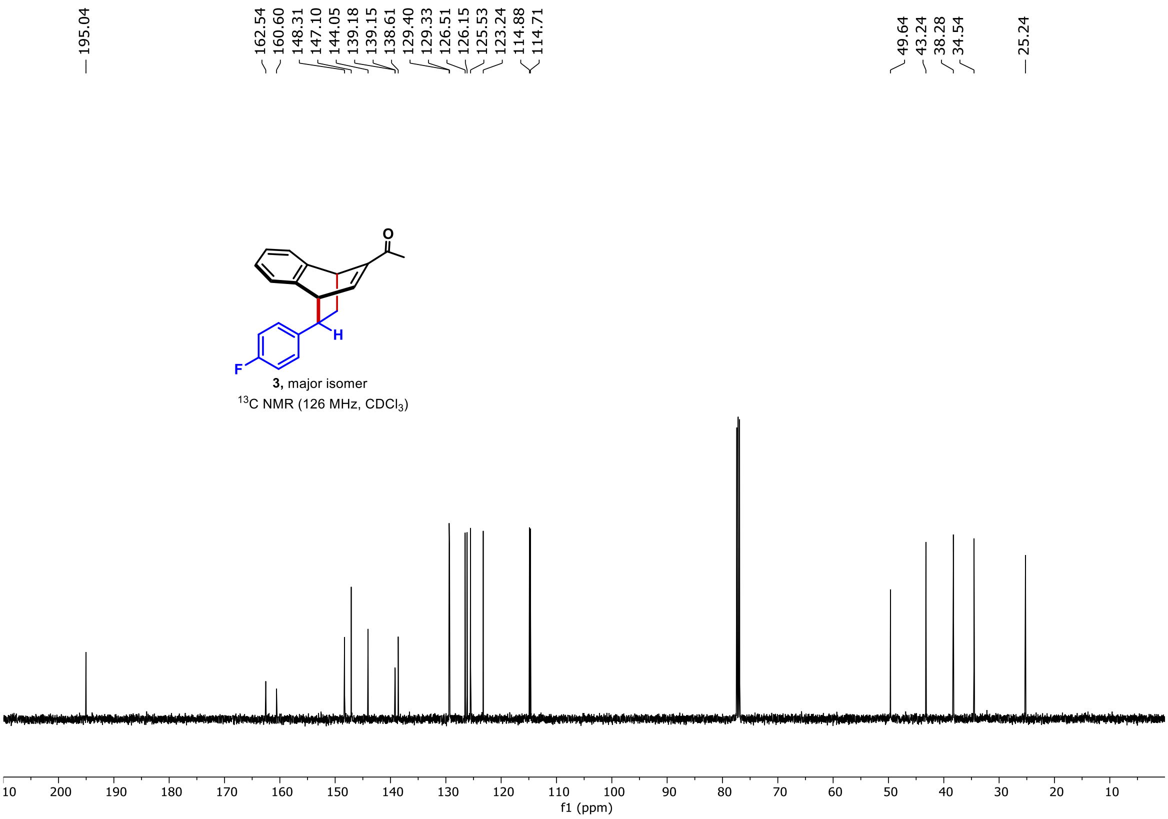
[3] S. T. Moe, A. B. Thompson, G. M. Smith, R. A. Fredenburg, R. L. Stein, A. R. Jacobson, *Bioorg. Med. Chem.* **2009**, *17*, 3072-3079.

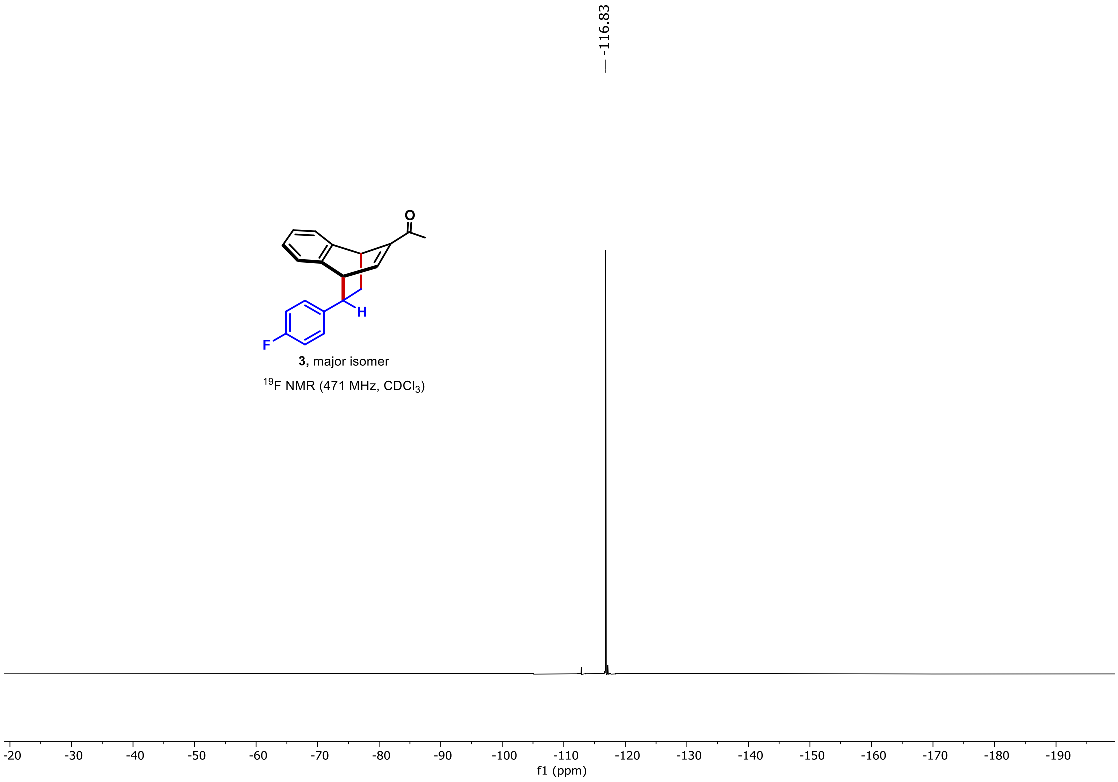
[4] F. M. Hörmann, T. S. Chung, E. Rodriguez, M. Jakob, T. Bach, *Angew. Chem. Int. Ed.* **2018**, *57*, 827-831.

[5] a) R. Guo, Y.-C. Chang, L. Herter, C. Salome, S. E. Braley, T. C. Fessard, M. K. Brown, *J. Am. Chem. Soc.* **2022**, *144*, 7988-7994; b) T. R. Blum, Z. D. Miller, D. M. Bates, I. A. Guzei, T. P. Yoon, *Science* **2016**, *354*, 1391-1395.

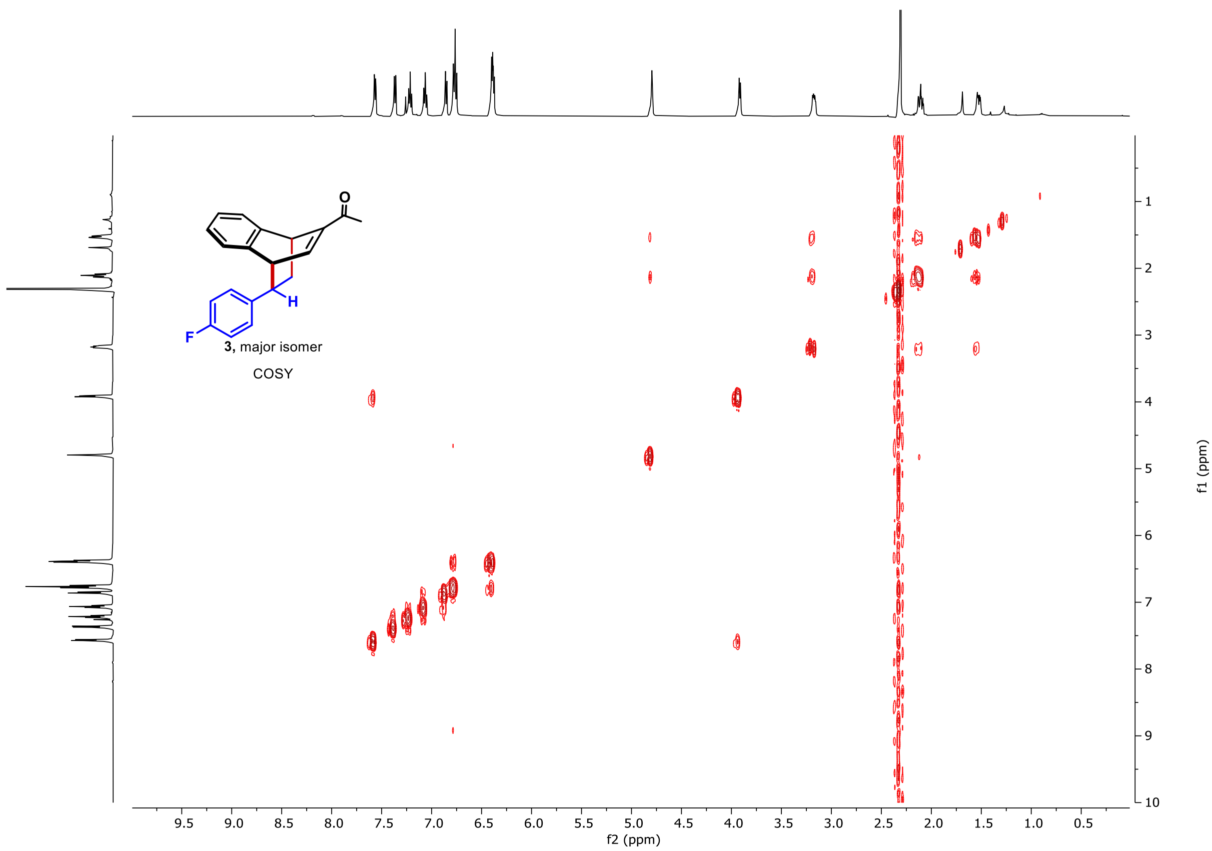
15. Copies of NMR spectra



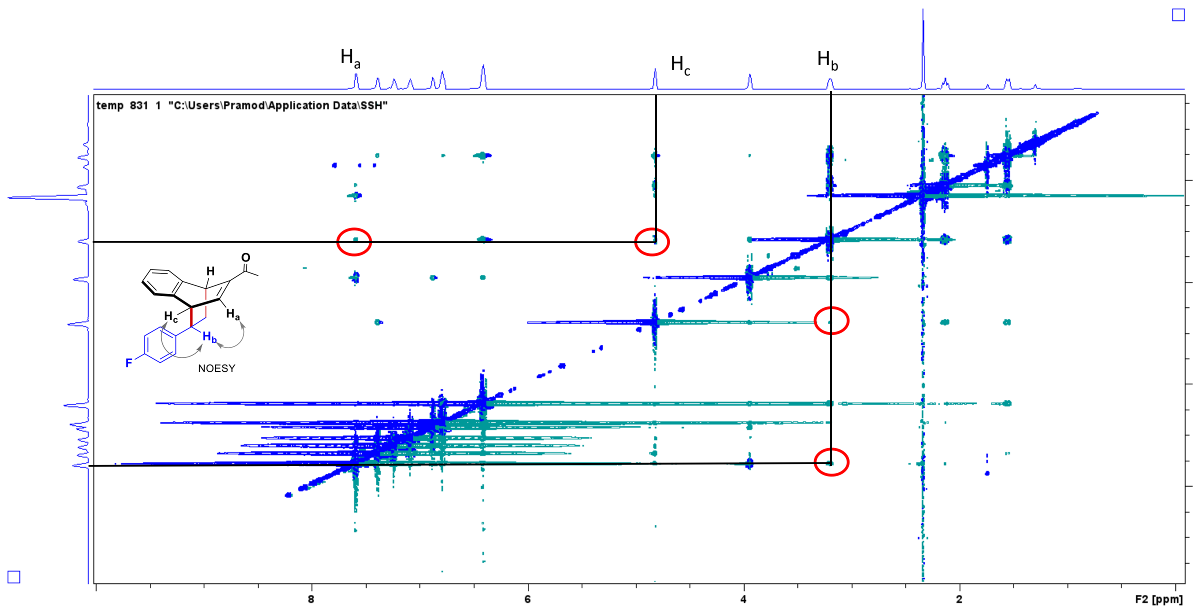


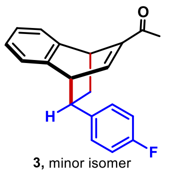


-116.83
3, major isomer
19F NMR (471 MHz, CDCl3)
f1 (ppm)



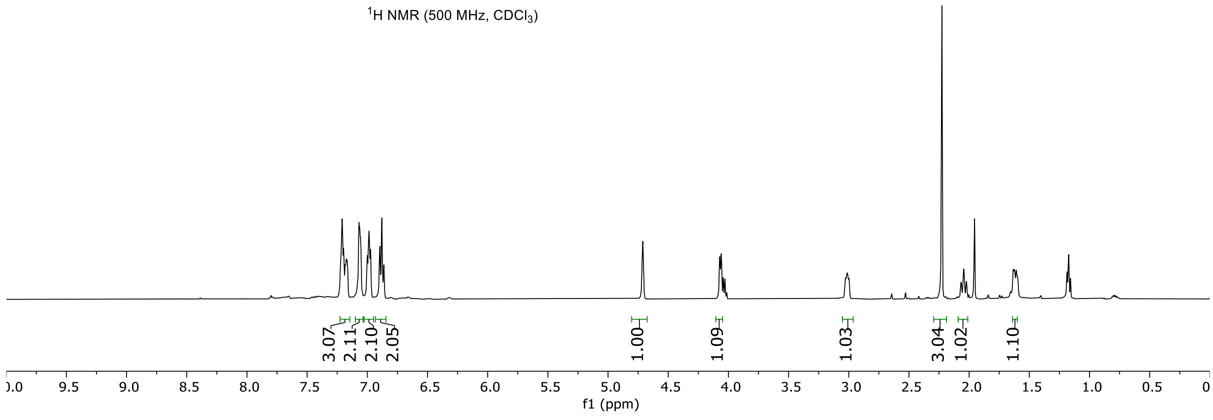
3, major isomer
COSY
f2 (ppm)
f1 (ppm)

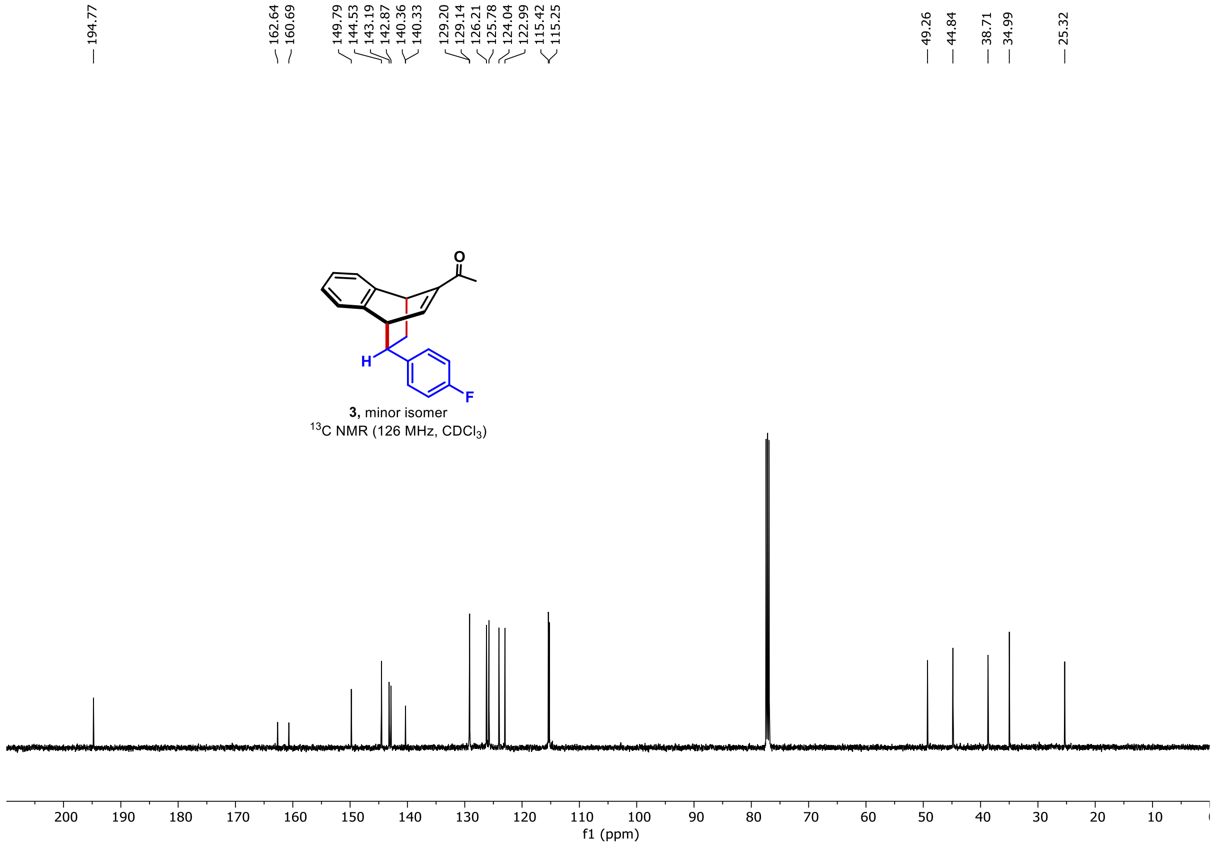


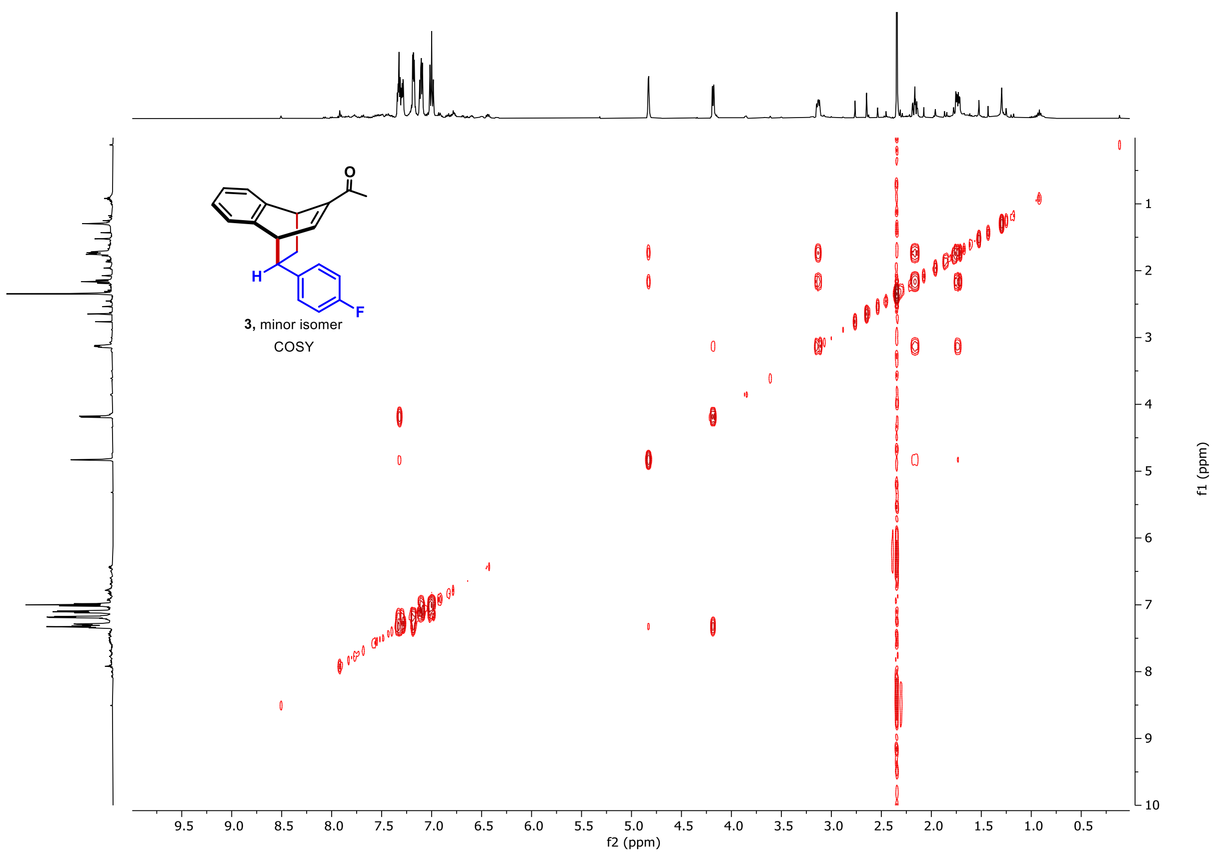


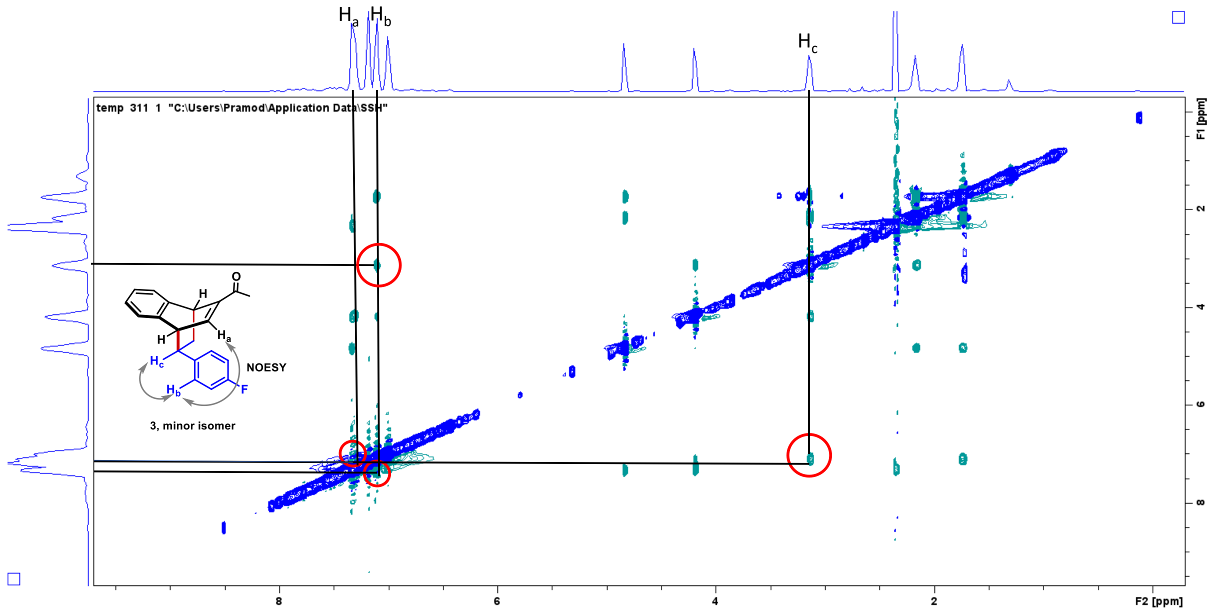
3, minor isomer

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

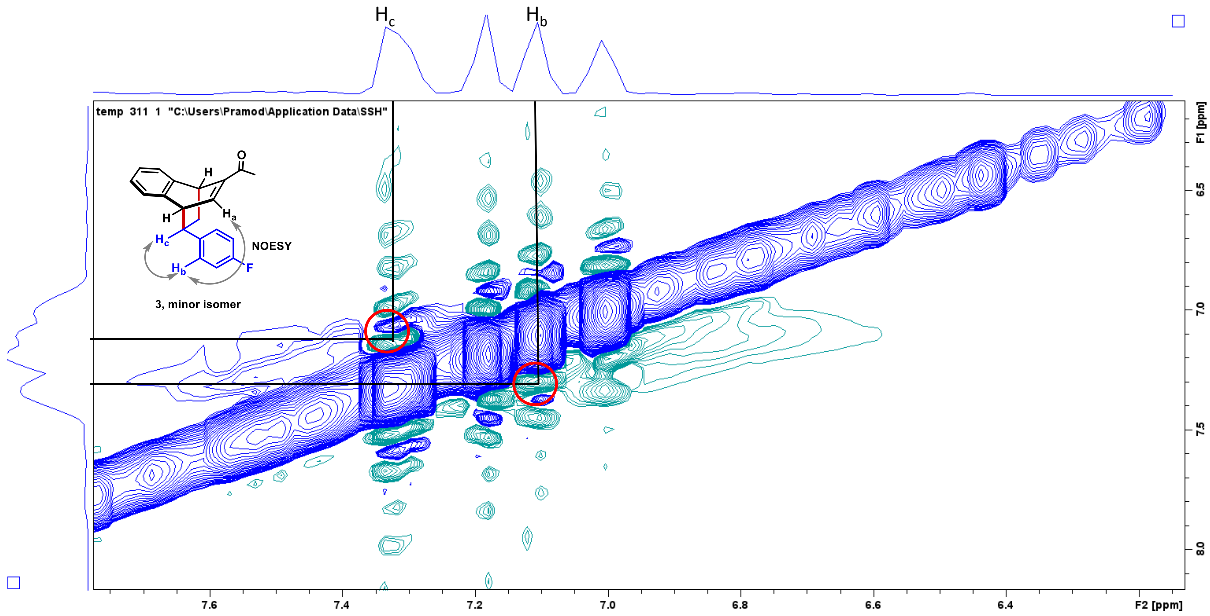



194.77
162.64
160.69
149.79
144.53
143.19
142.87
140.36
140.33
129.20
129.14
126.21
125.78
124.04
122.99
115.42
115.25
49.26
44.84
38.71
34.99
25.32
3, minor isomer
^{13}C NMR (126 MHz, $CDCl_3$)
f1 (ppm)

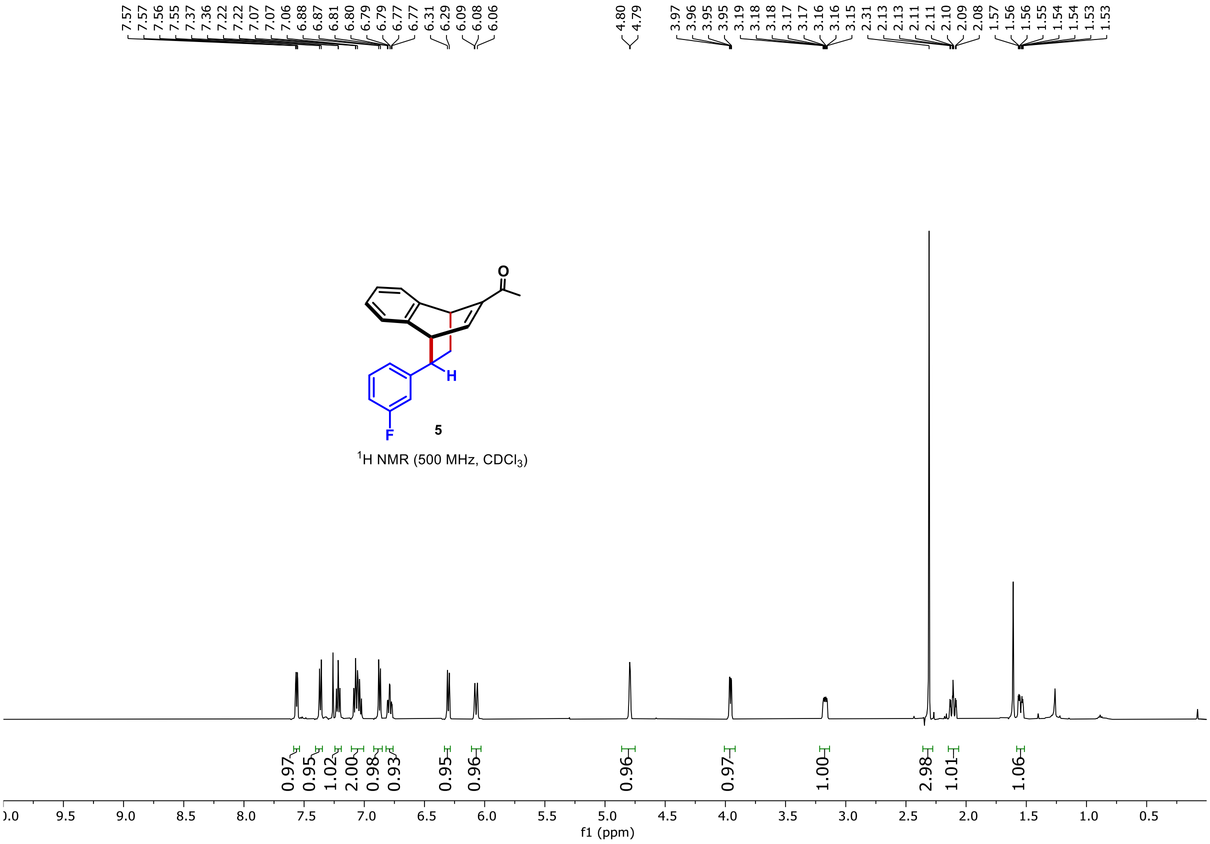

3, minor isomer
COSY
f2 (ppm)
f1 (ppm)

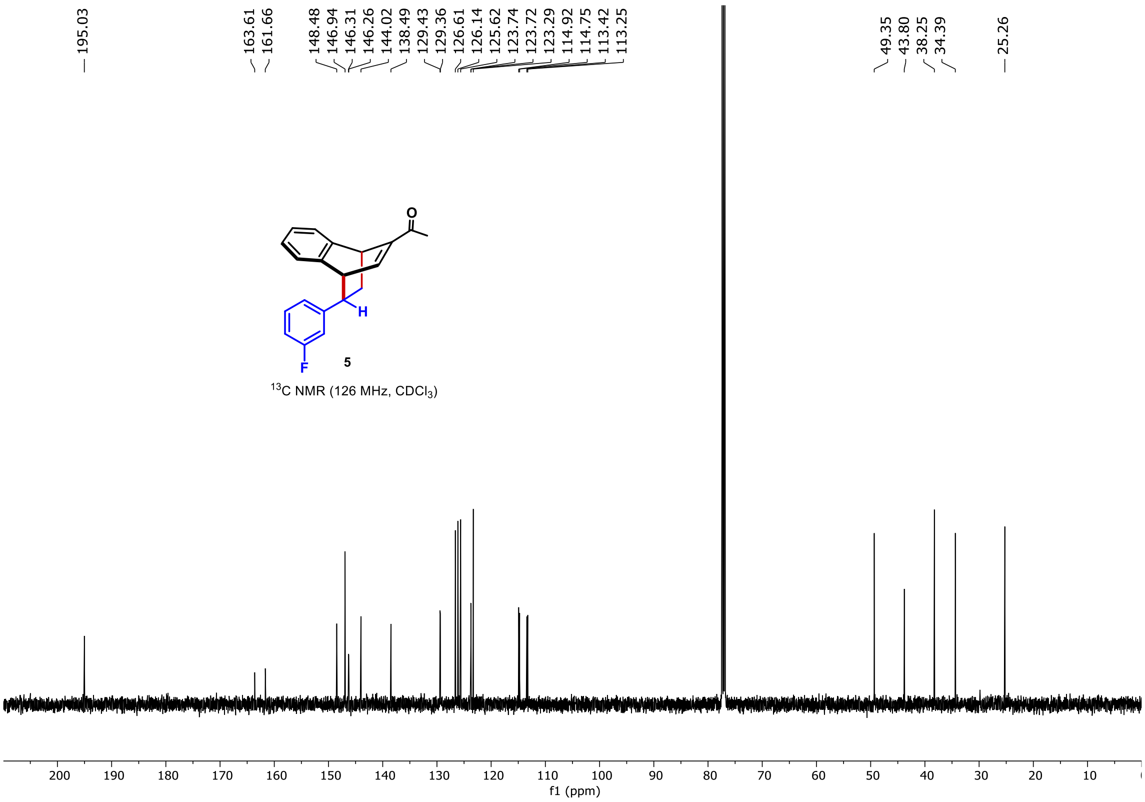


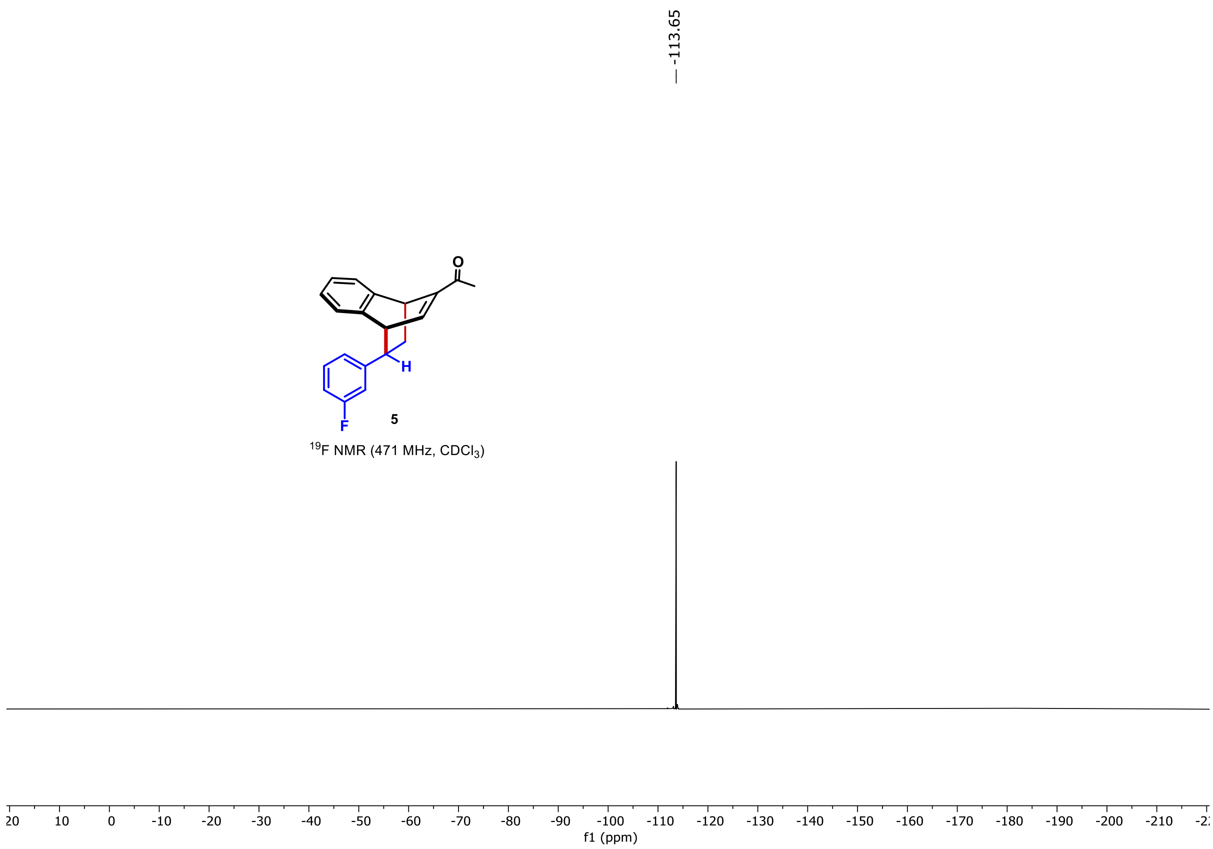
Ha
Hb
Hc
temp 311 1 "C:\Users\Pramod\Application Data\SSH"
NOESY
3, minor isomer
F1 [ppm]
F2 [ppm]



Hc
Hb
temp 311 1 "C:\Users\Pramod\Application Data\SSH"
NOESY
3, minor isomer
F1 [ppm]
F2 [ppm]

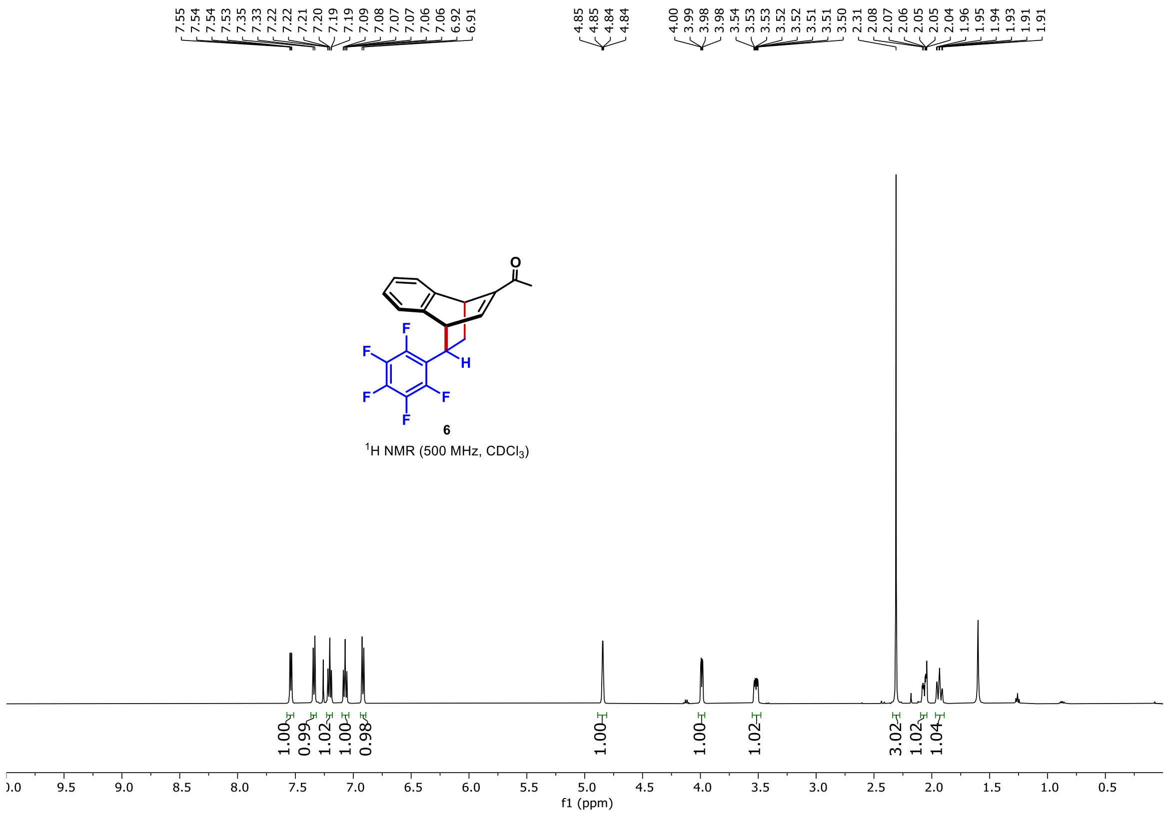

7.57 7.57 7.56 7.55 7.37 7.36 7.22 7.22 7.07 7.07 7.07 7.06 6.88 6.87 6.81 6.80 6.79 6.79 6.77 6.77 6.31 6.29 6.09 6.08 6.06
4.80 4.79
3.97 3.96 3.95 3.95 3.19 3.18 3.18 3.17 3.17 3.16 3.16 3.15 2.31 2.13 2.13 2.11 2.11 2.10 2.09 2.08 1.57 1.56 1.56 1.55 1.54 1.54 1.53 1.53
O
H
F
5
1H NMR (500 MHz, CDCl3)
0.97 0.95 1.02 2.00 0.98 0.93 0.95 0.96 0.96 0.97 1.00 2.98 1.01 1.06
f1 (ppm)


195.03
163.61 161.66
148.48 146.94 146.31 146.26 144.02 138.49 129.43 129.36 126.61 126.14 125.62 123.74 123.72 123.29 114.92 114.75 113.42 113.25
49.35 43.80 38.25 34.39
25.26
O
H
F
5
13C NMR (126 MHz, CDCl3)
f1 (ppm)



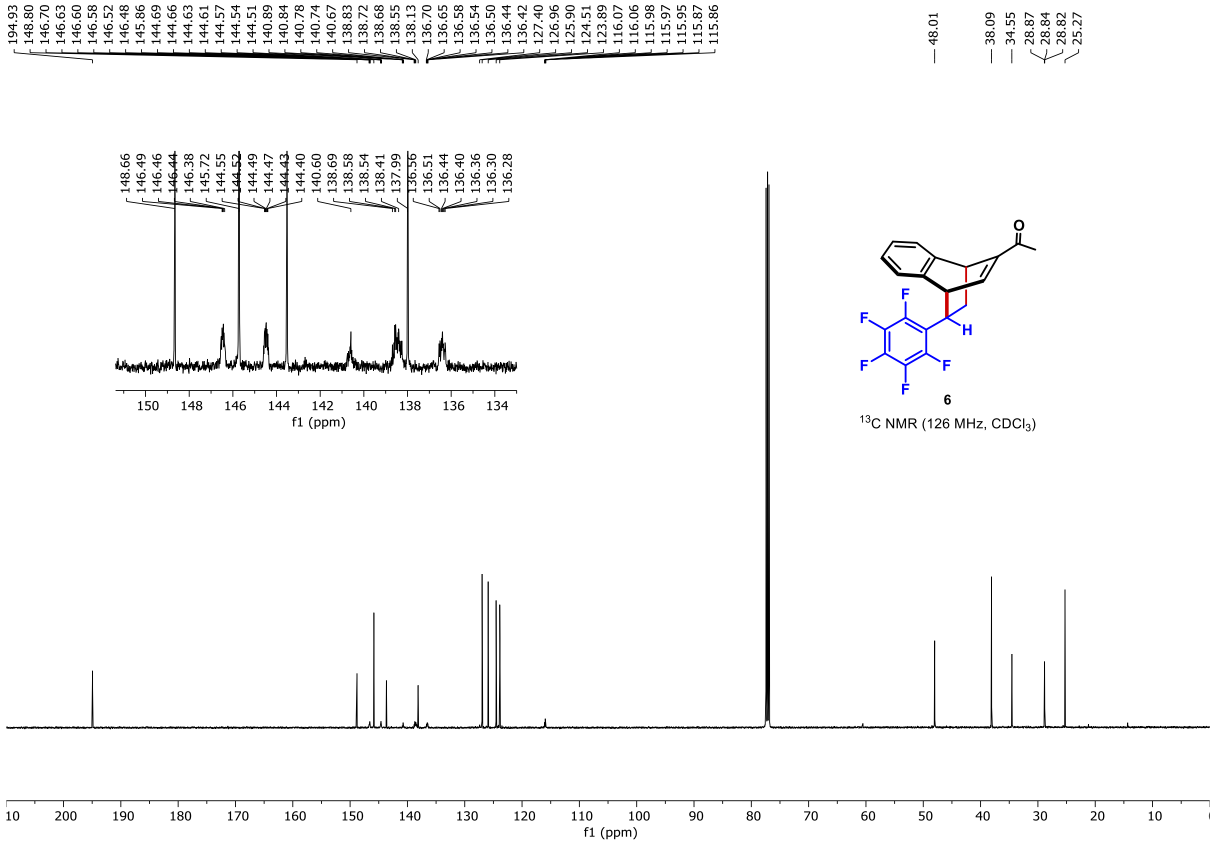
5

^{19}F NMR (471 MHz, CDCl$_3$)



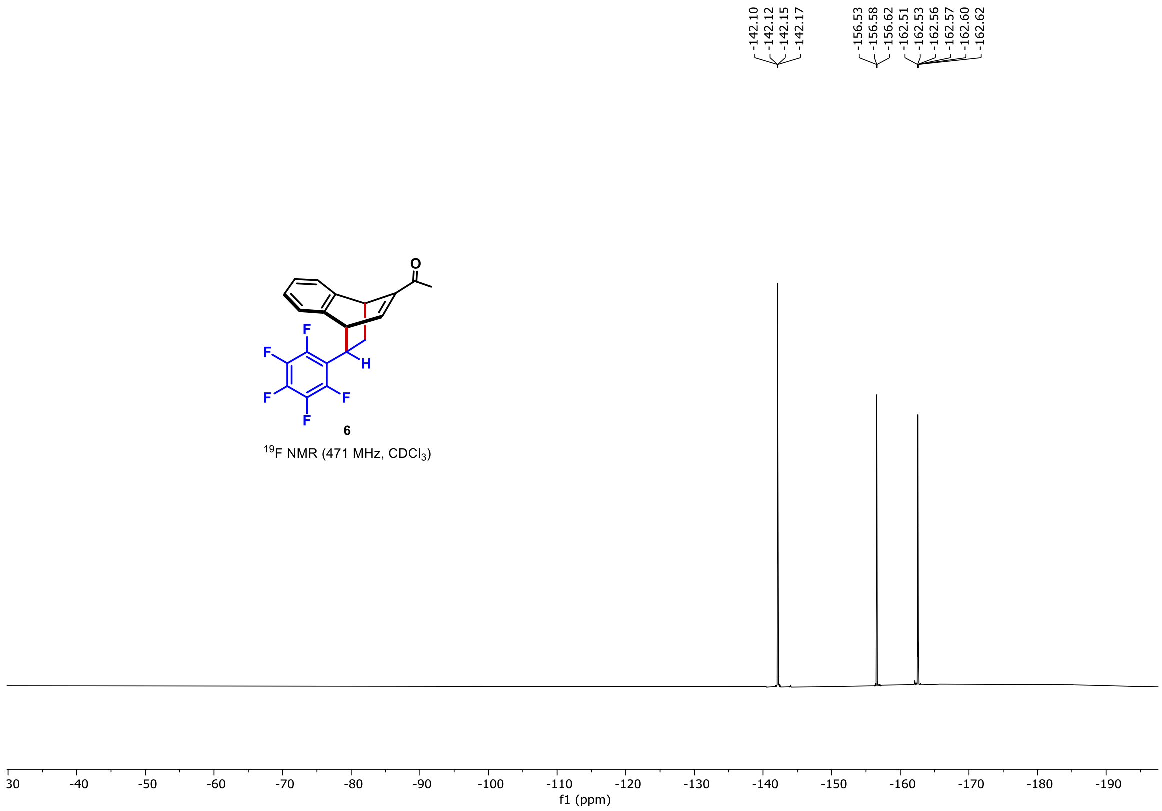
6

^{1}H NMR (500 MHz, CDCl$_3$)



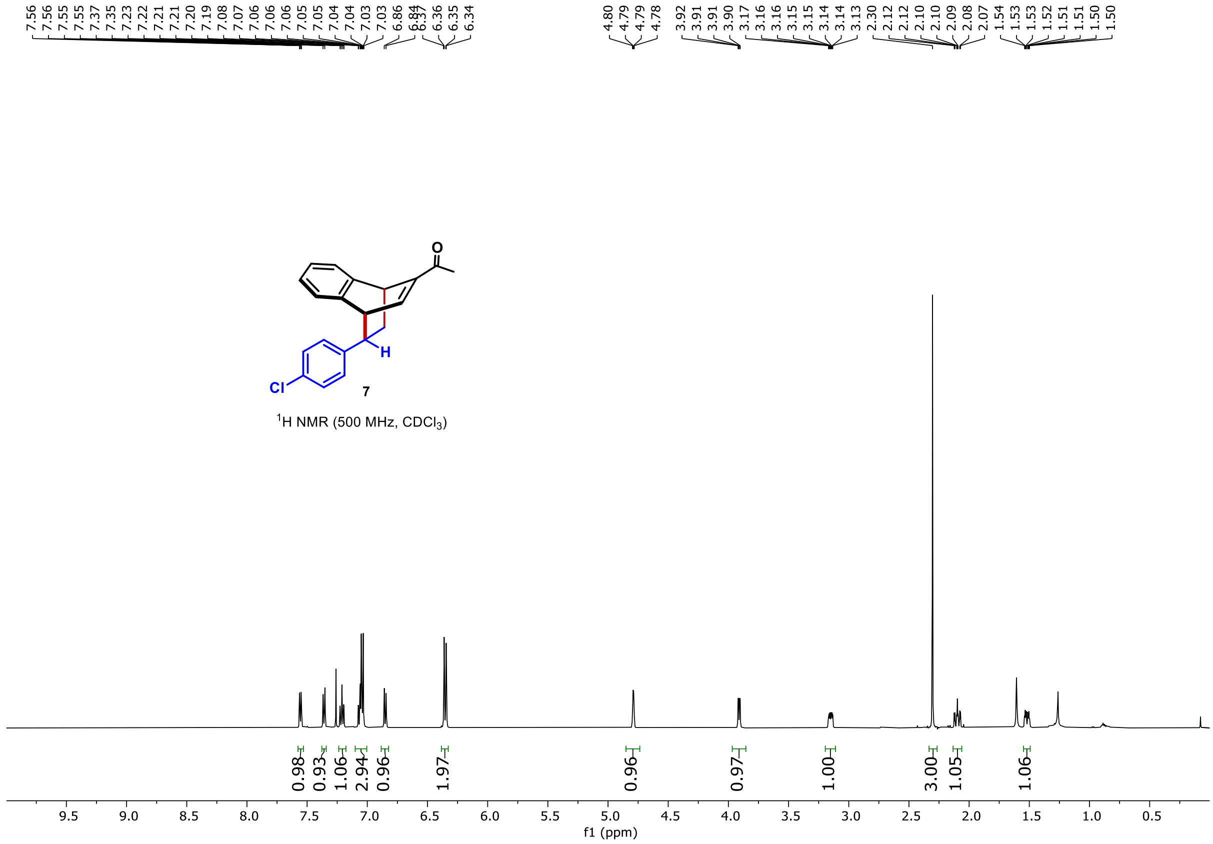
6

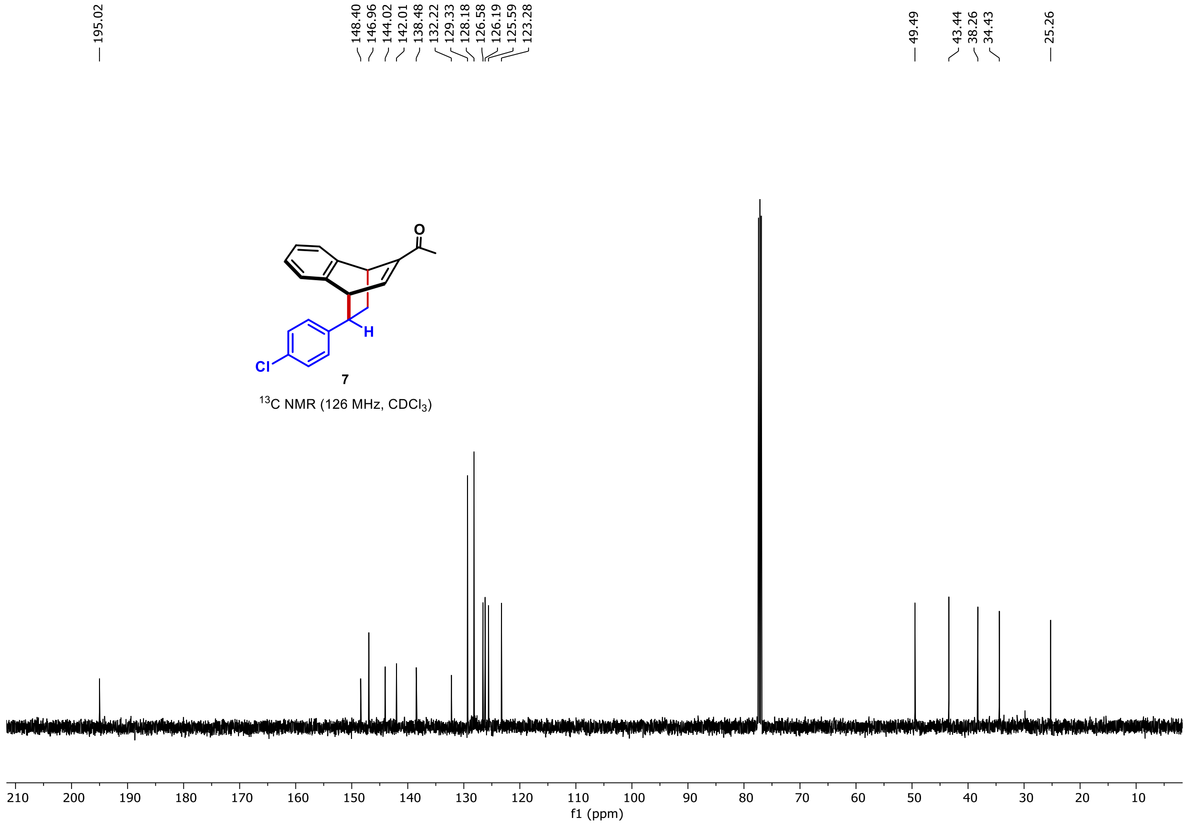
^{13}C NMR (126 MHz, $CDCl_3$)

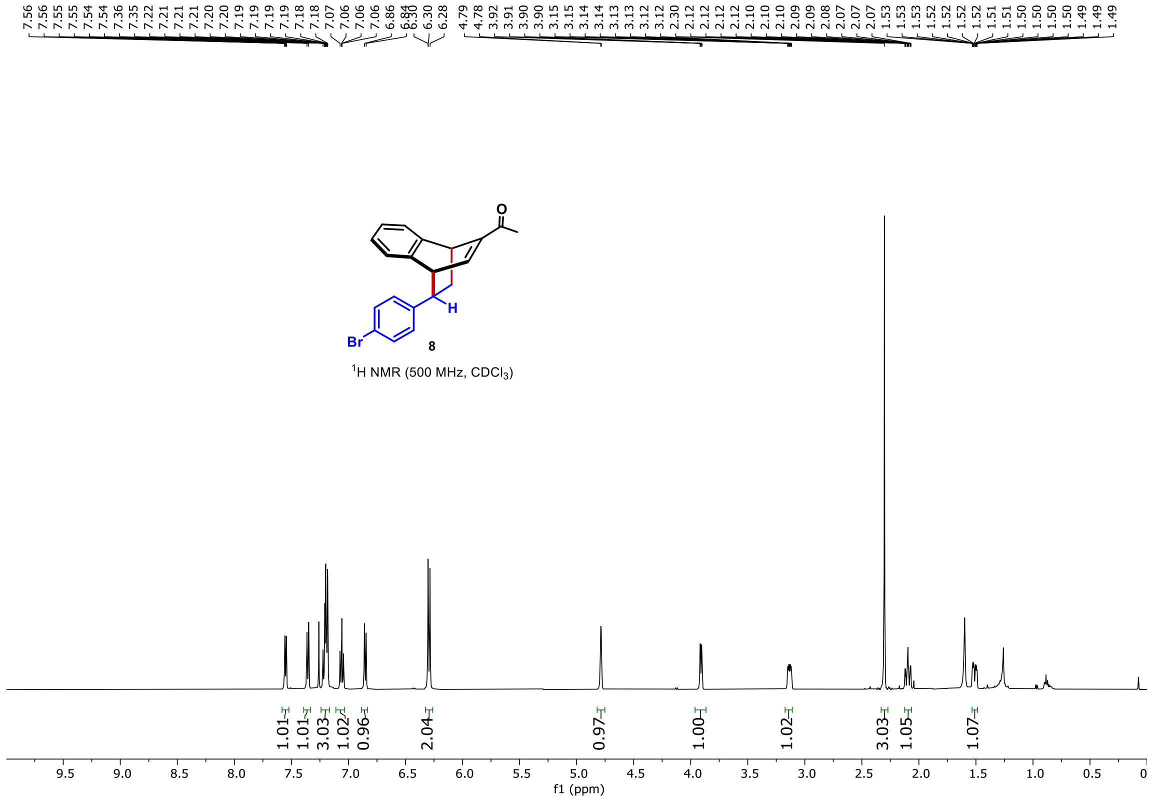


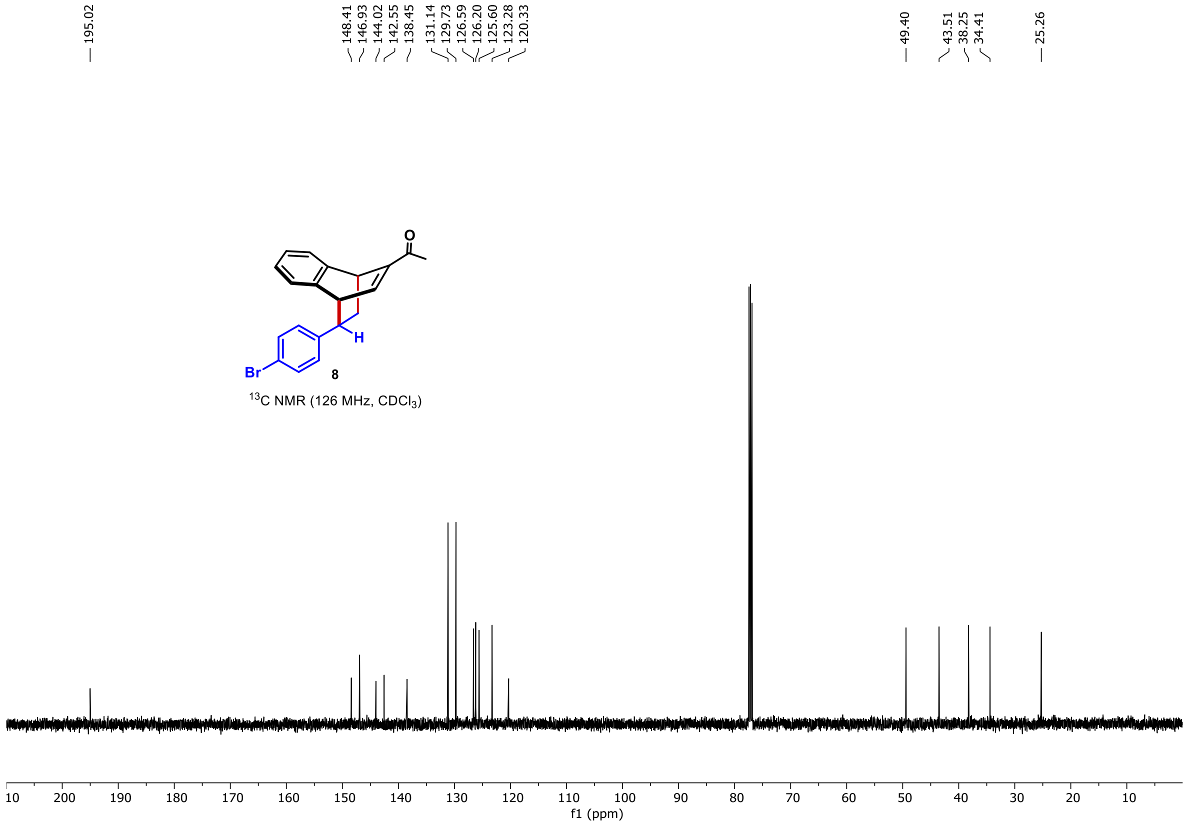
6

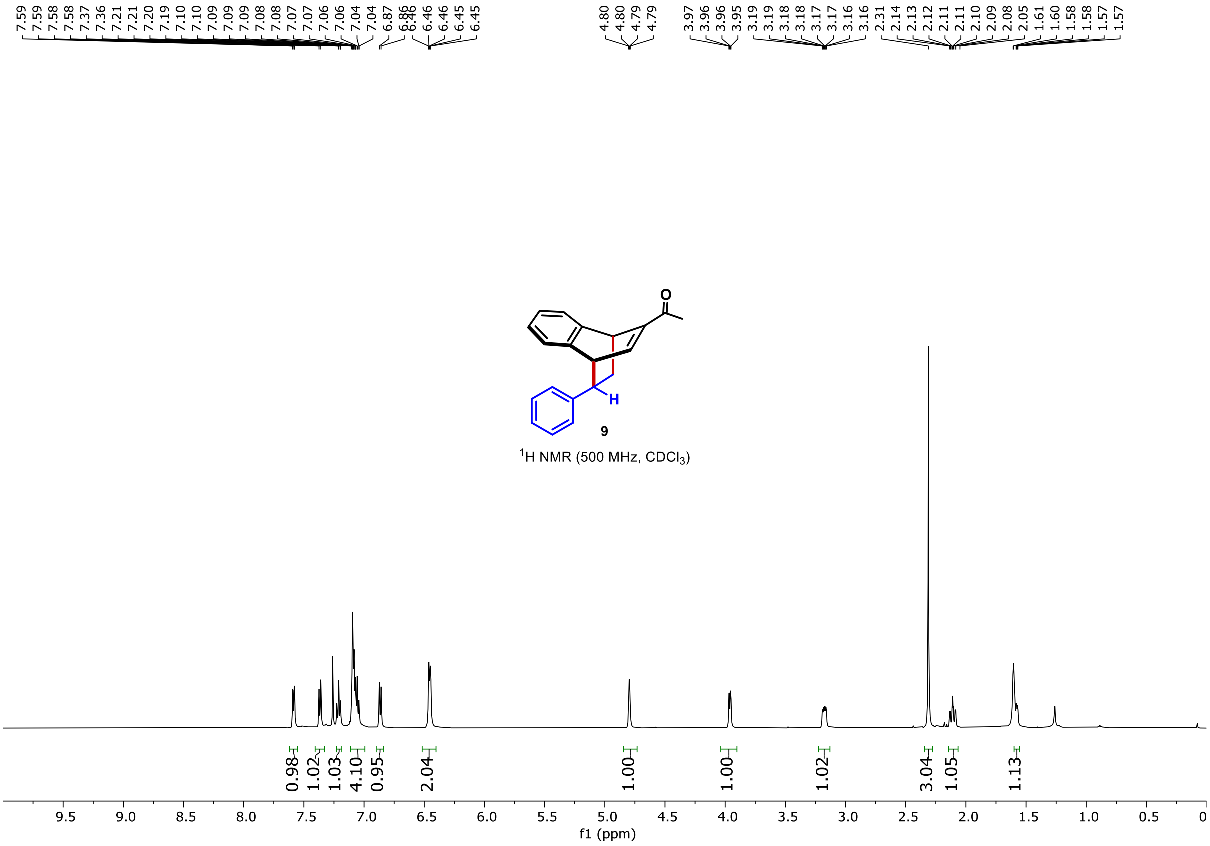
^{19}F NMR (471 MHz, $CDCl_3$)


7.56 7.56 7.55 7.37 7.35 7.23 7.22 7.21 7.21 7.20 7.19 7.08 7.07 7.06 7.06 7.05 7.05 7.04 7.03 7.03 6.86 6.84 6.37 6.36 6.35 6.34
4.80 4.79 4.79 4.78 3.92 3.91 3.91 3.90 3.17 3.16 3.16 3.15 3.15 3.14 3.14 3.13 2.30 2.12 2.12 2.10 2.10 2.09 2.08 2.07 1.54 1.53 1.53 1.52 1.51 1.51 1.50 1.50
O
H
Cl
7
^{1}H NMR (500 MHz, CDCl$_3$)
0.98 0.93 1.06 2.94 0.96 1.97 0.96 0.97 1.00 3.00 1.05 1.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


195.02
148.40 146.96 144.02 142.01 138.48 132.22 129.33 128.18 126.58 126.19 125.59 123.28
49.49 43.44 38.26 34.43 25.26
O
H
Cl
7
^{13}C NMR (126 MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

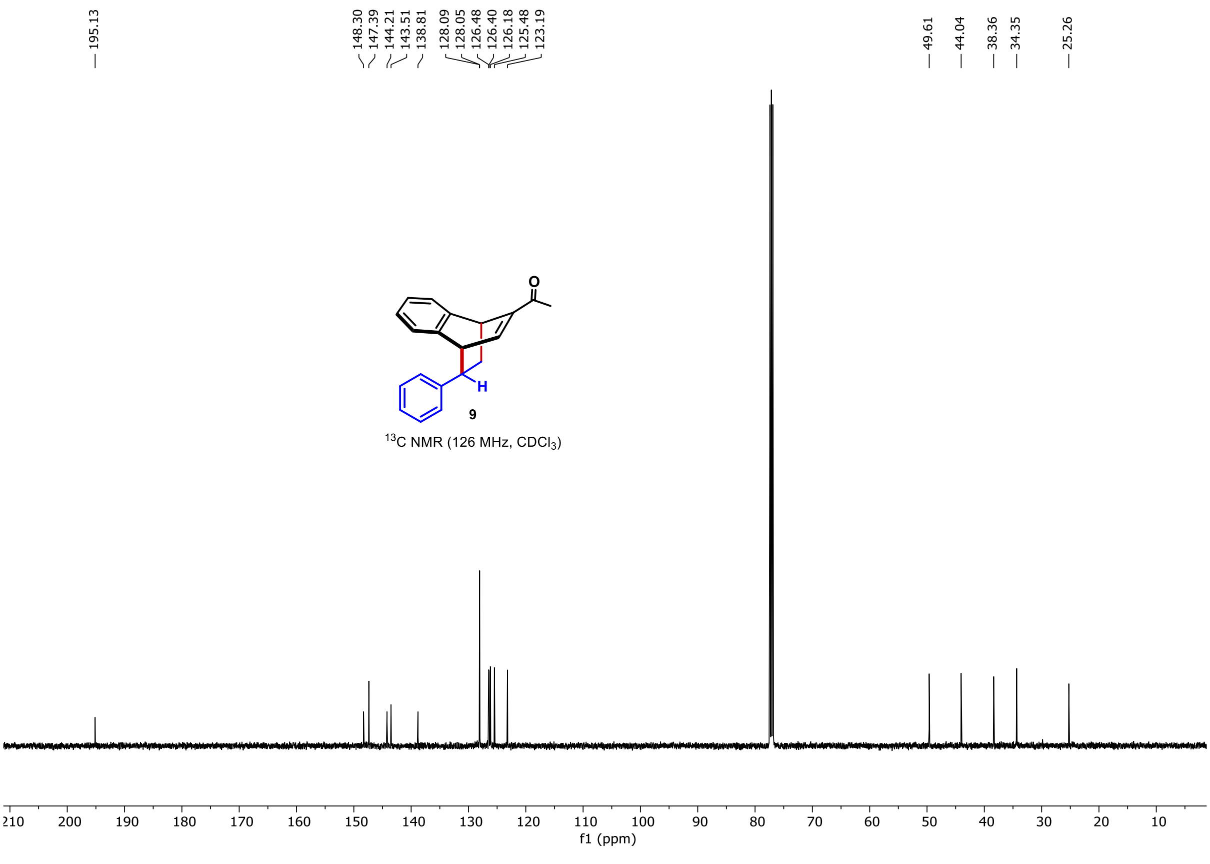

7.56 7.56 7.55 7.55 7.54 7.54 7.36 7.35 7.22 7.21 7.21 7.21 7.20 7.19 7.19 7.19 7.19 7.18 7.18 7.07 7.06 7.06 7.06 6.86 6.84 6.30 6.30 6.28 4.79 4.78 3.92 3.91 3.90 3.90 3.15 3.15 3.14 3.14 3.13 3.13 3.12 3.12 2.30 2.12 2.12 2.12 2.10 2.10 2.10 2.09 2.09 2.08 2.07 2.07 2.07 1.53 1.53 1.53 1.52 1.52 1.52 1.52 1.51 1.51 1.50 1.50 1.50 1.50 1.49 1.49 1.49
O
H
Br
8
^{1}H NMR (500 MHz, CDCl$_3$)
1.01 1.01 3.03 1.02 0.96 2.04 0.97 1.00 1.02 3.03 1.05 1.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)


195.02
148.41 146.93 144.02 142.55 138.45 131.14 129.73 126.59 126.20 125.60 123.28 120.33
49.40 43.51 38.25 34.41 25.26
O
H
Br
8
^{13}C NMR (126 MHz, CDCl$_3$)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)



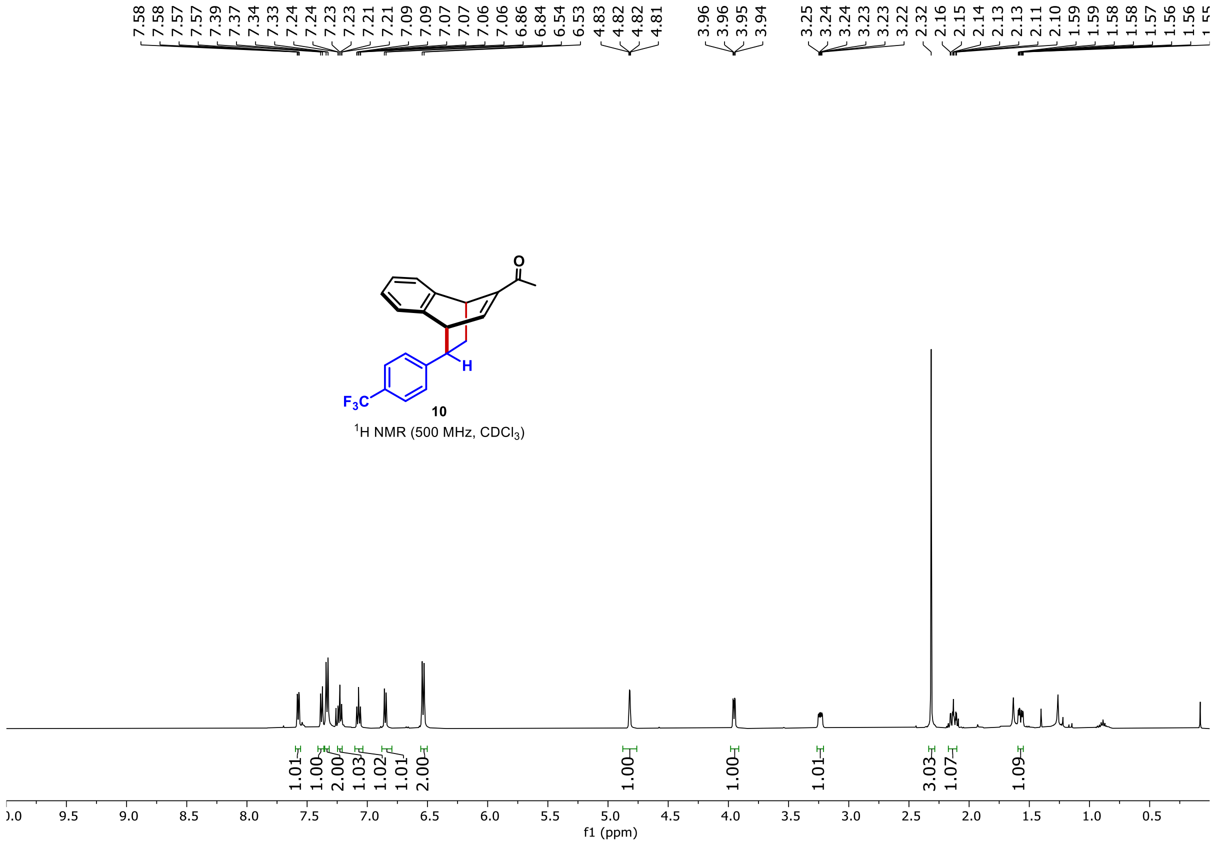
9

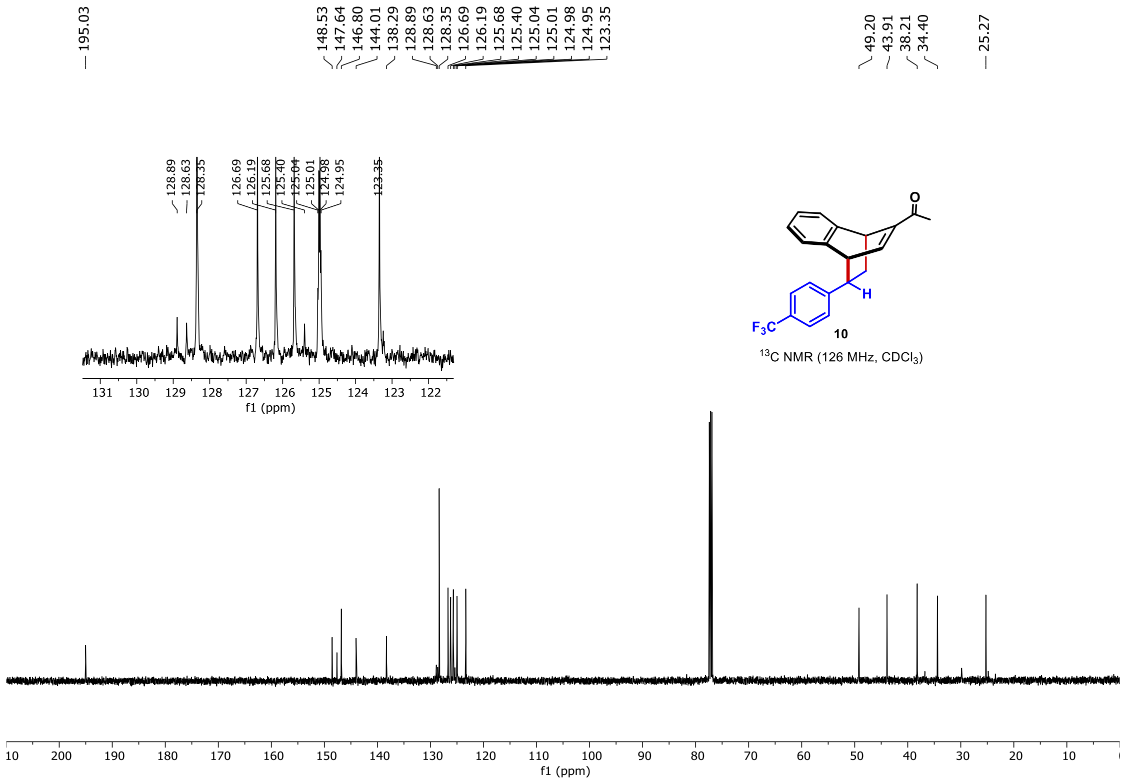
^{1}H NMR (500 MHz, $CDCl_3$)

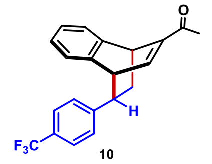


9

^{13}C NMR (126 MHz, $CDCl_3$)

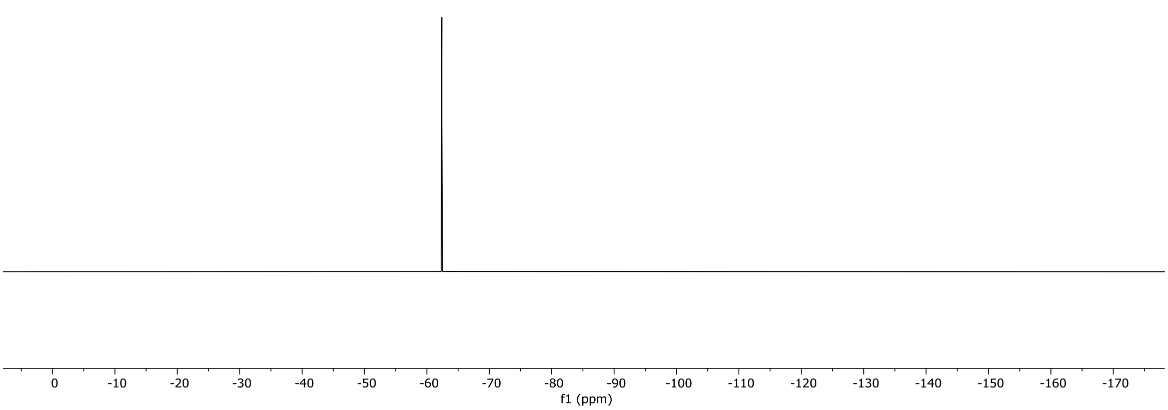

10
^{1}H NMR (500 MHz, CDCl$_3$)
f1 (ppm)

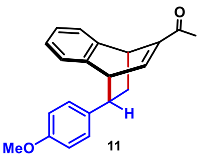

10
^{13}C NMR (126 MHz, CDCl$_3$)
f1 (ppm)



10

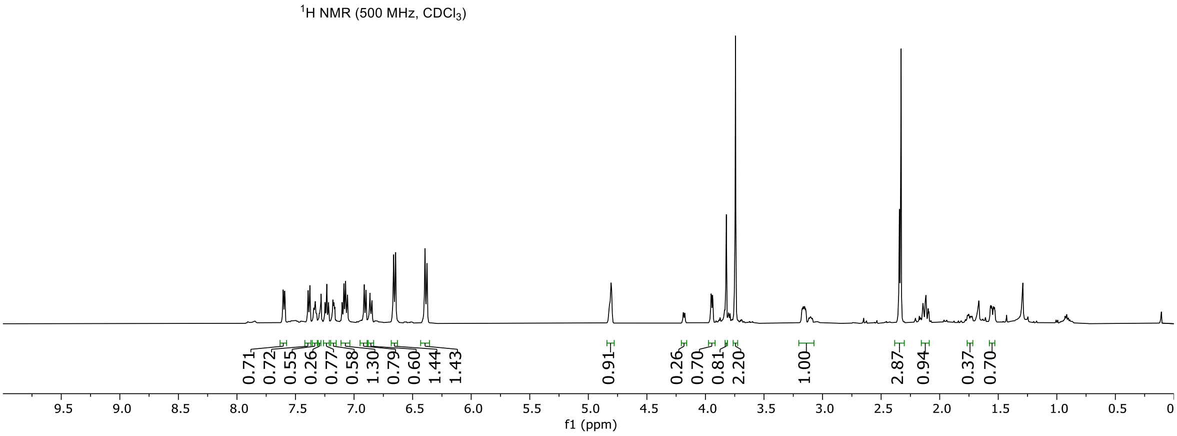
^{19}F NMR (471 MHz, $CDCl_3$)

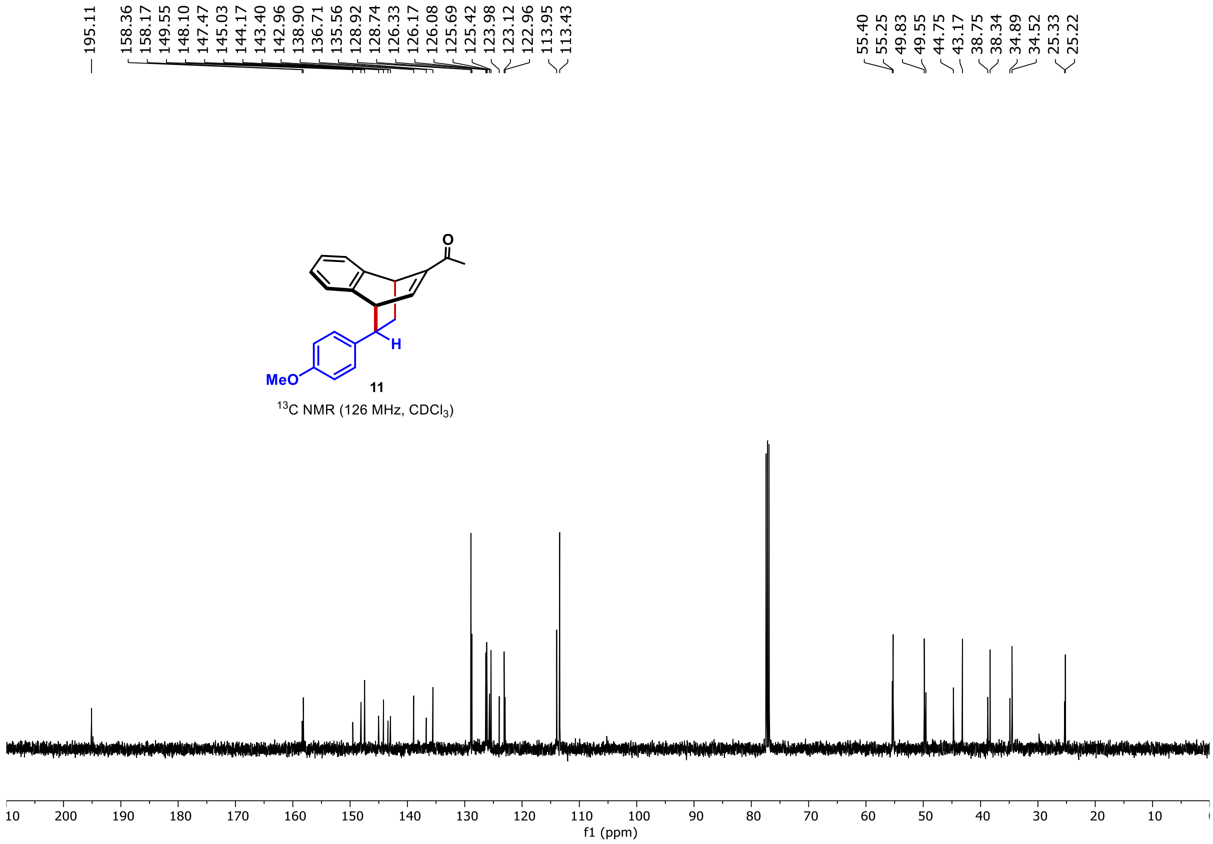




11

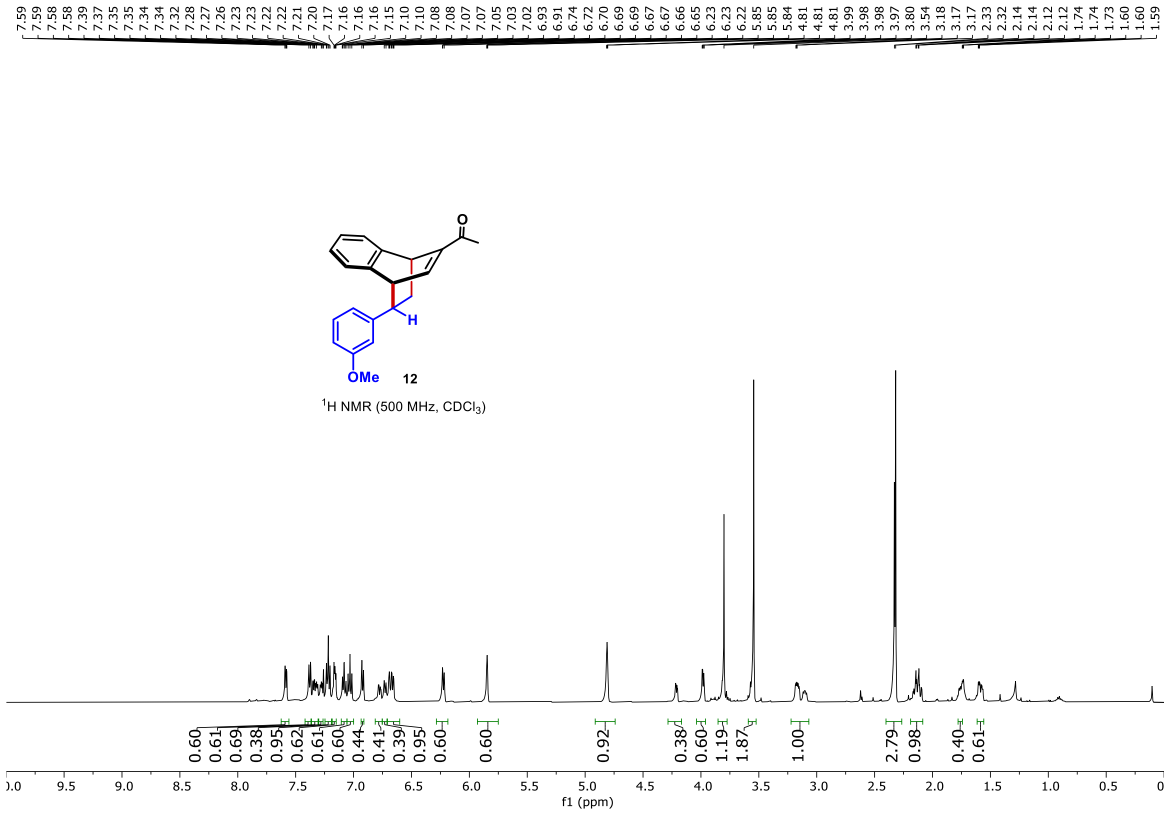
^{1}H NMR (500 MHz, $CDCl_3$)





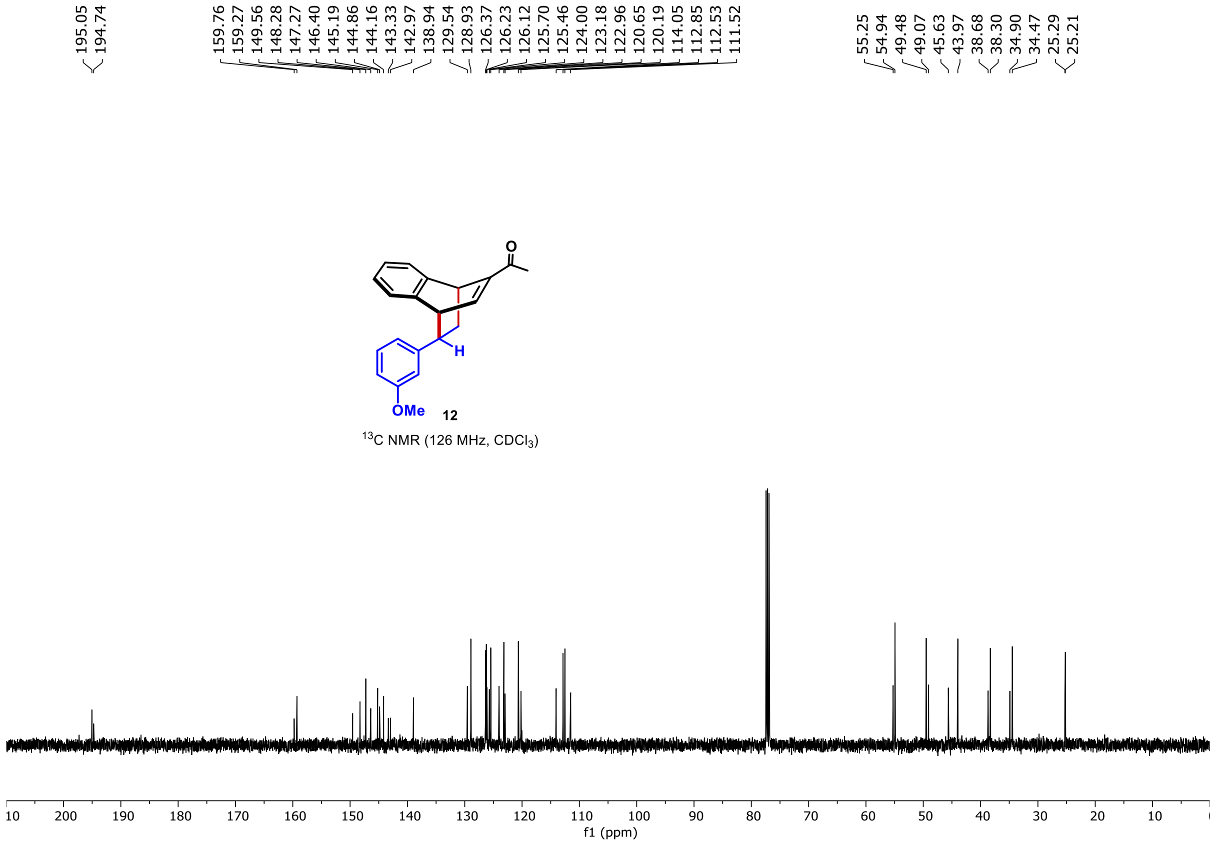
11

^{13}C NMR (126 MHz, $CDCl_3$)



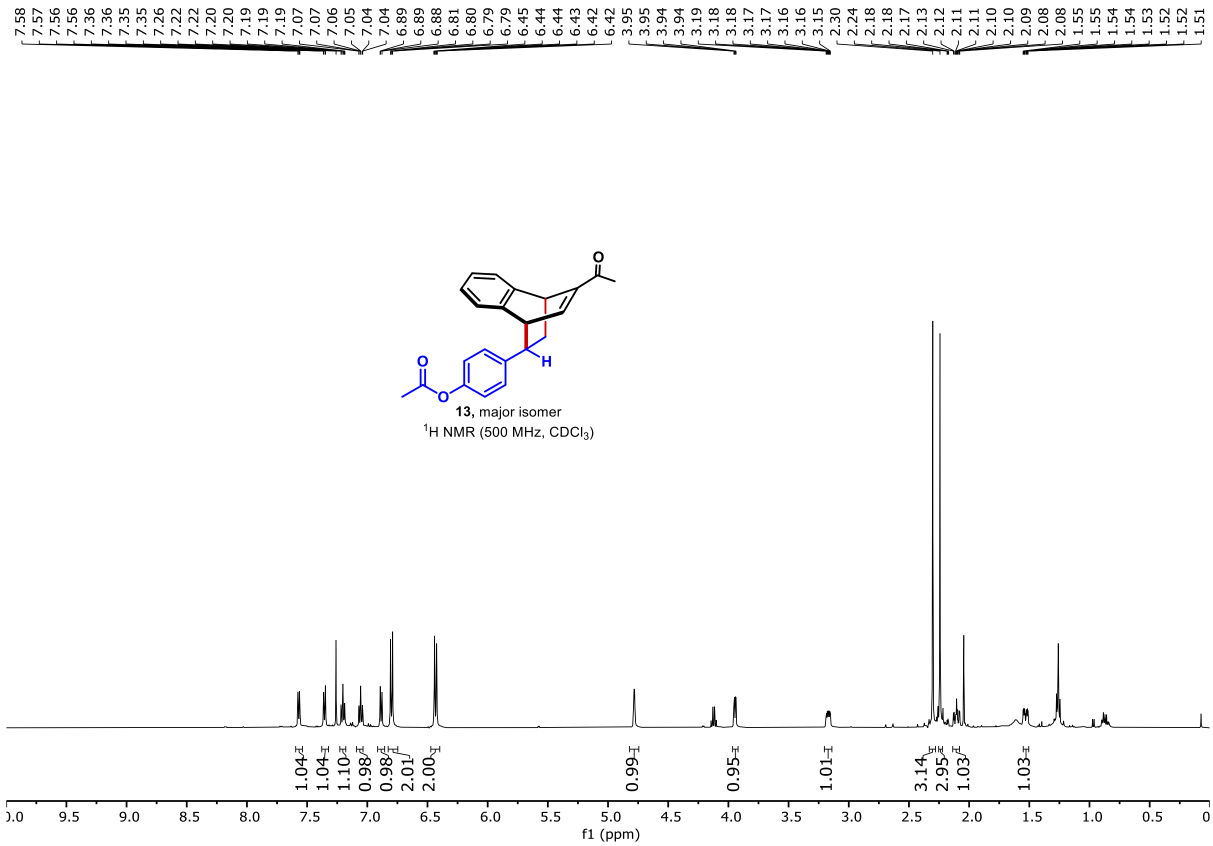
12

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



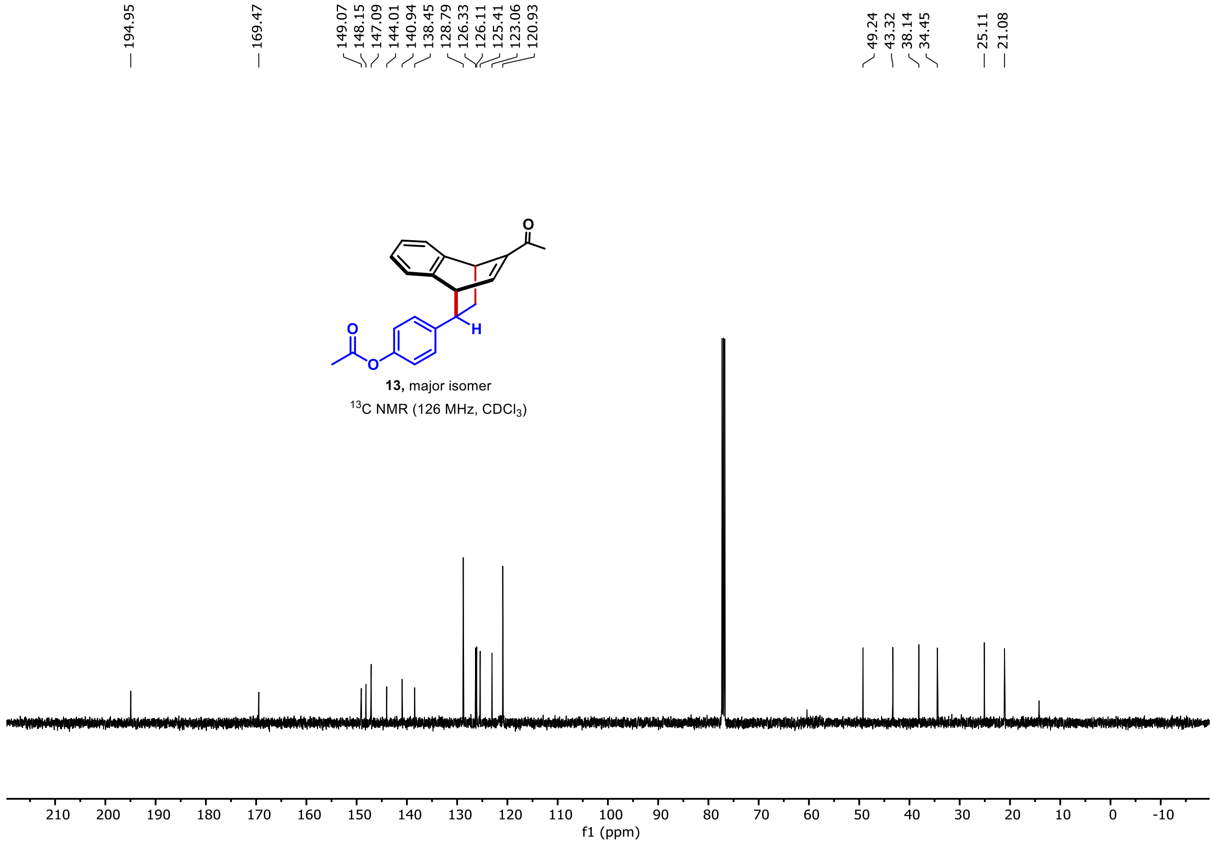
12

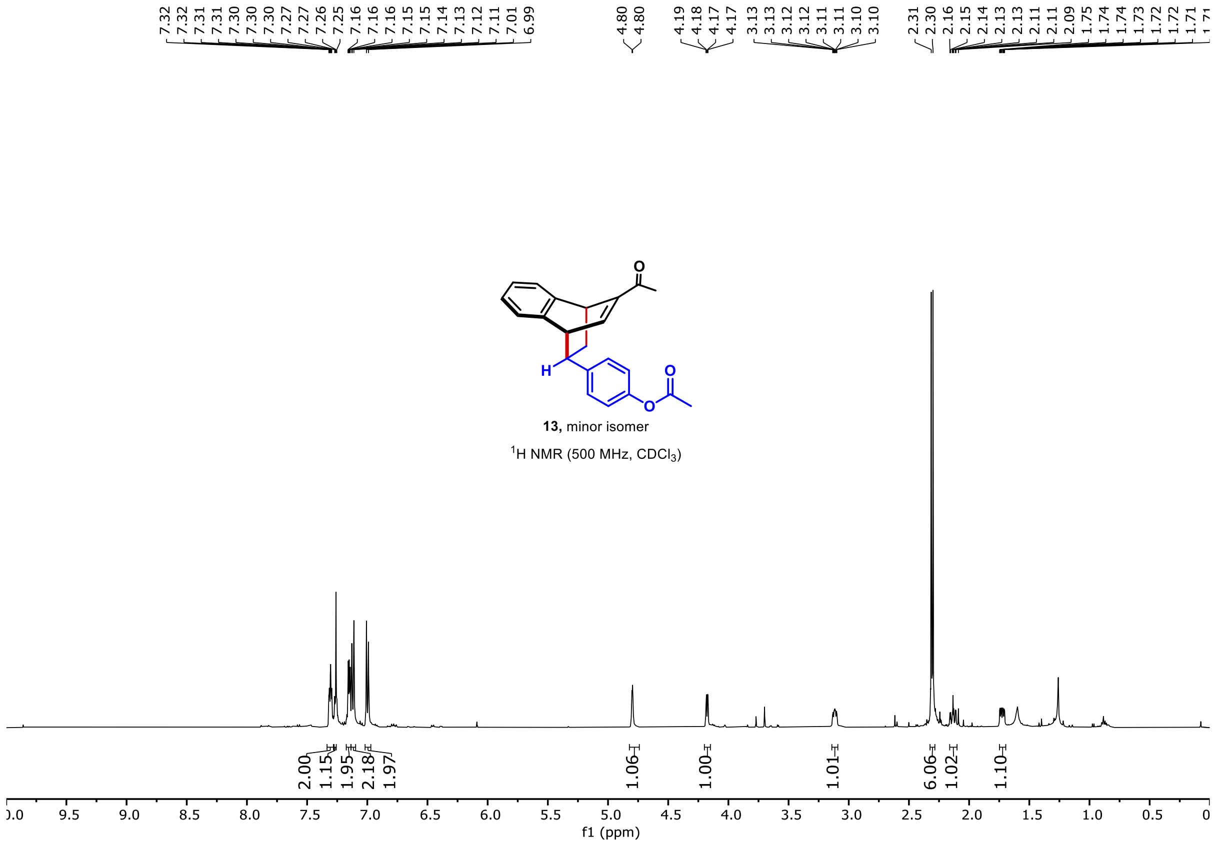
^{13}C NMR (126 MHz, $CDCl_3$)

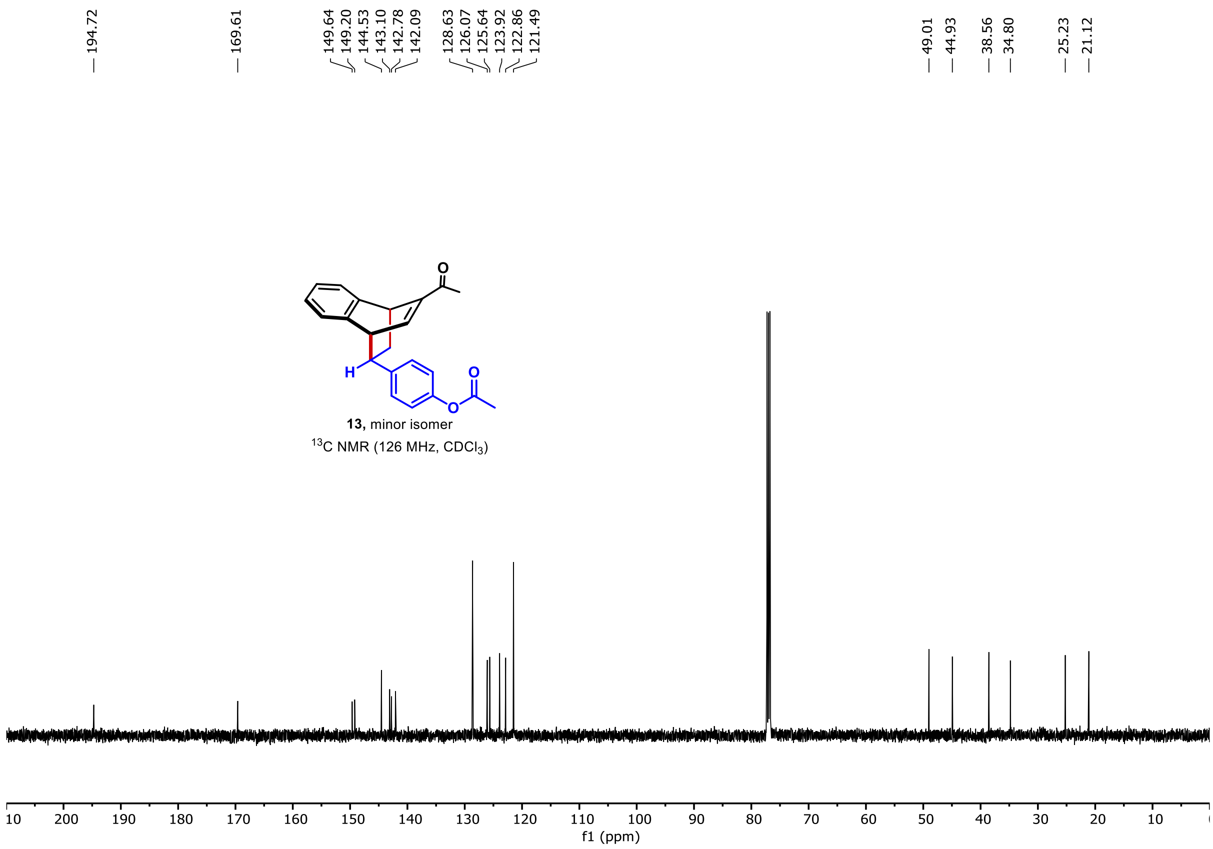


13, major isomer

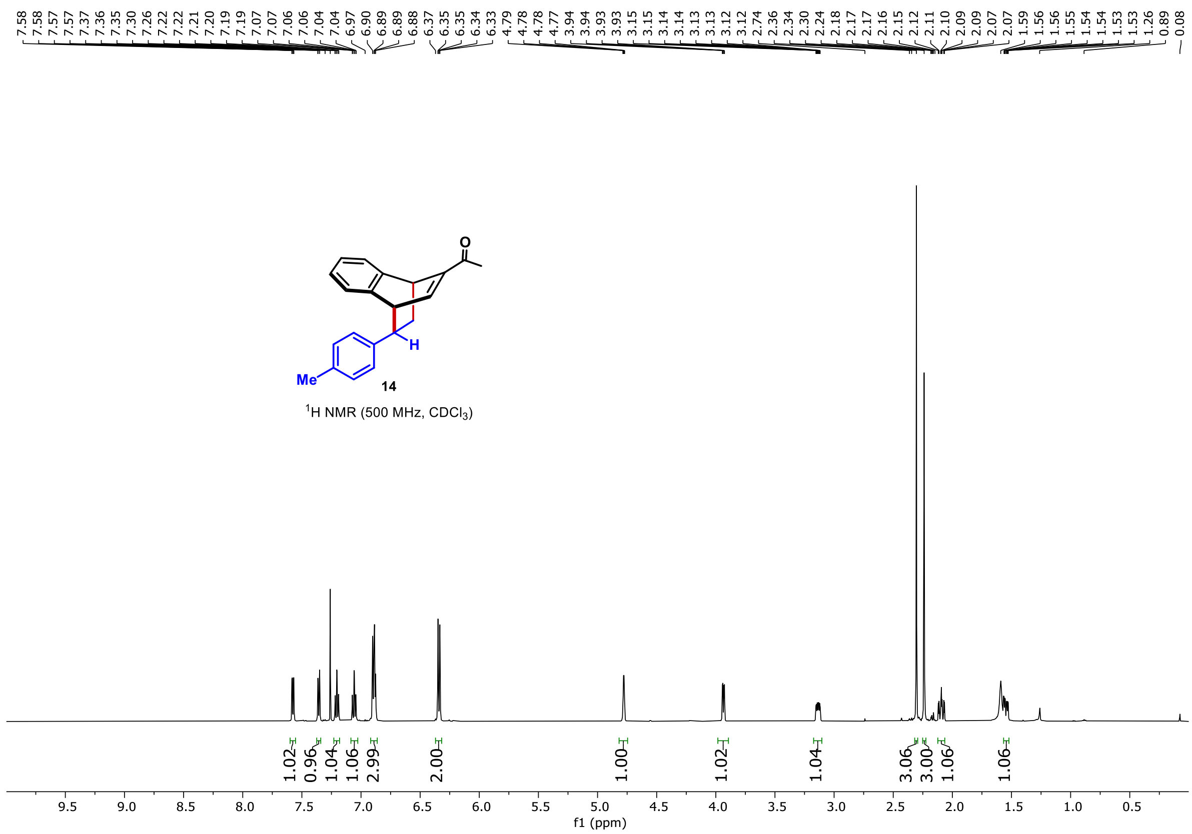
^{1}H NMR (500 MHz, $CDCl_3$)


194.95
169.47
149.07
148.15
147.09
144.01
140.94
138.45
128.79
126.33
126.11
125.41
123.06
120.93
49.24
43.32
38.14
34.45
25.11
21.08
13, major isomer
^{13}C NMR (126 MHz, CDCl$_3$)
f1 (ppm)

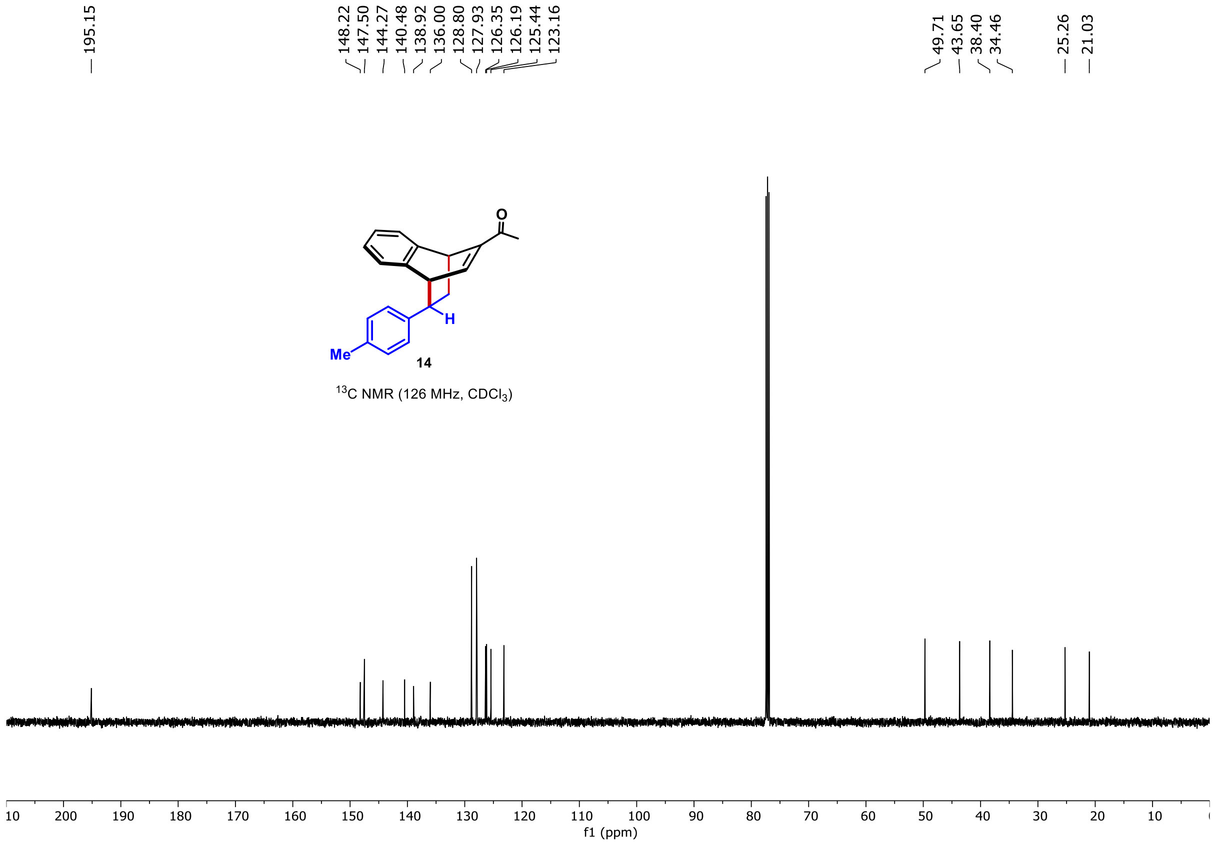

13, minor isomer
^{1}H NMR (500 MHz, CDCl$_3$)
2.00
1.15
1.95
2.18
1.97
1.06
1.00
1.01
6.06
1.02
1.10
f1 (ppm)

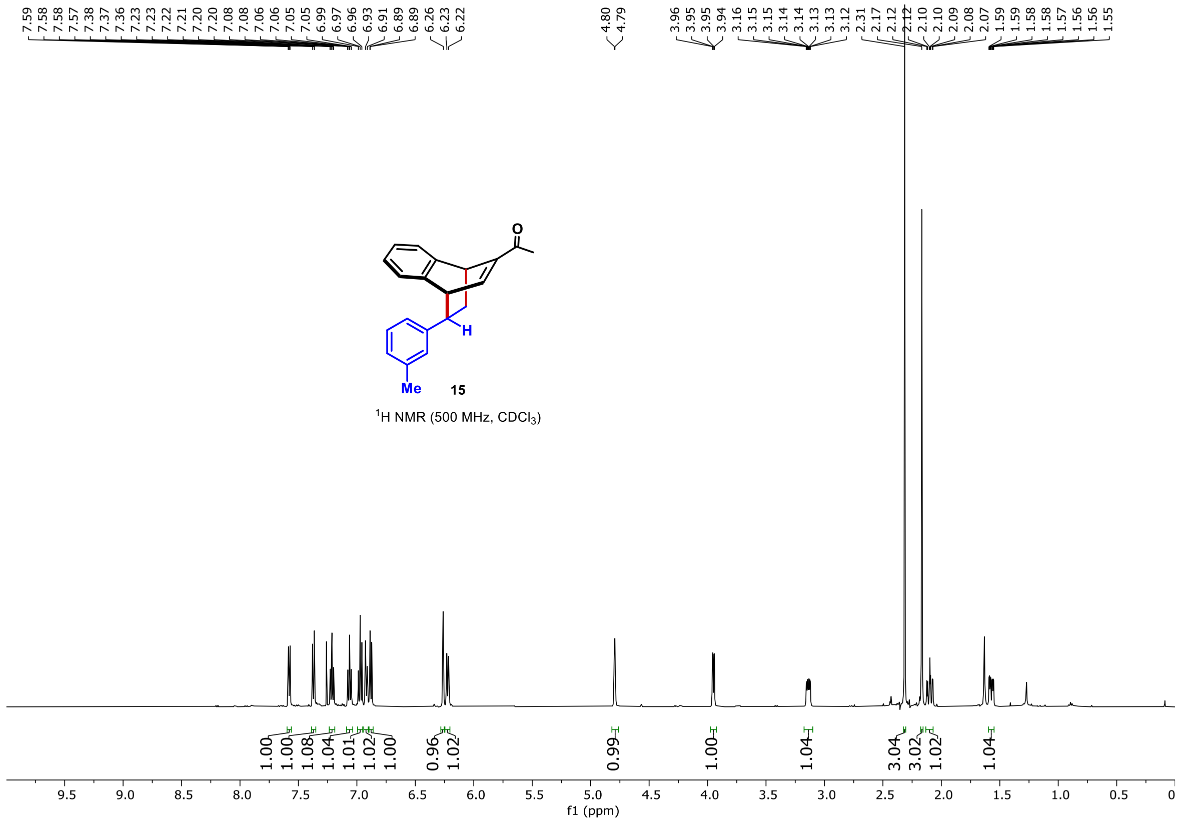


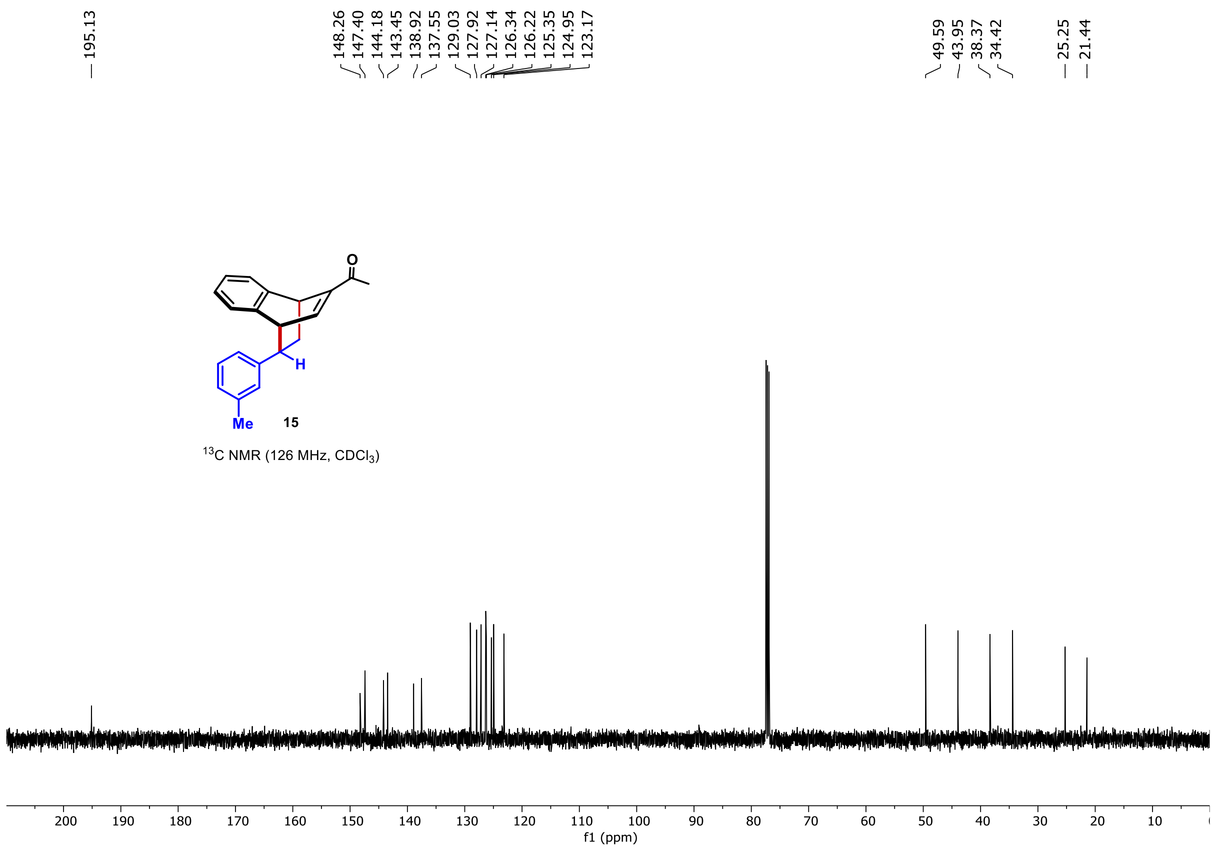
194.72
169.61
149.64
149.20
144.53
143.10
142.78
142.09
128.63
126.07
125.64
123.92
122.86
121.49
49.01
44.93
38.56
34.80
25.23
21.12
13, minor isomer
^{13}C NMR (126 MHz, CDCl$_3$)
f1 (ppm)



Me
H
14
^{1}H NMR (500 MHz, CDCl$_3$)
1.02
0.96
1.04
1.06
2.99
2.00
1.00
1.02
1.04
3.06
3.00
1.06
1.06
f1 (ppm)

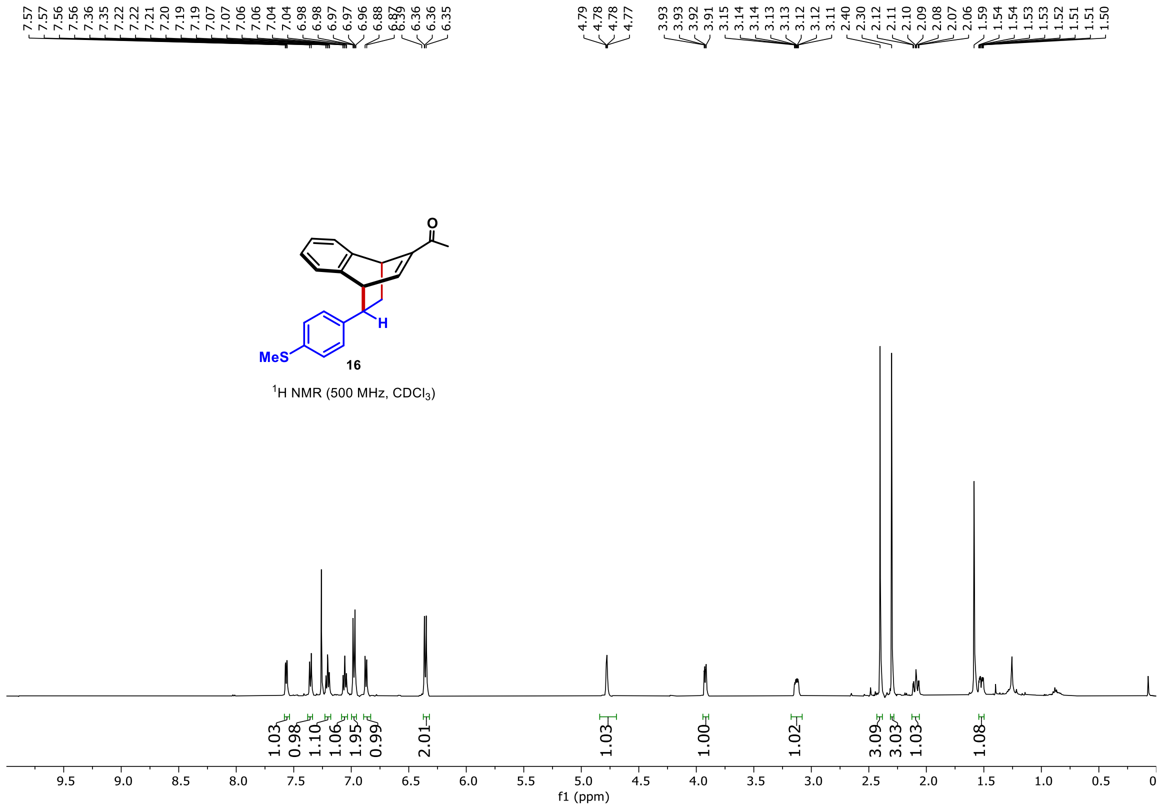

195.15
148.22
147.50
144.27
140.48
138.92
136.00
128.80
127.93
126.35
126.19
125.44
123.16
49.71
43.65
38.40
34.46
25.26
21.03
O
H
Me
14
^{13}C NMR (126 MHz, CDCl$_3$)
f1 (ppm)


7.59
7.58
7.58
7.57
7.38
7.37
7.36
7.23
7.23
7.22
7.22
7.21
7.20
7.20
7.08
7.08
7.06
7.06
7.05
7.05
6.99
6.97
6.96
6.93
6.91
6.89
6.89
6.26
6.23
6.22
4.80
4.79
3.96
3.95
3.95
3.94
3.16
3.15
3.15
3.14
3.14
3.13
3.13
3.12
2.31
2.17
2.12
2.12
2.10
2.10
2.09
2.08
2.07
1.59
1.59
1.58
1.58
1.57
1.56
1.56
1.55
O
H
Me
15
^{1}H NMR (500 MHz, CDCl$_3$)
1.00
1.00
1.08
1.04
1.01
1.02
1.00
0.96
1.02
0.99
1.00
1.04
3.04
3.02
1.02
1.04
f1 (ppm)



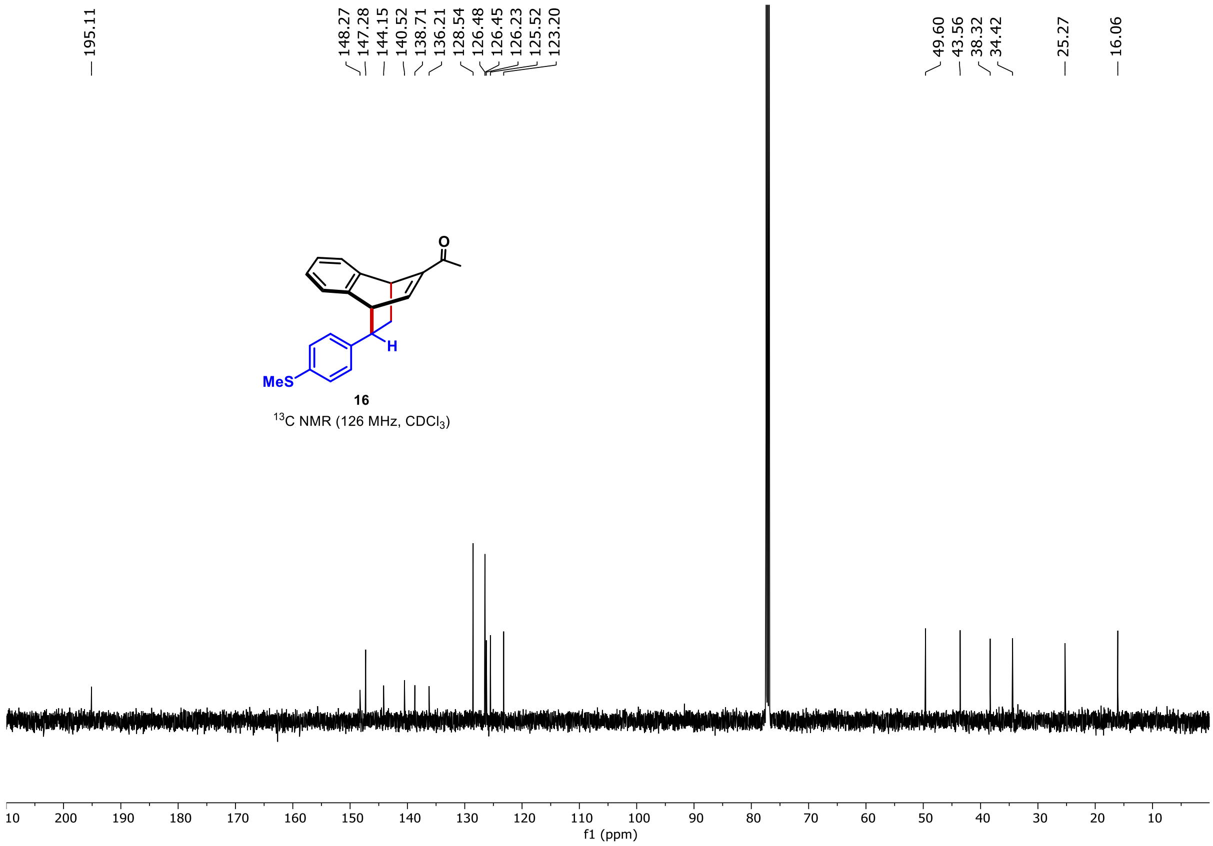
15

^{13}C NMR (126 MHz, $CDCl_3$)



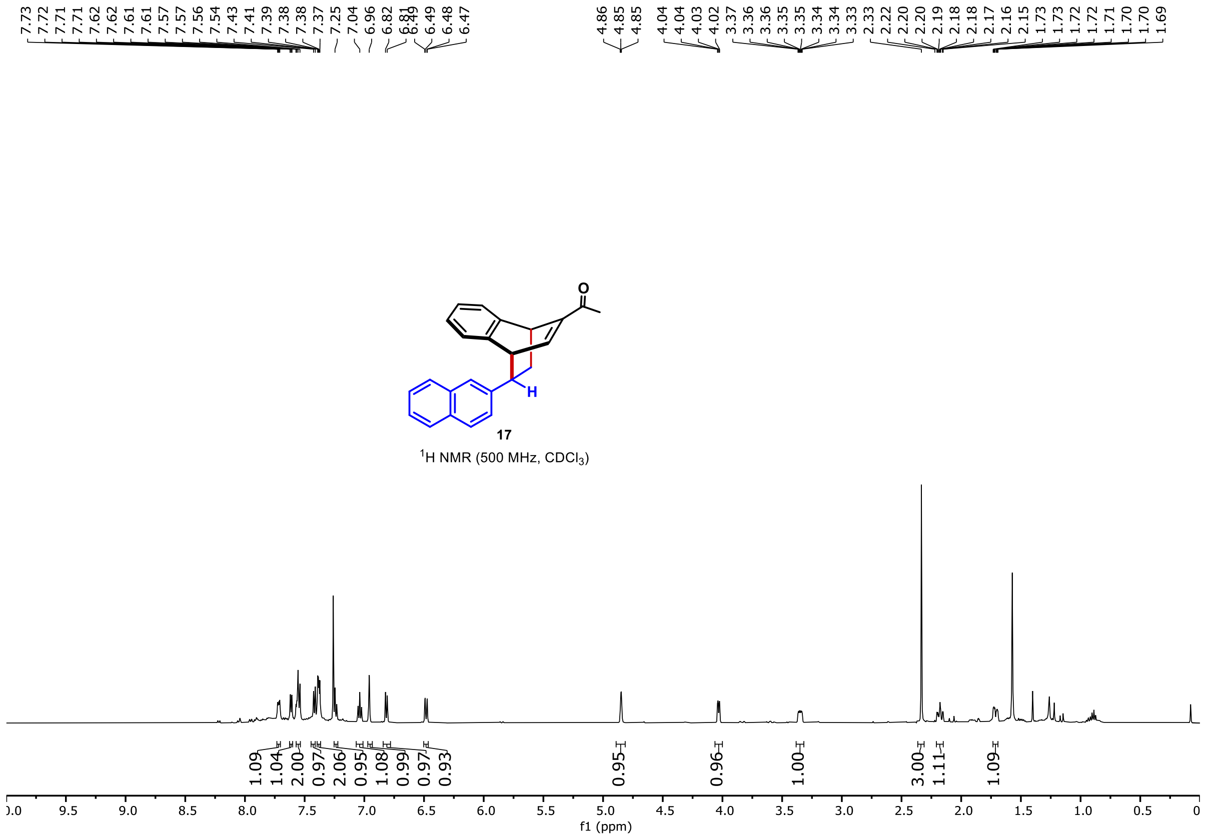
16

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



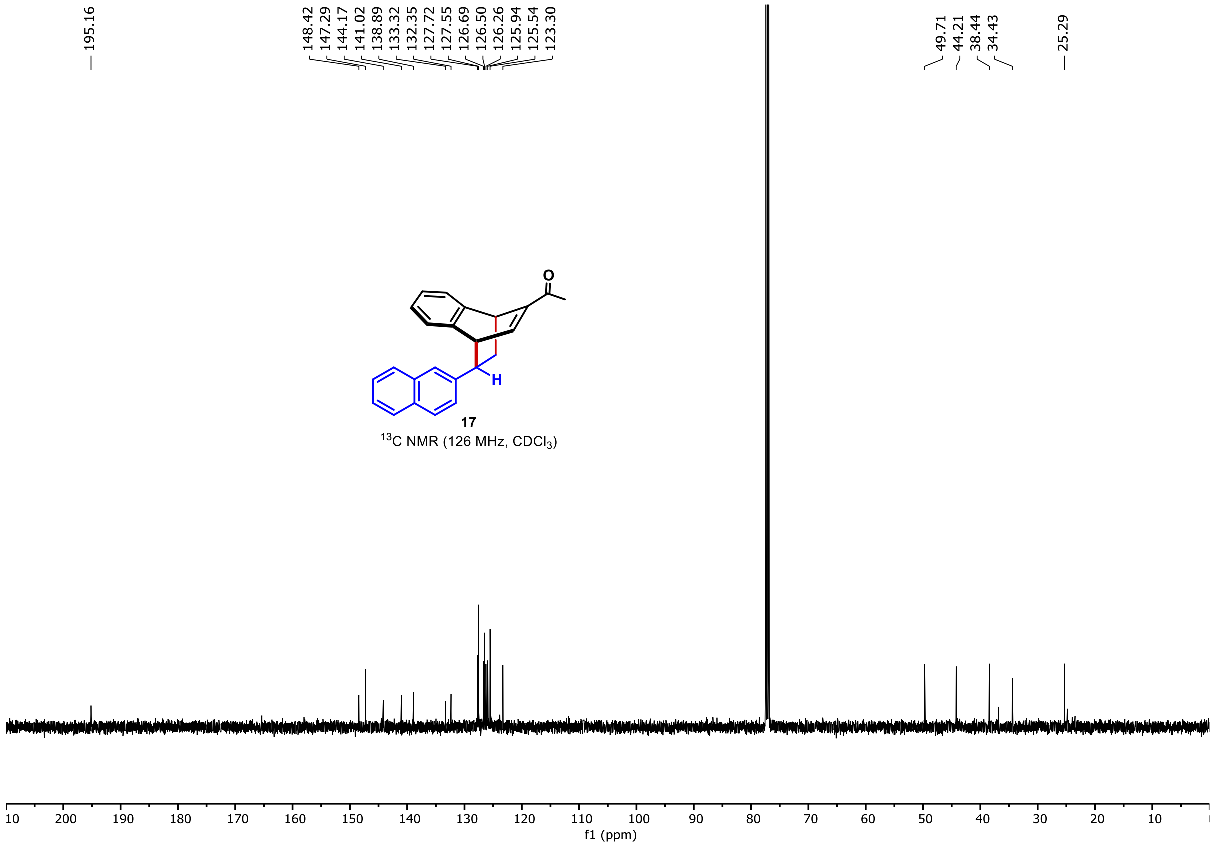
16

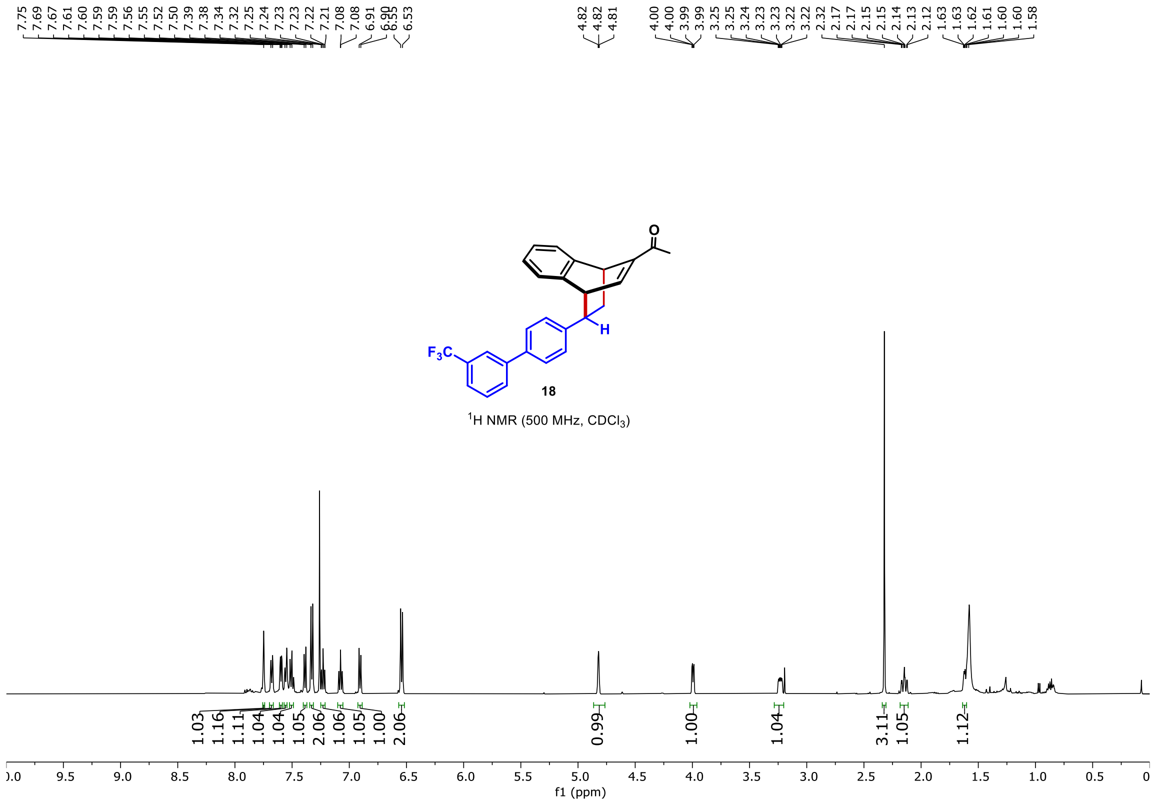
^{13}C NMR (126 MHz, $CDCl_3$)

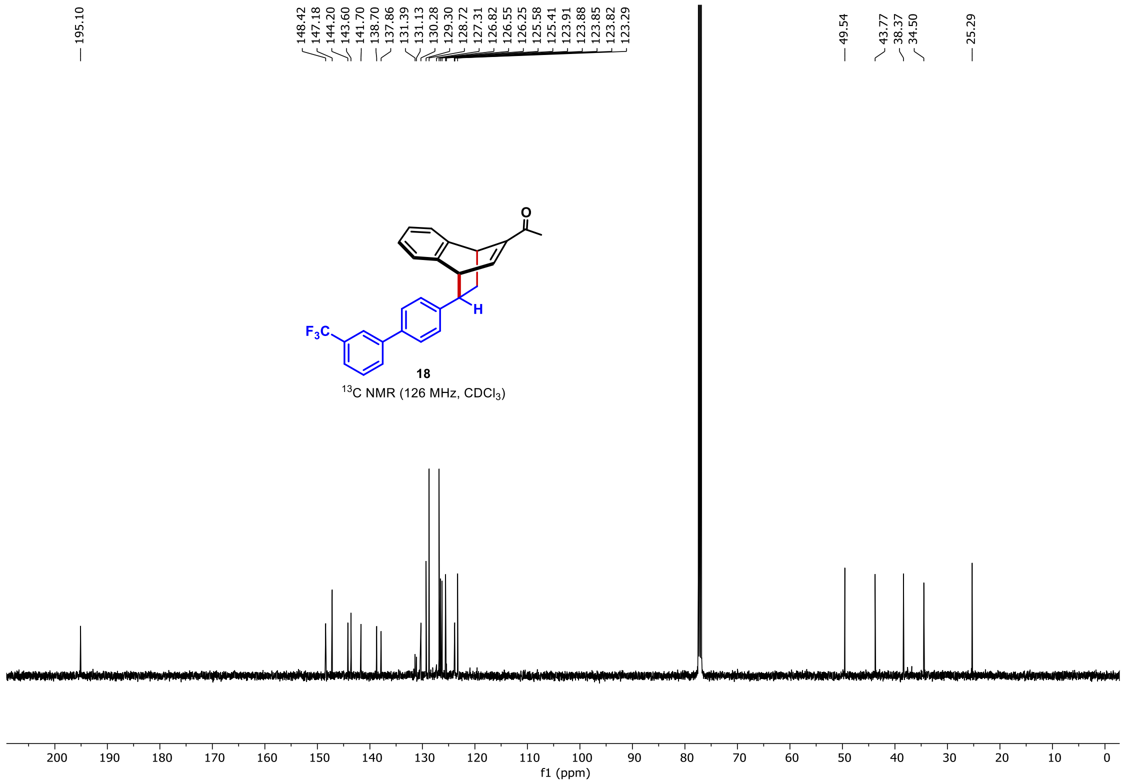


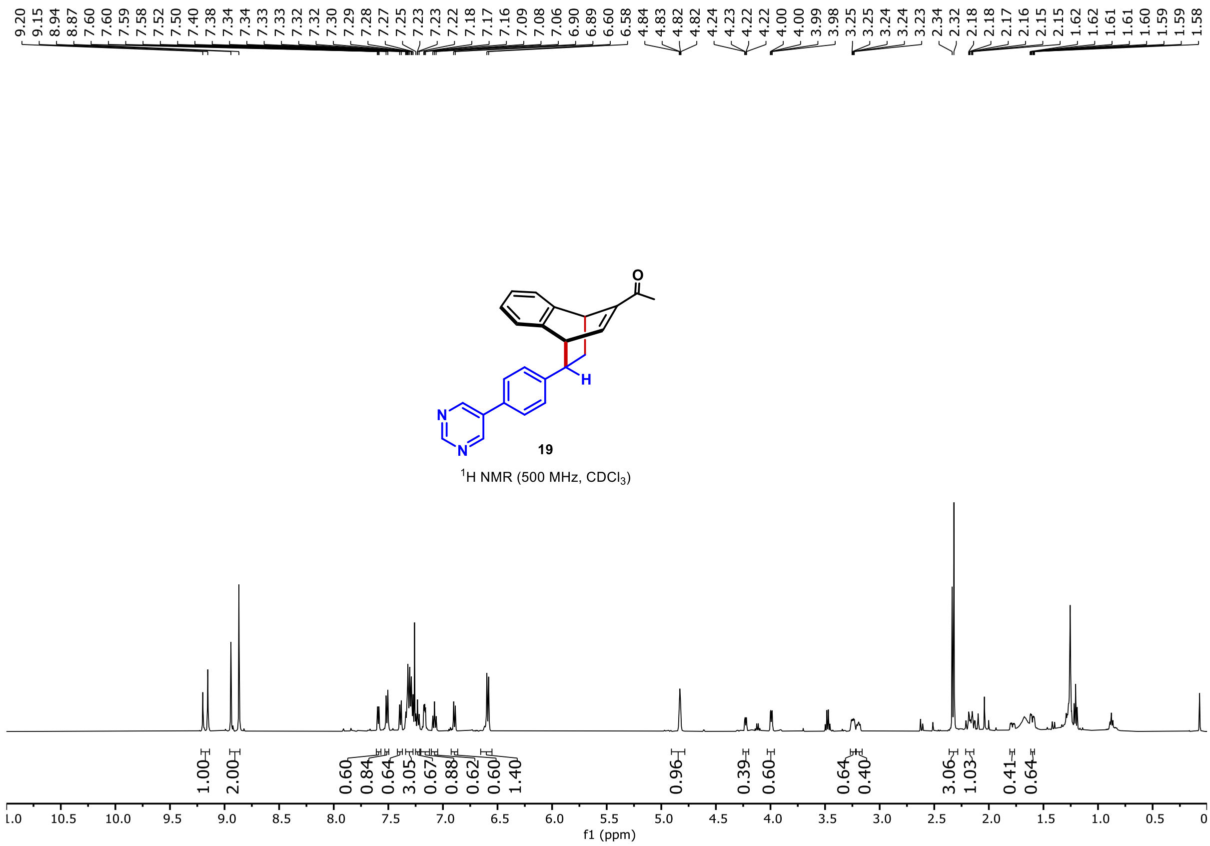
17

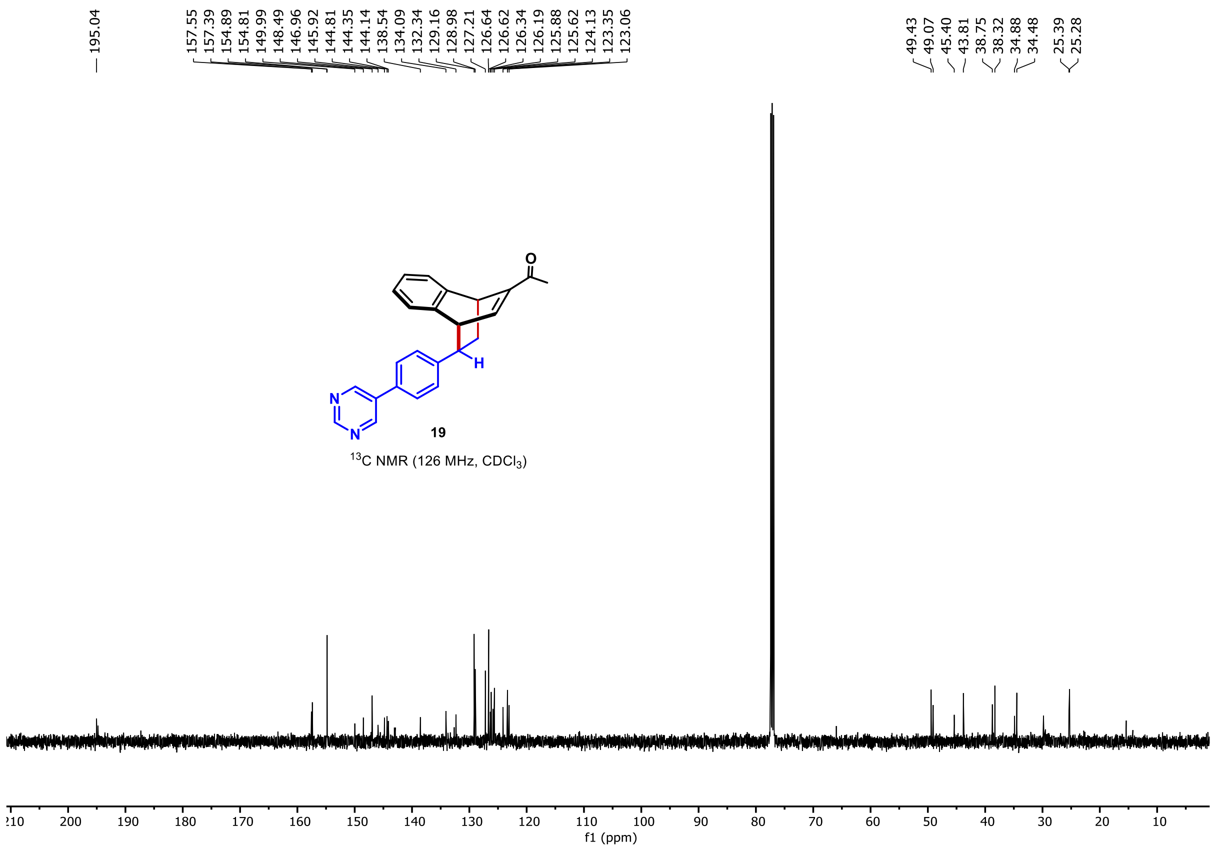
^{1}H NMR (500 MHz, $CDCl_3$)

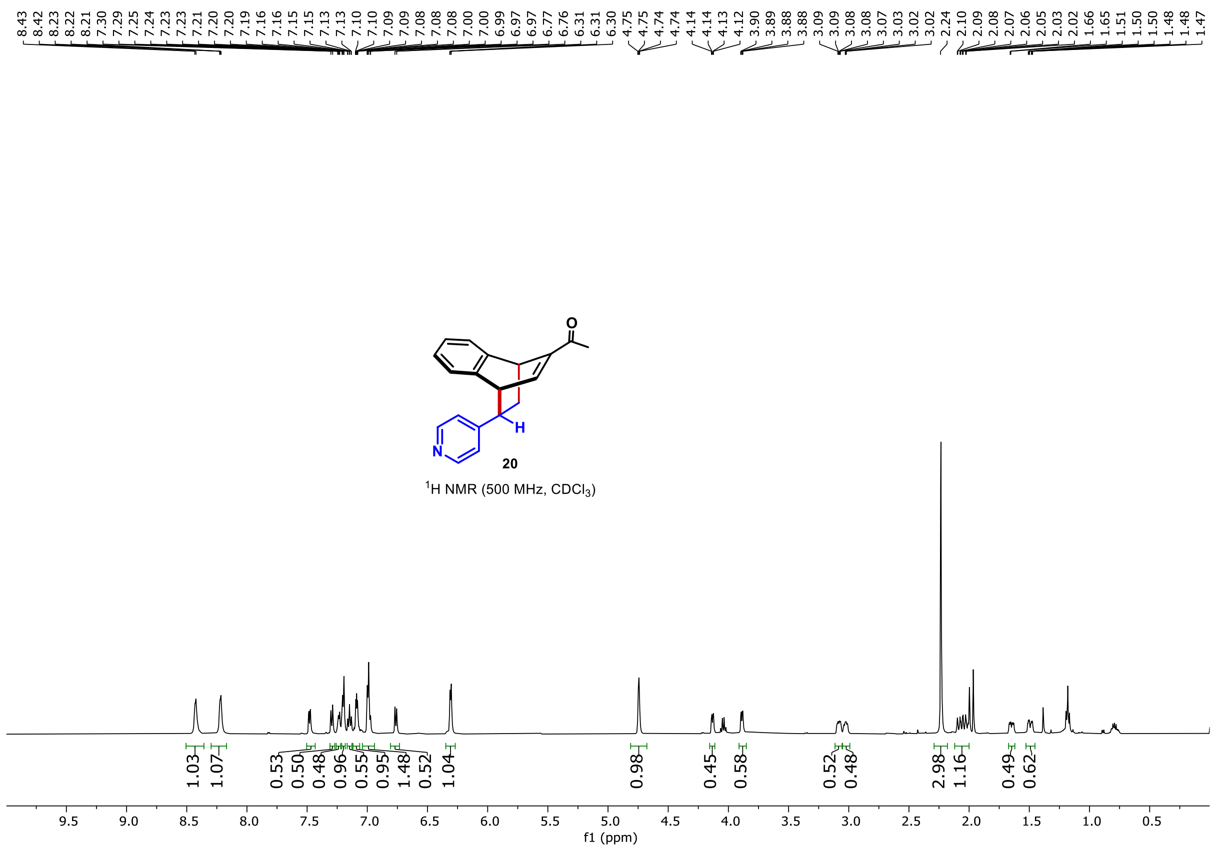

195.16
148.42
147.29
144.17
141.02
138.89
133.32
132.35
127.72
127.55
126.69
126.50
126.26
125.94
125.54
123.30
49.71
44.21
38.44
34.43
25.29
O
H
17
^{13}C NMR (126 MHz, $CDCl_3$)
f1 (ppm)

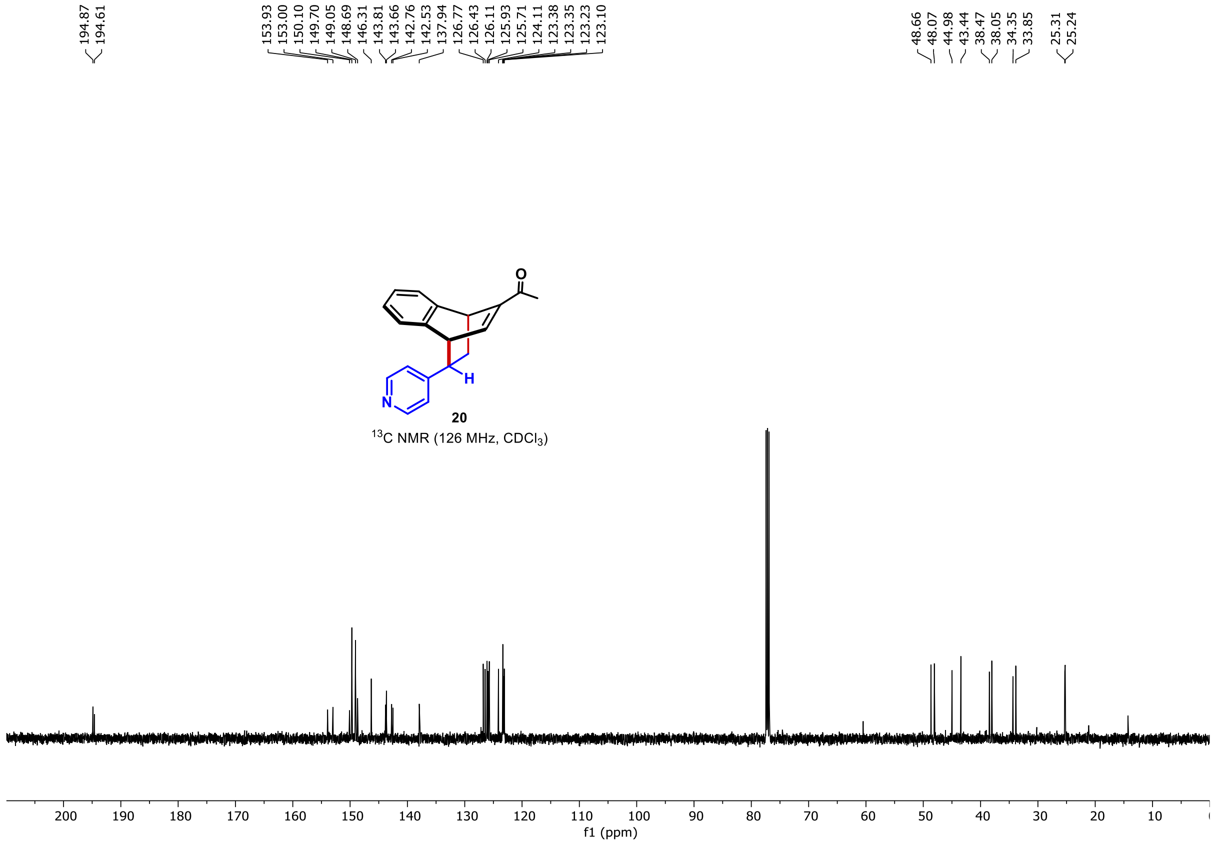

7.75
7.69
7.67
7.61
7.60
7.59
7.59
7.56
7.55
7.52
7.50
7.39
7.38
7.34
7.32
7.25
7.24
7.23
7.23
7.22
7.21
7.08
7.08
6.91
6.90
6.55
6.53
4.82
4.82
4.81
4.00
4.00
3.99
3.99
3.25
3.24
3.23
3.23
3.22
3.22
2.32
2.17
2.15
2.14
2.13
2.12
1.63
1.63
1.62
1.61
1.60
1.58
O
H
F_3C
18
^1H NMR (500 MHz, $CDCl_3$)
1.03
1.16
1.11
1.04
1.04
1.05
2.06
1.06
1.05
1.00
2.06
0.99
1.00
1.04
3.11
1.05
1.12
f1 (ppm)

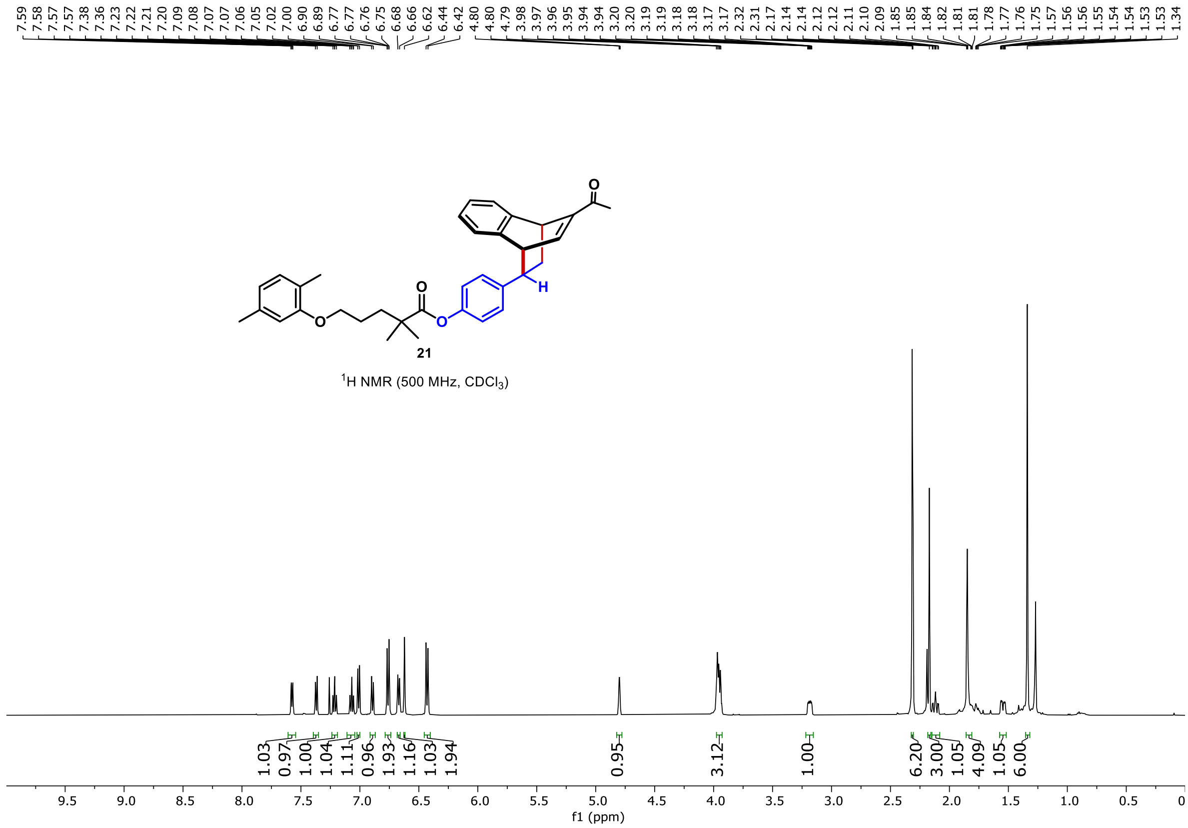

195.10
148.42
147.18
144.20
143.60
141.70
138.70
137.86
131.39
131.13
130.28
129.30
128.72
127.31
126.82
126.55
126.25
125.58
125.41
123.91
123.88
123.85
123.82
123.29
49.54
43.77
38.37
34.50
25.29
O
F_3C
H
18
^{13}C NMR (126 MHz, $CDCl_3$)
f1 (ppm)

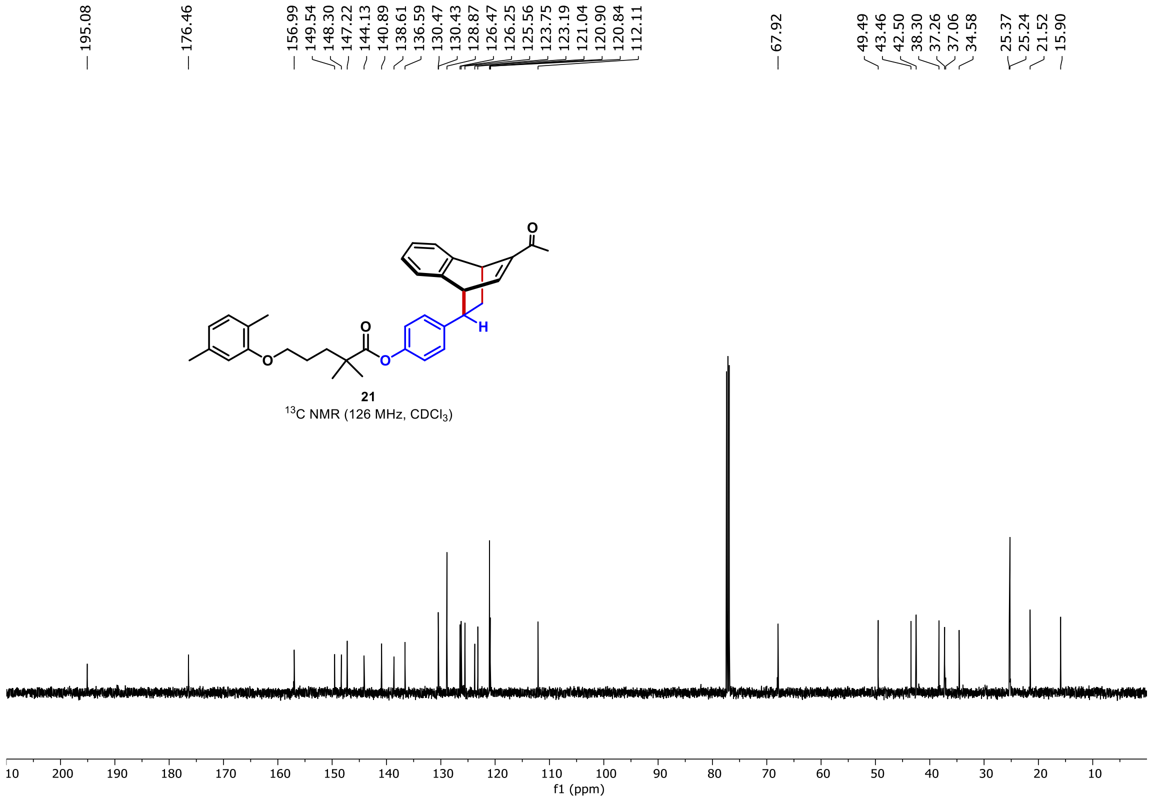

9.20
9.15
8.94
8.87
7.60
7.60
7.59
7.58
7.52
7.50
7.40
7.38
7.34
7.34
7.33
7.33
7.32
7.32
7.30
7.29
7.28
7.27
7.25
7.23
7.23
7.22
7.18
7.17
7.16
7.09
7.08
7.06
6.90
6.89
6.60
6.58
4.84
4.83
4.82
4.82
4.24
4.23
4.22
4.22
4.00
4.00
3.99
3.98
3.25
3.25
3.24
3.24
3.23
2.34
2.32
2.18
2.18
2.17
2.16
2.15
1.62
1.62
1.61
1.60
1.59
1.59
1.58
O
N
N
H
19
^1H NMR (500 MHz, $CDCl_3$)
1.00
2.00
0.60
0.84
0.64
3.05
0.67
0.88
0.62
0.60
1.40
0.96
0.39
0.60
0.64
0.40
3.06
1.03
0.41
0.64
f1 (ppm)


195.04
157.55 157.39 154.89 154.81 149.99 148.49 146.96 145.92 144.81 144.35 144.14 138.54 134.09 132.34 129.16 128.98 127.21 126.64 126.62 126.34 126.19 125.88 125.62 124.13 123.35 123.06
49.43 49.07 45.40 43.81 38.75 38.32 34.88 34.48 25.39 25.28
O
N
N
H
19
13C NMR (126 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

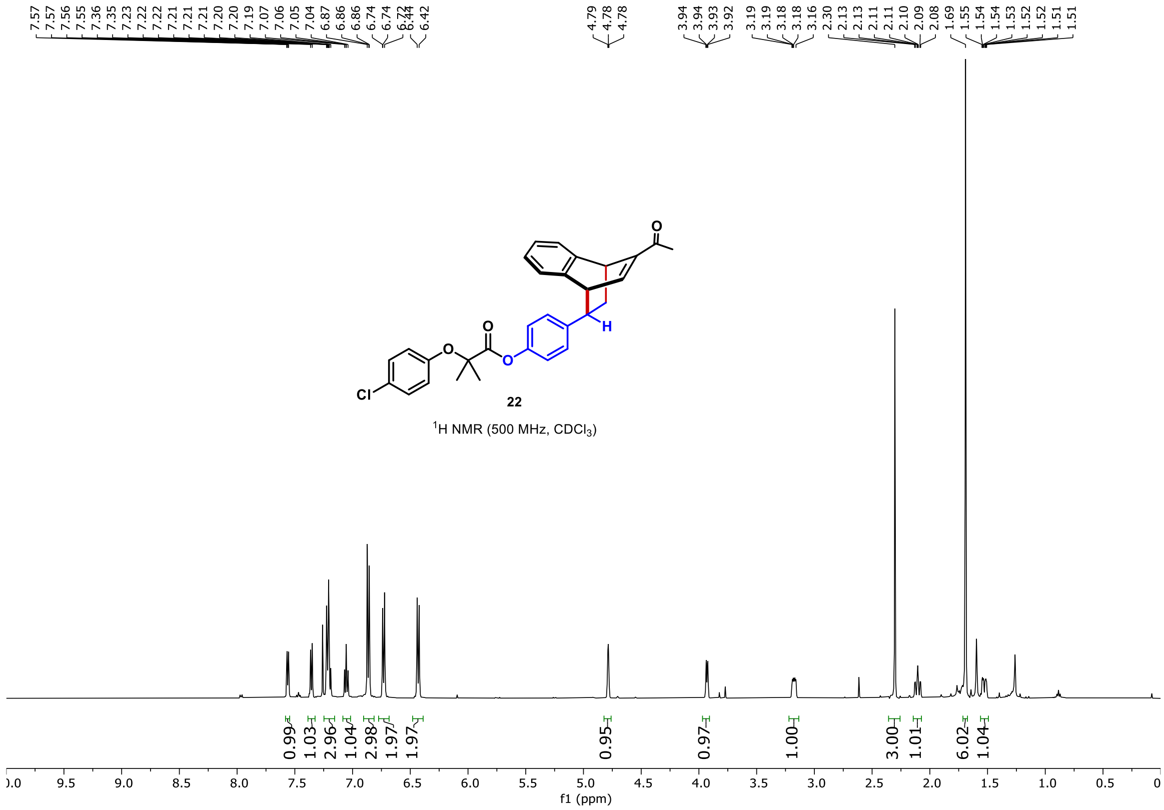

8.43 8.42 8.23 8.22 8.21 7.30 7.29 7.25 7.24 7.23 7.23 7.21 7.20 7.19 7.16 7.16 7.15 7.13 7.13 7.10 7.10 7.09 7.09 7.08 7.08 7.08 7.00 7.00 6.99 6.97 6.97 6.77 6.76 6.31 6.31 6.30 4.75 4.75 4.74 4.74 4.14 4.14 4.13 4.12 3.90 3.89 3.88 3.88 3.09 3.09 3.08 3.08 3.07 3.03 3.02 3.02 2.24 2.10 2.09 2.08 2.07 2.06 2.05 2.03 2.02 1.66 1.65 1.51 1.50 1.50 1.48 1.47
O
N
H
20
1H NMR (500 MHz, CDCl3)
1.03 1.07 0.53 0.50 0.48 0.96 0.55 0.95 1.48 0.52 1.04 0.98 0.45 0.58 0.52 0.48 2.98 1.16 0.49 0.62
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


194.87
194.61
153.93
153.00
150.10
149.70
149.05
148.69
146.31
143.81
143.66
142.76
142.53
137.94
126.77
126.43
126.11
125.93
125.71
124.11
123.38
123.35
123.23
123.10
48.66
48.07
44.98
43.44
38.47
38.05
34.35
33.85
25.31
25.24
O
N
H
20
^{13}C NMR (126 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

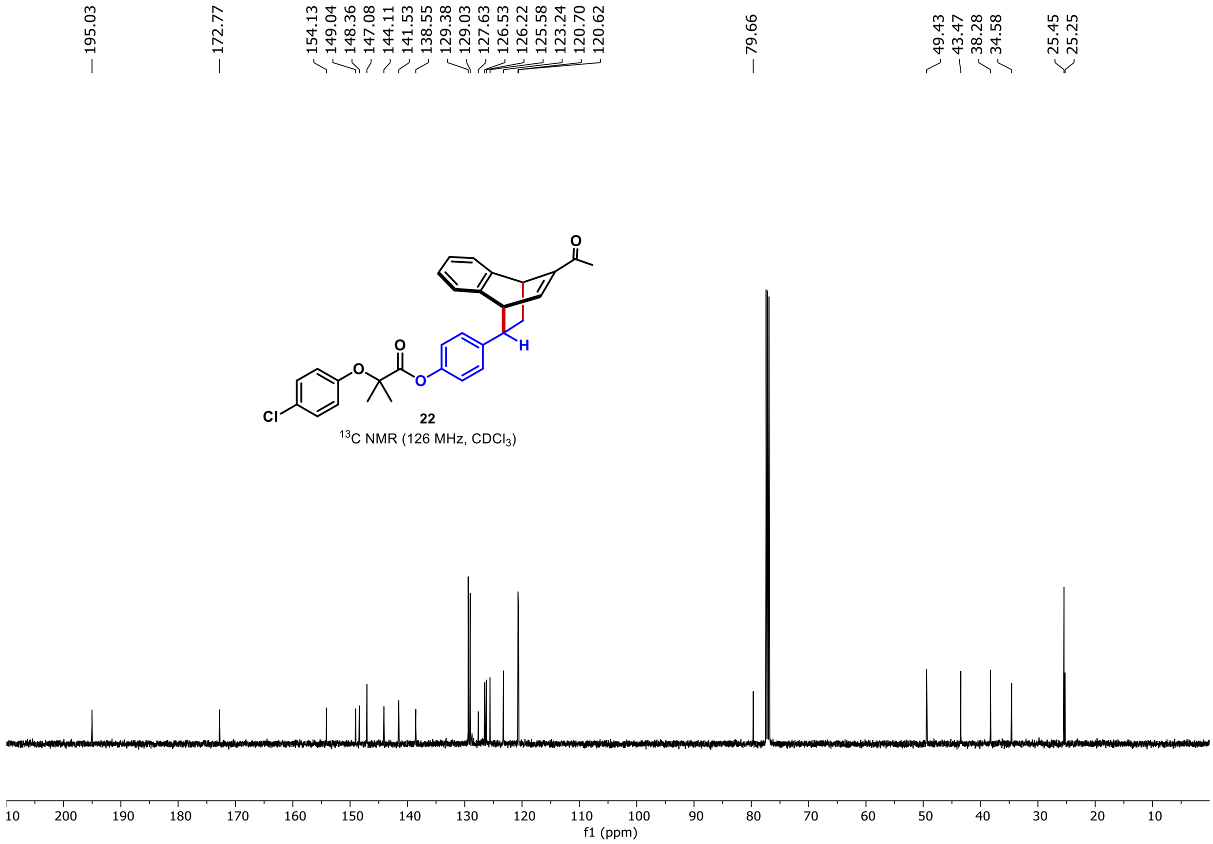

7.59
7.58
7.57
7.38
7.36
7.23
7.22
7.21
7.20
7.09
7.08
7.07
7.06
7.05
7.02
7.00
6.90
6.89
6.77
6.76
6.75
6.68
6.66
6.62
6.44
6.42
4.80
4.79
3.98
3.97
3.96
3.95
3.94
3.20
3.19
3.18
3.18
3.17
3.17
2.32
2.31
2.17
2.14
2.14
2.12
2.12
2.11
2.10
2.09
1.85
1.85
1.84
1.82
1.81
1.81
1.78
1.77
1.76
1.75
1.57
1.56
1.56
1.55
1.54
1.53
1.53
1.34
O
O
O
O
H
21
^{1}H NMR (500 MHz, CDCl$_3$)
1.03
0.97
1.00
1.04
1.11
0.96
1.93
1.16
1.03
1.94
0.95
3.12
1.00
6.20
3.00
1.05
4.09
1.05
6.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)



21
^{13}C NMR (126 MHz, $CDCl_3$)

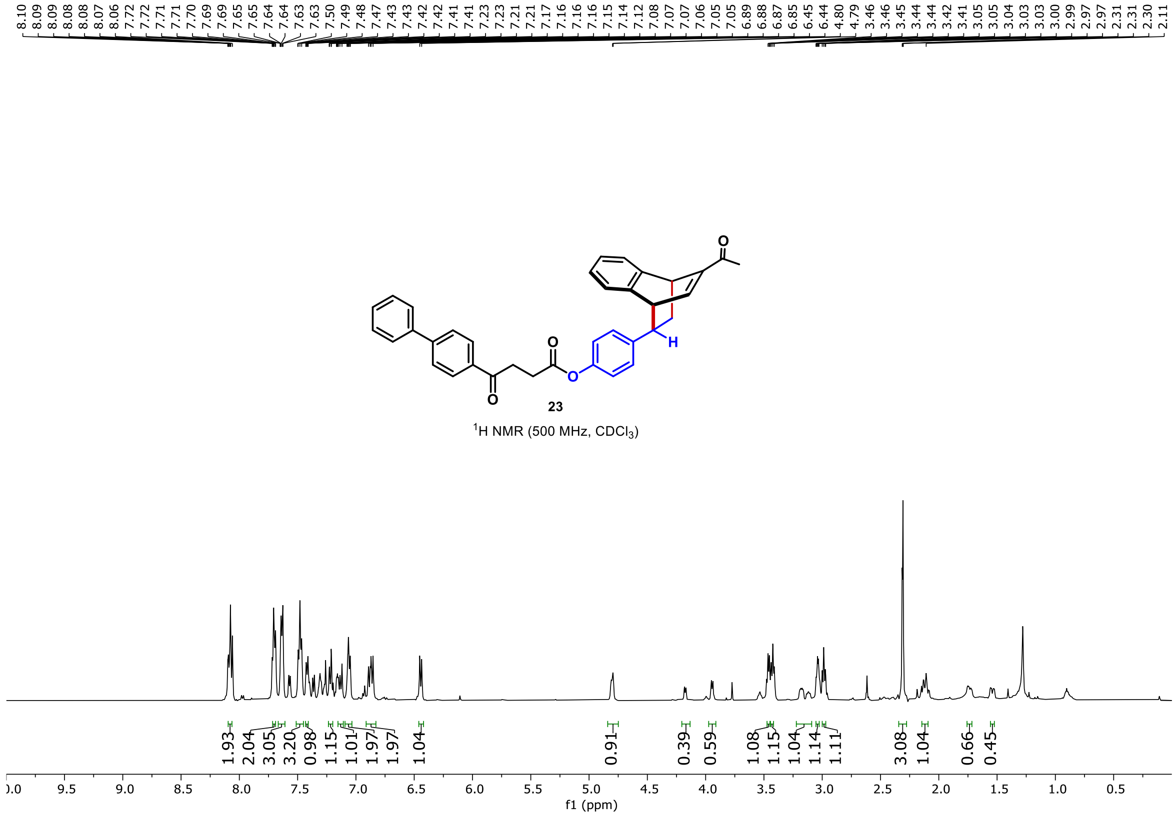


22
^{1}H NMR (500 MHz, $CDCl_3$)



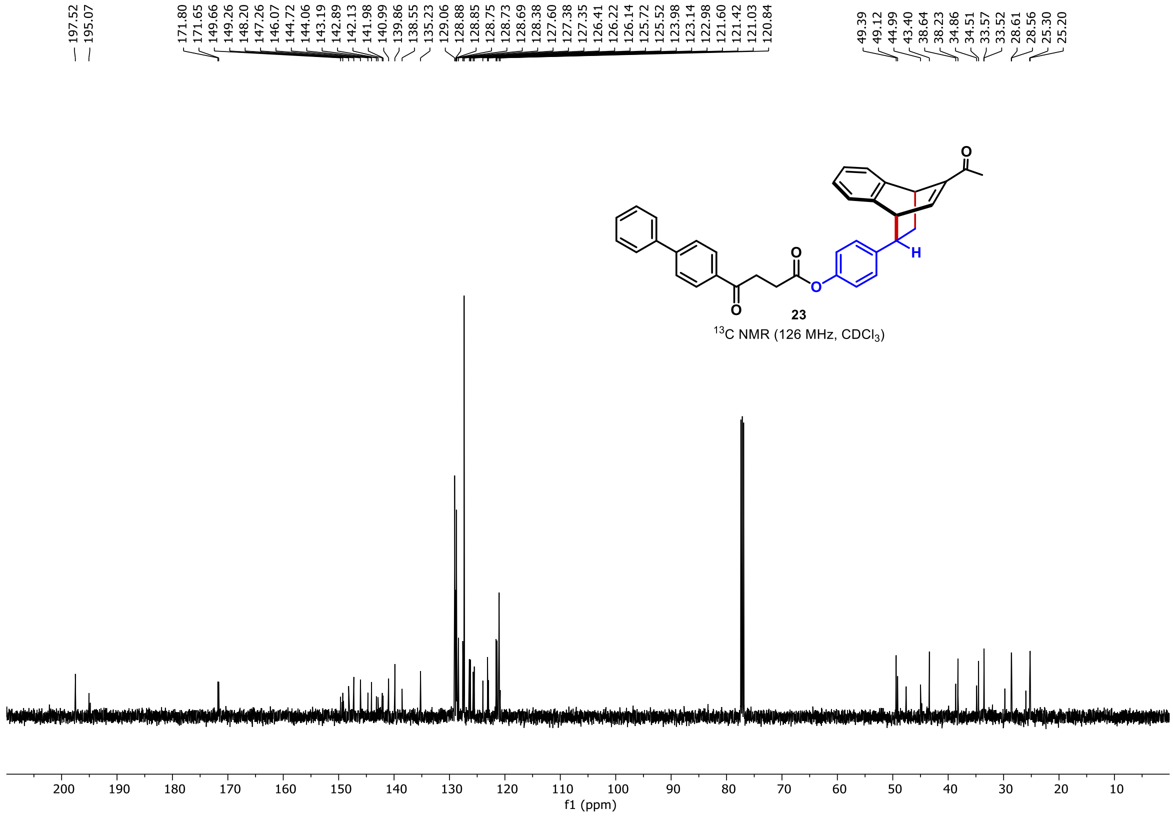
22

^{13}C NMR (126 MHz, $CDCl_3$)



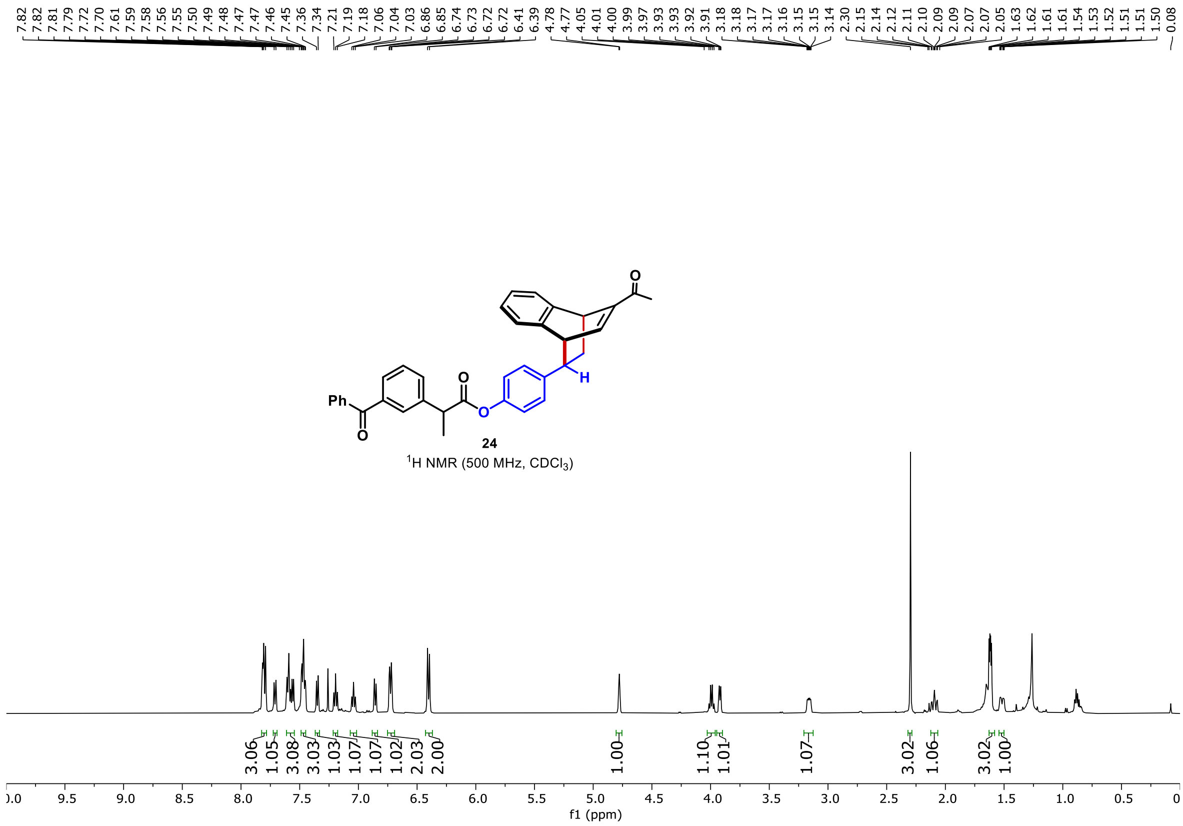
23

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



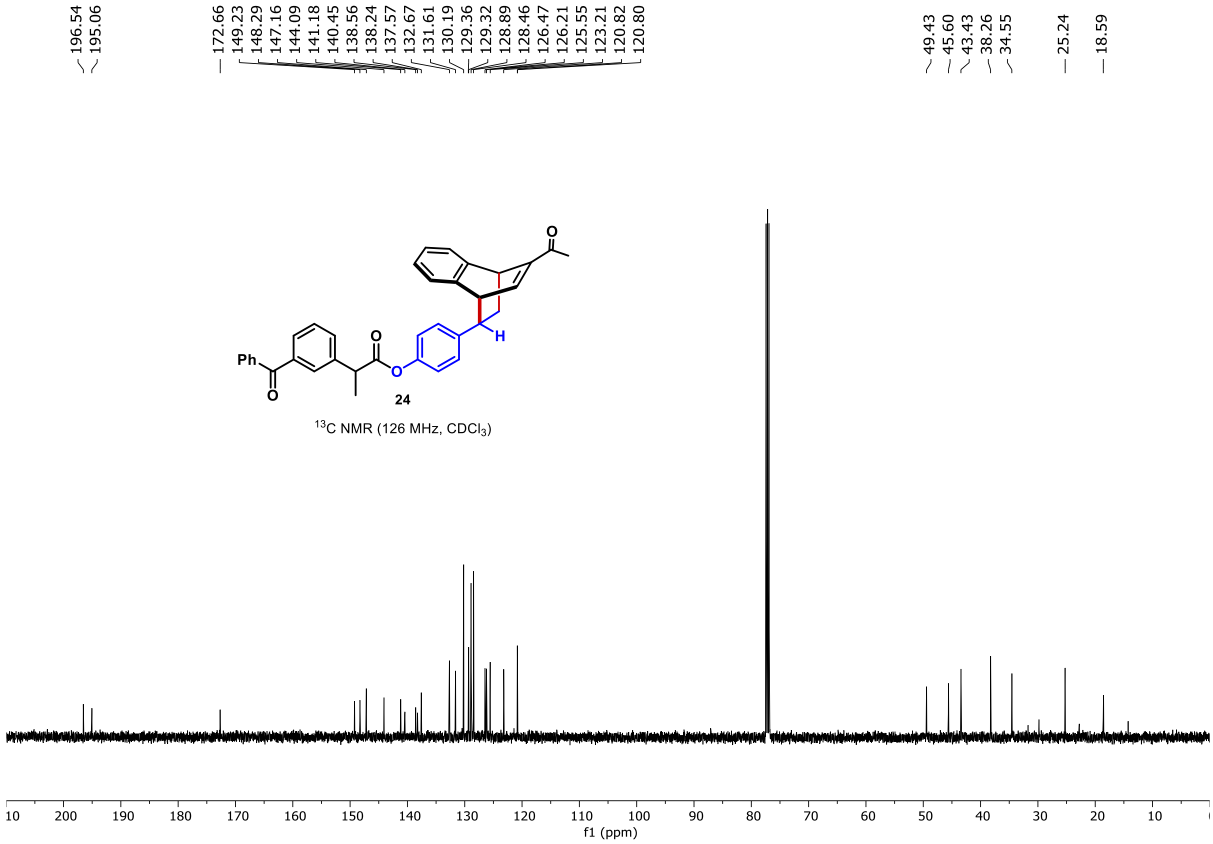
23

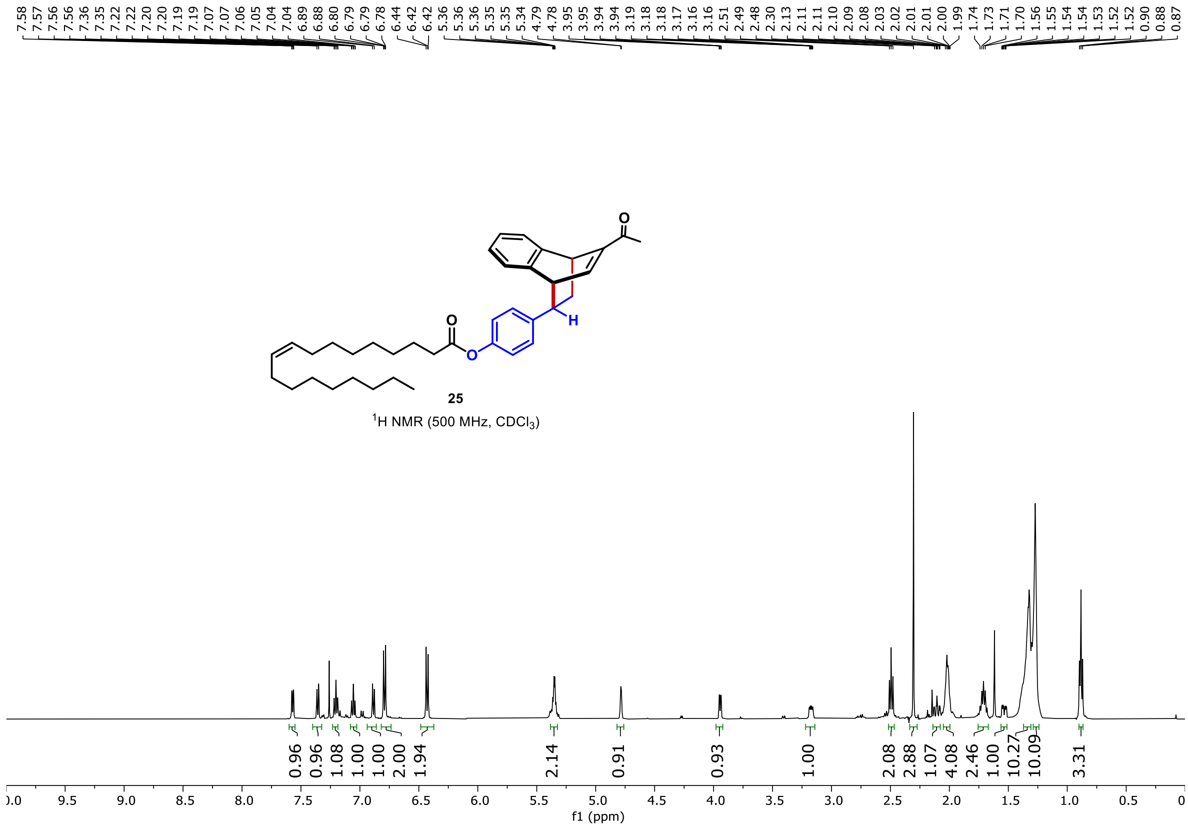
^{13}C NMR (126 MHz, $CDCl_3$)

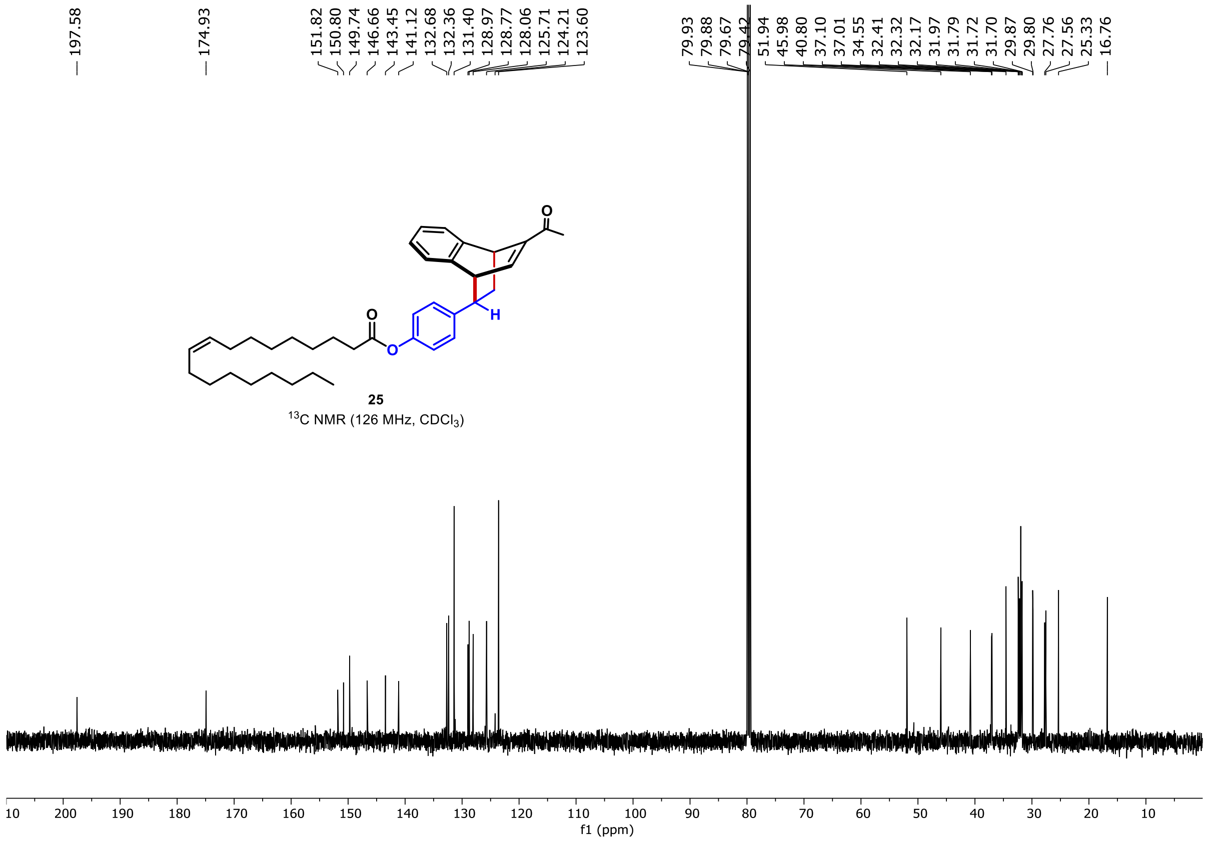


24

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

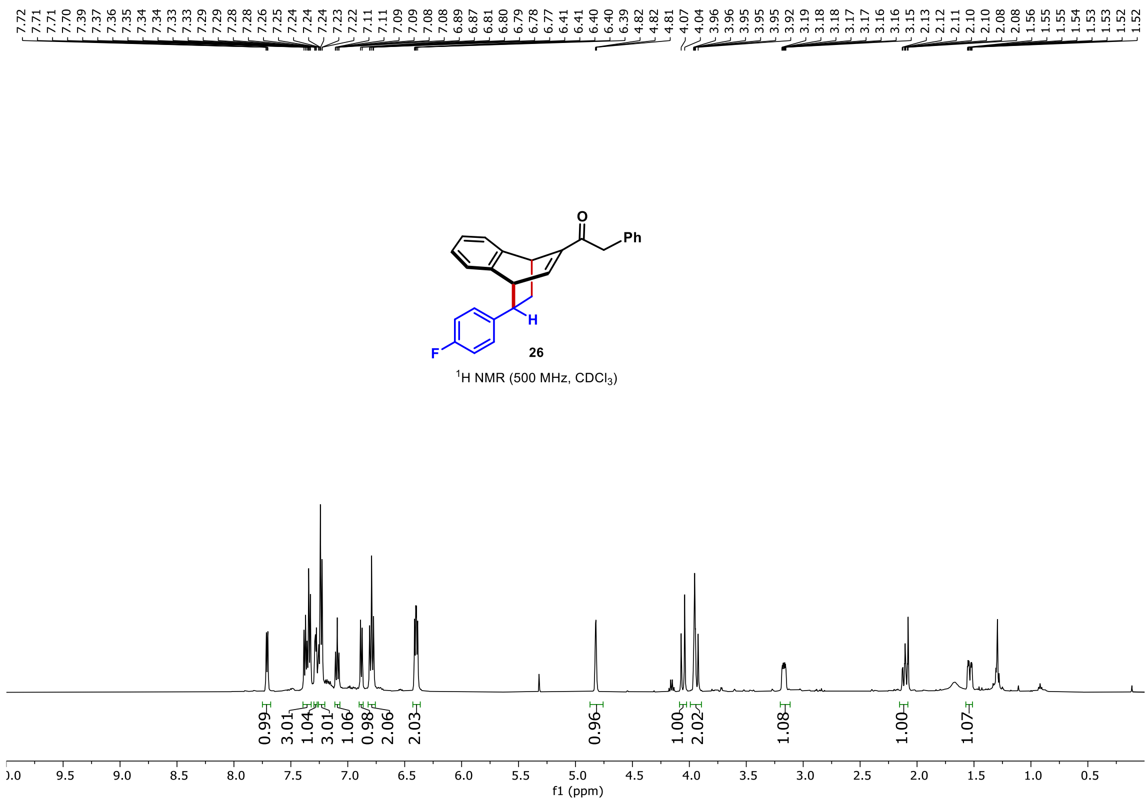

196.54
195.06
172.66
149.23
148.29
147.16
144.09
141.18
140.45
138.56
138.24
137.57
132.67
131.61
130.19
129.36
129.32
128.89
128.46
126.47
126.21
125.55
123.21
120.82
120.80
49.43
45.60
43.43
38.26
34.55
25.24
18.59
Ph
O
O
O
O
H
24
13C NMR (126 MHz, CDCl3)
f1 (ppm)


7.58 7.57 7.56 7.56 7.36 7.35 7.22 7.22 7.20 7.20 7.19 7.19 7.07 7.06 7.05 7.04 7.04 6.89 6.88 6.80 6.79 6.79 6.78 6.44 6.42 6.42 5.36 5.36 5.35 5.35 5.34 4.79 4.78 3.95 3.95 3.94 3.94 3.19 3.18 3.17 3.16 2.51 2.49 2.48 2.30 2.13 2.11 2.11 2.10 2.09 2.08 2.03 2.02 2.01 2.00 1.99 1.74 1.73 1.71 1.70 1.56 1.55 1.54 1.54 1.53 1.52 1.52 0.90 0.88 0.87
O
O
O
H
25
1H NMR (500 MHz, CDCl3)
0.96 0.96 1.08 1.00 1.00 2.00 1.94 2.14 0.91 0.93 1.00 2.08 2.88 1.07 4.08 2.46 1.00 10.27 10.09 3.31
f1 (ppm)



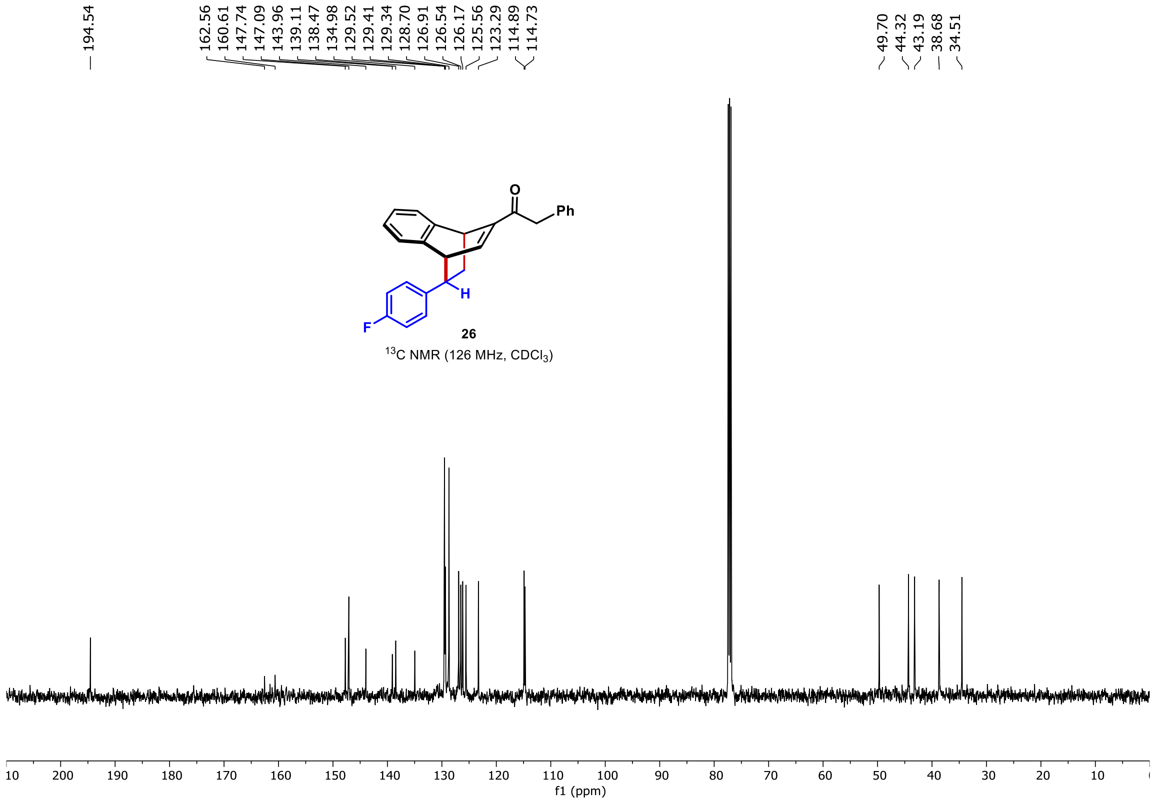
25

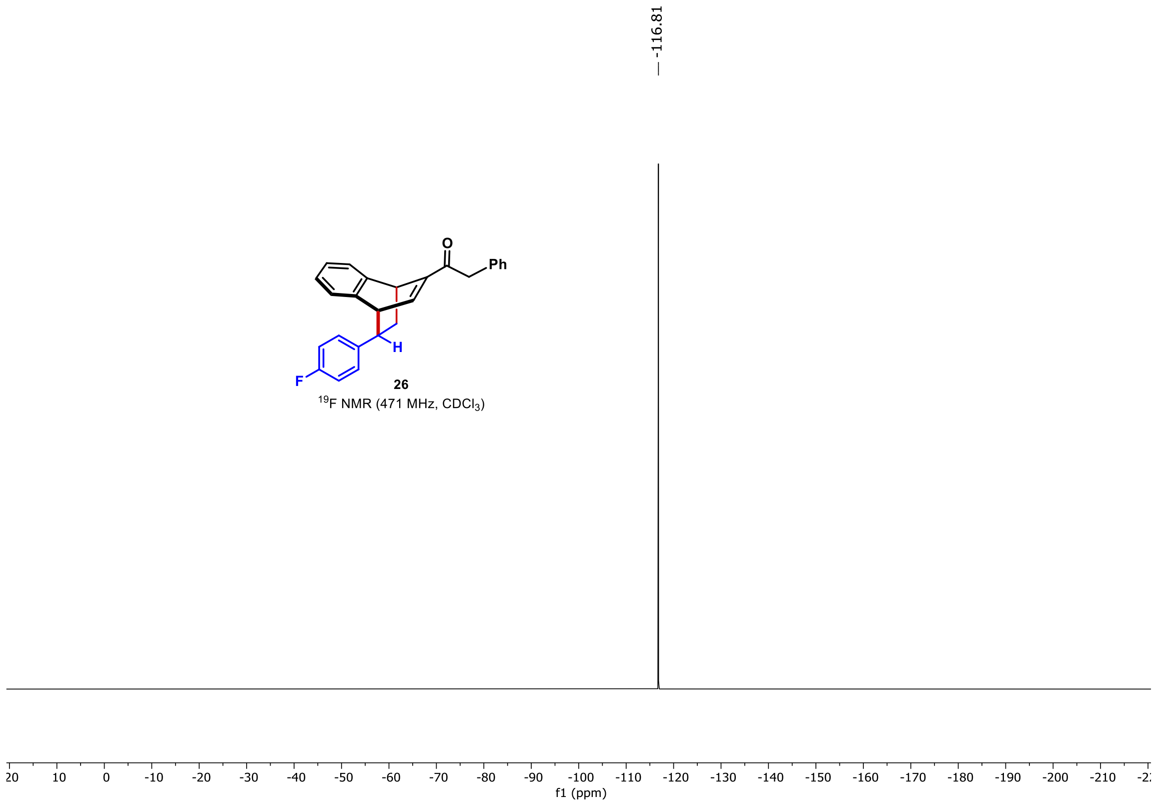
^{13}C NMR (126 MHz, $CDCl_3$)

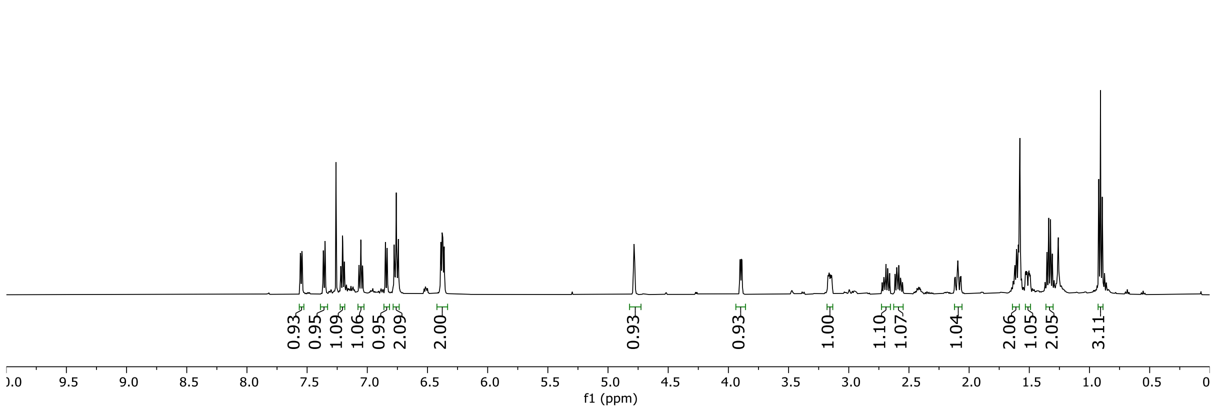


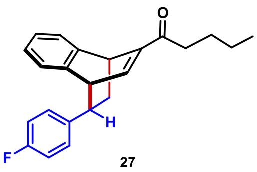
26

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


194.54
162.56
160.61
147.74
147.09
143.96
139.11
138.47
134.98
129.52
129.41
129.34
128.70
126.91
126.54
126.17
125.56
123.29
114.89
114.73
49.70
44.32
43.19
38.68
34.51
O
Ph
H
F
26
^{13}C NMR (126 MHz, CDCl$_3$)
f1 (ppm)

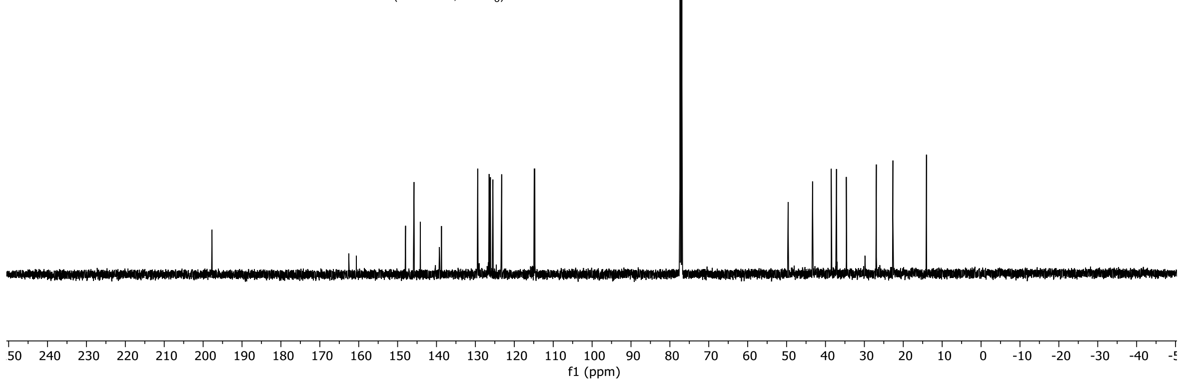

-116.81
O
Ph
H
F
26
^{19}F NMR (471 MHz, CDCl$_3$)
f1 (ppm)

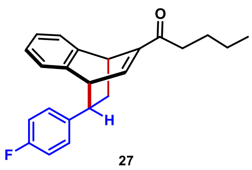




27

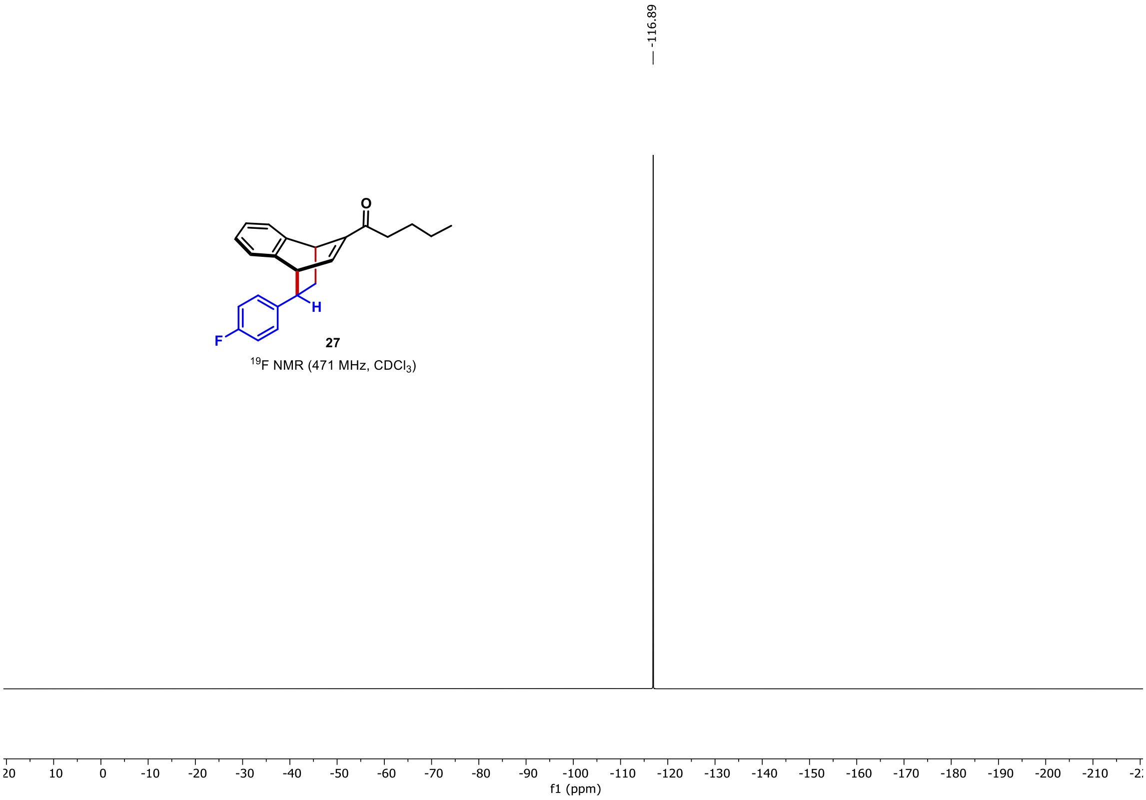
^{1}H NMR (500 MHz, $CDCl_3$)



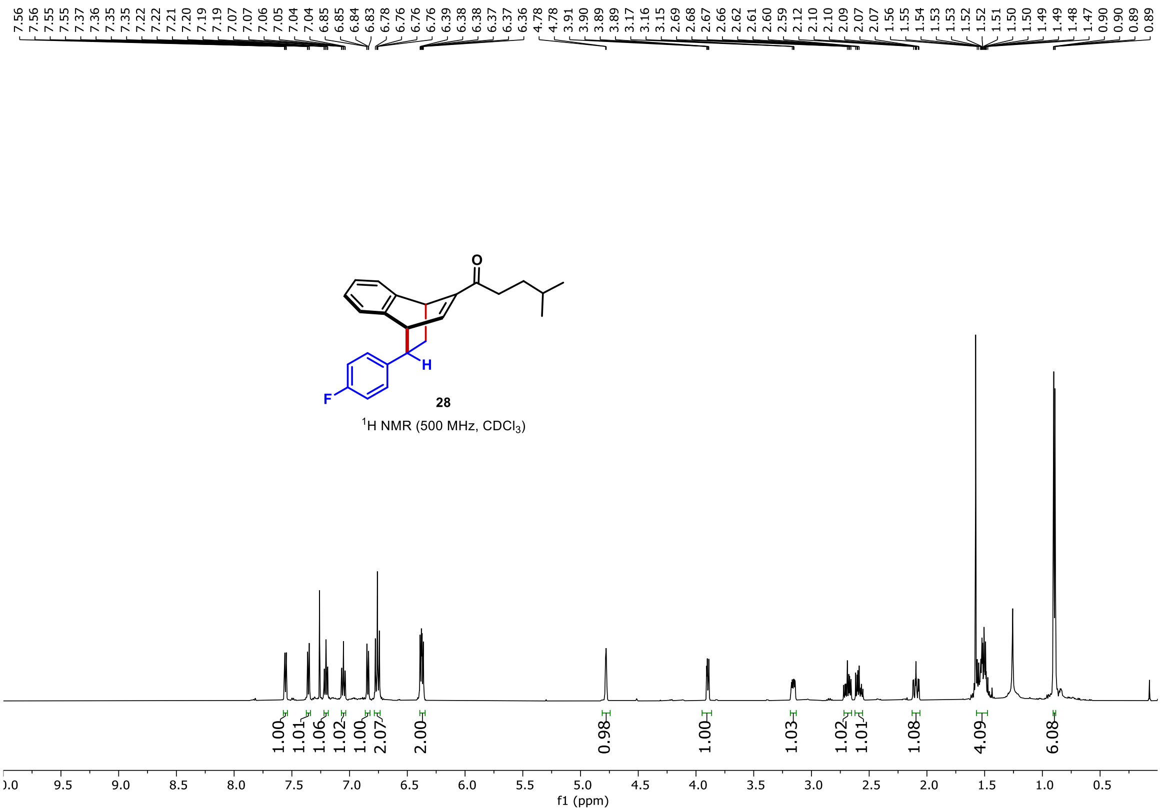


27

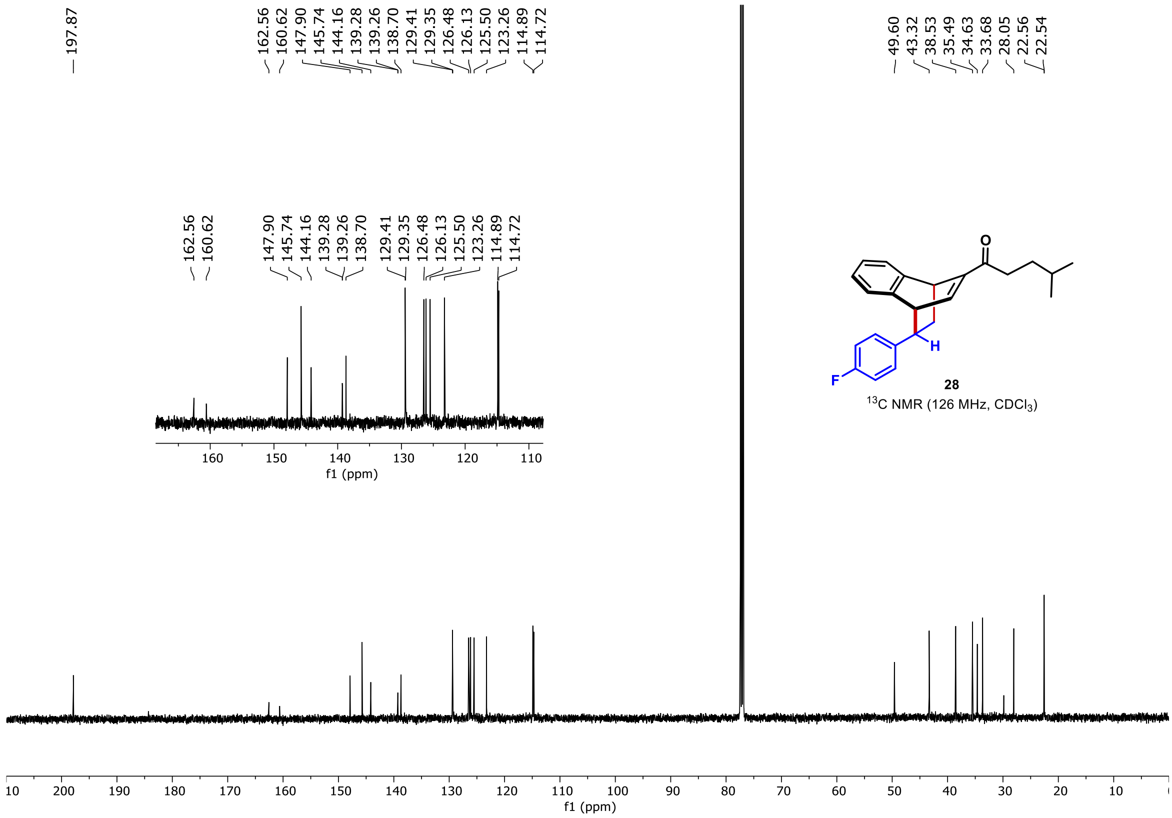
^{13}C NMR (126 MHz, $CDCl_3$)

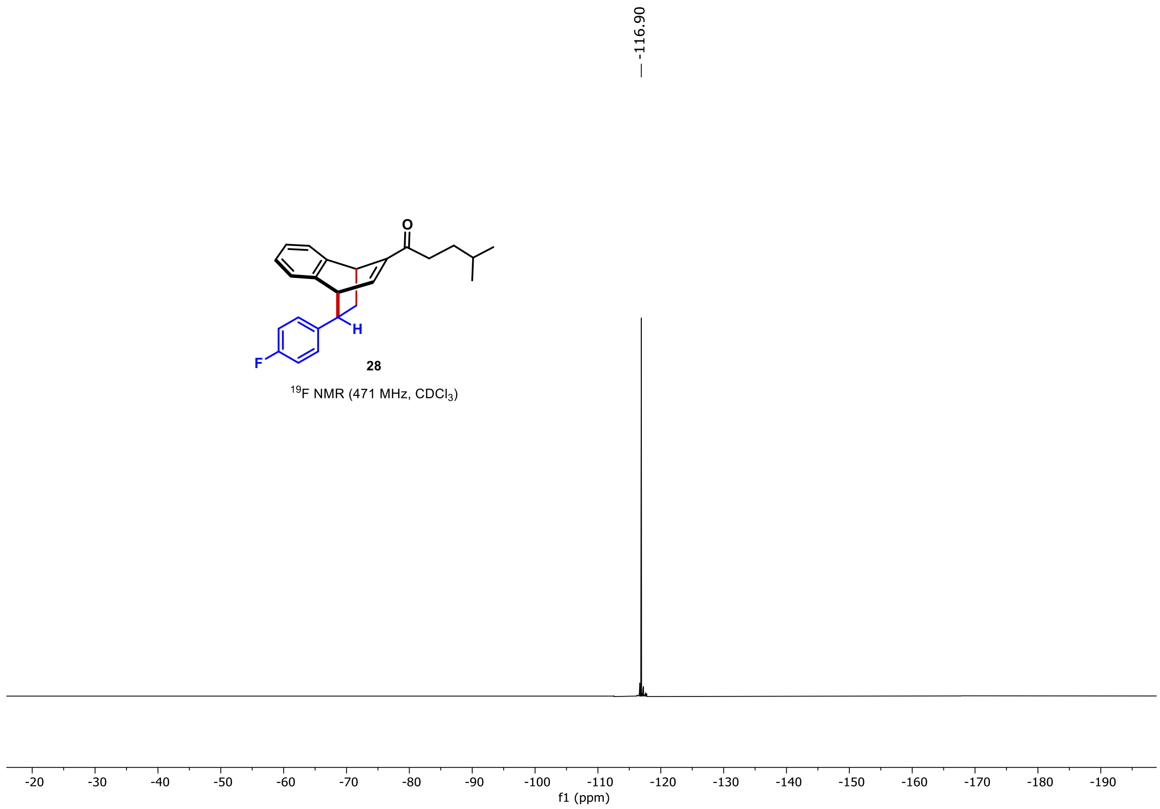


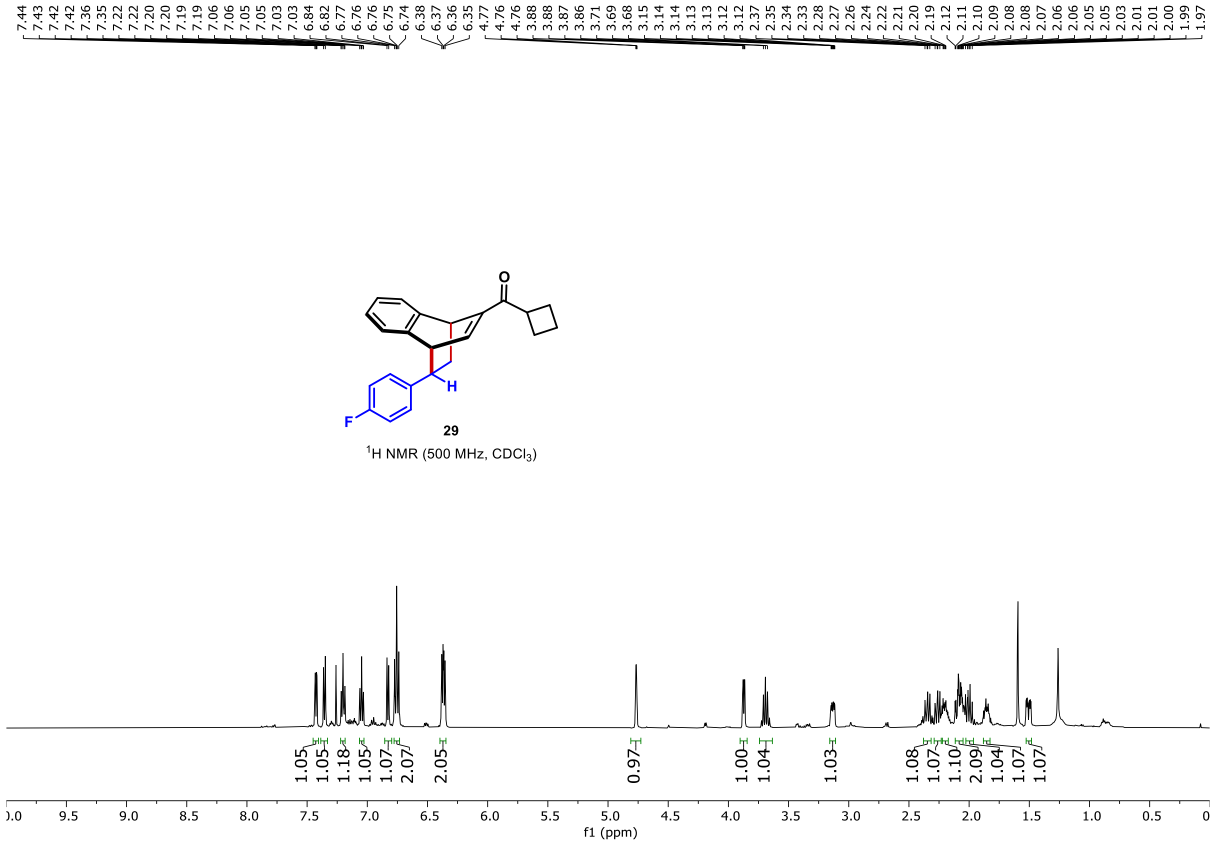
-116.89
O
H
F
27
19F NMR (471 MHz, CDCl3)
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

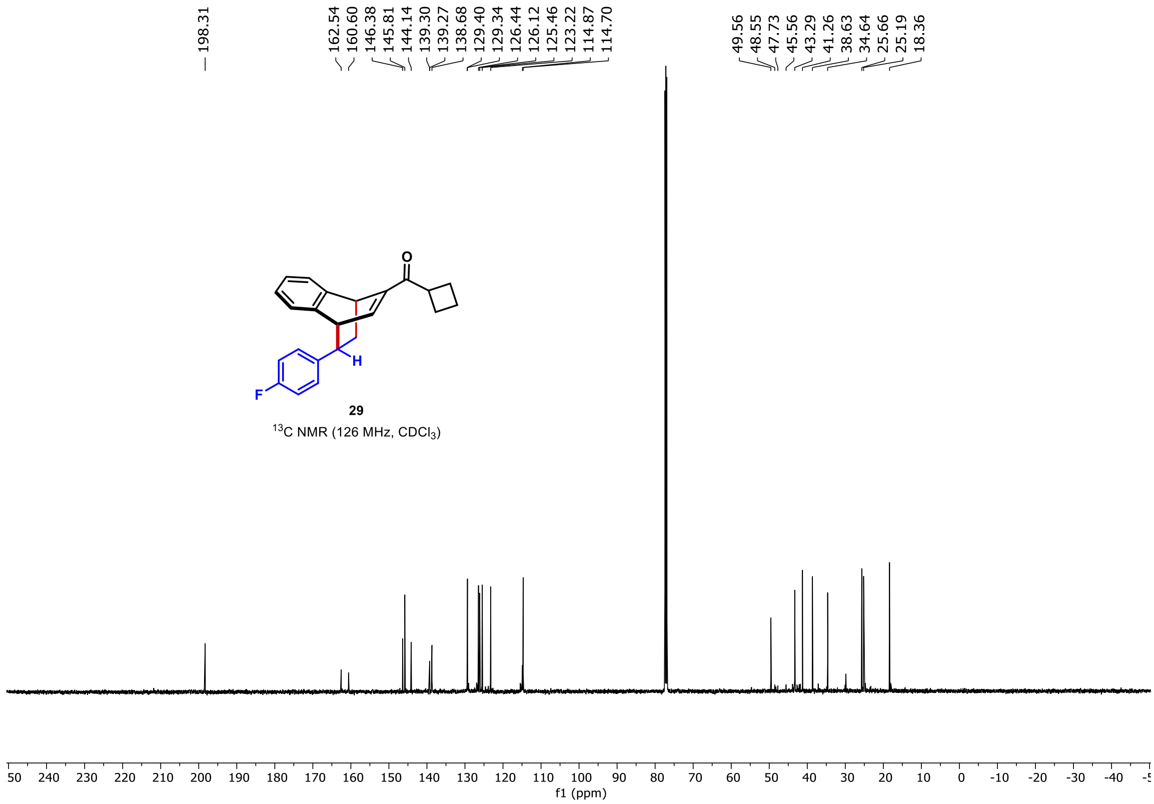


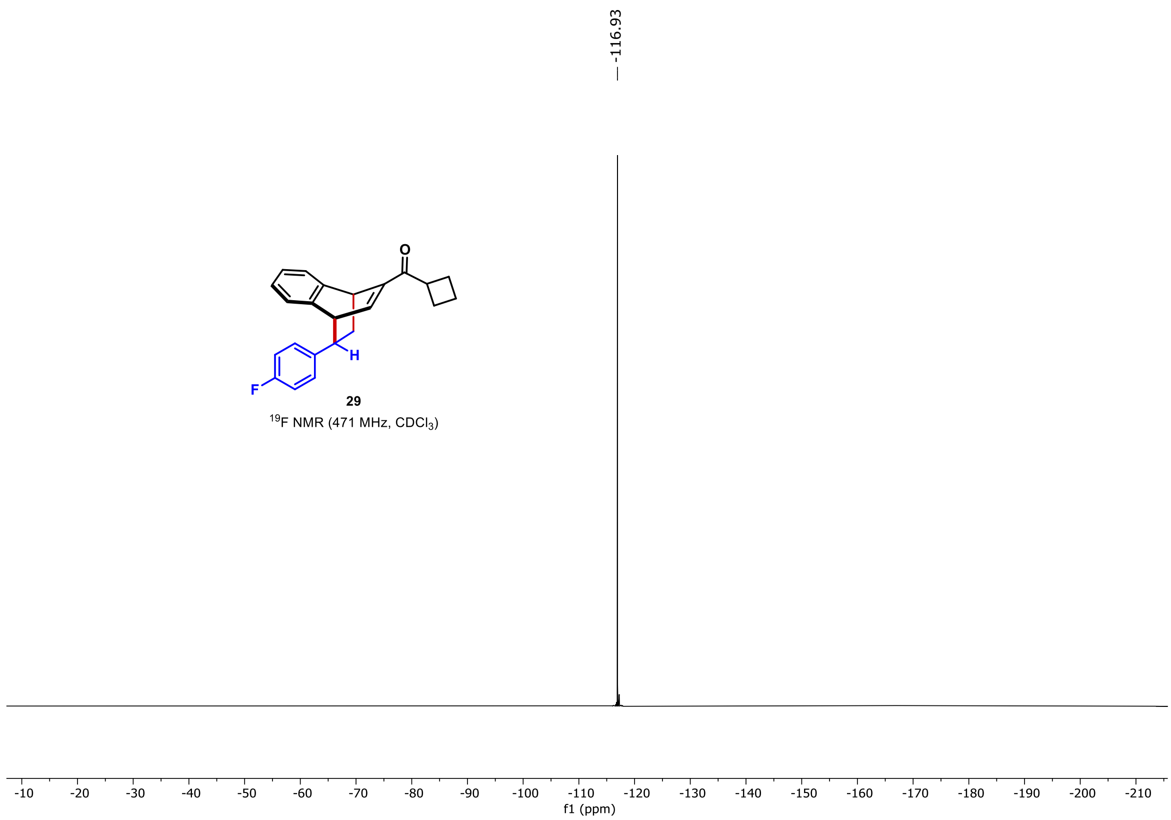
7.56 7.56 7.55 7.55 7.37 7.36 7.35 7.35 7.22 7.22 7.21 7.20 7.19 7.19 7.07 7.07 7.06 7.05 7.04 7.04 6.85 6.85 6.84 6.83 6.78 6.76 6.76 6.76 6.39 6.38 6.38 6.37 6.37 6.36 4.78 4.78 3.91 3.90 3.89 3.89 3.17 3.16 3.15 2.69 2.68 2.67 2.66 2.62 2.61 2.60 2.59 2.12 2.10 2.10 2.09 2.07 2.07 1.56 1.55 1.54 1.53 1.53 1.52 1.52 1.51 1.50 1.50 1.49 1.49 1.48 1.47 0.90 0.90 0.89 0.89
O
H
F
28
1H NMR (500 MHz, CDCl3)
1.00 1.01 1.06 1.02 1.00 2.07 2.00 0.98 1.00 1.03 1.02 1.01 1.08 4.09 6.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

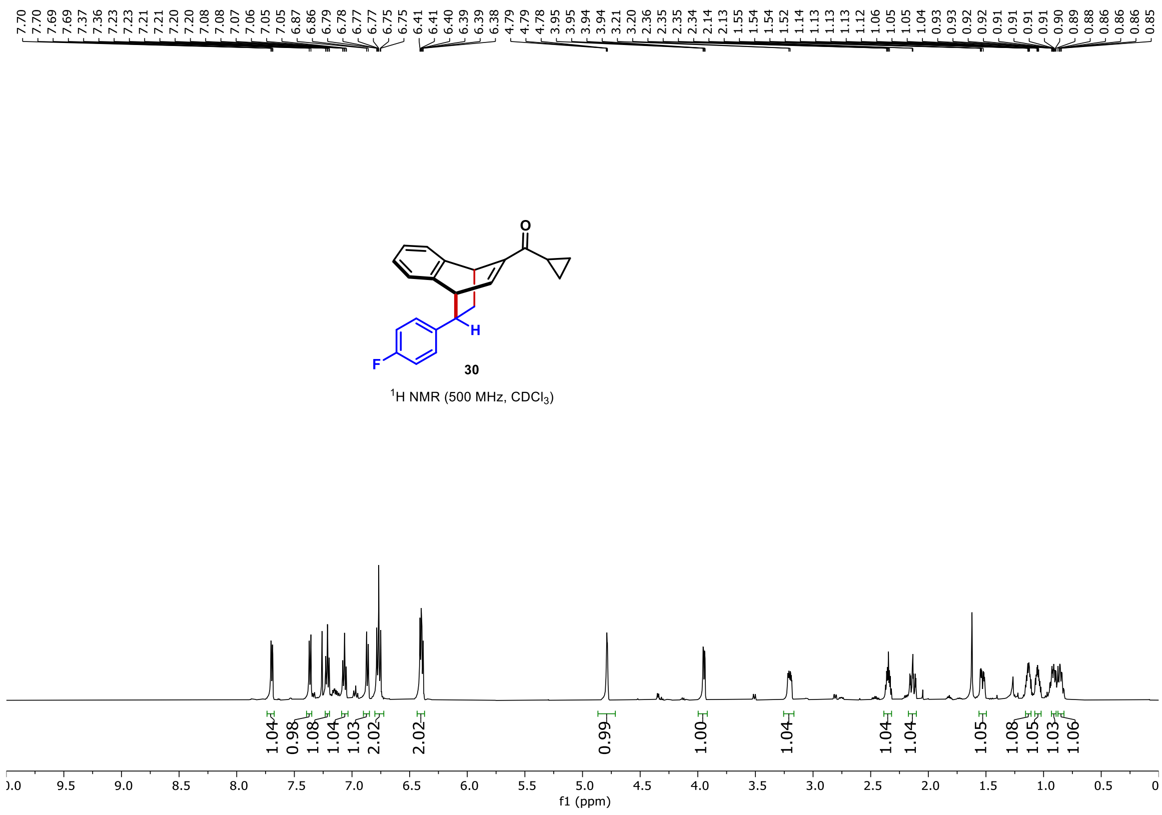

197.87
162.56
160.62
147.90
145.74
144.16
139.28
139.26
138.70
129.41
129.35
126.48
126.13
125.50
123.26
114.89
114.72
49.60
43.32
38.53
35.49
34.63
33.68
28.05
22.56
22.54
28
^{13}C NMR (126 MHz, CDCl$_3$)
f1 (ppm)

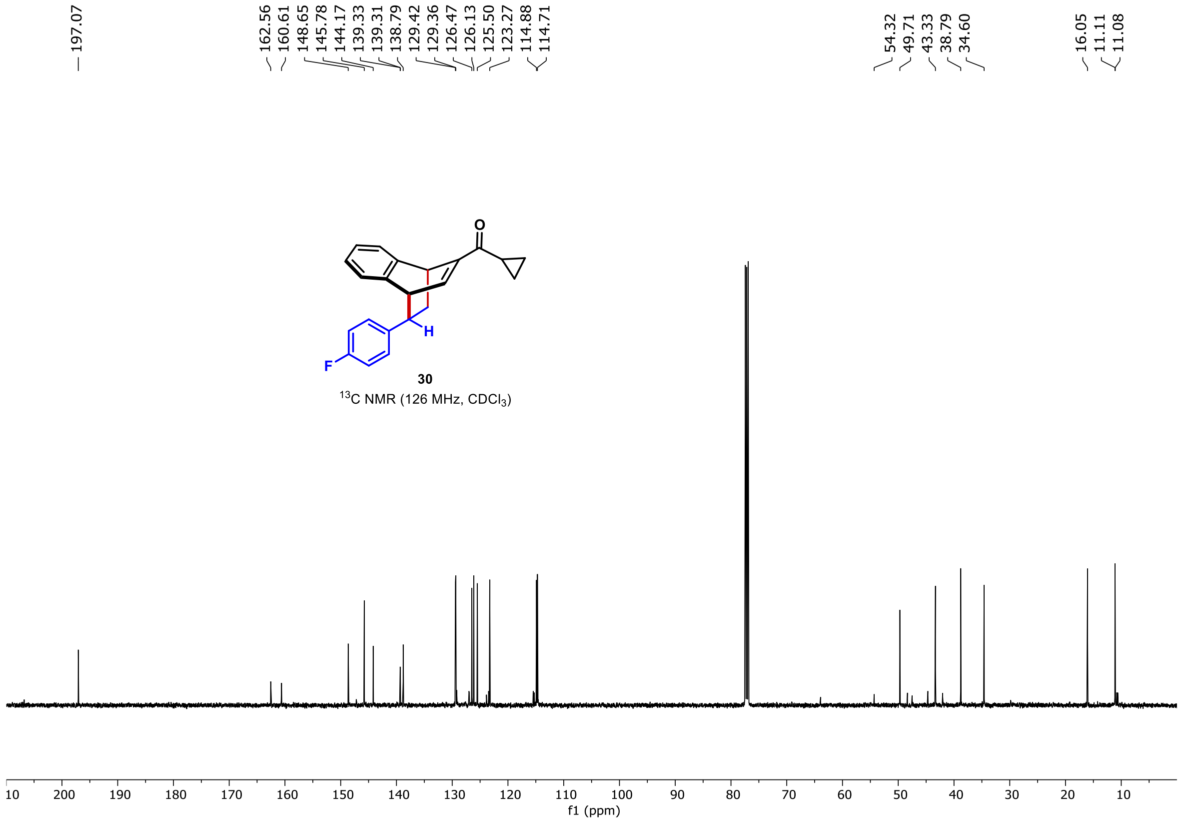

-116.90
28
^{19}F NMR (471 MHz, CDCl$_3$)
f1 (ppm)

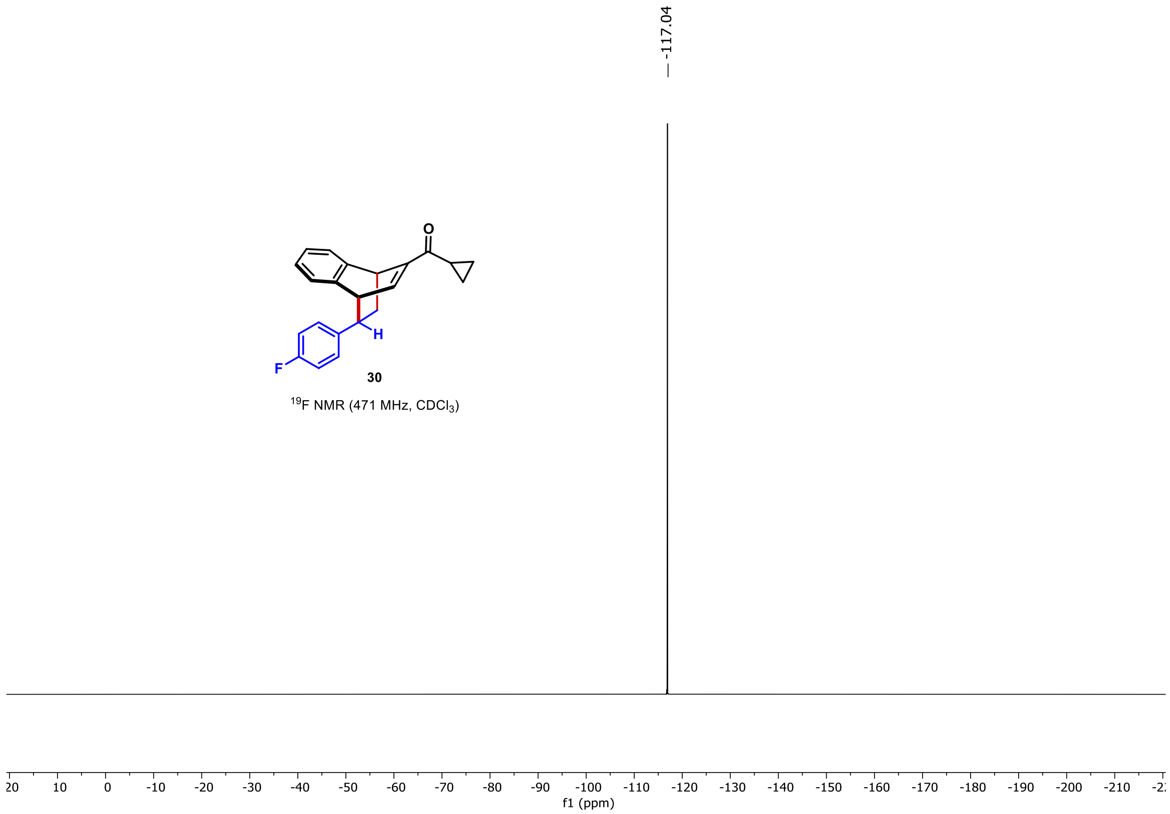

O
F
H
29
^{1}H NMR (500 MHz, CDCl$_3$)
f1 (ppm)

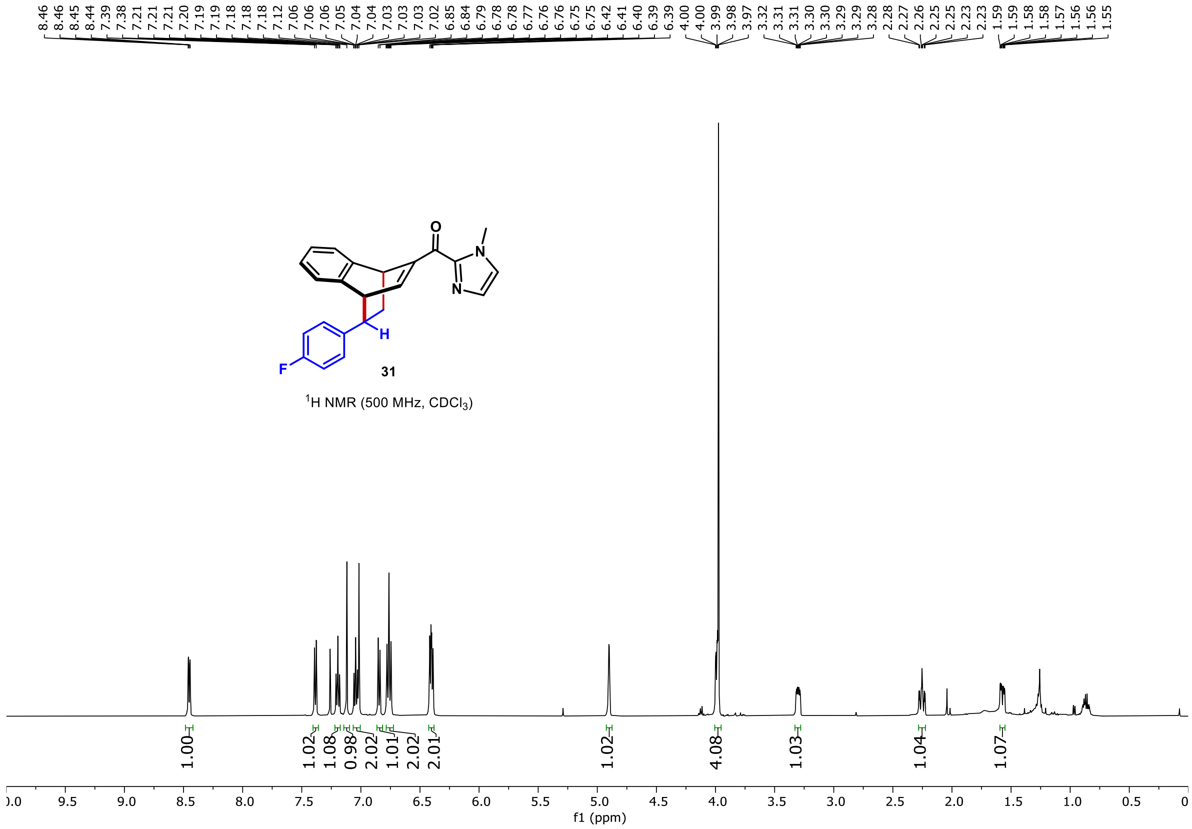

O
F
H
29
^{13}C NMR (126 MHz, CDCl$_3$)
f1 (ppm)

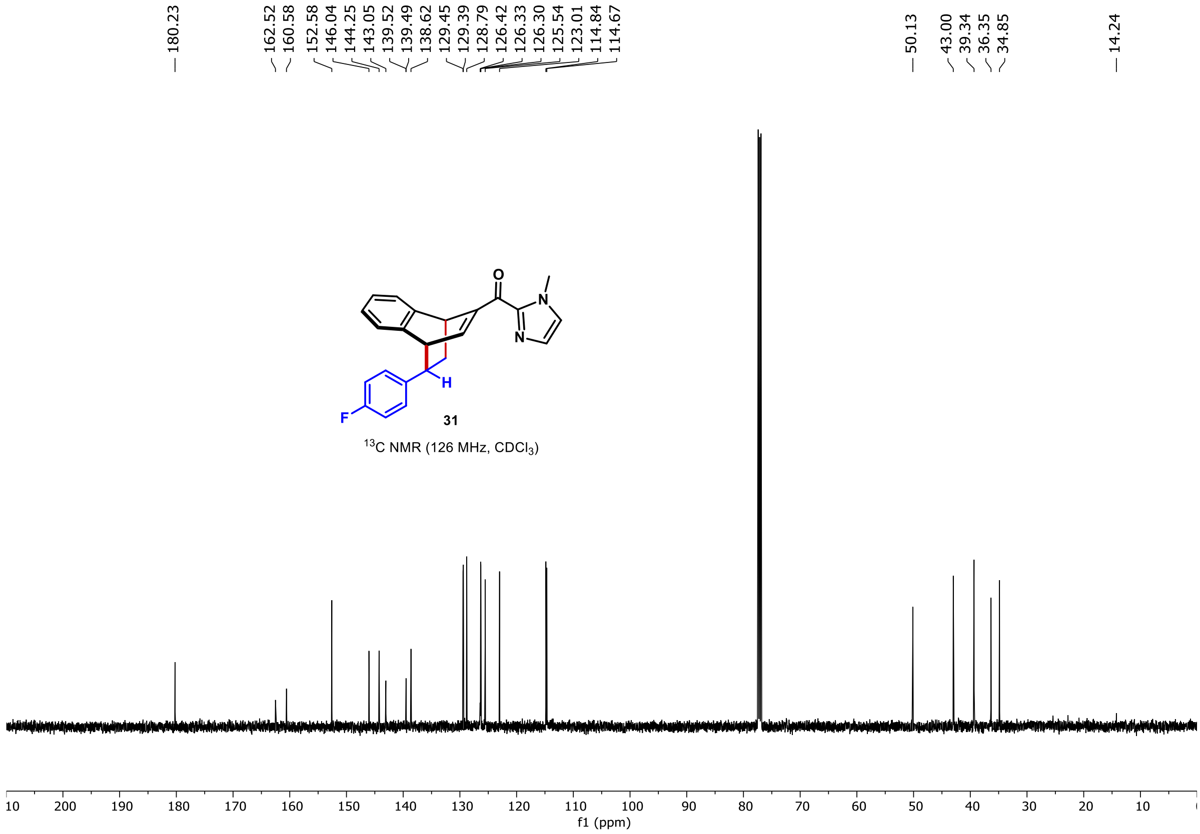

-116.93
O
H
F
29
^{19}F NMR (471 MHz, CDCl$_3$)
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

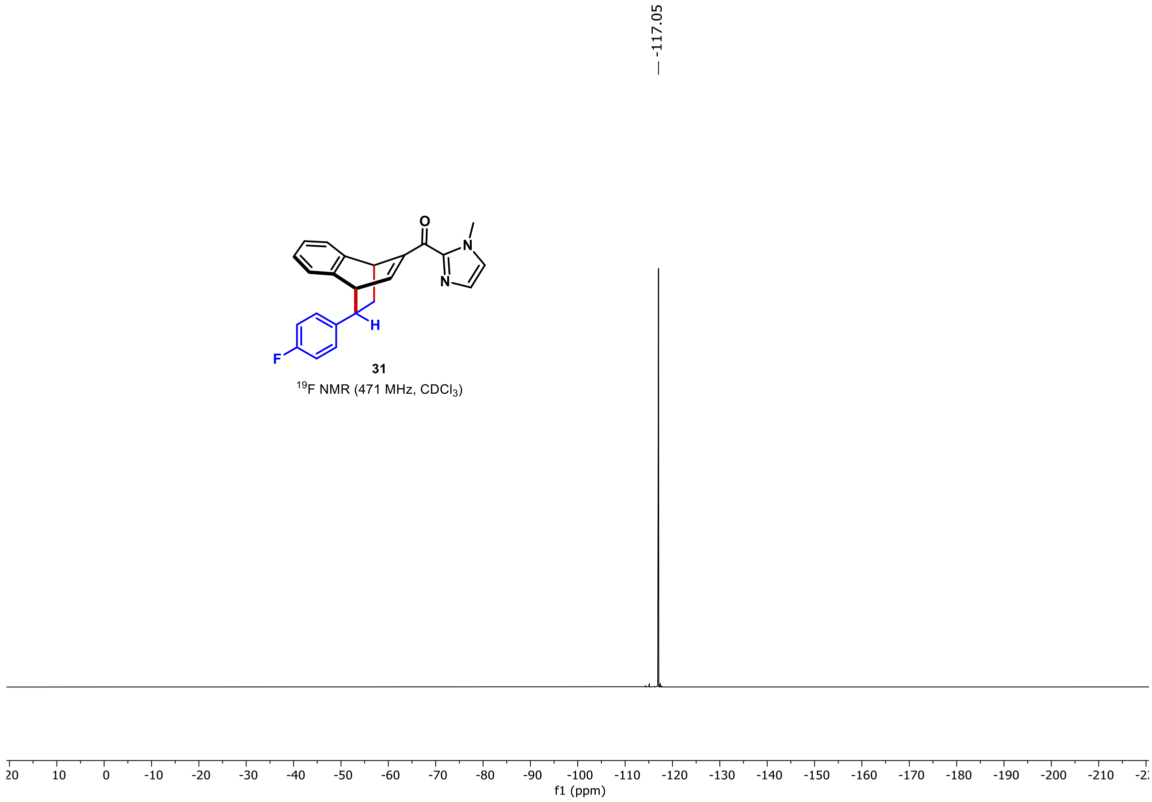

7.70 7.70 7.69 7.69 7.37 7.36 7.23 7.23 7.21 7.21 7.20 7.08 7.08 7.07 7.06 7.05 7.05 6.87 6.86 6.79 6.78 6.77 6.77 6.75 6.75 6.41 6.41 6.40 6.39 6.39 6.38 4.79 4.79 4.78 3.95 3.95 3.94 3.94 3.21 3.20 2.36 2.35 2.35 2.34 2.14 2.13 1.55 1.54 1.54 1.52 1.14 1.13 1.13 1.13 1.12 1.06 1.05 1.05 1.04 0.93 0.93 0.92 0.92 0.91 0.91 0.91 0.91 0.90 0.89 0.88 0.86 0.86 0.85
O
H
F
30
^{1}H NMR (500 MHz, CDCl$_3$)
1.04 0.98 1.08 1.04 1.03 2.02 2.02 0.99 1.00 1.04 1.04 1.04 1.05 1.08 1.05 1.03 1.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)


197.07
162.56
160.61
148.65
145.78
144.17
139.33
139.31
138.79
129.42
129.36
126.47
126.13
125.50
123.27
114.88
114.71
54.32
49.71
43.33
38.79
34.60
16.05
11.11
11.08
O
H
F
30
^{13}C NMR (126 MHz, CDCl$_3$)
f1 (ppm)

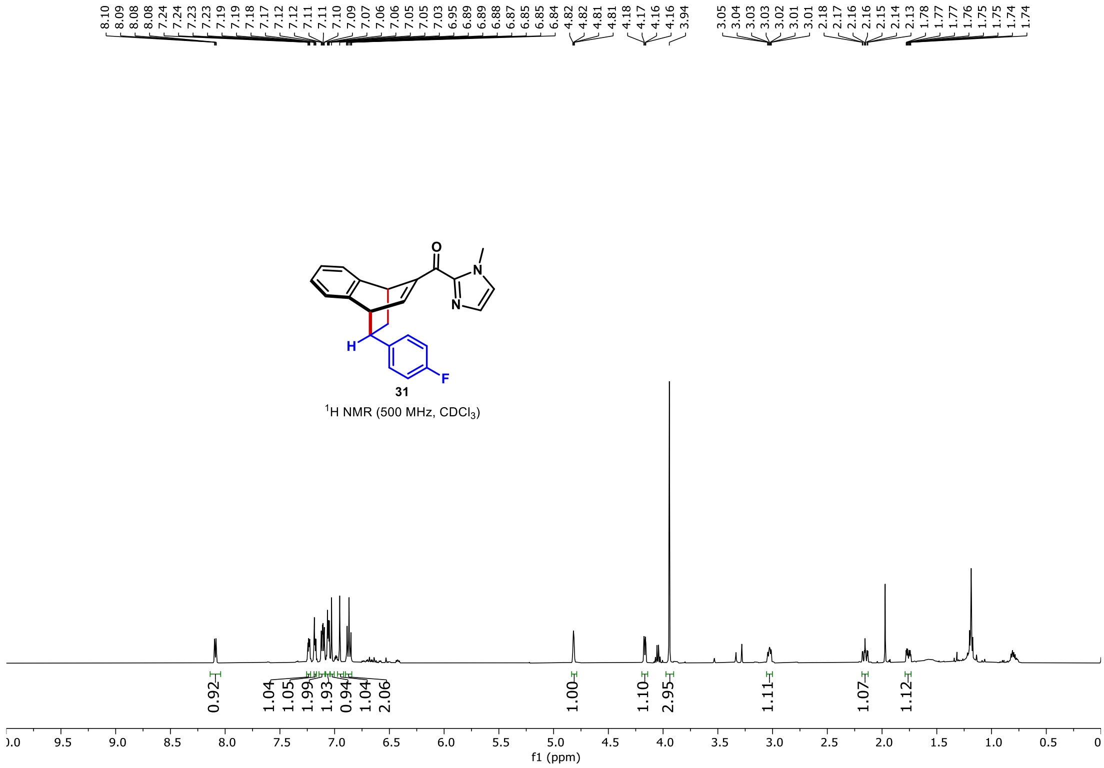

-117.04
O
H
F
30
^{19}F NMR (471 MHz, CDCl$_3$)
f1 (ppm)


8.46 8.46 8.45 8.44 7.39 7.38 7.21 7.21 7.21 7.20 7.19 7.19 7.18 7.18 7.18 7.12 7.06 7.06 7.05 7.04 7.04 7.03 7.03 7.03 7.02 6.85 6.84 6.79 6.78 6.78 6.77 6.76 6.76 6.75 6.75 6.42 6.41 6.40 6.39 6.39 4.00 3.99 3.98 3.97 3.32 3.31 3.31 3.30 3.30 3.29 3.29 3.28 2.28 2.27 2.26 2.25 2.25 2.23 2.23 1.59 1.59 1.58 1.58 1.57 1.56 1.56 1.55
O
N
N
H
F
31
1H NMR (500 MHz, CDCl3)
1.00 1.02 1.08 0.98 2.02 1.01 2.02 2.01 1.02 4.08 1.03 1.04 1.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)

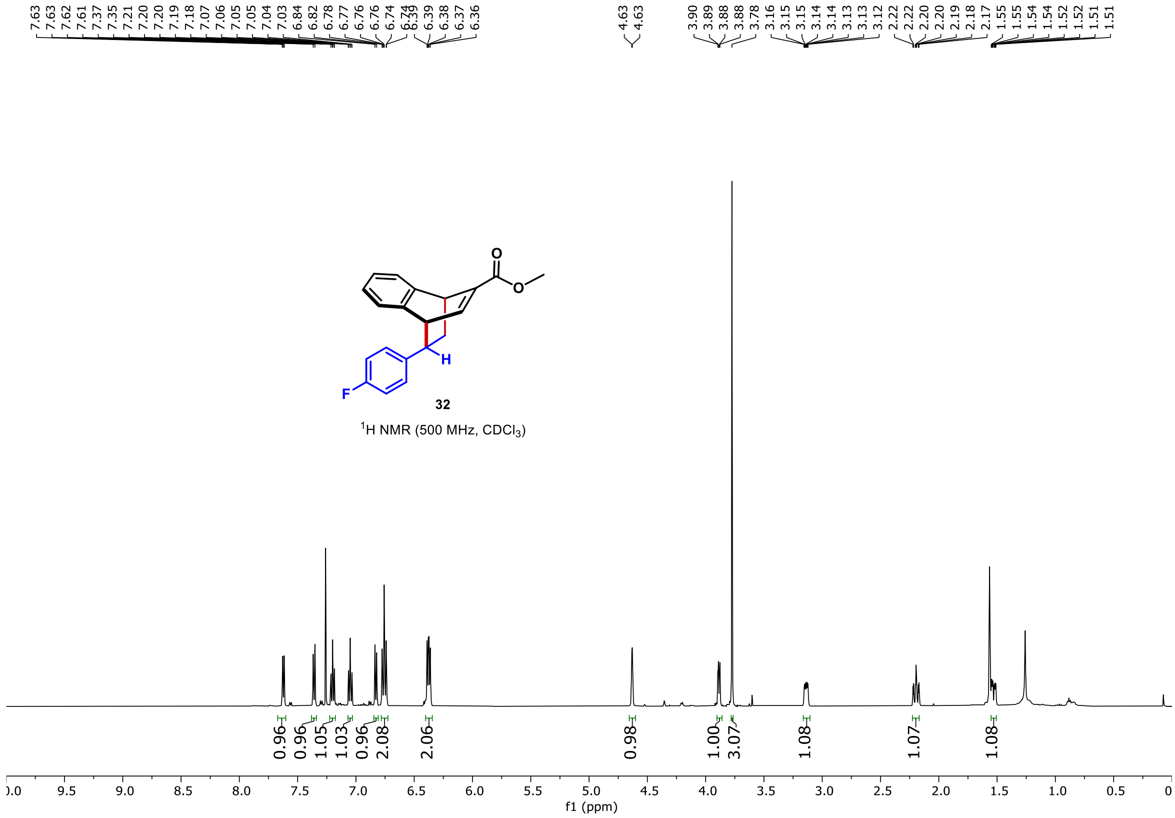

180.23
162.52 160.58 152.58 146.04 144.25 143.05 139.52 139.49 138.62 129.45 129.39 128.79 126.42 126.33 126.30 125.54 123.01 114.84 114.67
50.13 43.00 39.34 36.35 34.85
14.24
O
N
N
H
F
31
13C NMR (126 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

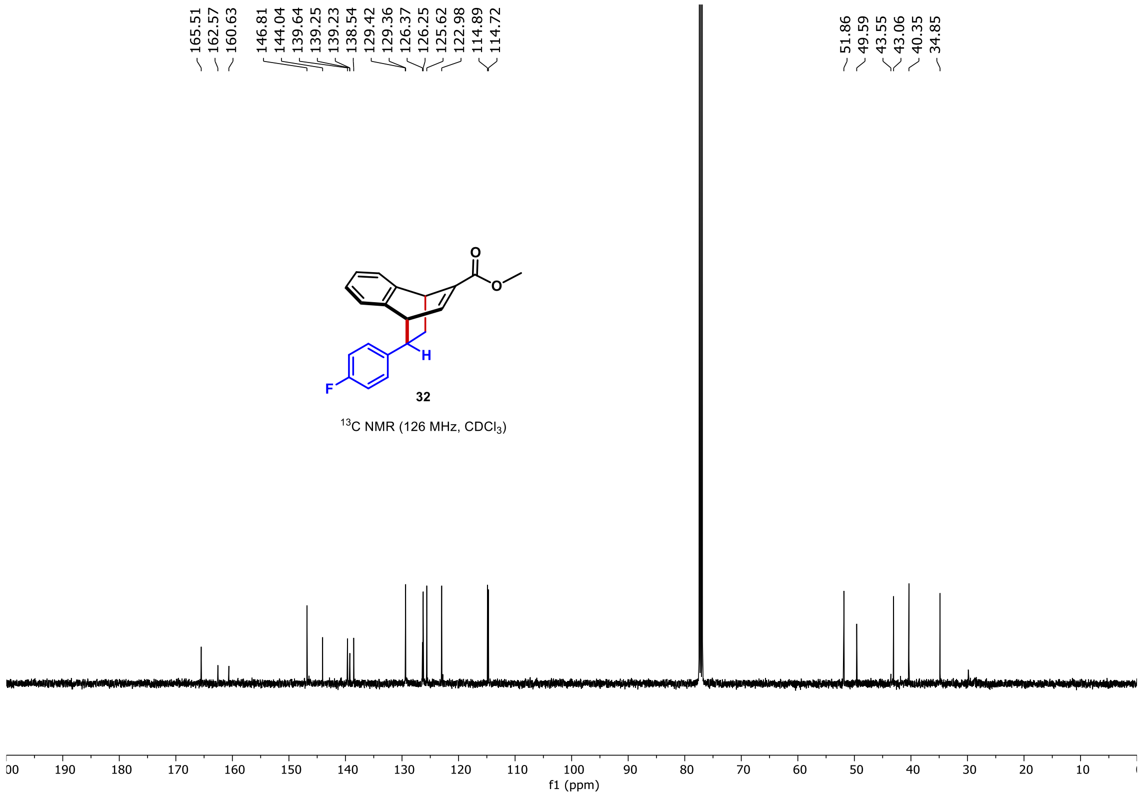


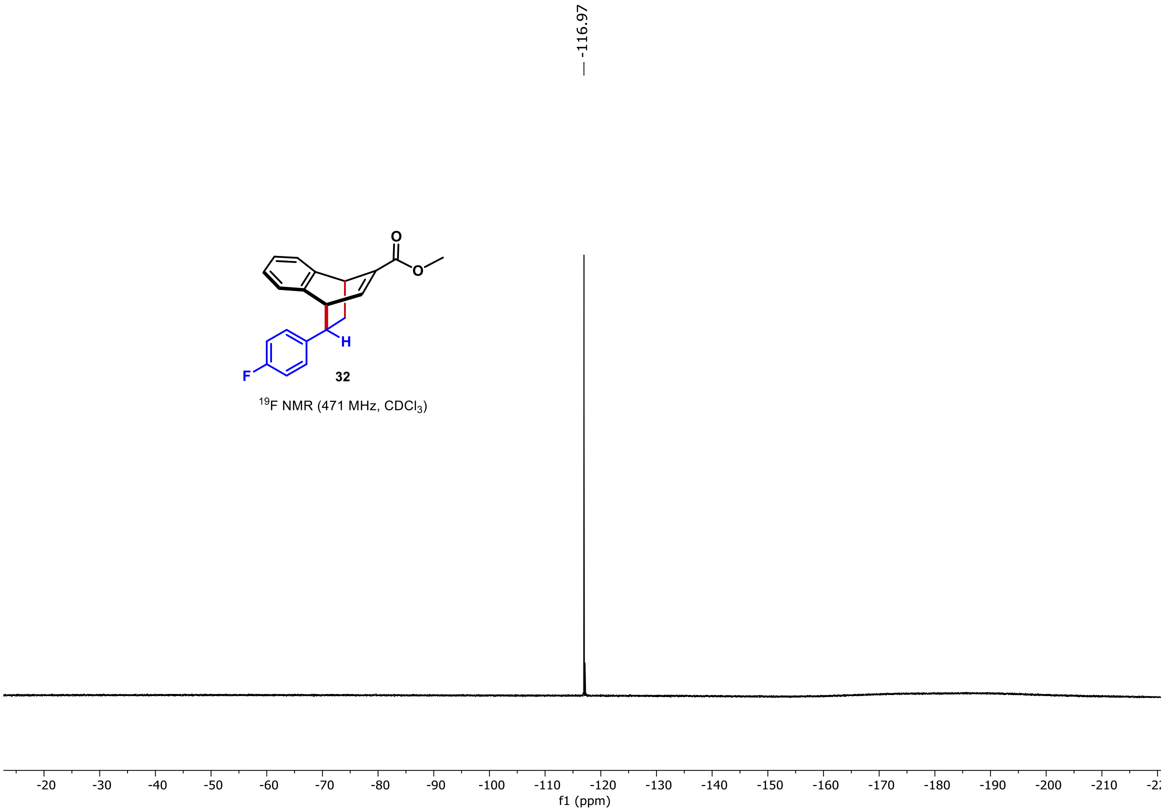
-117.05
O
N
N
H
F
31
^{19}F NMR (471 MHz, CDCl$_3$)
f1 (ppm)



8.10 8.09 8.08 8.08 7.24 7.24 7.23 7.23 7.19 7.19 7.18 7.17 7.12 7.12 7.11 7.11 7.10 7.09 7.07 7.06 7.05 7.05 7.03 6.95 6.89 6.89 6.88 6.87 6.85 6.85 6.84 4.82 4.82 4.81 4.81 4.18 4.17 4.16 4.16 3.94 3.05 3.04 3.03 3.03 3.02 3.01 3.01 2.18 2.17 2.16 2.16 2.15 2.14 2.13 1.78 1.77 1.77 1.76 1.75 1.75 1.74 1.74
O
N
N
H
F
31
^{1}H NMR (500 MHz, CDCl$_3$)
0.92 1.04 1.05 1.99 1.93 0.94 1.04 2.06 1.00 1.10 2.95 1.11 1.07 1.12
f1 (ppm)

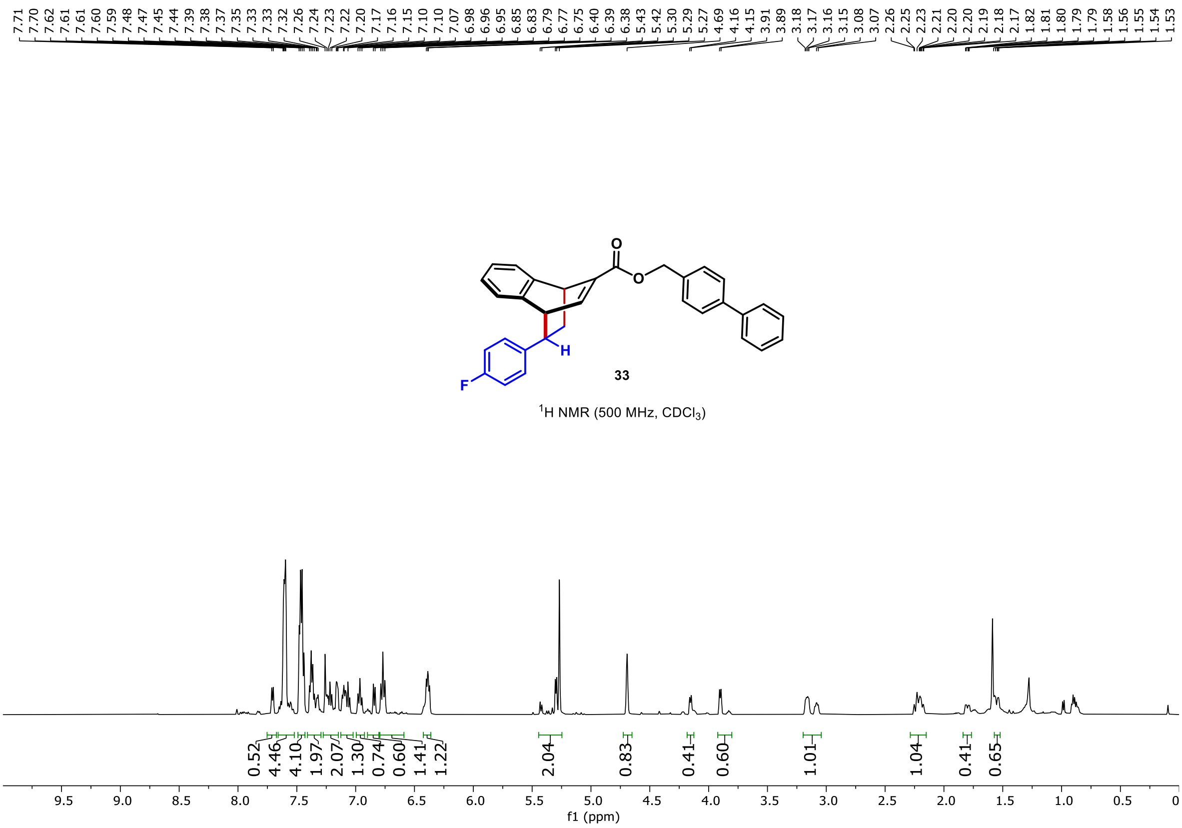

32
^{1}H NMR (500 MHz, CDCl$_3$)
f1 (ppm)


32
^{13}C NMR (126 MHz, CDCl$_3$)
f1 (ppm)



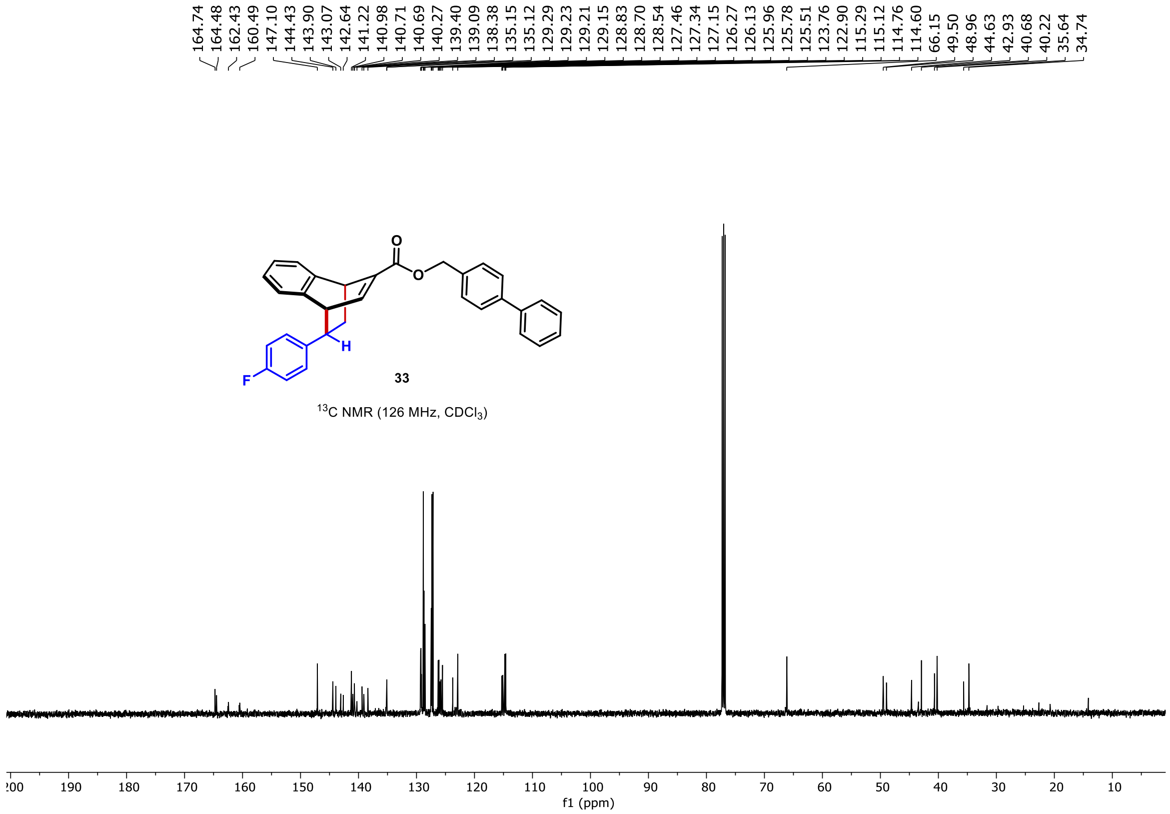
32

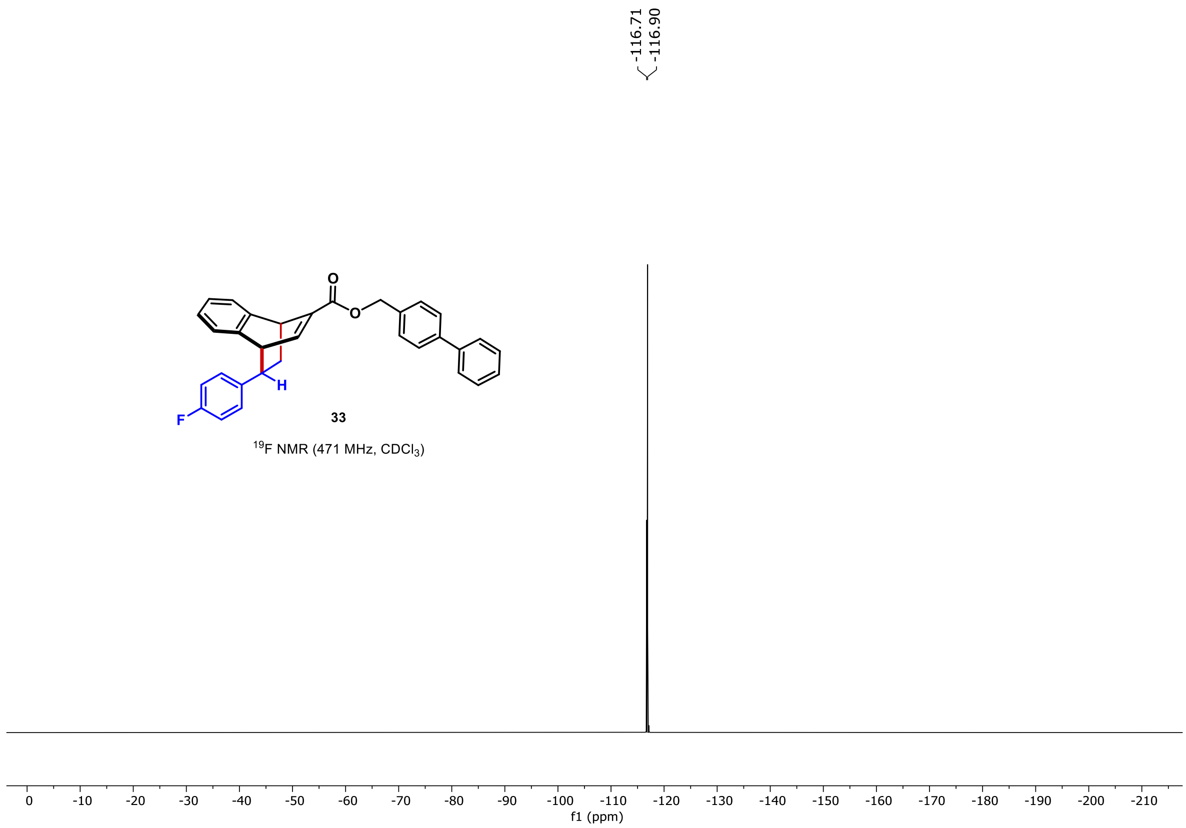
^{19}F NMR (471 MHz, $CDCl_3$)

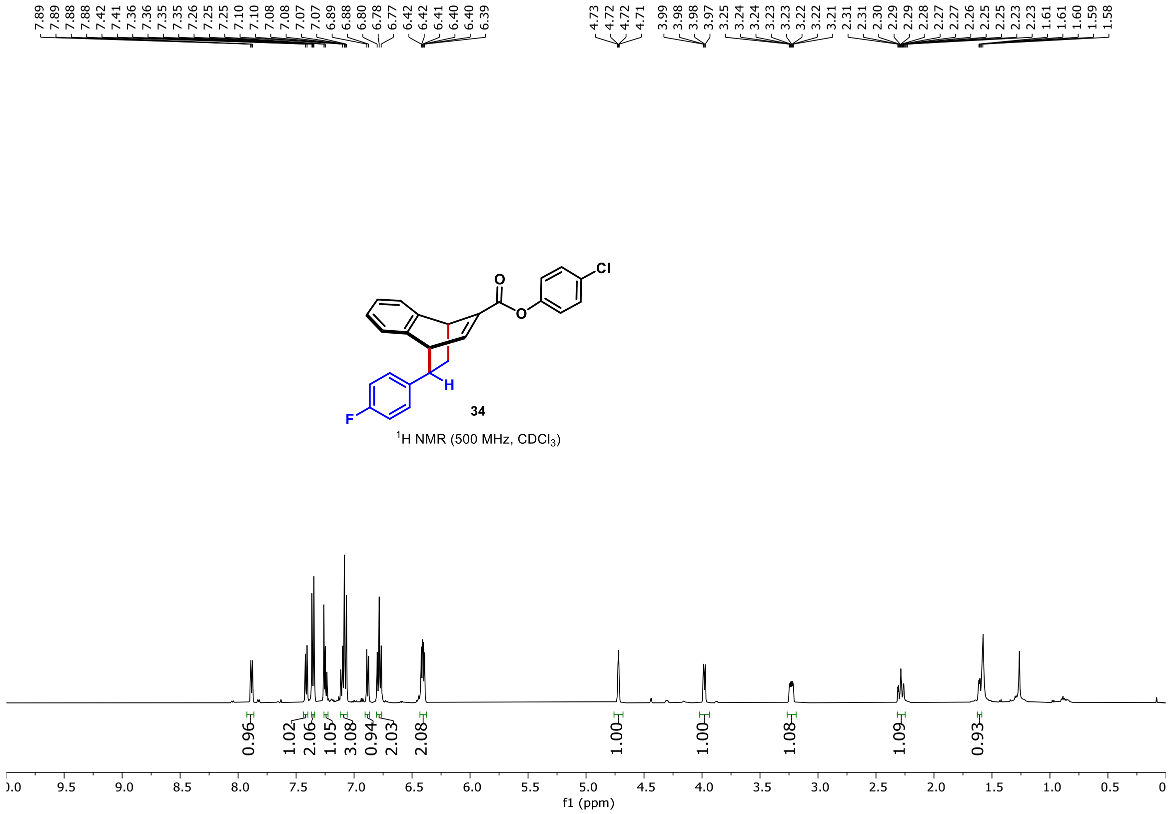


33

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

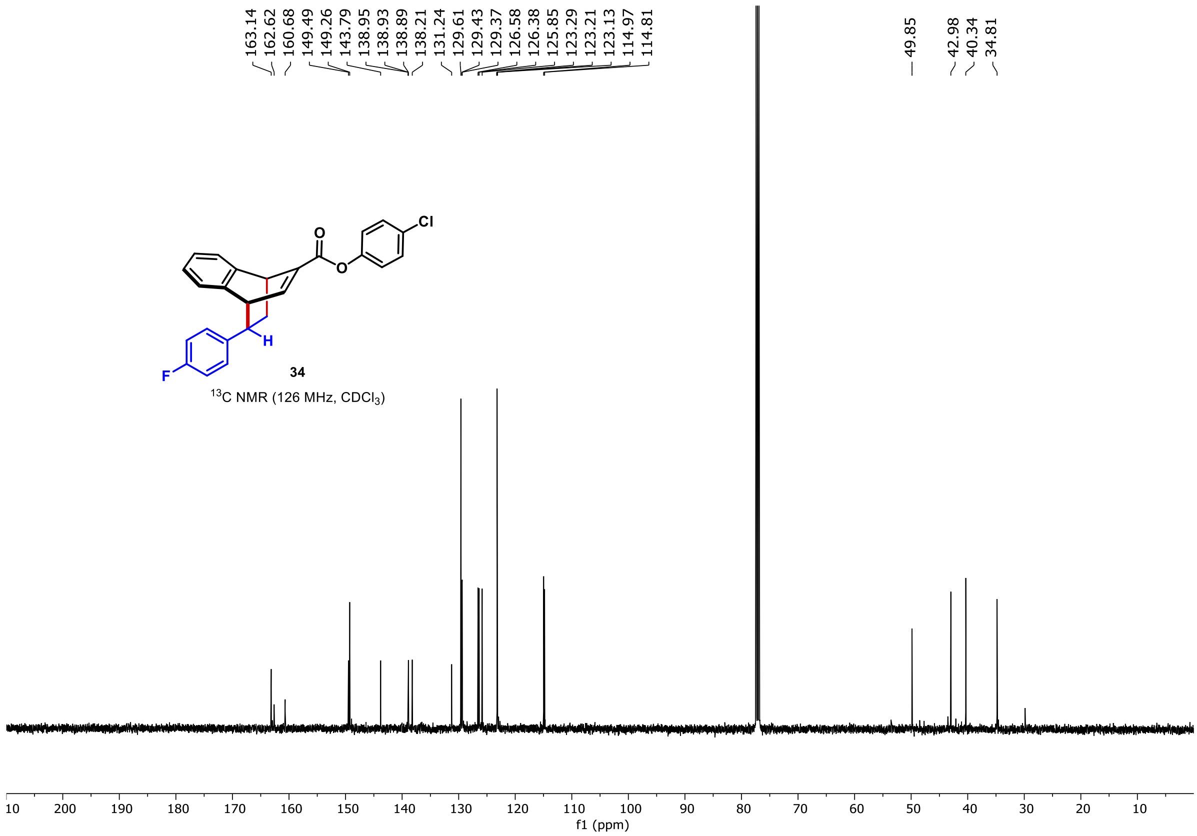

164.74
164.48
162.43
160.49
147.10
144.43
143.90
143.07
142.64
141.22
140.98
140.71
140.69
140.27
139.40
139.09
138.38
135.15
135.12
129.29
129.23
129.21
129.15
128.83
128.70
128.54
127.46
127.34
127.15
126.27
126.13
125.96
125.78
125.51
123.76
122.90
115.29
115.12
114.76
114.60
66.15
49.50
48.96
44.63
42.93
40.68
40.22
35.64
34.74
O
O
H
F
33
13C NMR (126 MHz, CDCl3)
f1 (ppm)


-116.71
-116.90
O
O
H
F
33
19F NMR (471 MHz, CDCl3)
f1 (ppm)



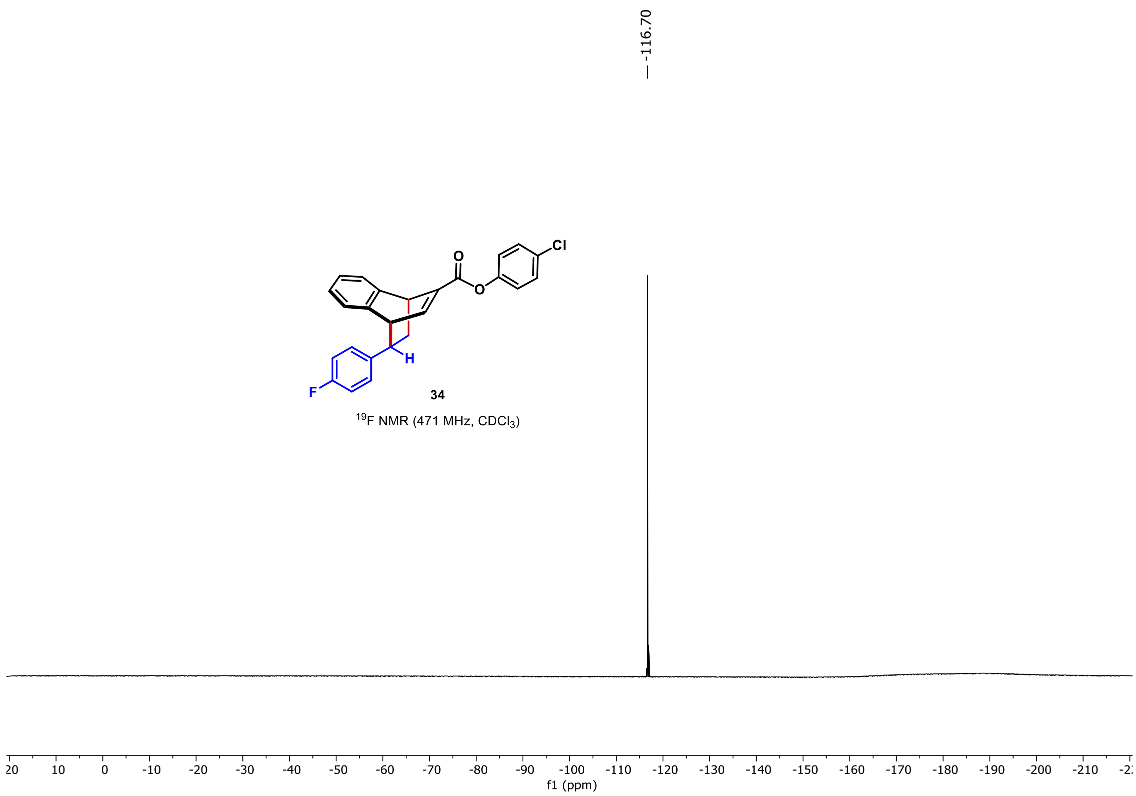
34

^{1}H NMR (500 MHz, CDCl$_3$)



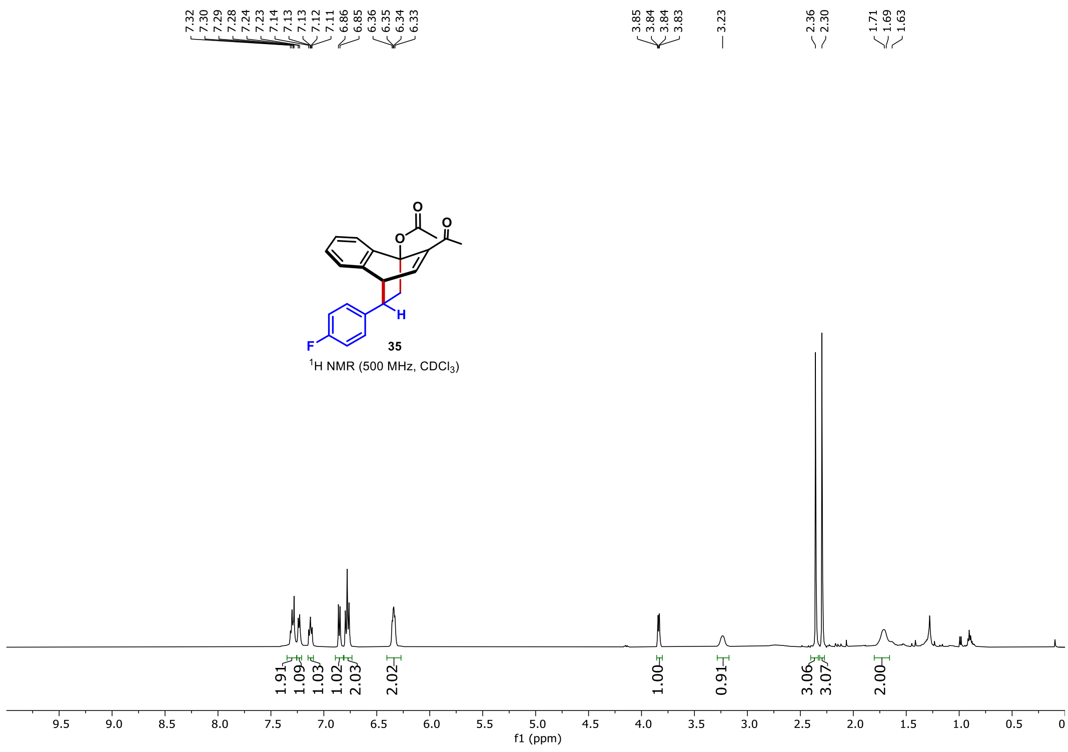
34

^{13}C NMR (126 MHz, CDCl$_3$)



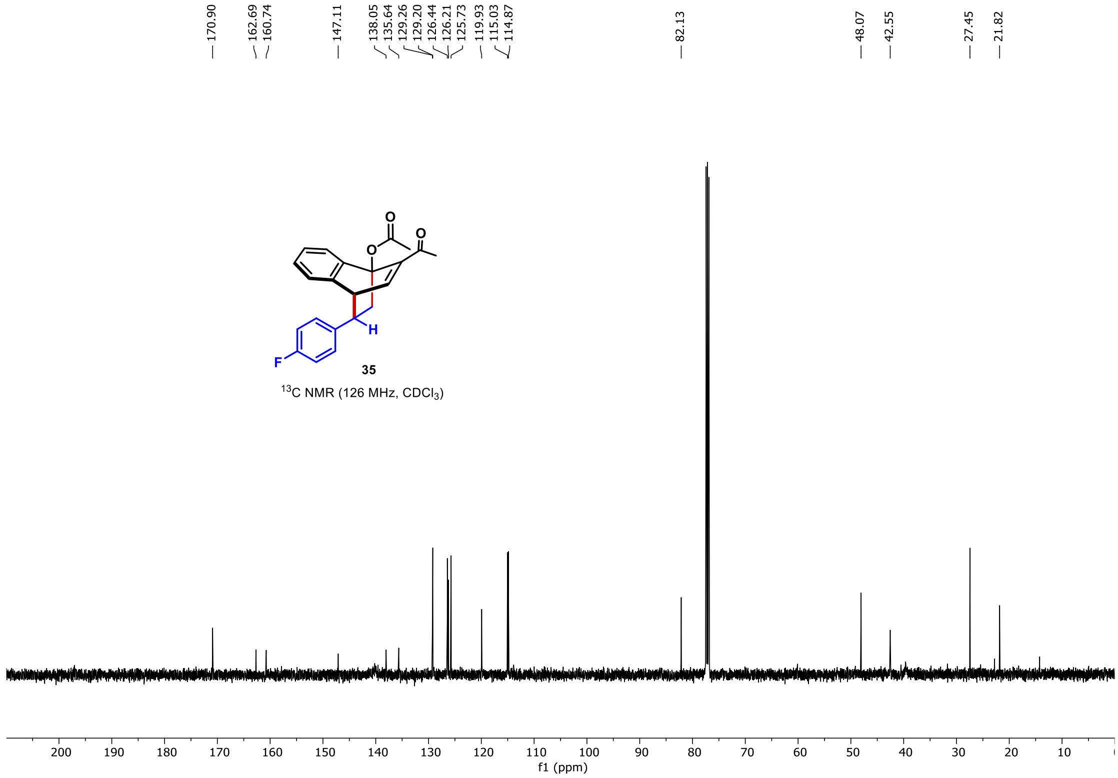
34

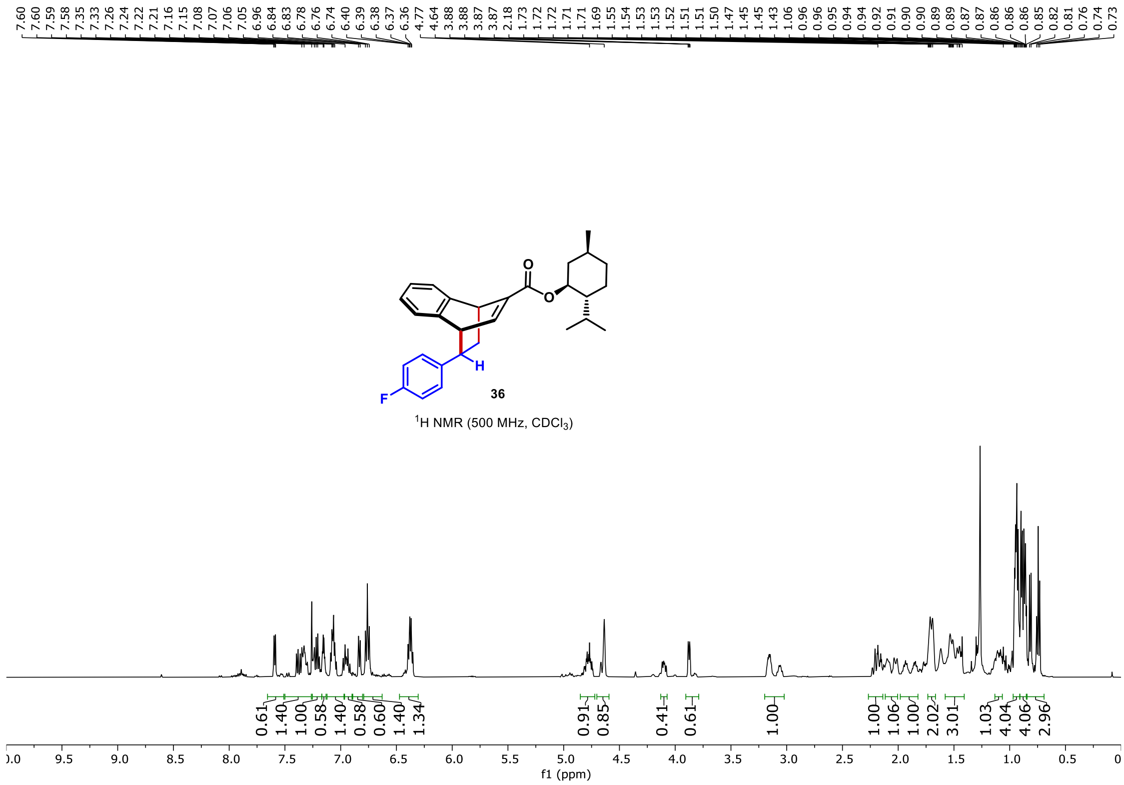
^{19}F NMR (471 MHz, $CDCl_3$)

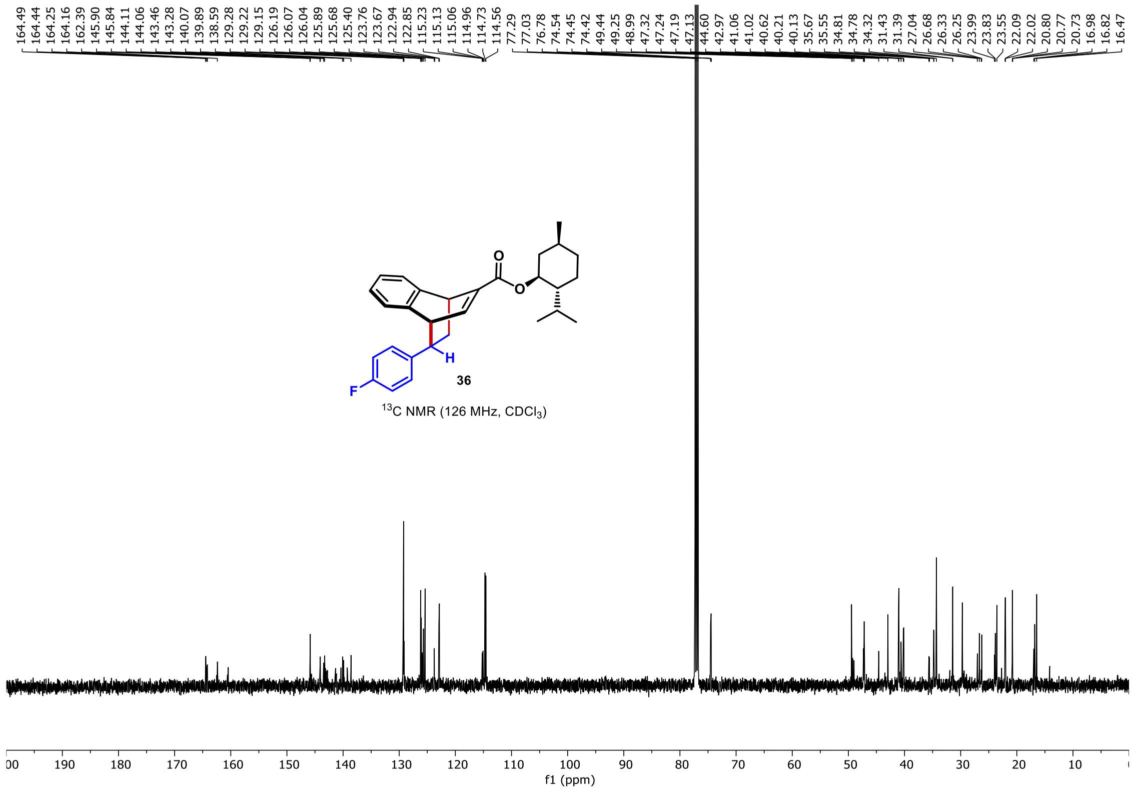


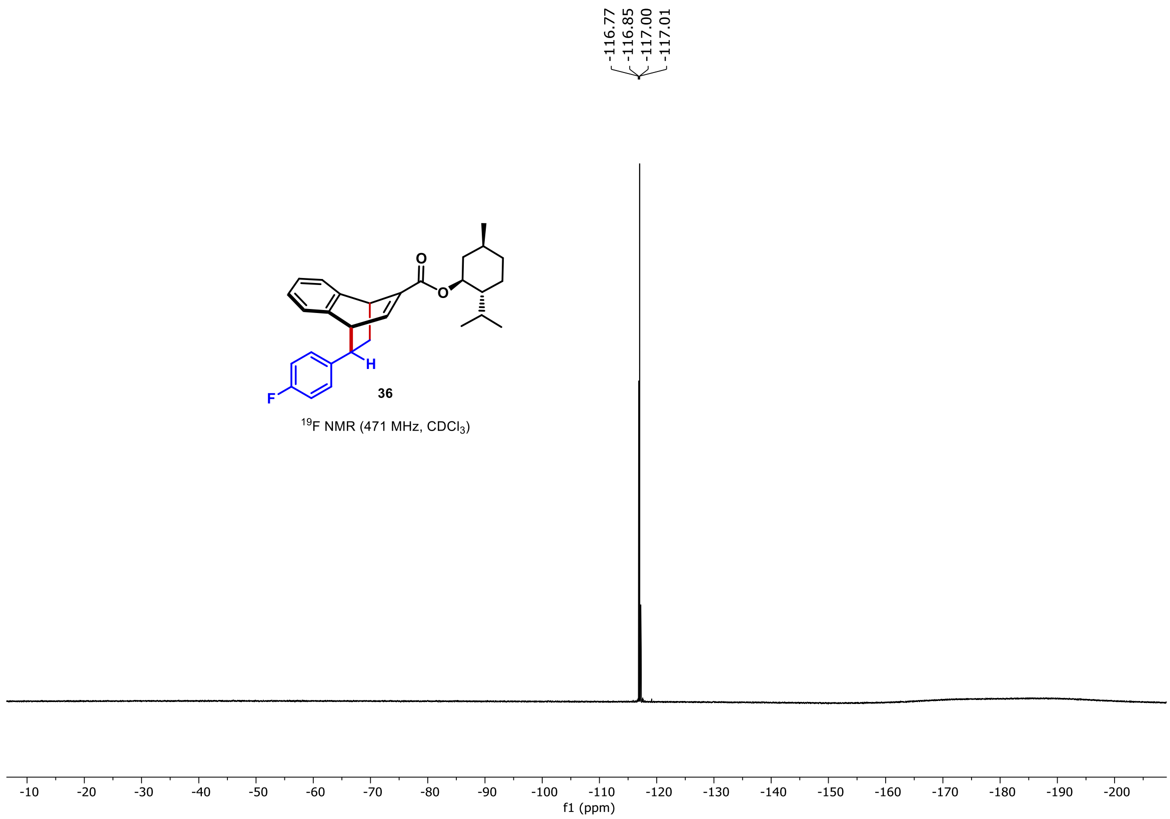
35

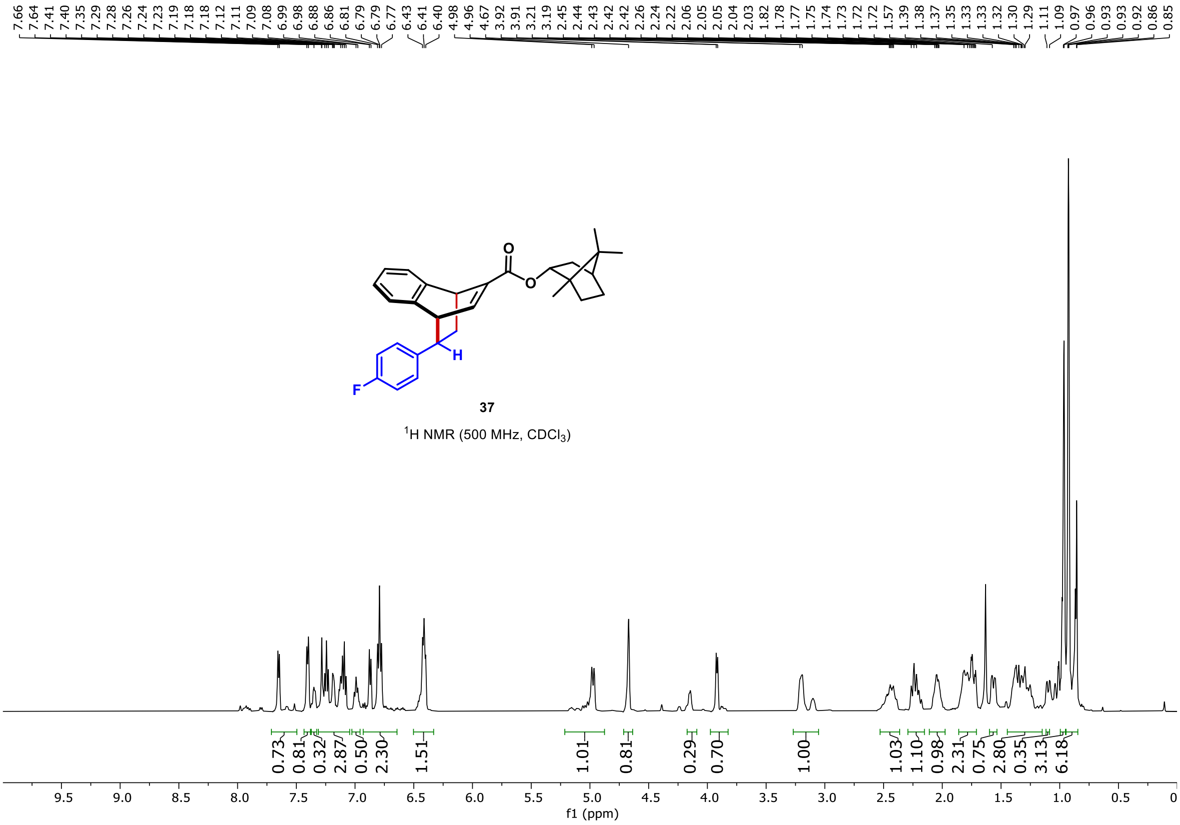
^{1}H NMR (500 MHz, $CDCl_3$)

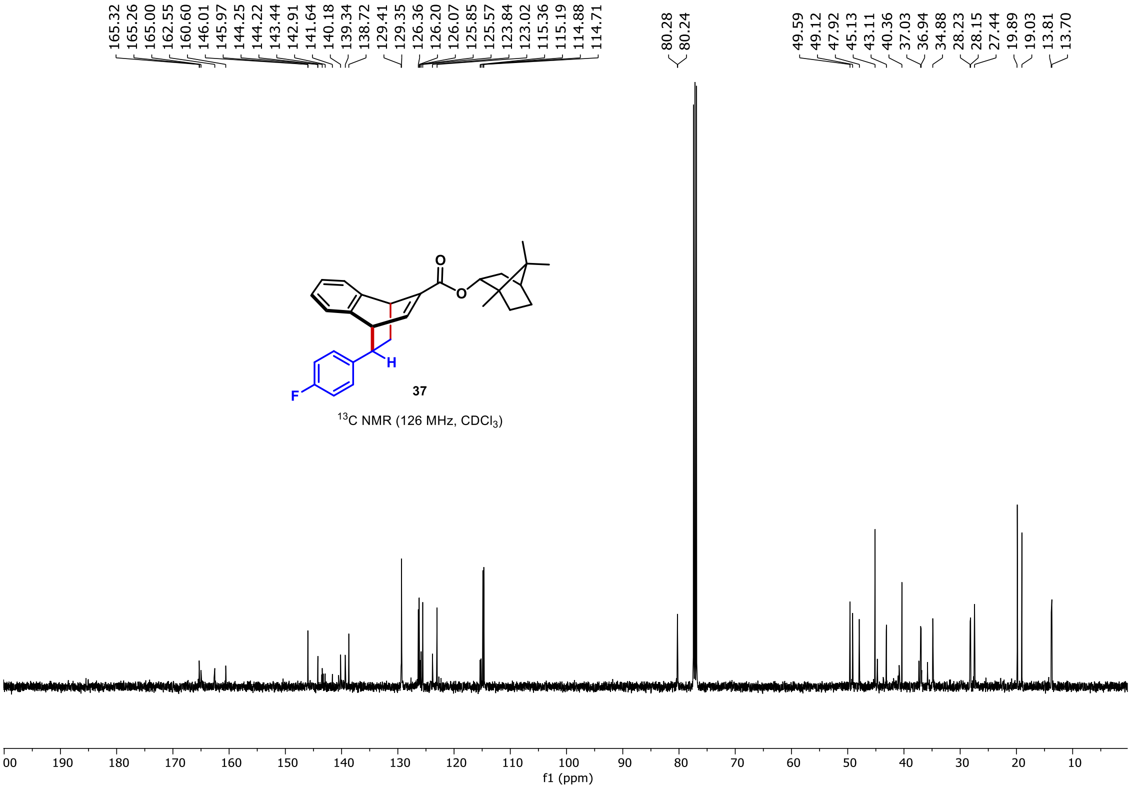

170.90
162.69
160.74
147.11
138.05
135.64
129.26
129.20
126.44
126.21
125.73
119.93
115.03
114.87
82.13
48.07
42.55
27.45
21.82
35
13C NMR (126 MHz, CDCl3)
f1 (ppm)

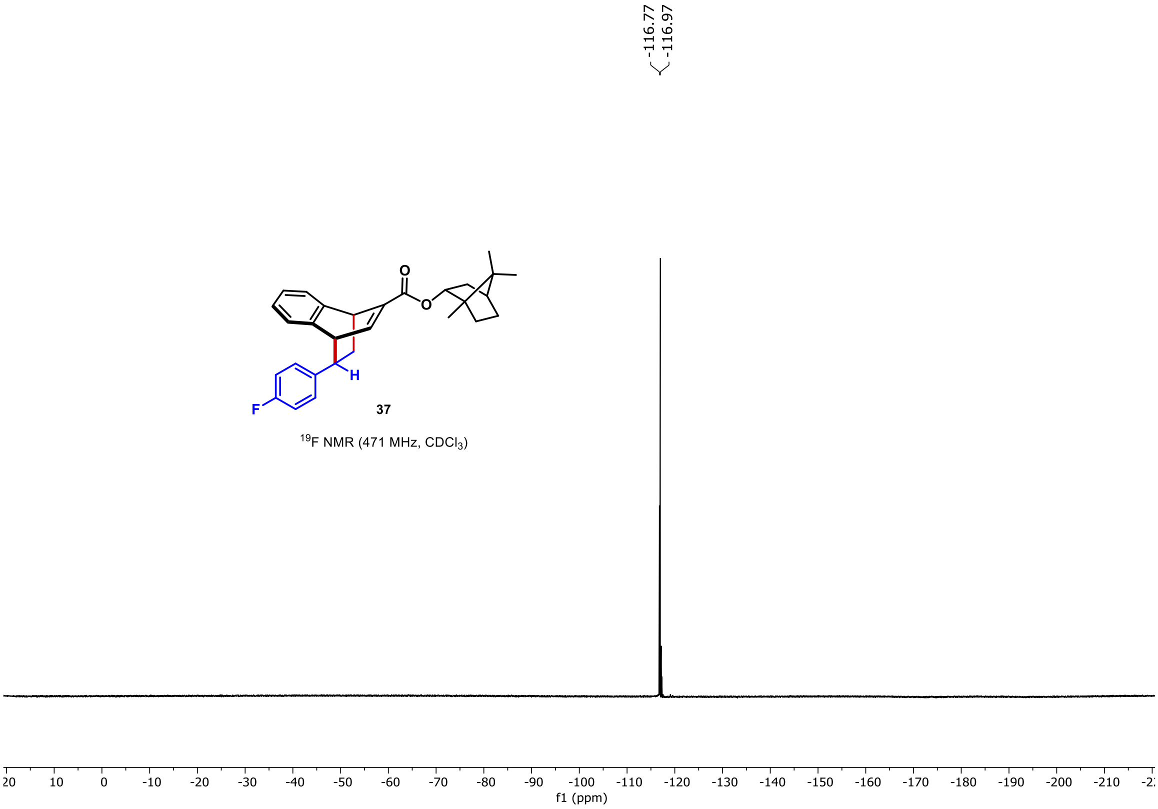

7.60 7.60 7.59 7.58 7.35 7.33 7.26 7.24 7.22 7.21 7.16 7.15 7.08 7.07 7.06 7.05 6.96 6.84 6.83 6.78 6.76 6.74 6.40 6.39 6.38 6.37 6.36 4.77 4.64 3.88 3.88 3.87 3.87 2.18 1.73 1.72 1.72 1.71 1.71 1.69 1.55 1.54 1.53 1.53 1.52 1.51 1.51 1.50 1.47 1.45 1.45 1.43 1.06 0.96 0.96 0.95 0.94 0.94 0.92 0.91 0.90 0.90 0.89 0.89 0.87 0.87 0.86 0.86 0.86 0.85 0.82 0.81 0.76 0.74 0.73
36
1H NMR (500 MHz, CDCl3)
0.61 1.40 1.00 0.58 1.40 0.58 0.60 1.40 1.34 0.91 0.85 0.41 0.61 1.00 1.00 1.06 1.00 2.02 3.01 1.03 4.04 4.06 2.96
f1 (ppm)

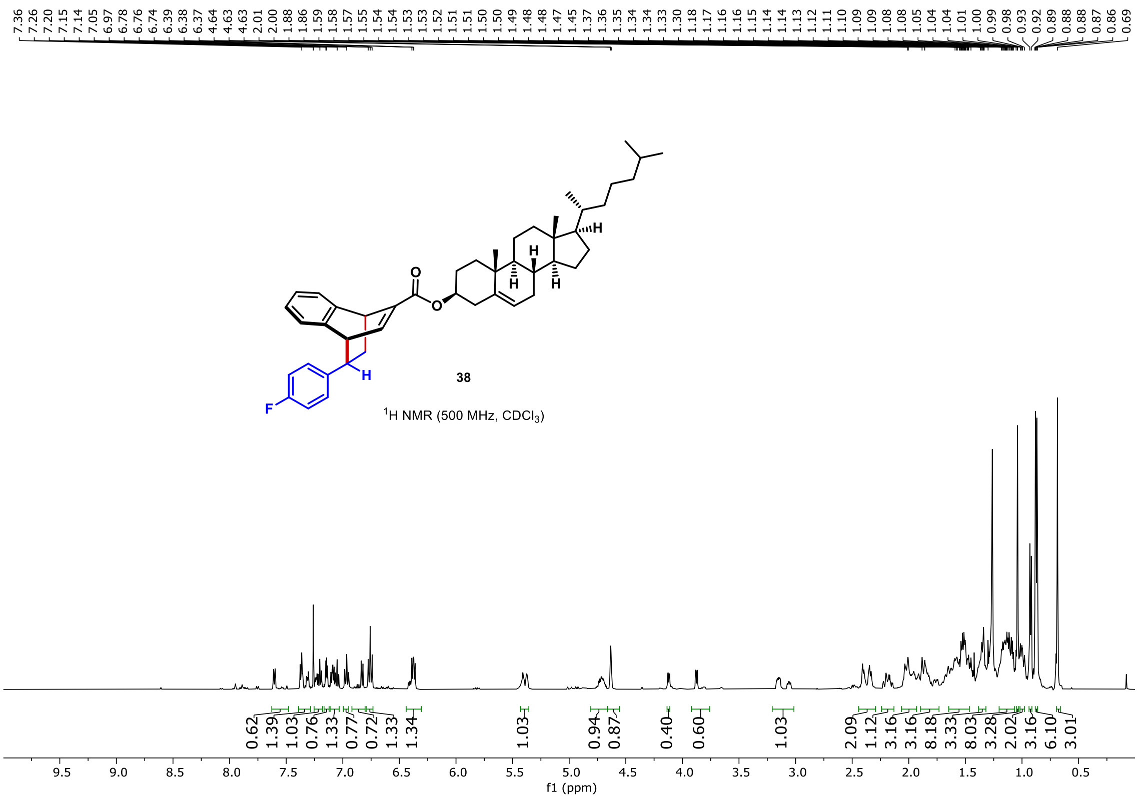

164.49
164.44
164.25
164.16
162.39
145.90
145.84
144.11
144.06
143.46
143.28
140.07
139.89
138.59
129.28
129.22
129.15
126.19
126.07
126.04
125.89
125.68
125.40
123.76
123.67
122.94
122.85
115.23
115.13
115.06
114.96
114.73
114.56
77.29
77.03
76.78
74.54
74.45
74.42
49.44
49.25
48.99
47.32
47.24
47.19
47.13
44.60
42.97
41.06
41.02
40.62
40.21
40.13
35.67
35.55
34.81
34.78
34.32
31.43
31.39
27.04
26.68
26.33
26.25
23.99
23.83
23.55
22.09
22.02
20.80
20.77
20.73
16.98
16.82
16.47
O
O
H
F
36
^{13}C NMR (126 MHz, CDCl$_3$)
f1 (ppm)

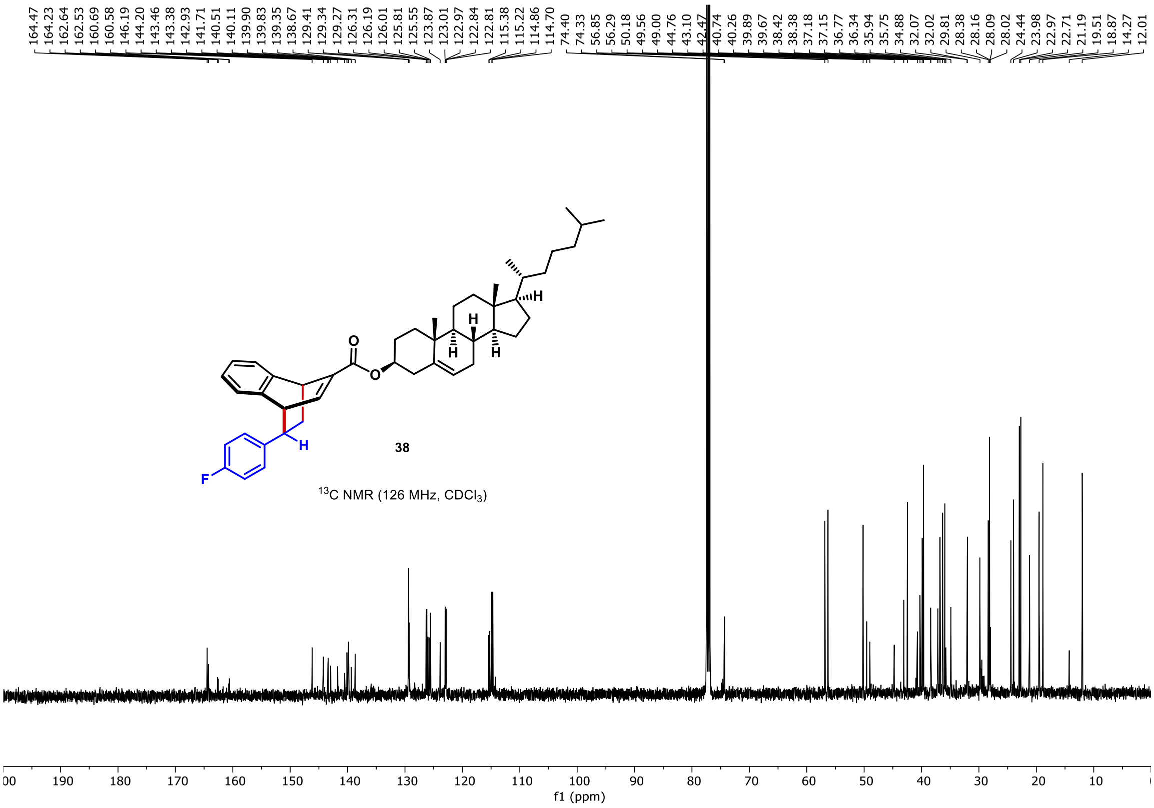

-116.77
-116.85
-117.00
-117.01
O
O
H
F
36
^{19}F NMR (471 MHz, CDCl$_3$)
f1 (ppm)


7.66 7.64 7.41 7.40 7.35 7.29 7.28 7.26 7.24 7.23 7.19 7.18 7.18 7.12 7.11 7.09 7.08 6.99 6.98 6.88 6.86 6.81 6.79 6.79 6.77 6.43 6.41 6.40 4.98 4.96 4.67 3.92 3.91 3.21 3.19 2.45 2.44 2.43 2.42 2.42 2.26 2.24 2.22 2.06 2.05 2.05 2.04 2.03 1.82 1.78 1.77 1.75 1.74 1.73 1.72 1.72 1.57 1.39 1.38 1.37 1.35 1.33 1.33 1.32 1.30 1.29 1.11 1.09 0.97 0.96 0.93 0.93 0.92 0.86 0.85
O
O
H
F
37
^{1}H NMR (500 MHz, $CDCl_3$)
0.73 0.81 0.32 2.87 0.50 2.30 1.51 1.01 0.81 0.29 0.70 1.00 1.03 1.10 0.98 2.31 0.75 2.80 0.35 3.13 6.18
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)


165.32 165.26 165.00 162.55 160.60 146.01 145.97 144.25 144.22 143.44 142.91 141.64 140.18 139.34 138.72 129.41 129.35 126.36 126.20 126.07 125.85 125.57 123.84 123.02 115.36 115.19 114.88 114.71
80.28 80.24
49.59 49.12 47.92 45.13 43.11 40.36 37.03 36.94 34.88 28.23 28.15 27.44 19.89 19.03 13.81 13.70
O
O
H
F
37
^{13}C NMR (126 MHz, $CDCl_3$)
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


-116.77
-116.97
37
19F NMR (471 MHz, CDCl3)
f1 (ppm)


7.36 7.26 7.20 7.15 7.14 7.05 6.97 6.78 6.76 6.74 6.39 6.38 6.37 4.64 4.63 2.01 2.00 1.88 1.86 1.59 1.58 1.57 1.55 1.54 1.54 1.53 1.53 1.51 1.51 1.50 1.49 1.48 1.48 1.47 1.45 1.37 1.36 1.35 1.34 1.34 1.33 1.30 1.18 1.17 1.16 1.15 1.14 1.14 1.13 1.12 1.11 1.10 1.09 1.09 1.08 1.08 1.05 1.04 1.04 1.01 1.00 0.99 0.98 0.93 0.92 0.89 0.88 0.88 0.87 0.86 0.69
38
1H NMR (500 MHz, CDCl3)
0.62 1.39 1.03 0.76 1.33 0.77 0.72 1.33 1.34 1.03 0.94 0.87 0.40 0.60 1.03 2.09 1.12 3.16 3.16 8.18 3.33 8.03 3.28 2.02 3.16 6.10 3.01
f1 (ppm)


164.47
164.23
162.64
162.53
160.69
160.58
146.19
144.20
143.46
143.38
142.93
141.71
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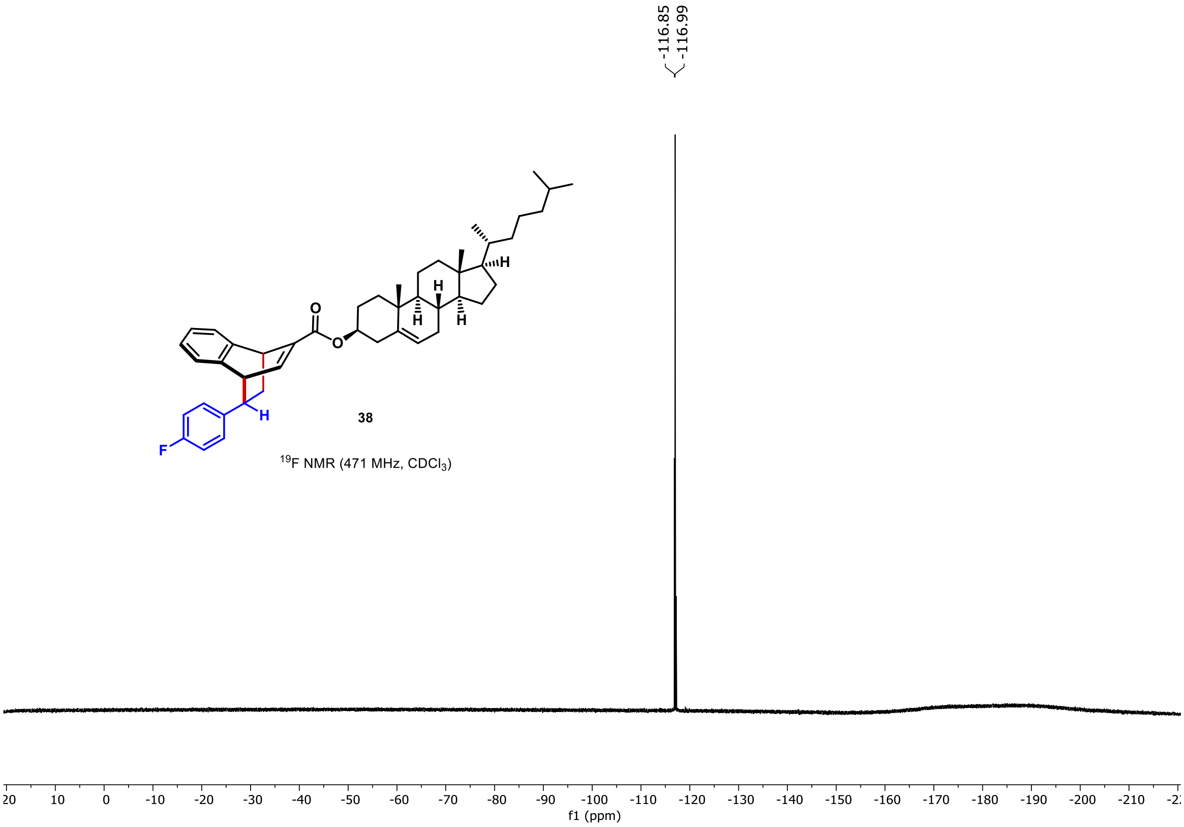
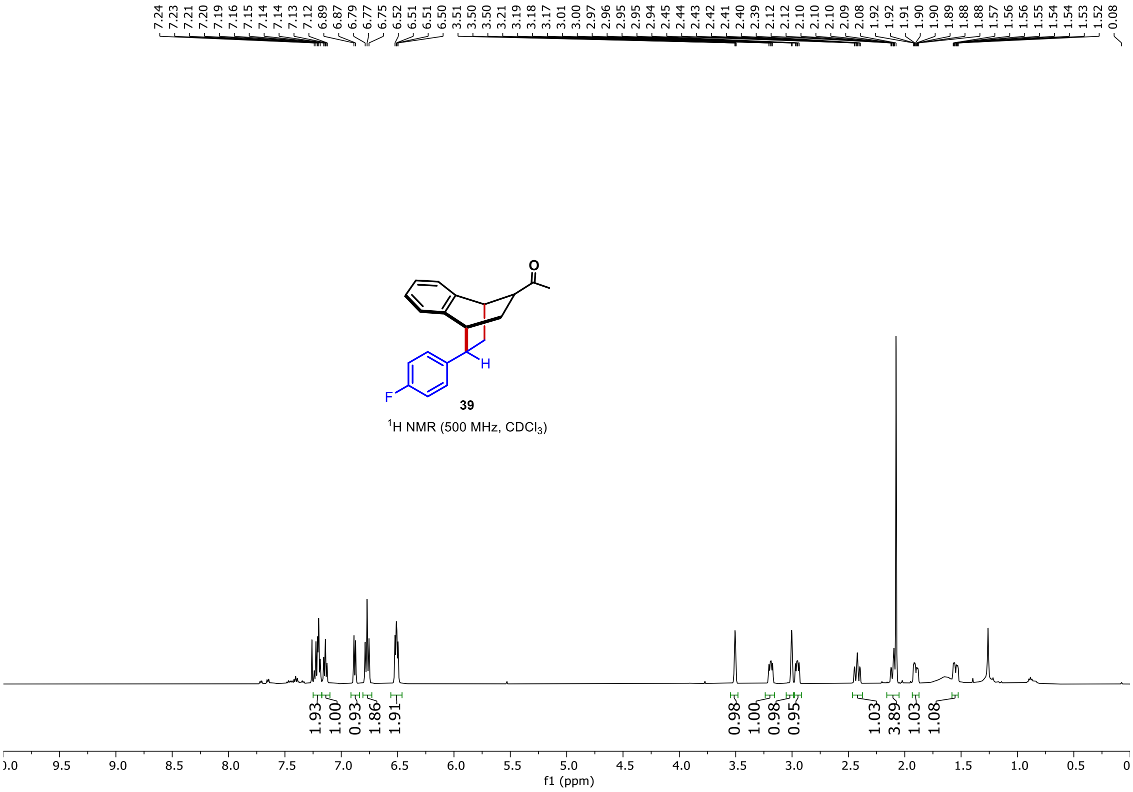
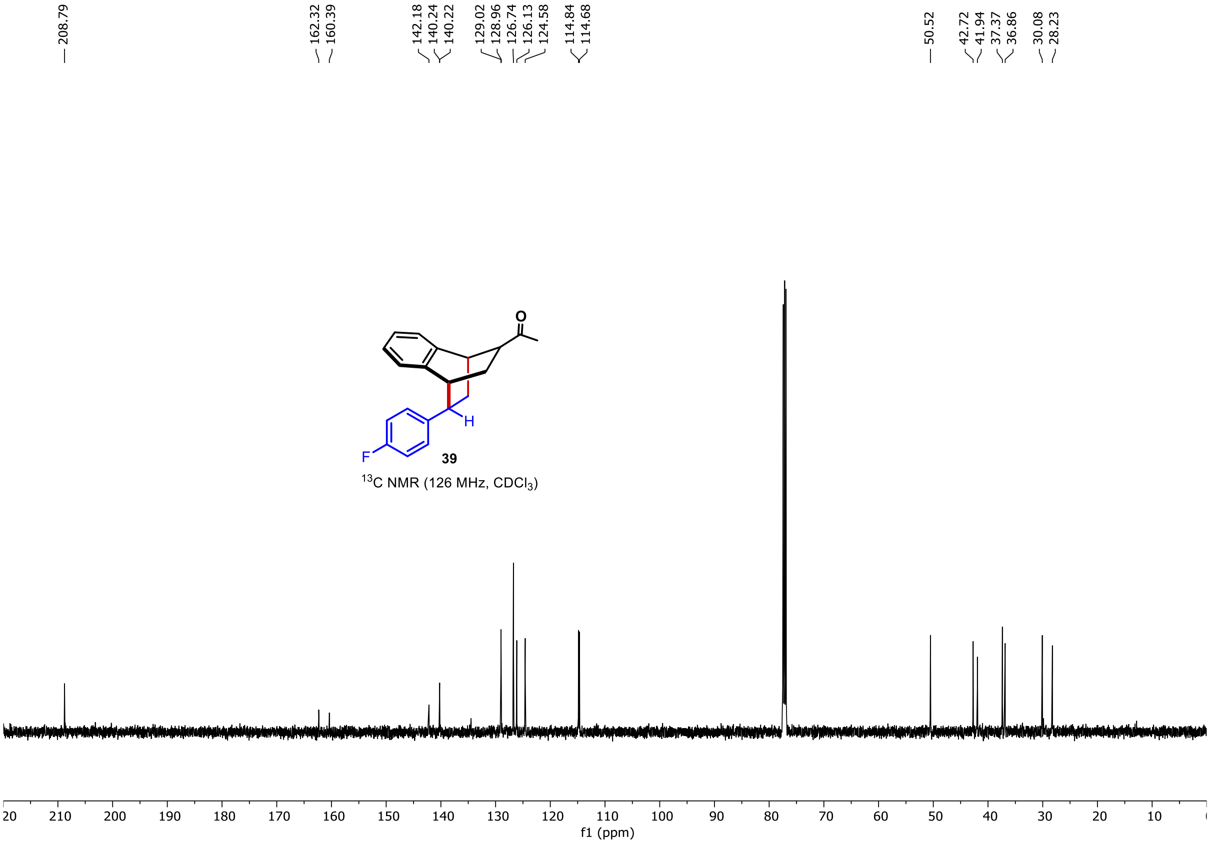
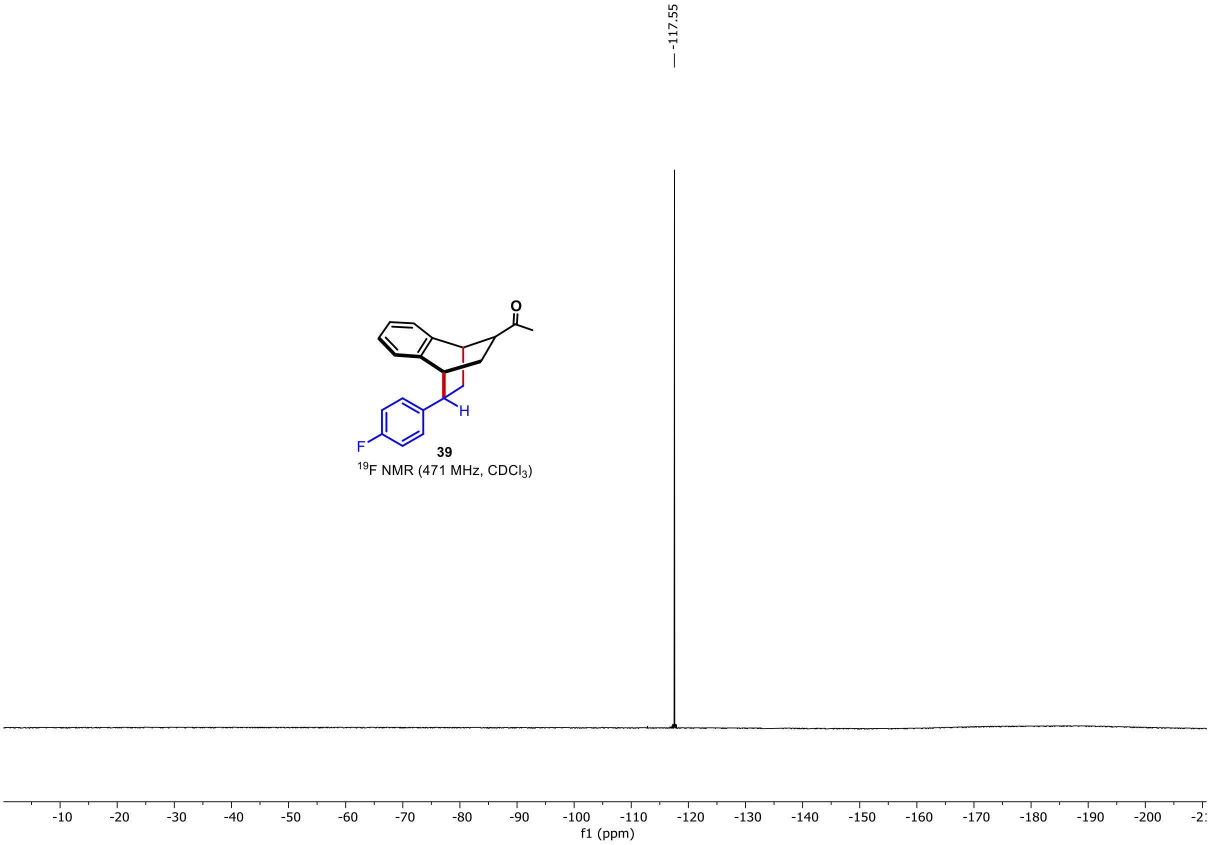
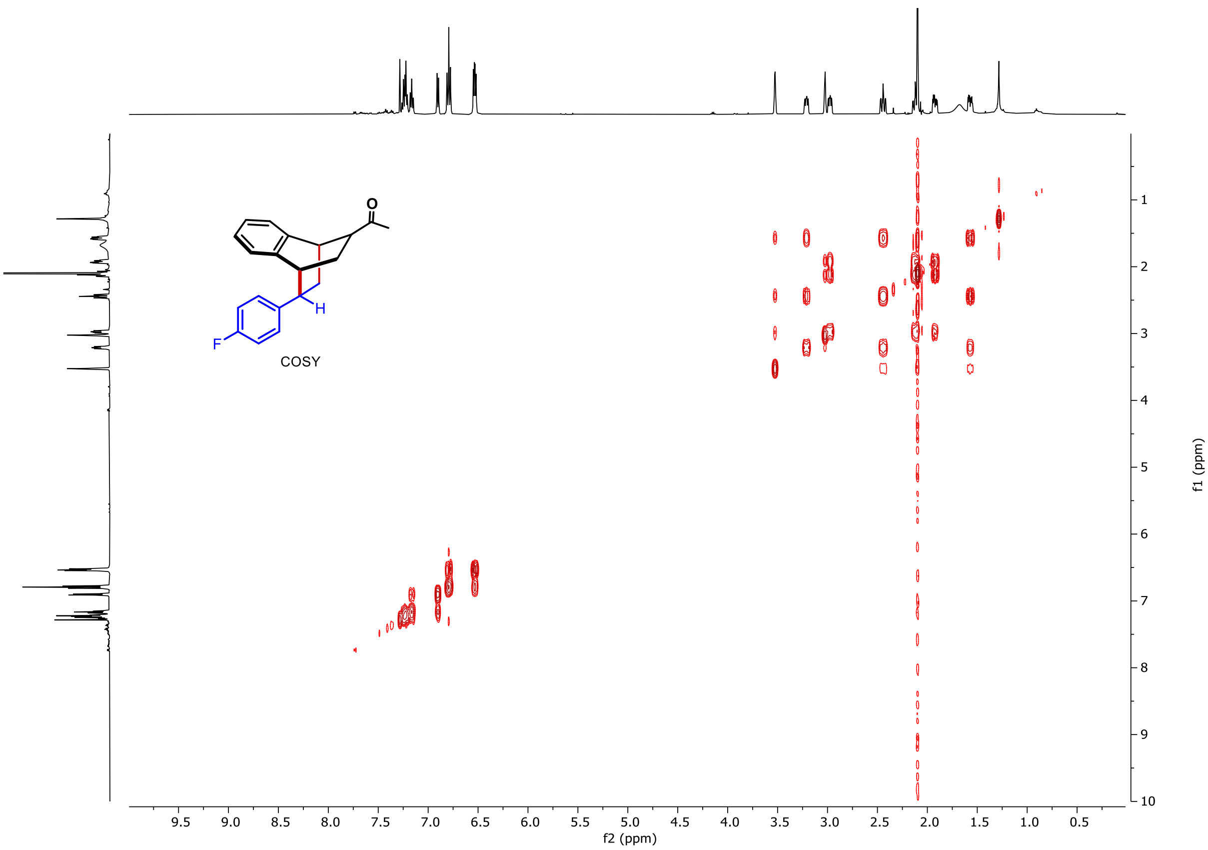
140.11
139.90
139.83
139.35
138.67
129.41
129.34
129.27
126.31
126.19
126.01
125.81
125.55
123.87
123.01
122.97
122.84
122.81
115.38
115.22
114.86
114.70
74.40
74.33
56.85
56.29
50.18
49.56
49.00
44.76
43.10
42.47
40.74
40.26
39.89
39.67
38.42
38.38
37.18
37.15
36.77
36.34
35.94
35.75
34.88
32.07
32.02
29.81
28.38
28.16
28.09
28.02
24.44
23.98
22.97
22.71
21.19
19.51
18.87
14.27
12.01
38
^{13}C NMR (126 MHz, CDCl$_3$)
f1 (ppm)

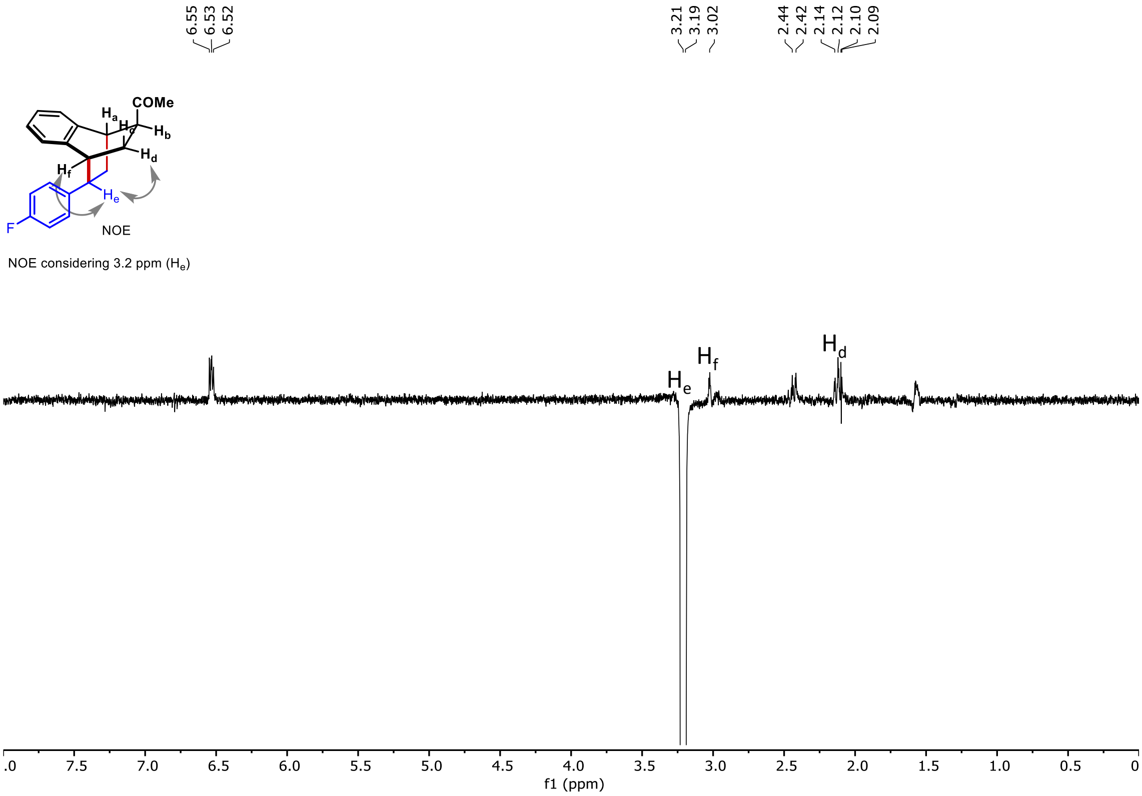

-116.85
-116.99
38
^{19}F NMR (471 MHz, CDCl$_3$)
f1 (ppm)


7.24 7.23 7.21 7.20 7.19 7.16 7.15 7.14 7.14 7.13 7.12 6.89 6.87 6.79 6.77 6.75 6.52 6.51 6.51 6.50 3.51 3.50 3.50 3.21 3.19 3.18 3.17 3.01 3.00 2.97 2.96 2.95 2.95 2.94 2.45 2.44 2.43 2.42 2.41 2.40 2.39 2.12 2.12 2.10 2.10 2.10 2.09 2.08 1.92 1.92 1.91 1.90 1.90 1.89 1.88 1.88 1.57 1.56 1.56 1.55 1.54 1.54 1.53 1.52 0.08
O
H
F
39
1H NMR (500 MHz, CDCl3)
1.93 1.00 0.93 1.86 1.91
0.98 1.00 0.98 0.95
1.03 3.89 1.03 1.08
f1 (ppm)

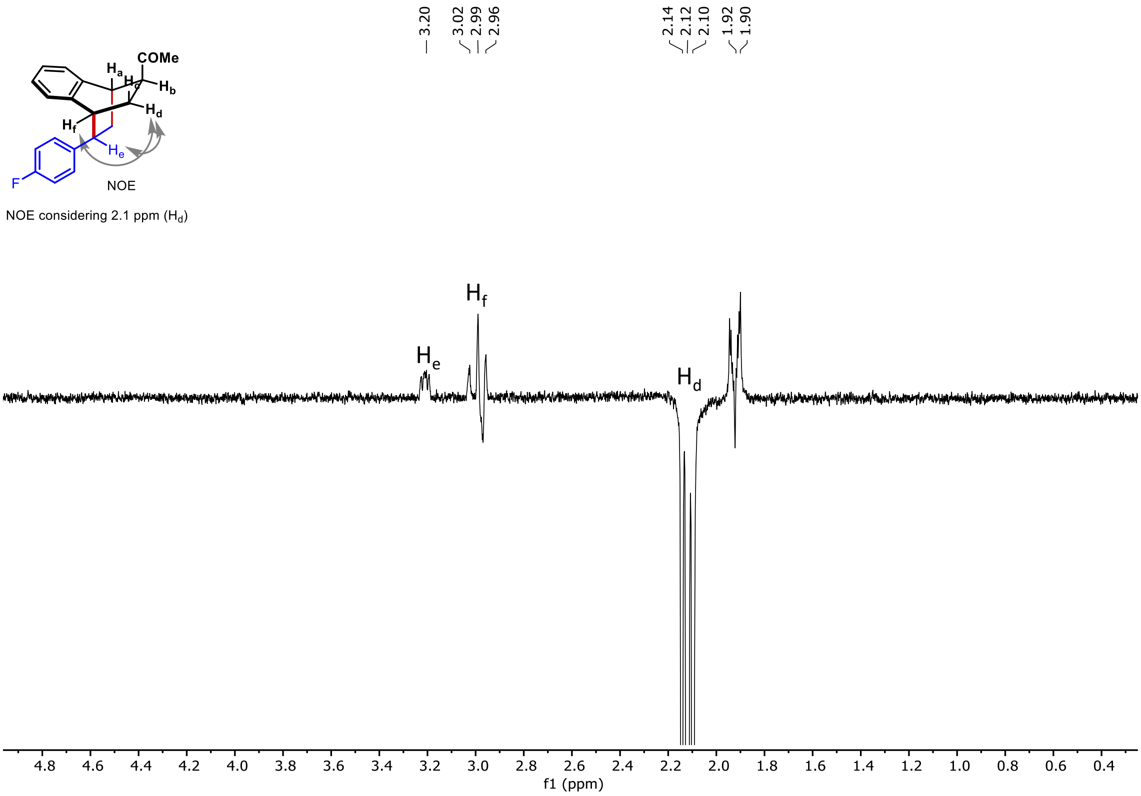

208.79
162.32 160.39
142.18 140.24 140.22
129.02 128.96 126.74 126.13 124.58
114.84 114.68
50.52
42.72 41.94 37.37 36.86 30.08 28.23
O
H
F
39
13C NMR (126 MHz, CDCl3)
f1 (ppm)


-117.55
39
19F NMR (471 MHz, CDCl3)
f1 (ppm)

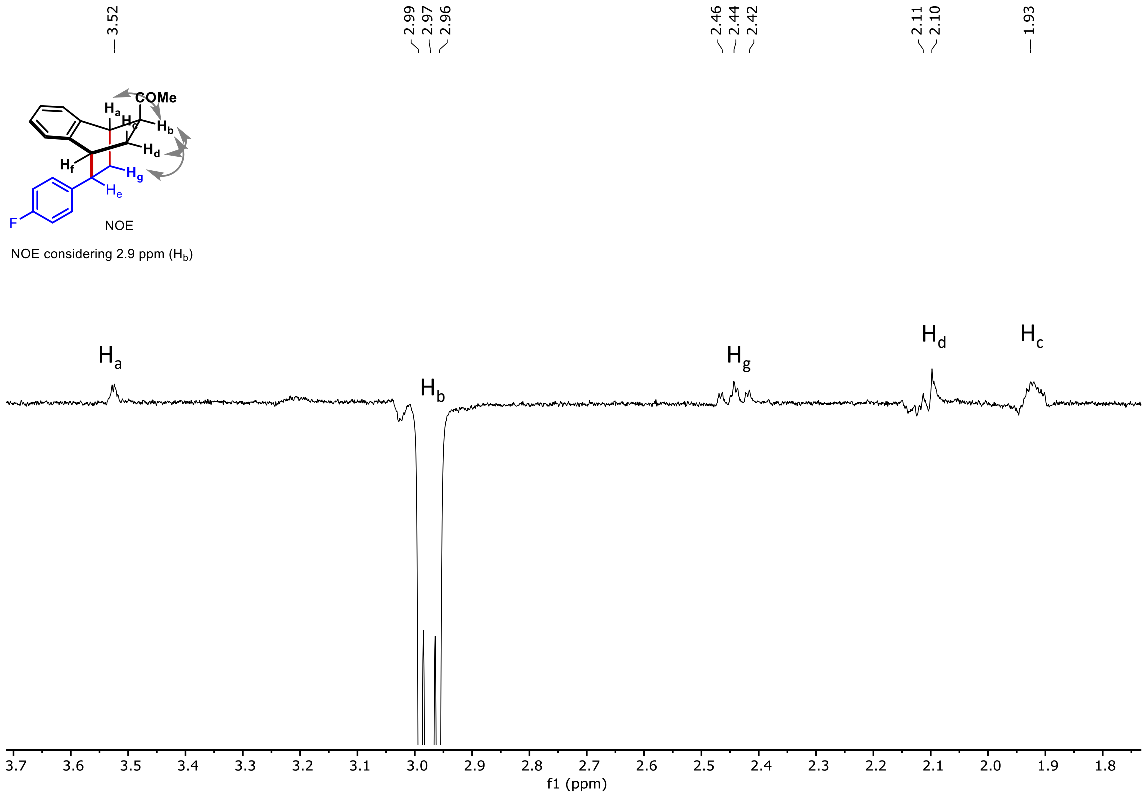

COSY
f2 (ppm)
f1 (ppm)

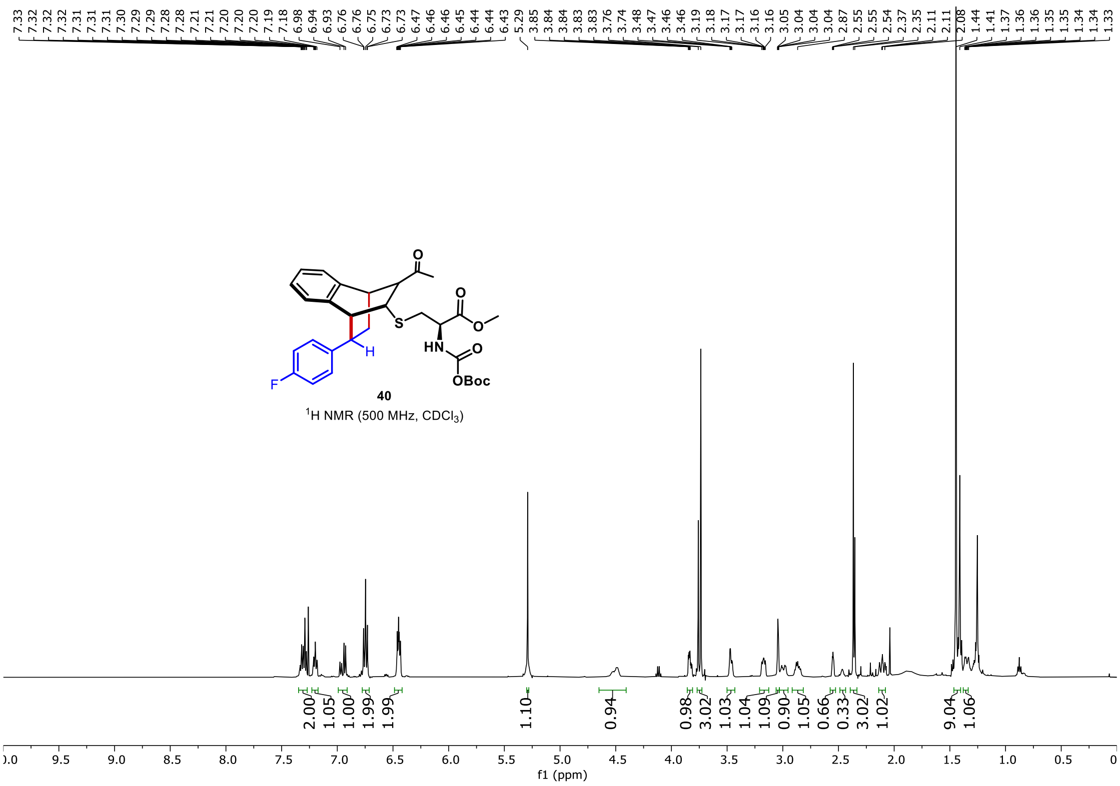


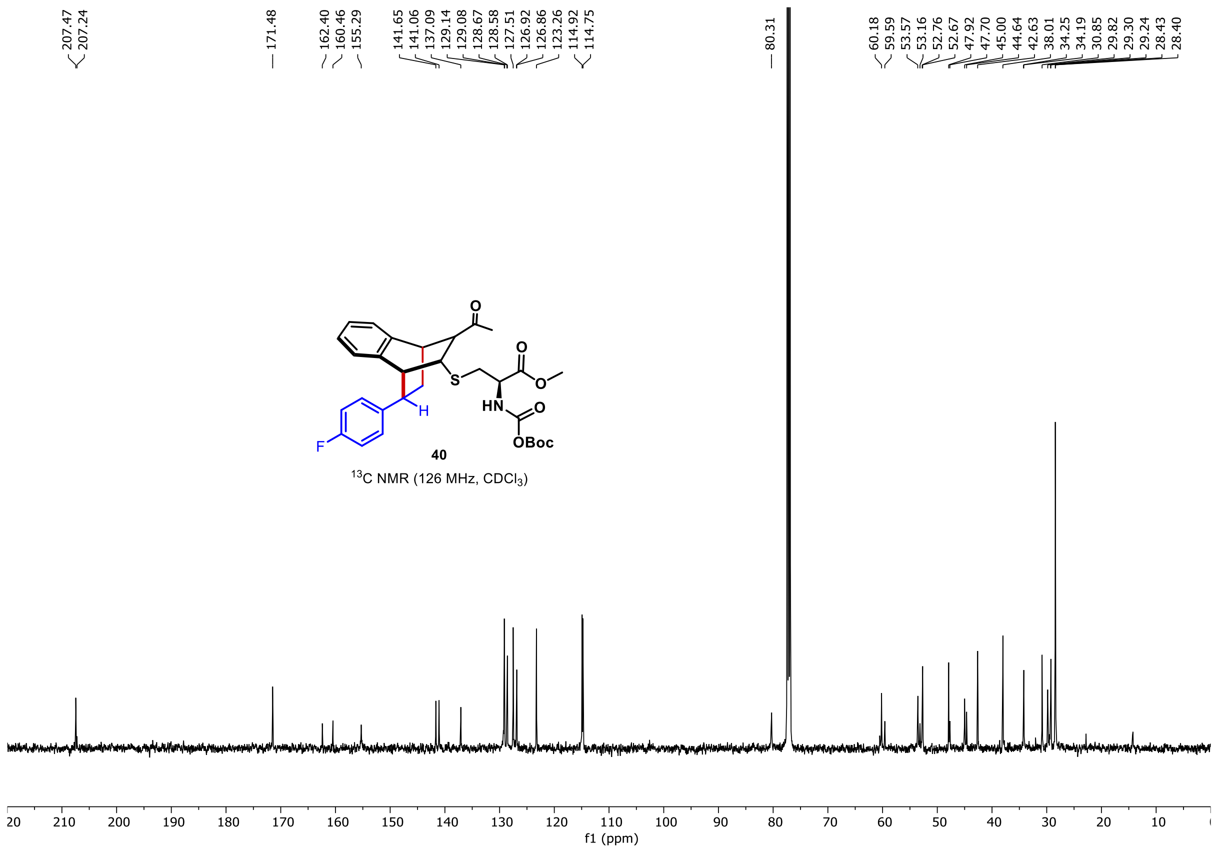
NOE considering 3.2 ppm (H_e)



NOE considering 2.1 ppm (H_d)

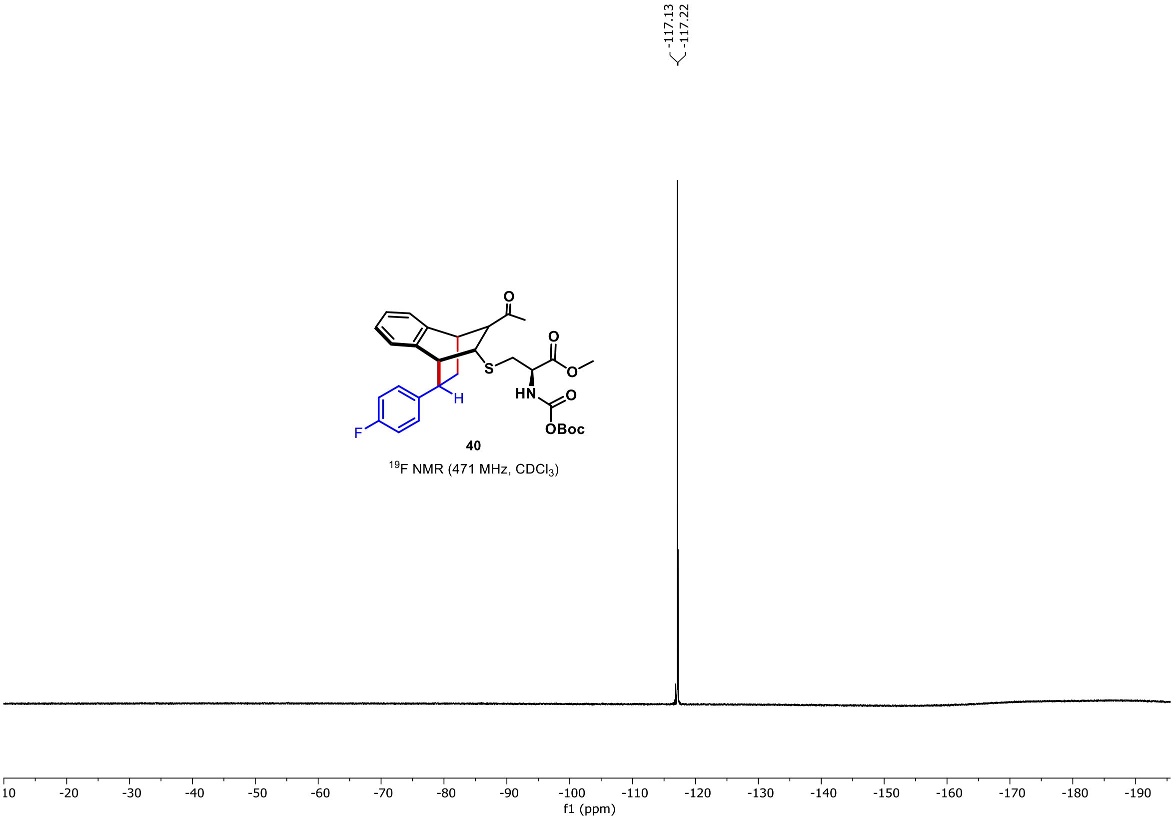

COMe
Ha
Hb
Hd
Hf
Hg
He
F
NOE
NOE considering 2.9 ppm (Hb)
Ha
Hb
Hg
Hd
Hc
f1 (ppm)

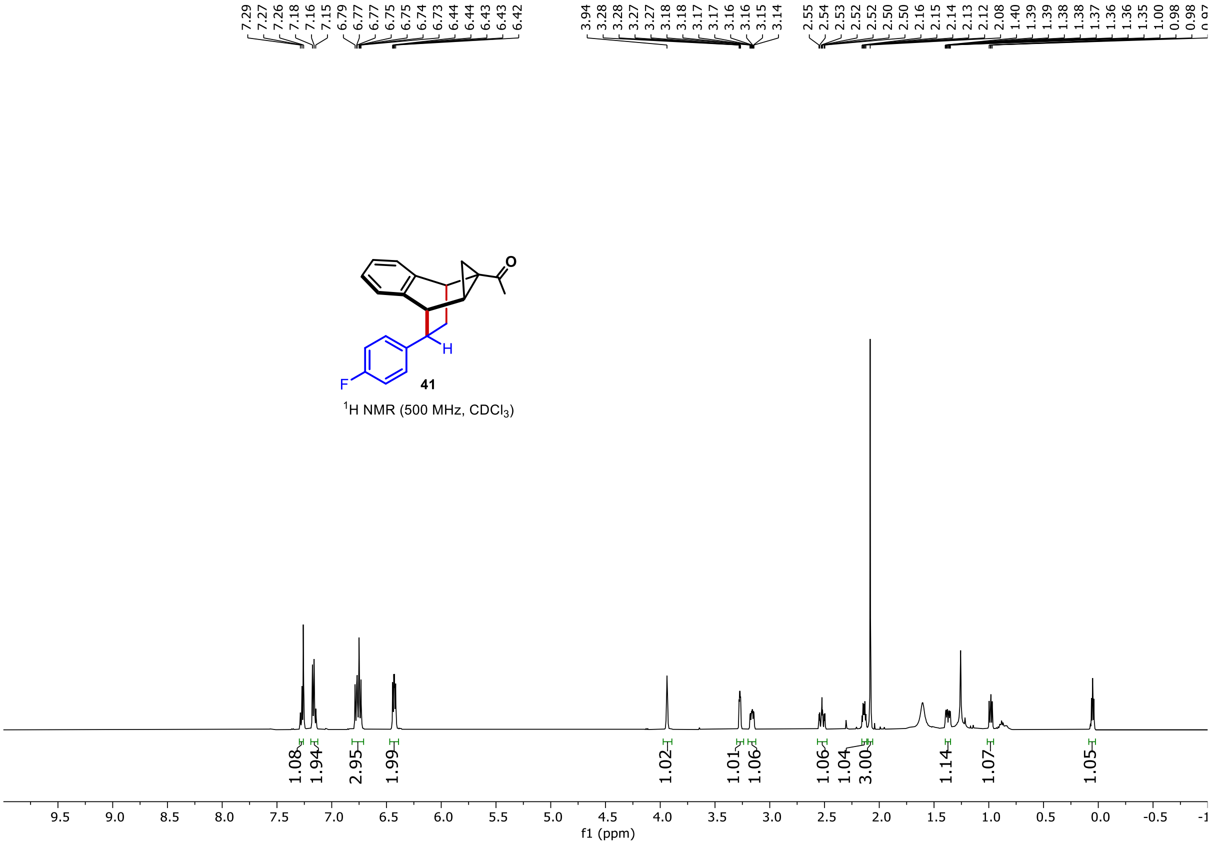

S
HN
OBoc
F
H
40
1H NMR (500 MHz, CDCl3)
f1 (ppm)

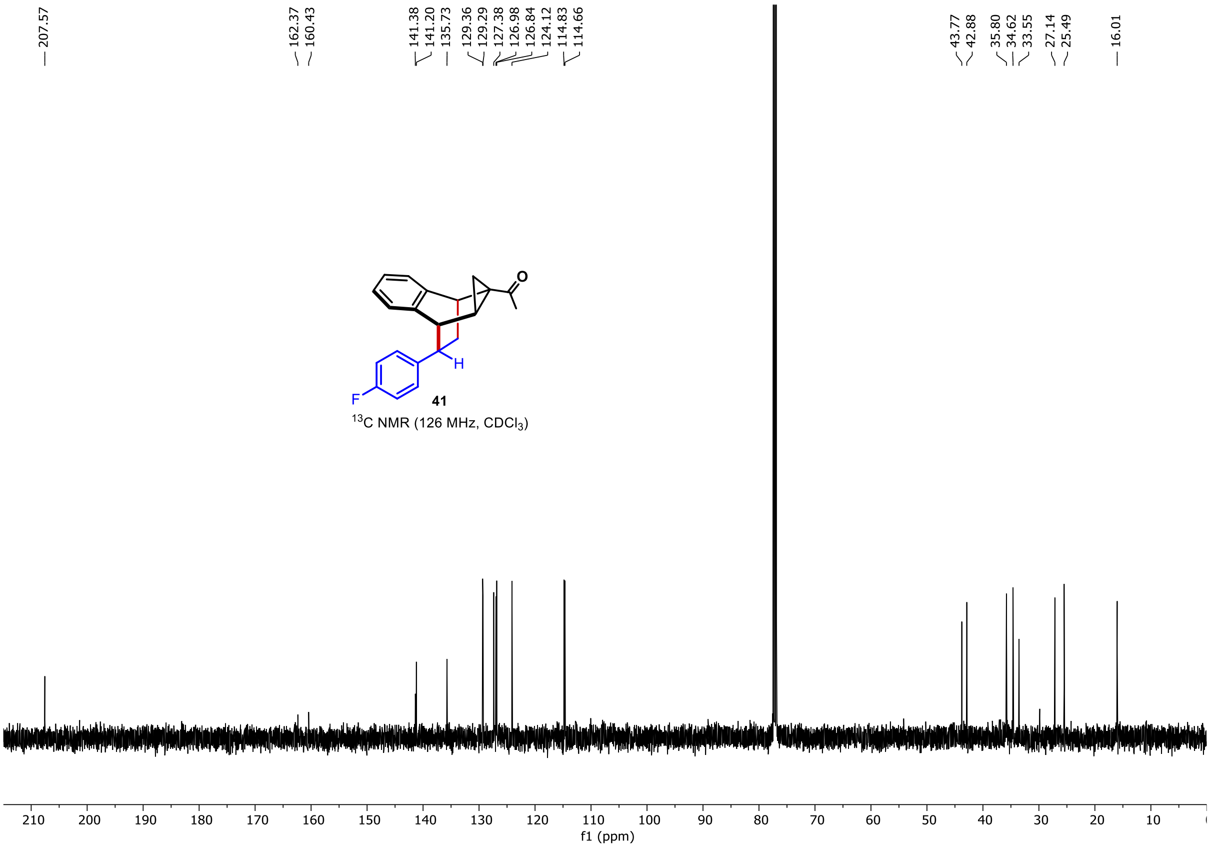


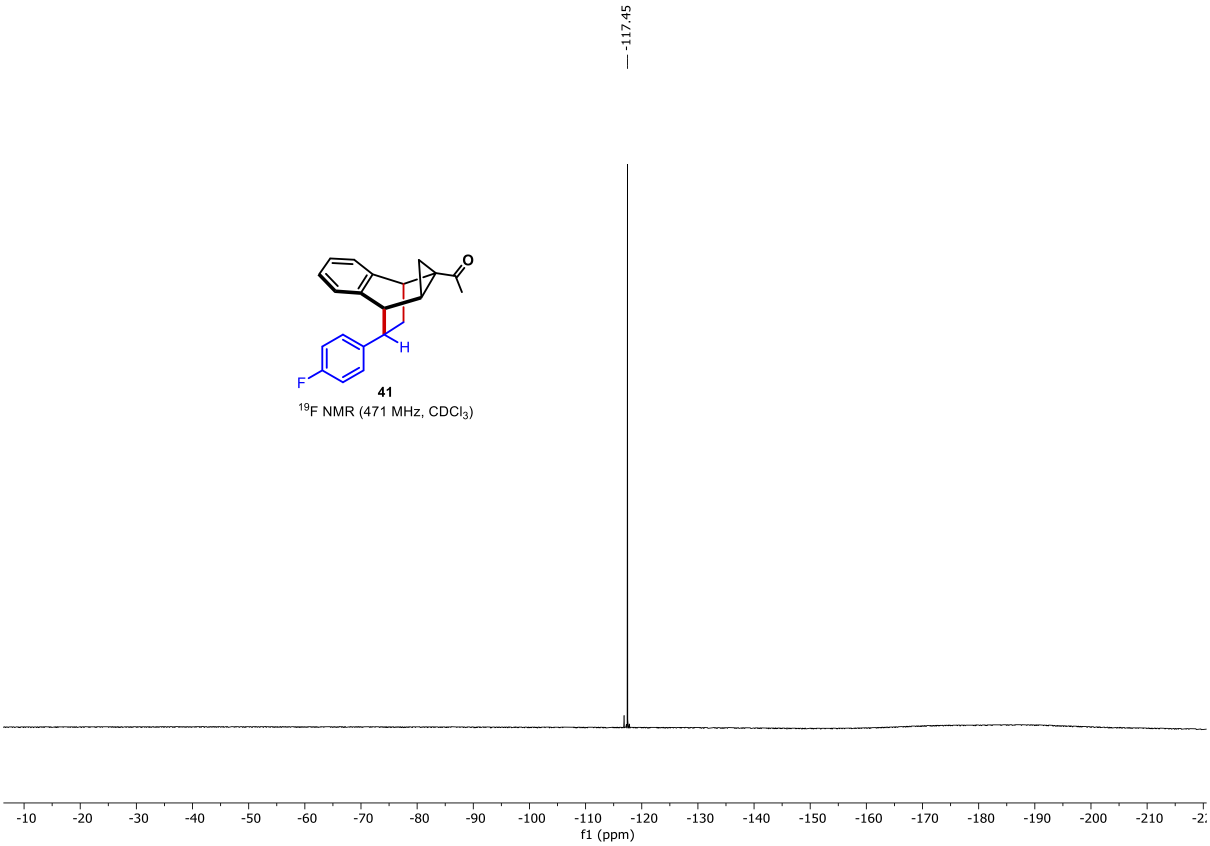
40

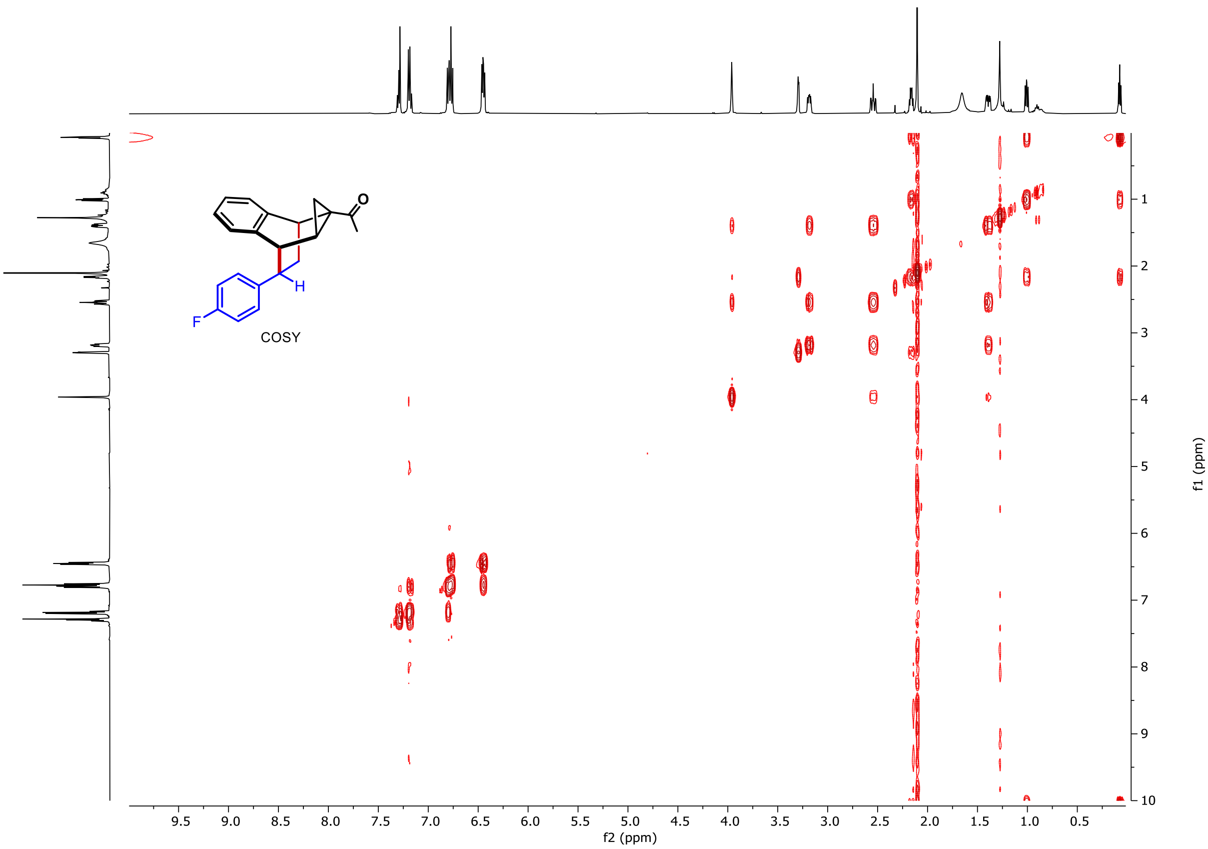
^{13}C NMR (126 MHz, $CDCl_3$)

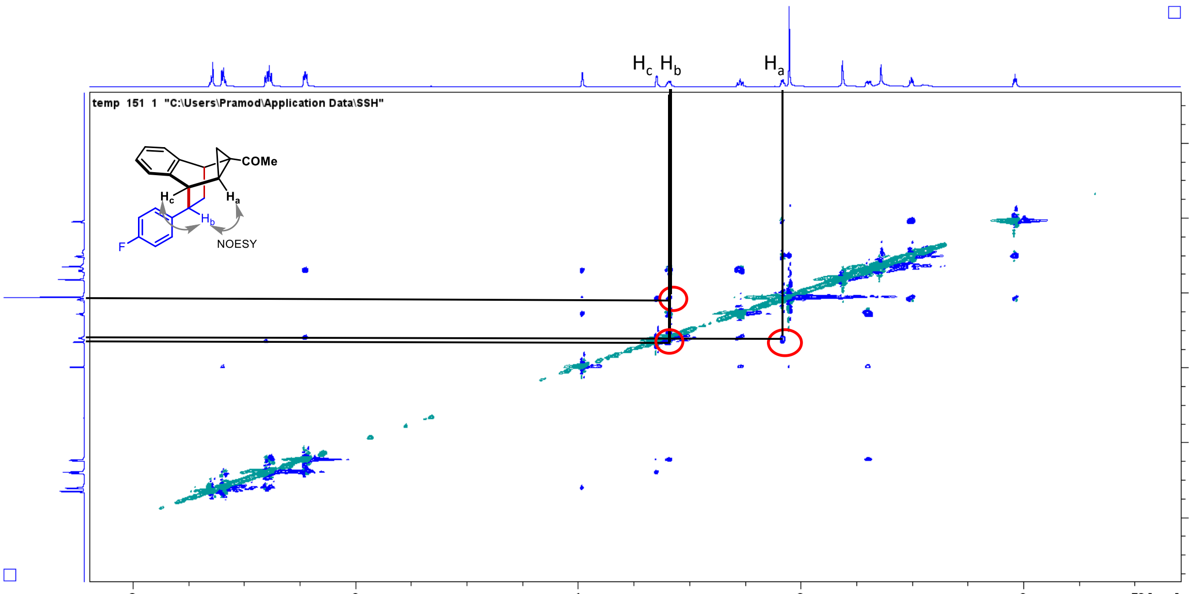

-117.13
-117.22
40
^{19}F NMR (471 MHz, CDCl$_3$)
f1 (ppm)

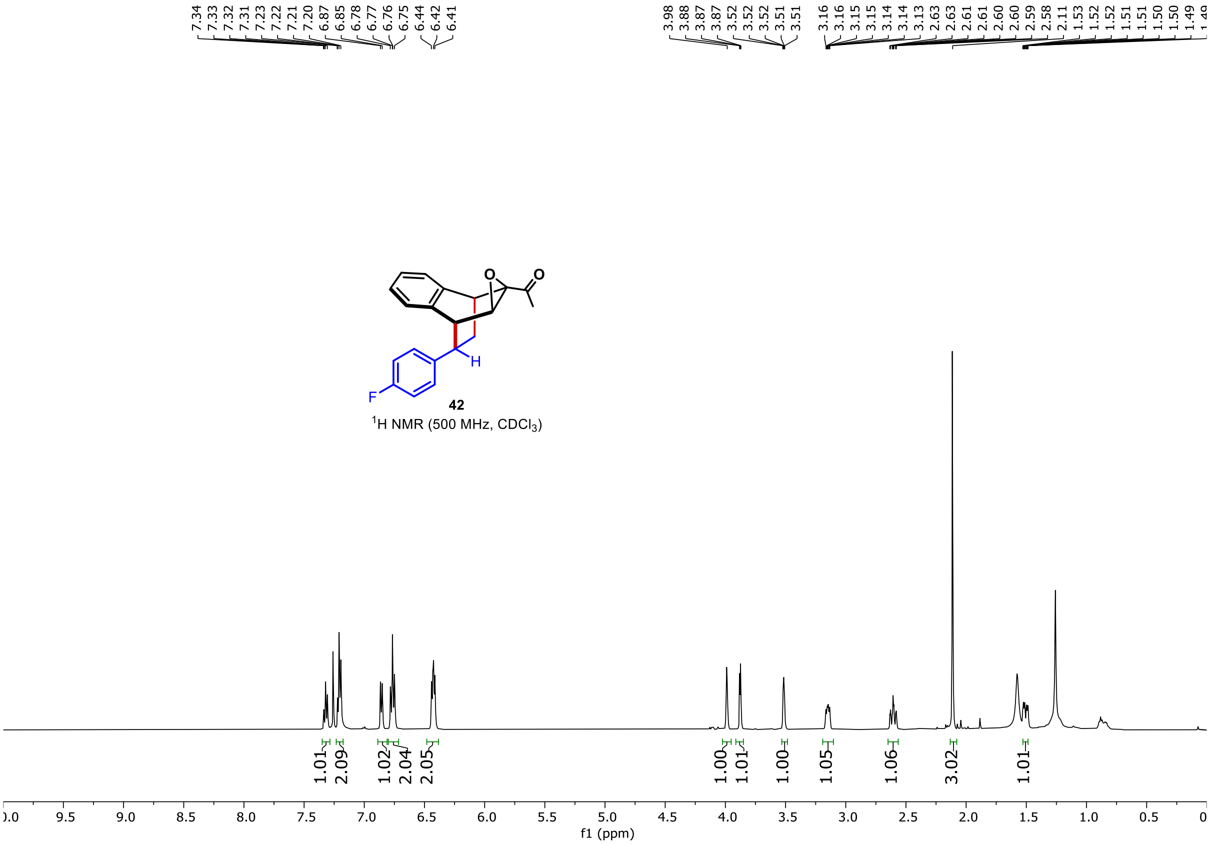

7.29 7.27 7.26 7.18 7.16 7.15 6.79 6.77 6.77 6.75 6.75 6.74 6.73 6.44 6.44 6.43 6.43 6.42
3.94 3.28 3.28 3.27 3.27 3.18 3.18 3.17 3.17 3.16 3.16 3.15 3.14
2.55 2.54 2.53 2.52 2.52 2.50 2.50 2.16 2.15 2.14 2.13 2.12 2.08 1.40 1.39 1.39 1.38 1.38 1.37 1.36 1.36 1.35 1.00 0.98 0.98
41
^{1}H NMR (500 MHz, CDCl$_3$)
1.08 1.94 2.95 1.99 1.02 1.01 1.06 1.06 1.04 3.00 1.14 1.07 1.05
f1 (ppm)

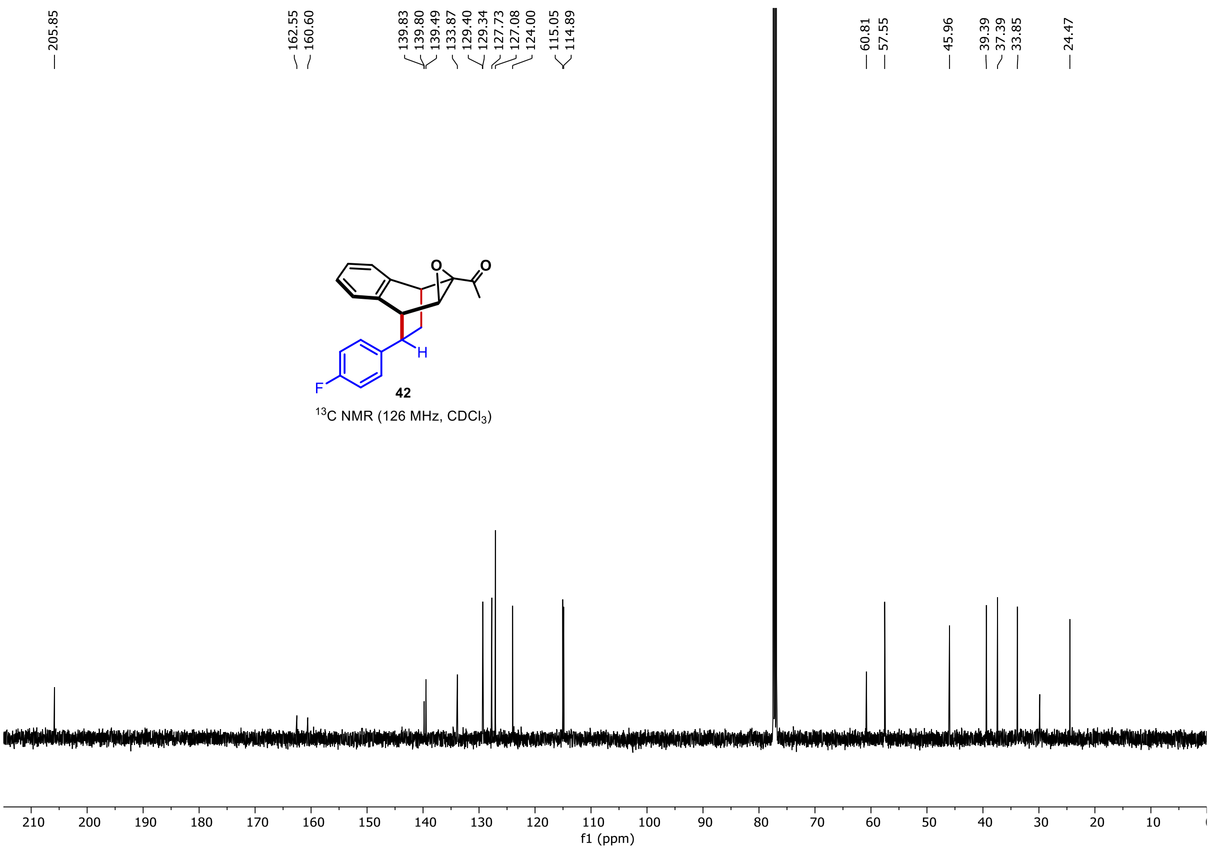

207.57
162.37
160.43
141.38
141.20
135.73
129.36
129.29
127.38
126.98
126.84
124.12
114.83
114.66
43.77
42.88
35.80
34.62
33.55
27.14
25.49
16.01
O
H
F
41
^{13}C NMR (126 MHz, CDCl$_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

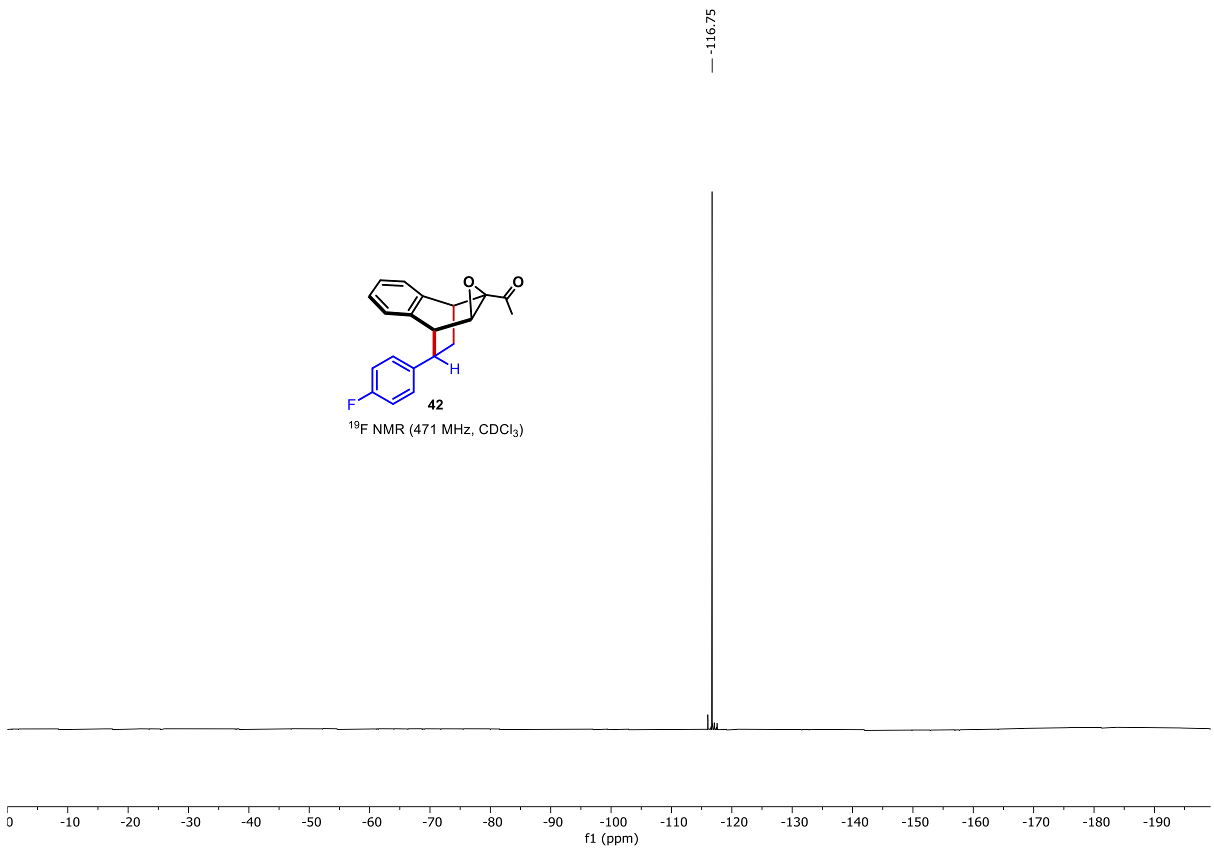

-117.45
O
H
F
41
^{19}F NMR (471 MHz, CDCl$_3$)
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

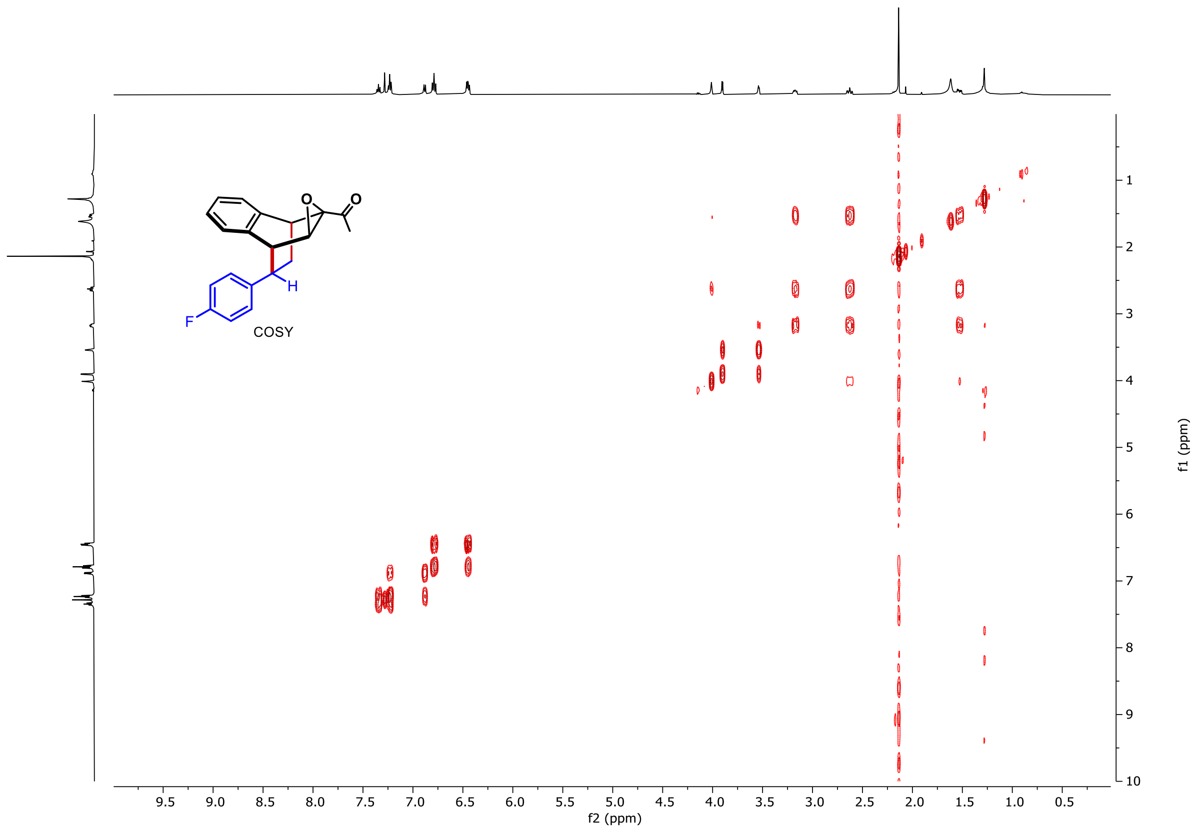

COSY
f2 (ppm)
f1 (ppm)

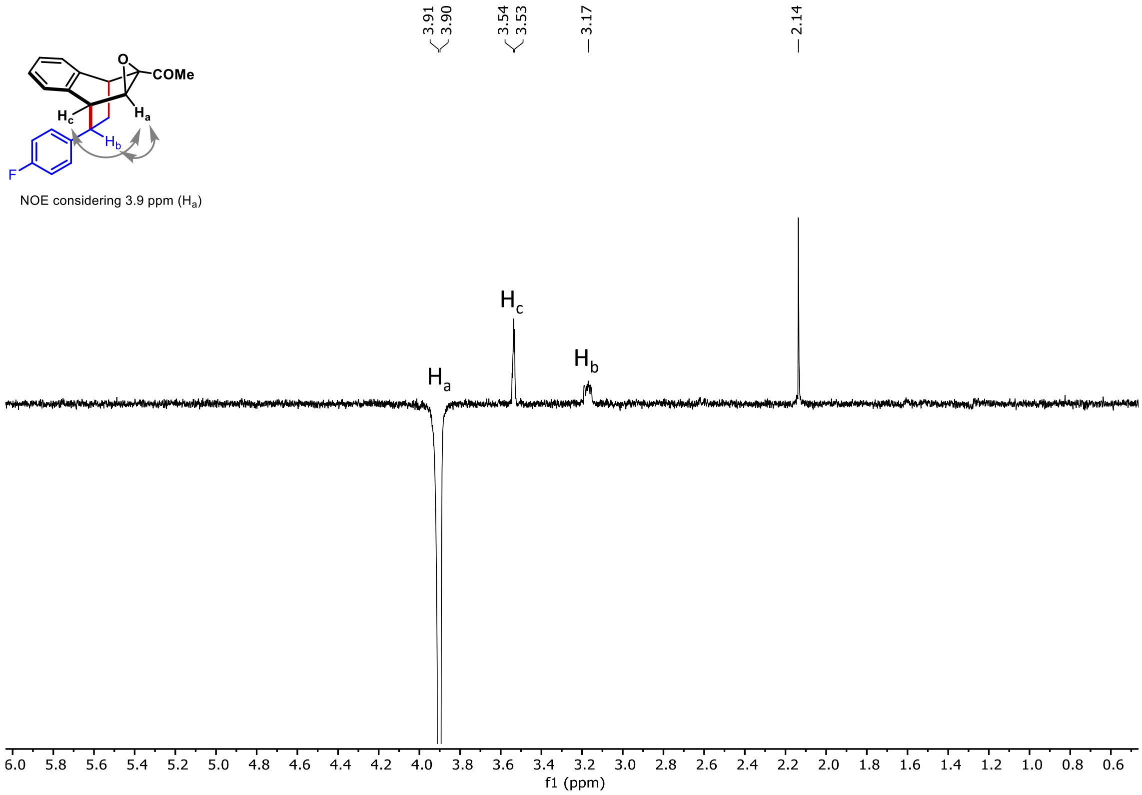

Hc Hb
Ha
temp 151 1 "C:\Users\Pramod\Application Data\SSH"
COMe
NOESY
F2 [ppm]
F1 [ppm]

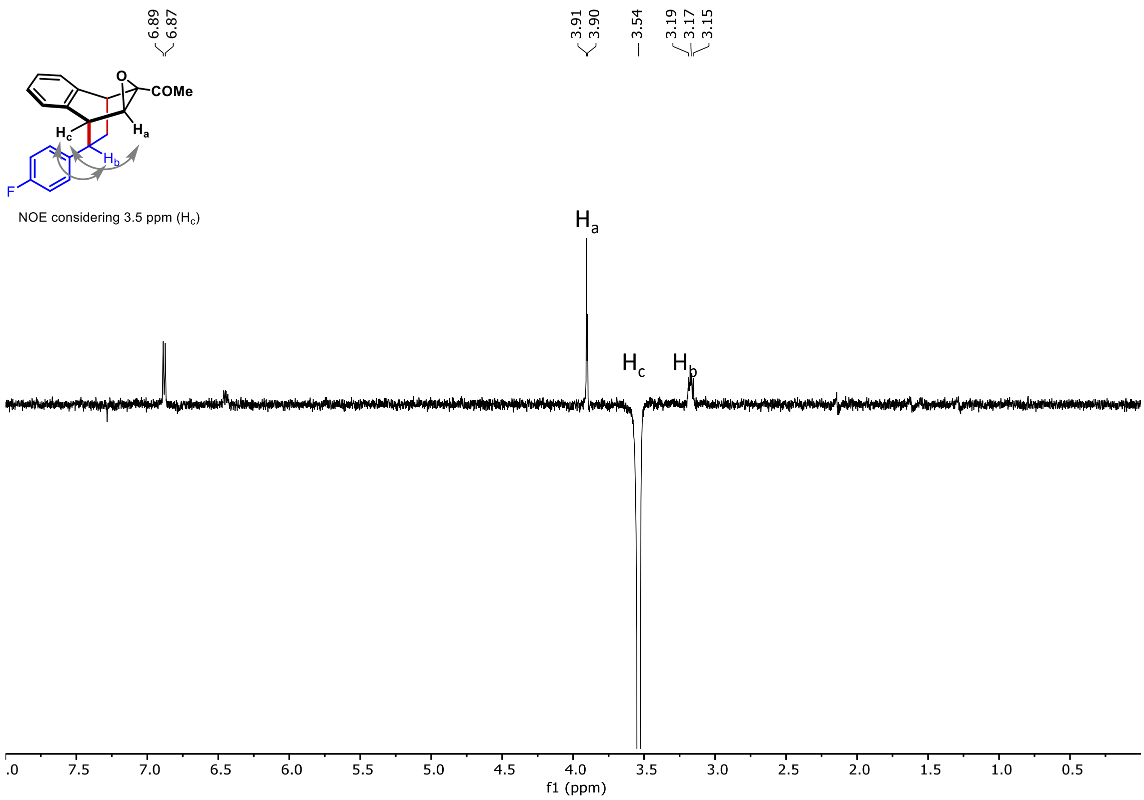

42
^{1}H NMR (500 MHz, CDCl$_3$)

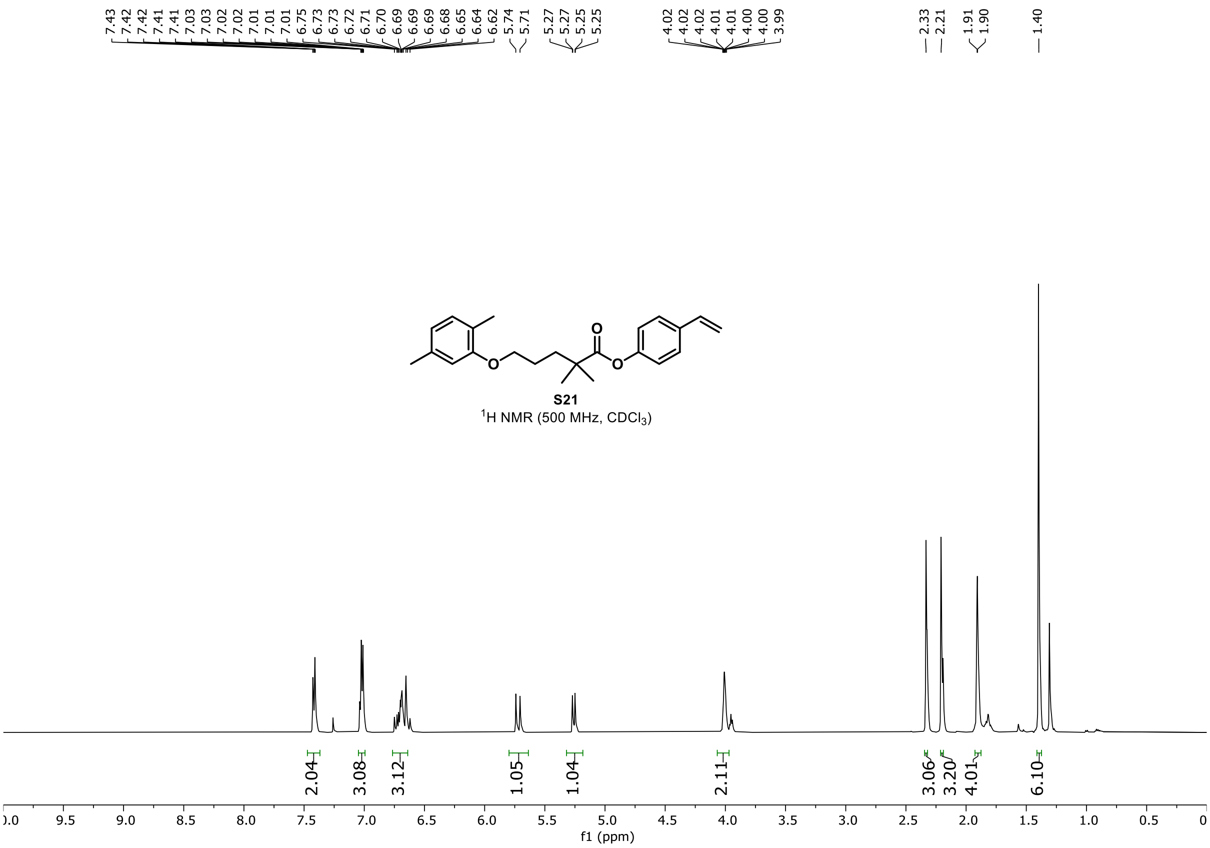

42
^{13}C NMR (126 MHz, CDCl$_3$)

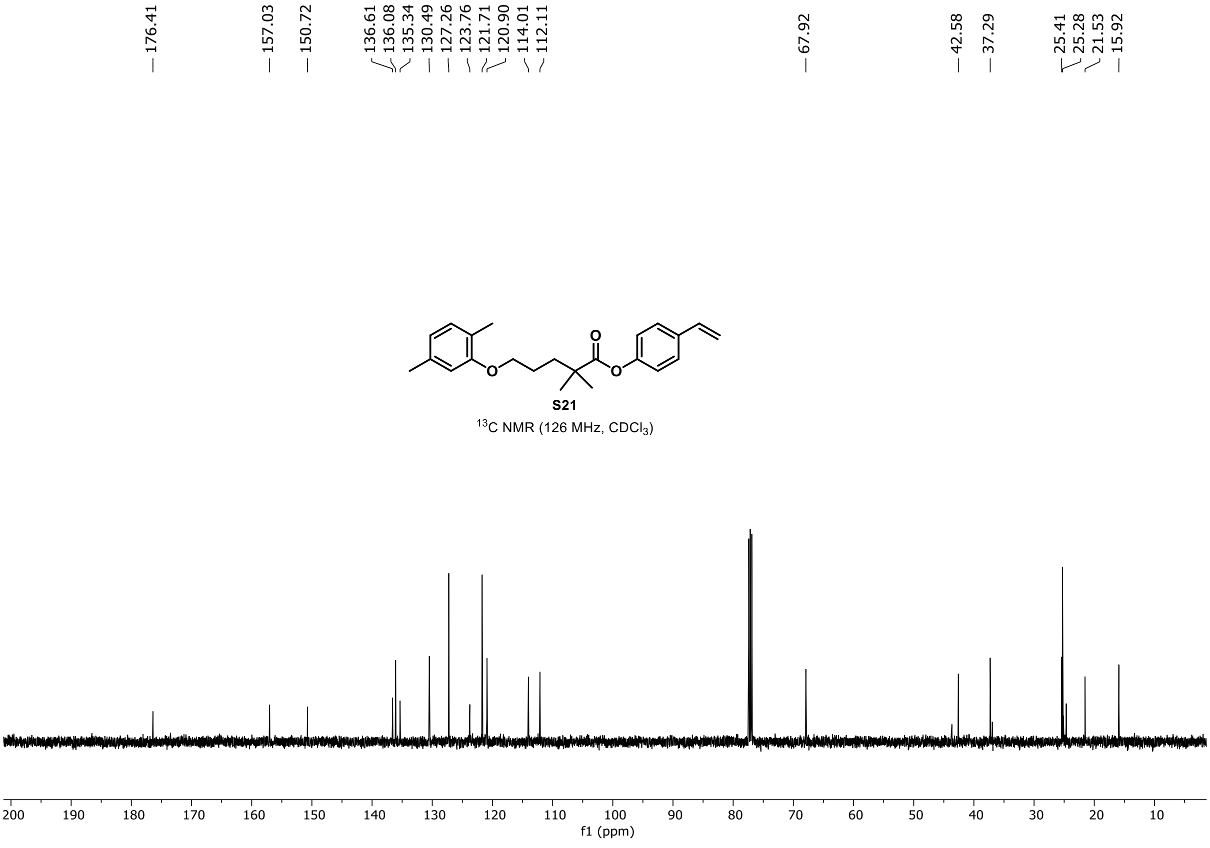

-116.75
42
19F NMR (471 MHz, CDCl3)
f1 (ppm)

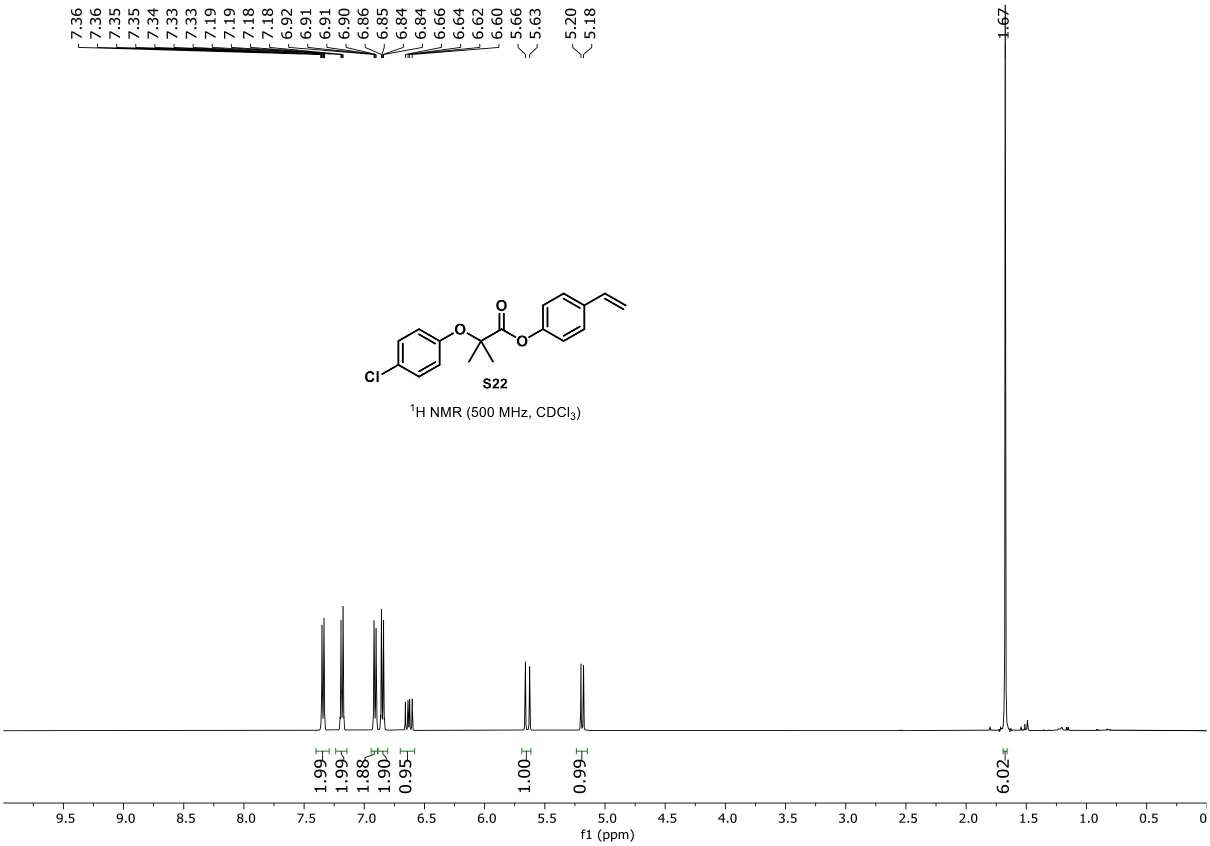

COSY
f2 (ppm)
f1 (ppm)


3.91
3.90
3.54
3.53
3.17
2.14
COMe
O
Hc
Ha
Hb
F
NOE considering 3.9 ppm (Ha)
Hc
Ha
Hb
6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6
f1 (ppm)

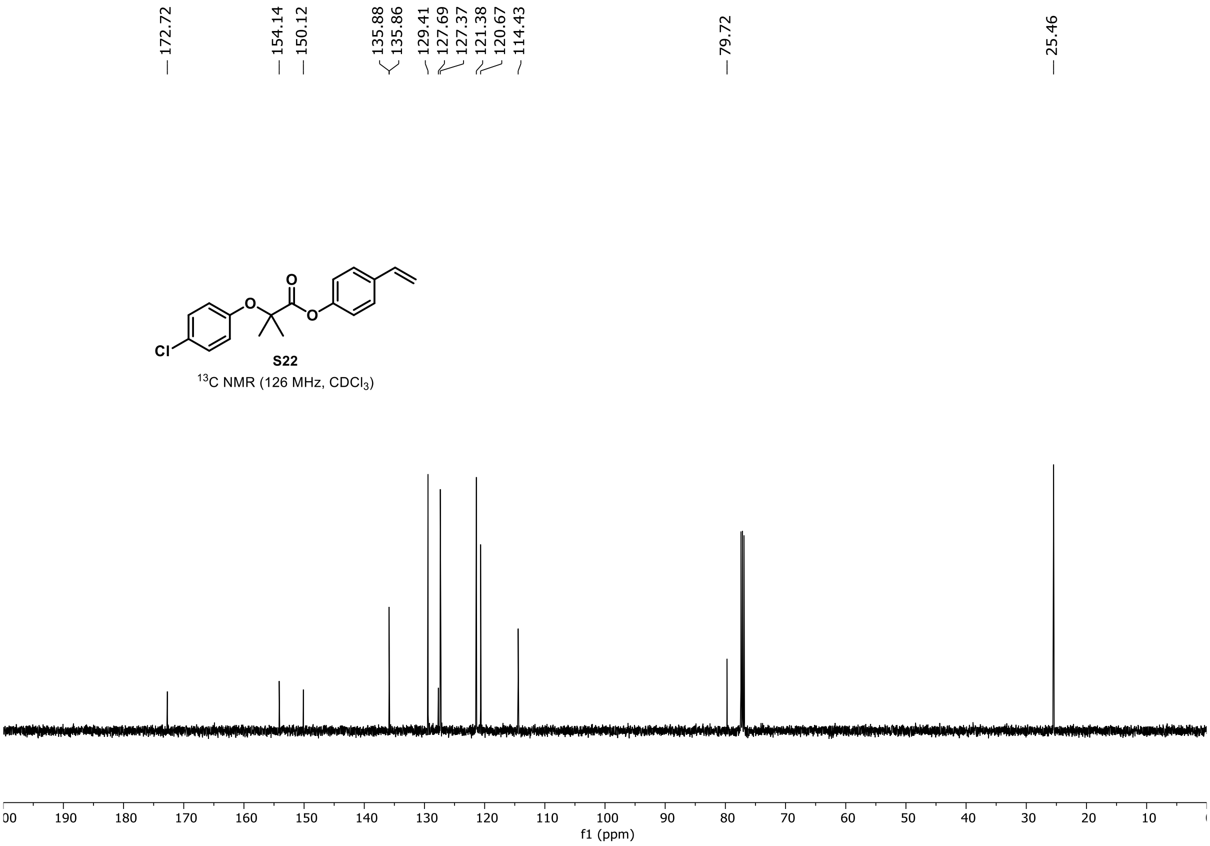

6.89
6.87
3.91
3.90
3.54
3.19
3.17
3.15
COMe
O
Hc
Ha
Hb
F
NOE considering 3.5 ppm (Hc)
Ha
Hc
Hb
.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


7.43 7.42 7.42 7.41 7.41 7.03 7.03 7.02 7.02 7.01 7.01 7.01 6.75 6.73 6.73 6.72 6.71 6.70 6.69 6.69 6.69 6.68 6.65 6.64 6.62 5.74 5.71 5.27 5.27 5.25 5.25 4.02 4.02 4.02 4.01 4.01 4.00 4.00 3.99 2.33 2.21 1.91 1.90 1.40
O
O
O
S21
^{1}H NMR (500 MHz, $CDCl_3$)
2.04 3.08 3.12 1.05 1.04 2.11 3.06 3.20 4.01 6.10
f1 (ppm)

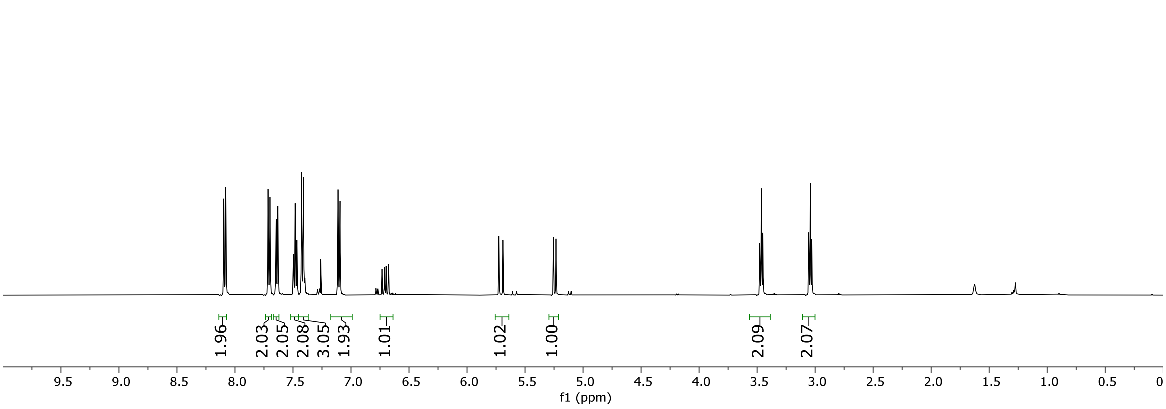

176.41 157.03 150.72 136.61 136.08 135.34 130.49 127.26 123.76 121.71 120.90 114.01 112.11 67.92 42.58 37.29 25.41 25.28 21.53 15.92
O
O
O
S21
^{13}C NMR (126 MHz, $CDCl_3$)
f1 (ppm)

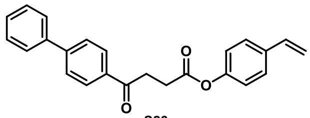


7.36
7.36
7.35
7.35
7.34
7.33
7.33
7.19
7.19
7.18
7.18
6.92
6.91
6.91
6.90
6.86
6.85
6.84
6.84
6.66
6.64
6.62
6.60
5.66
5.63
5.20
5.18
1.67
Cl
O
O
O
S22
1H NMR (500 MHz, CDCl3)
1.99
1.99
1.88
1.90
0.95
1.00
0.99
6.02
f1 (ppm)



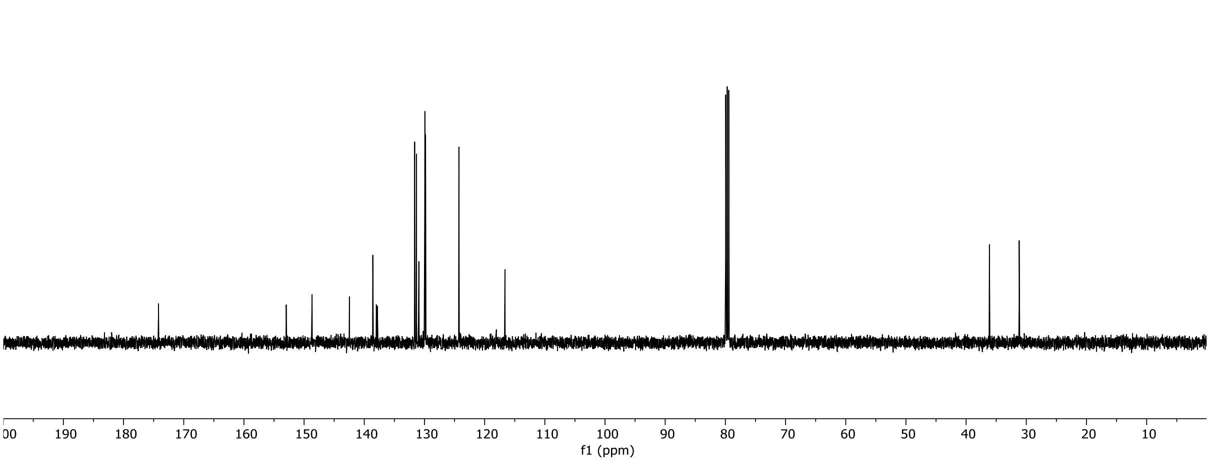
172.72
154.14
150.12
135.88
135.86
129.41
127.69
127.37
121.38
120.67
114.43
79.72
25.46
Cl
O
O
O
S22
13C NMR (126 MHz, CDCl3)
f1 (ppm)

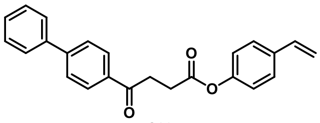




S23

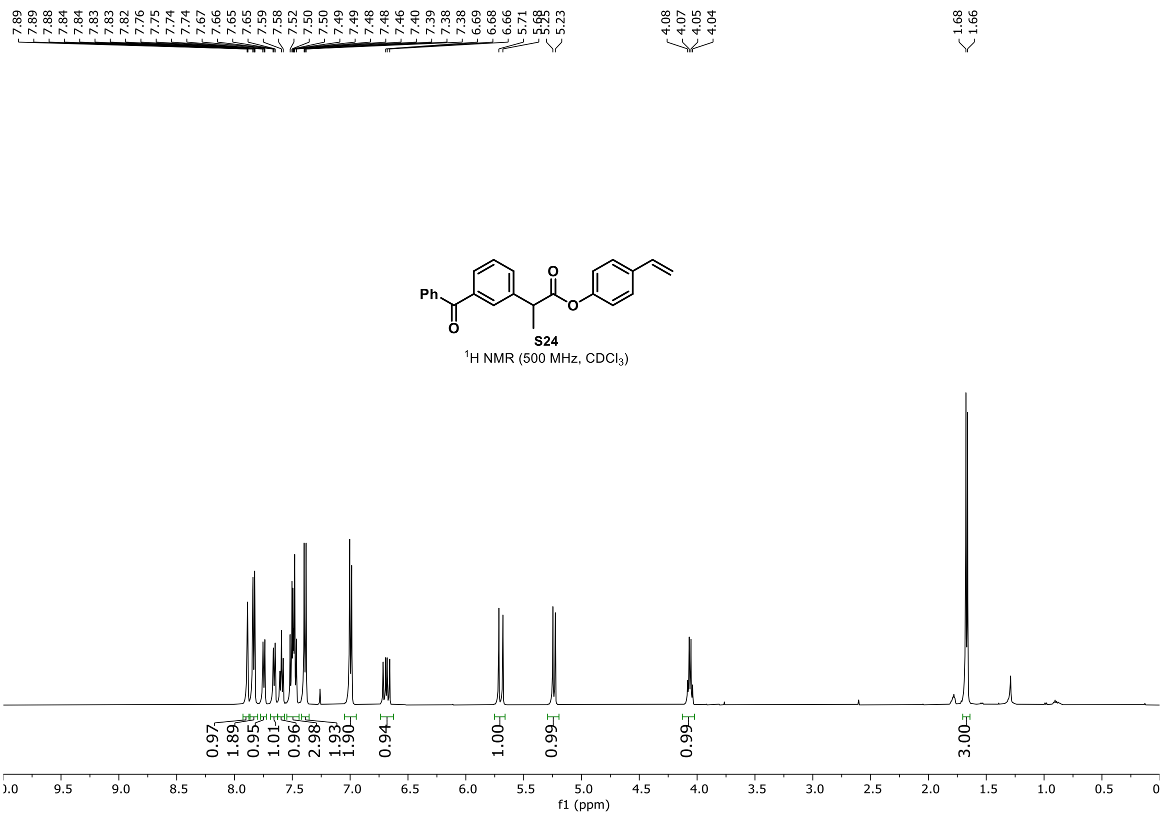
^{1}H NMR (500 MHz, $CDCl_3$)

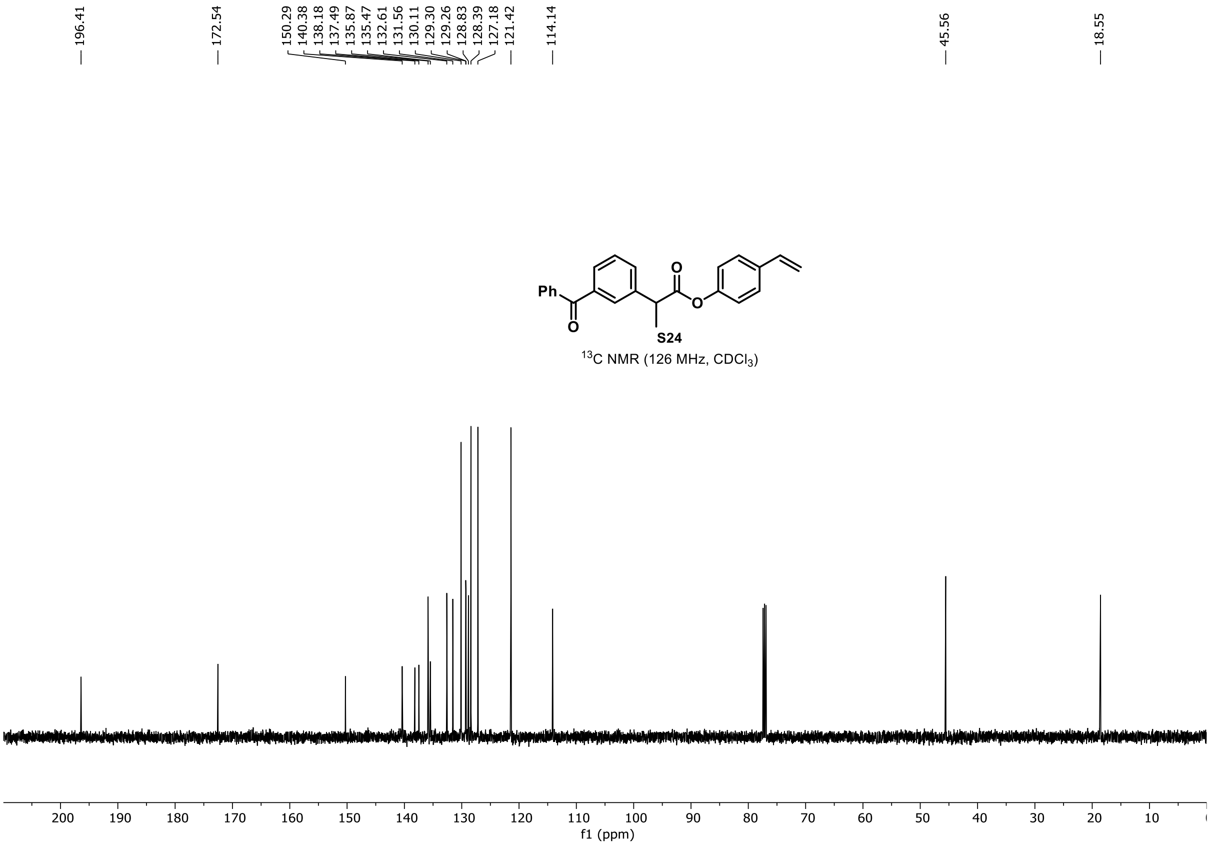


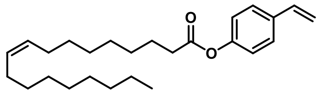


S23

^{13}C NMR (126 MHz, $CDCl_3$)

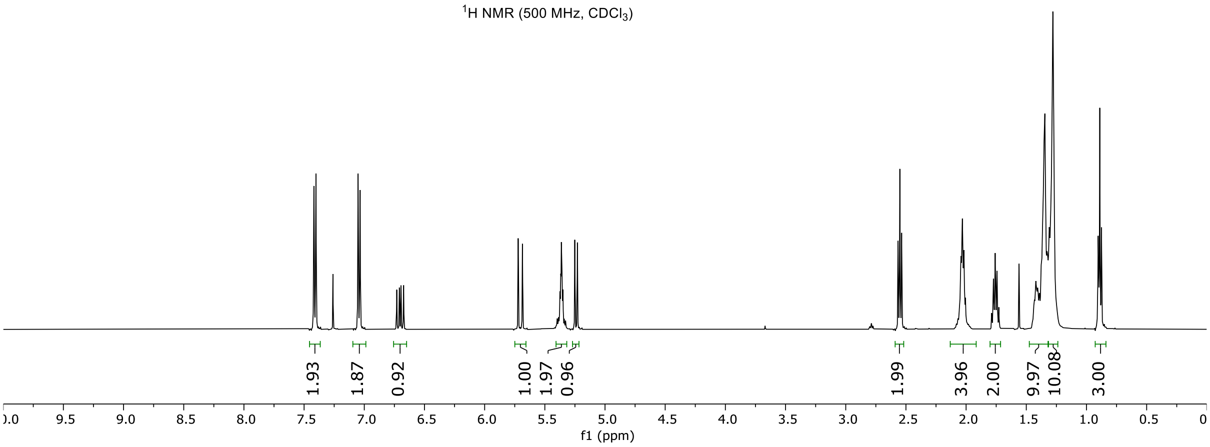


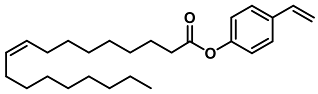




S25

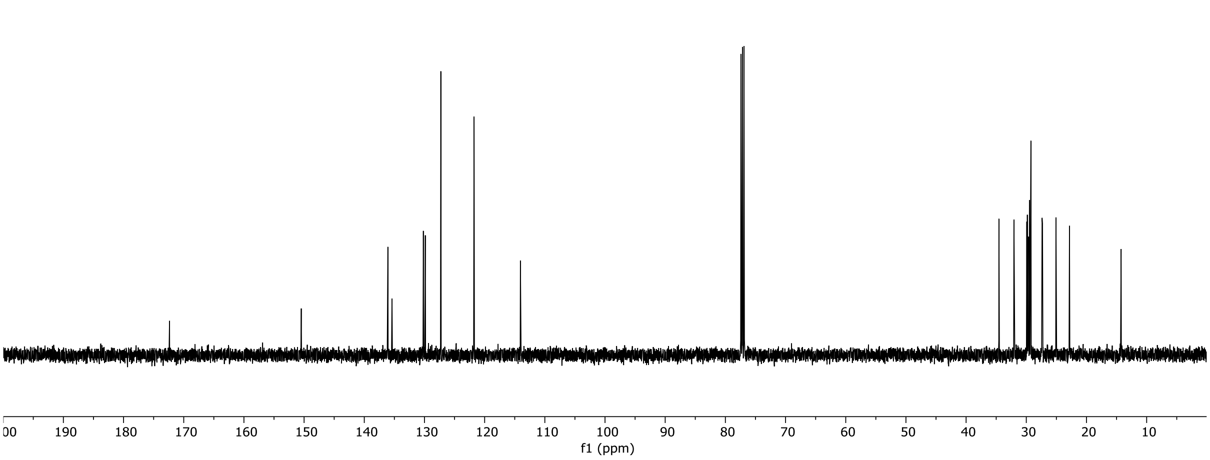
^{1}H NMR (500 MHz, $CDCl_3$)

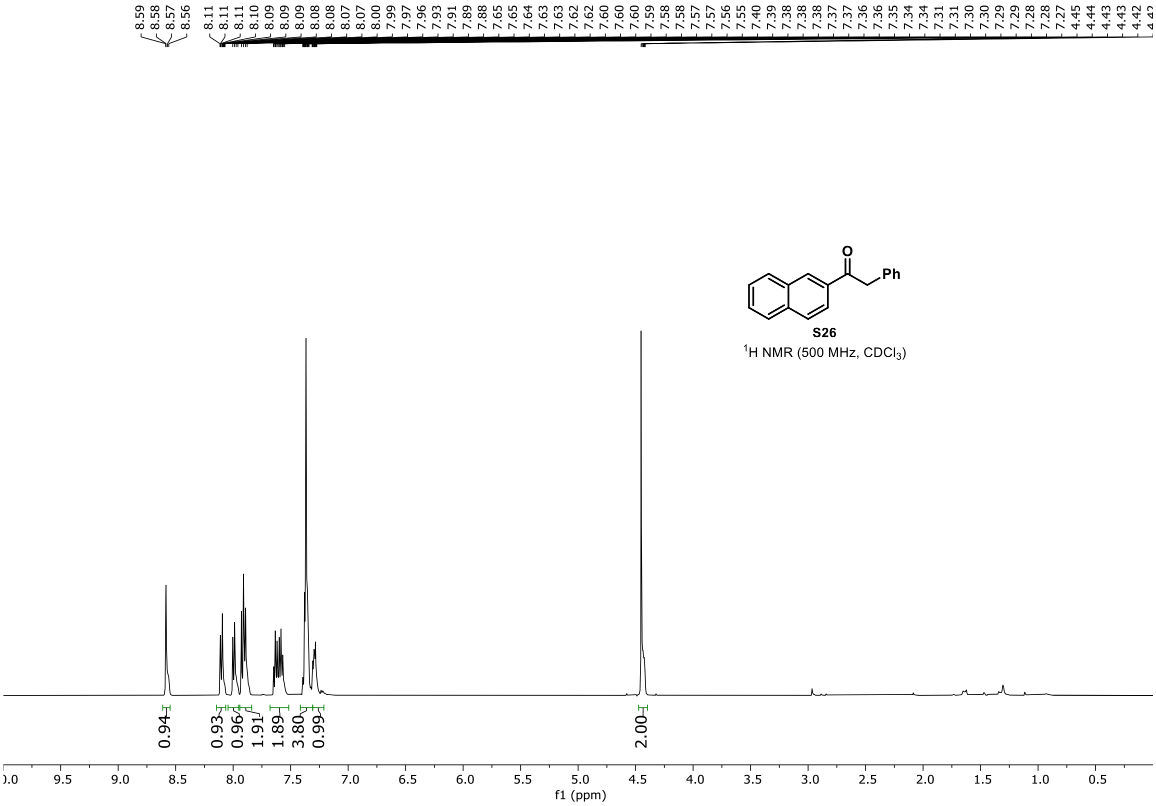


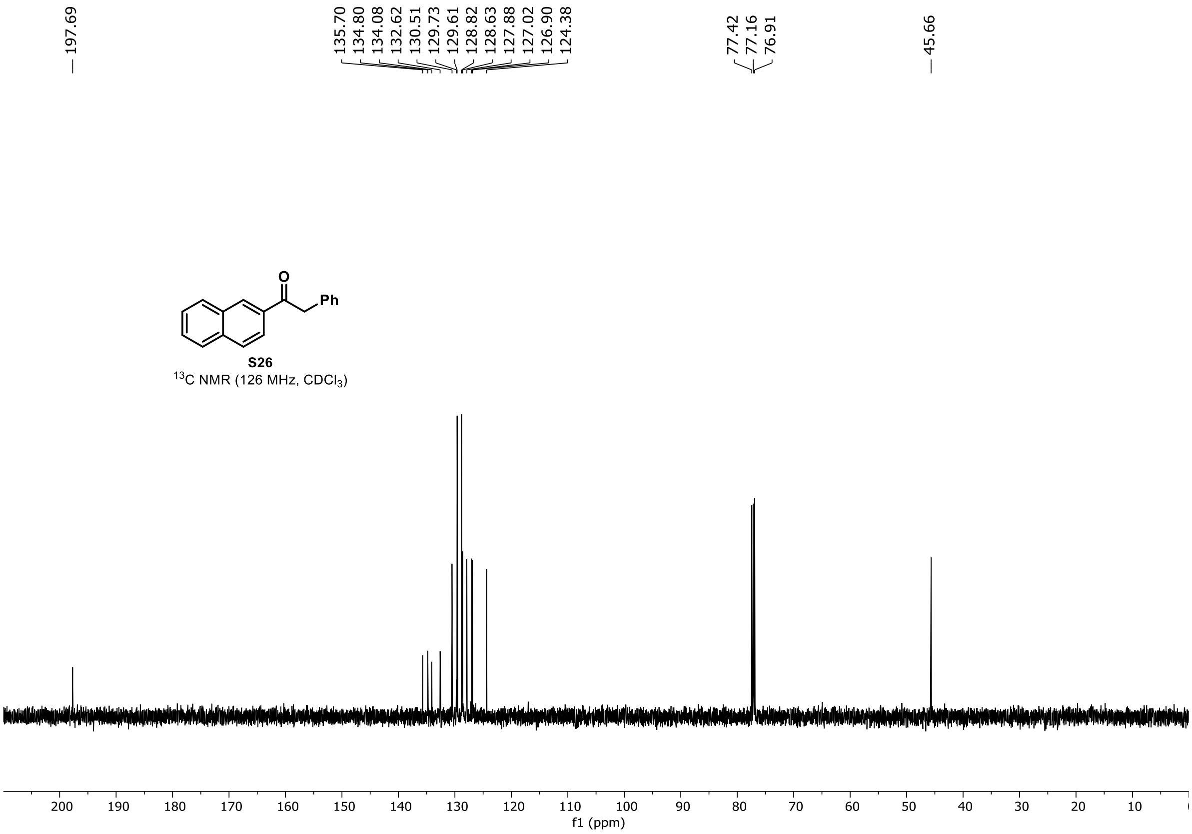


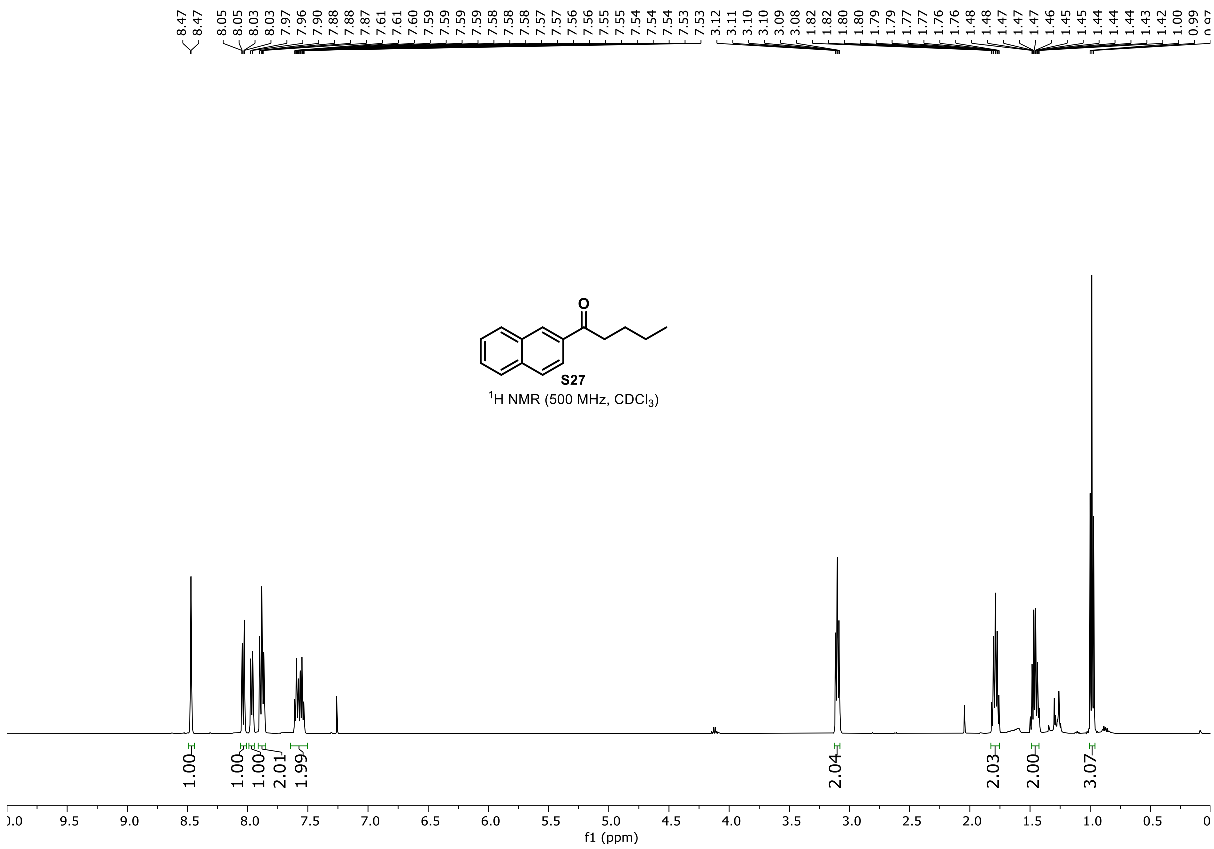
S25

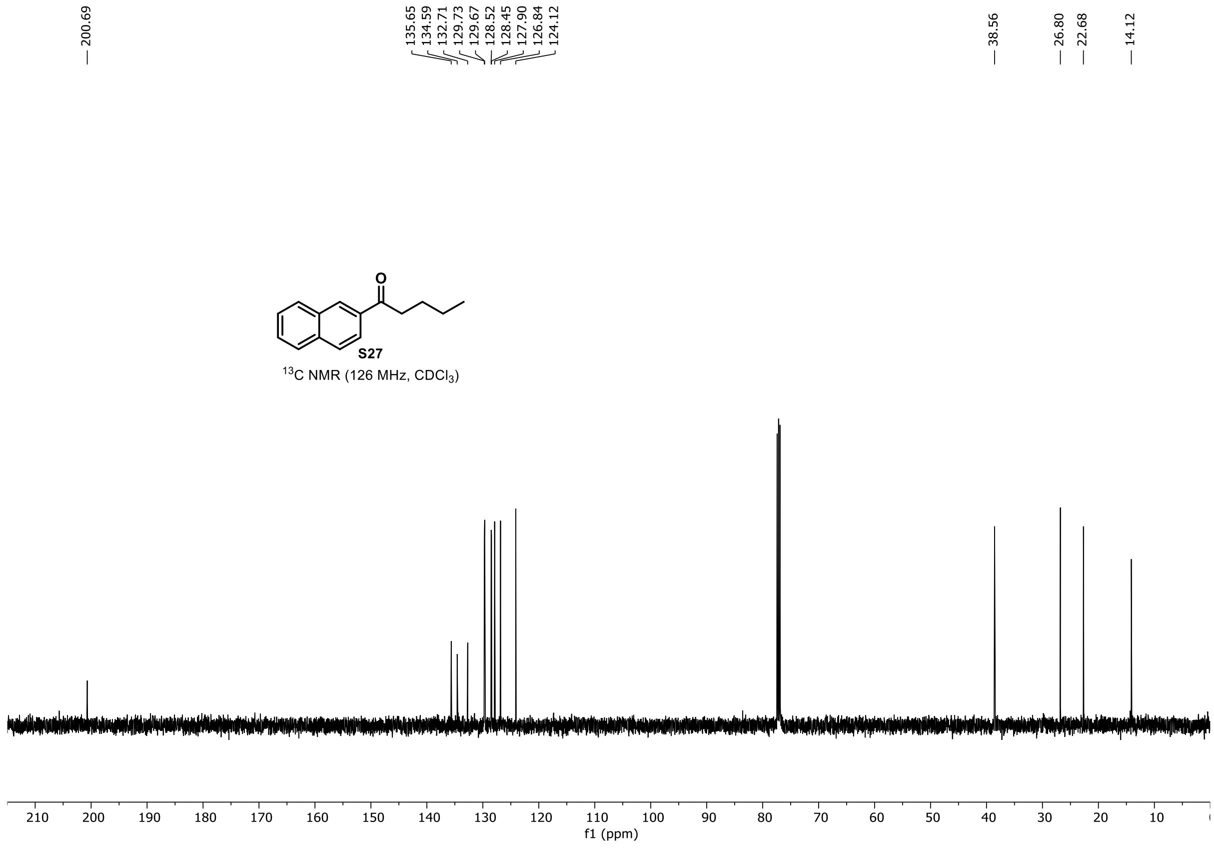
^{13}C NMR (126 MHz, $CDCl_3$)

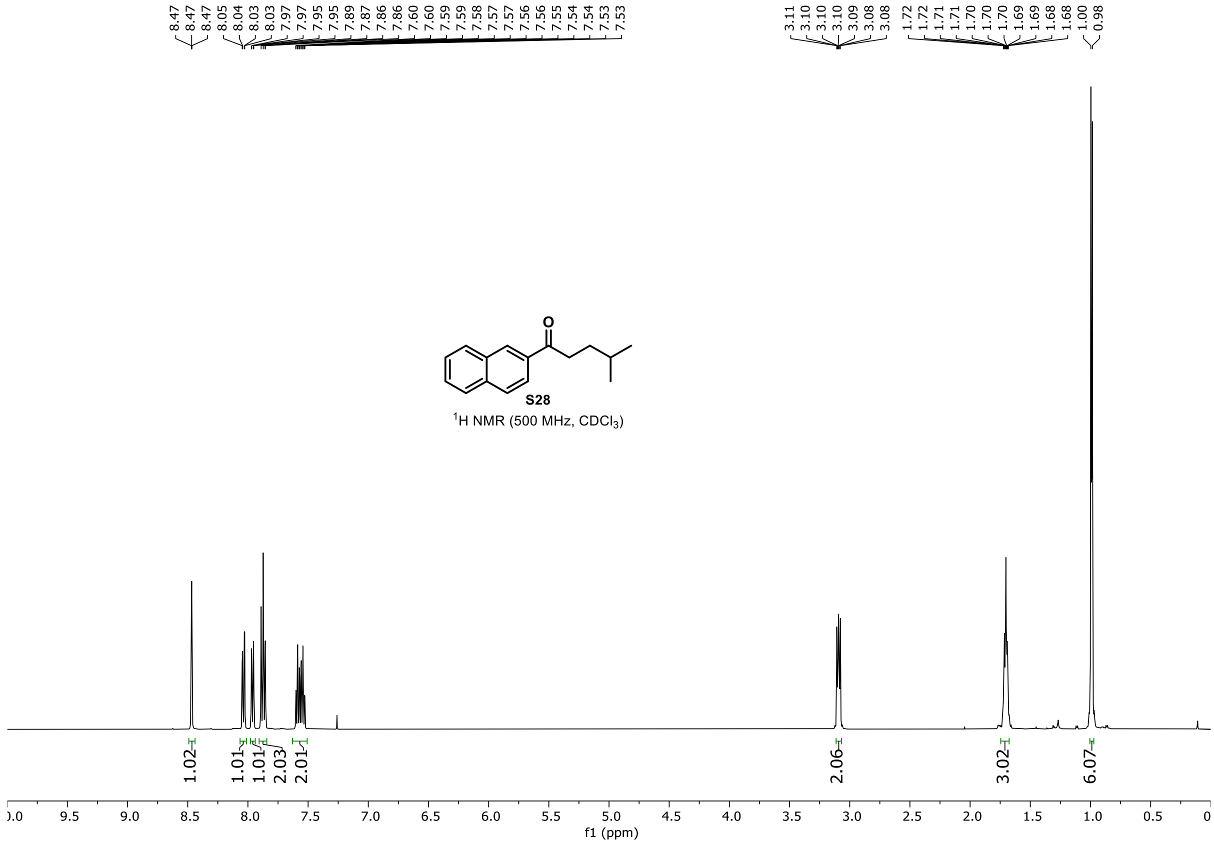



8.59 8.58 8.57 8.56 8.11 8.11 8.11 8.10 8.09 8.09 8.09 8.08 8.08 8.07 8.07 8.00 7.99 7.97 7.96 7.93 7.91 7.89 7.88 7.65 7.65 7.64 7.63 7.63 7.62 7.62 7.60 7.60 7.59 7.58 7.58 7.57 7.57 7.56 7.55 7.40 7.39 7.38 7.38 7.38 7.38 7.37 7.37 7.36 7.36 7.35 7.34 7.34 7.31 7.30 7.30 7.29 7.29 7.28 7.28 7.27 4.45 4.44 4.43 4.42
O
Ph
S26
1H NMR (500 MHz, CDCl3)
0.94 0.93 0.96 1.91 1.89 3.80 0.99 2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

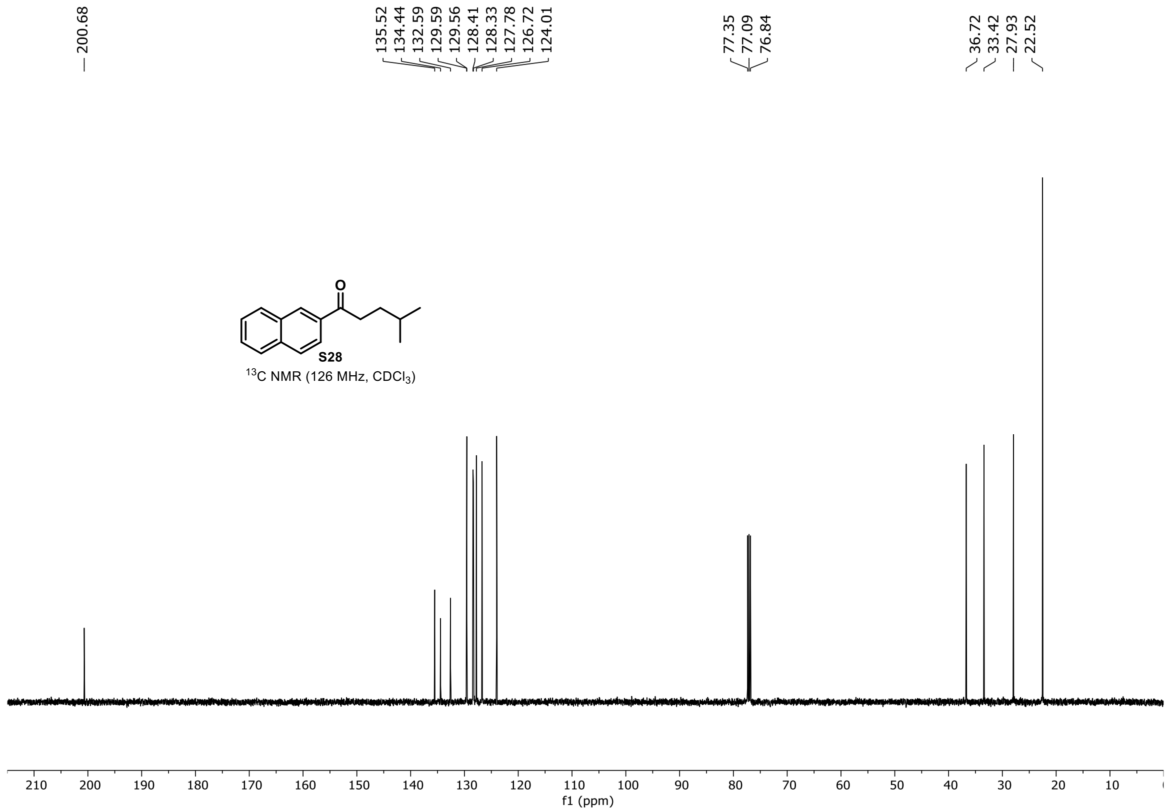

197.69
135.70 134.80 134.08 132.62 130.51 129.73 129.61 128.82 128.63 127.88 127.02 126.90 124.38
77.42 77.16 76.91
45.66
O
Ph
S26
13C NMR (126 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


S27
^{1}H NMR (500 MHz, $CDCl_3$)
f1 (ppm)

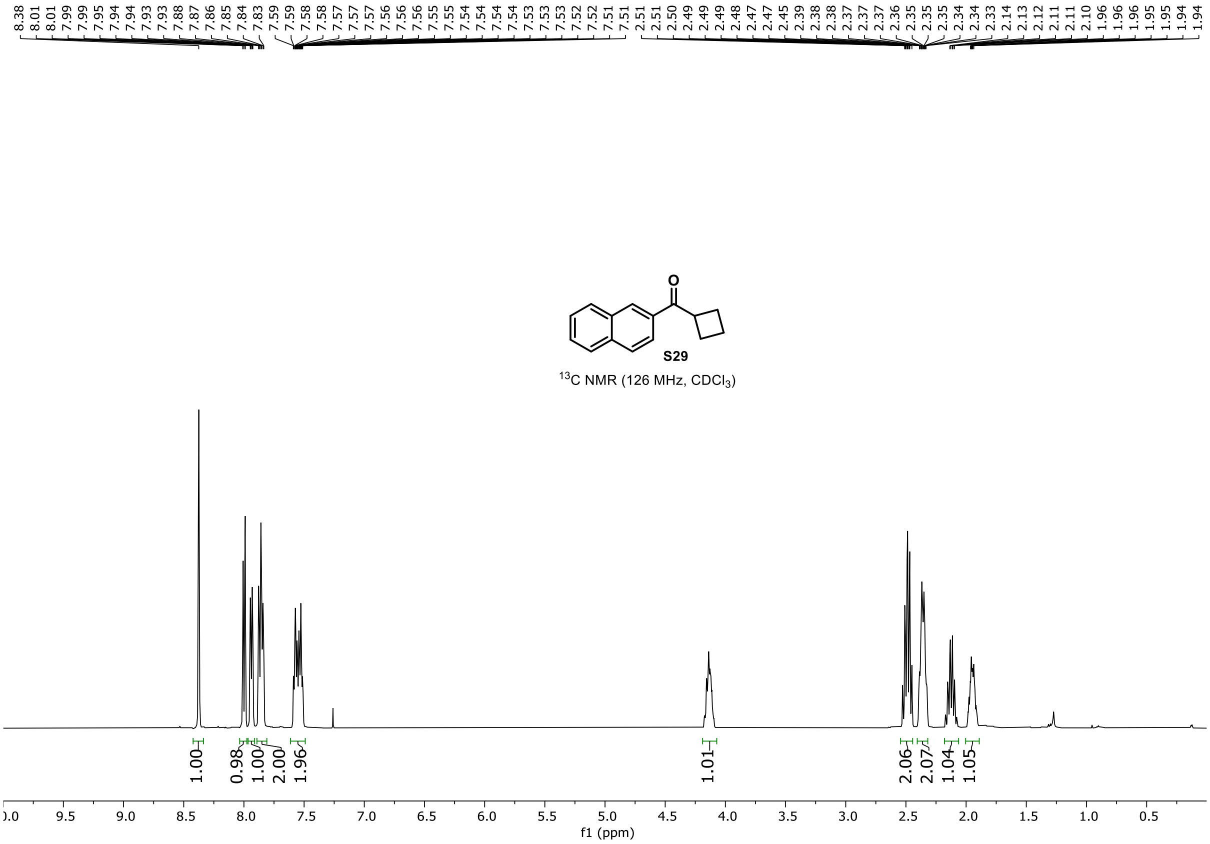

S27
^{13}C NMR (126 MHz, $CDCl_3$)
f1 (ppm)

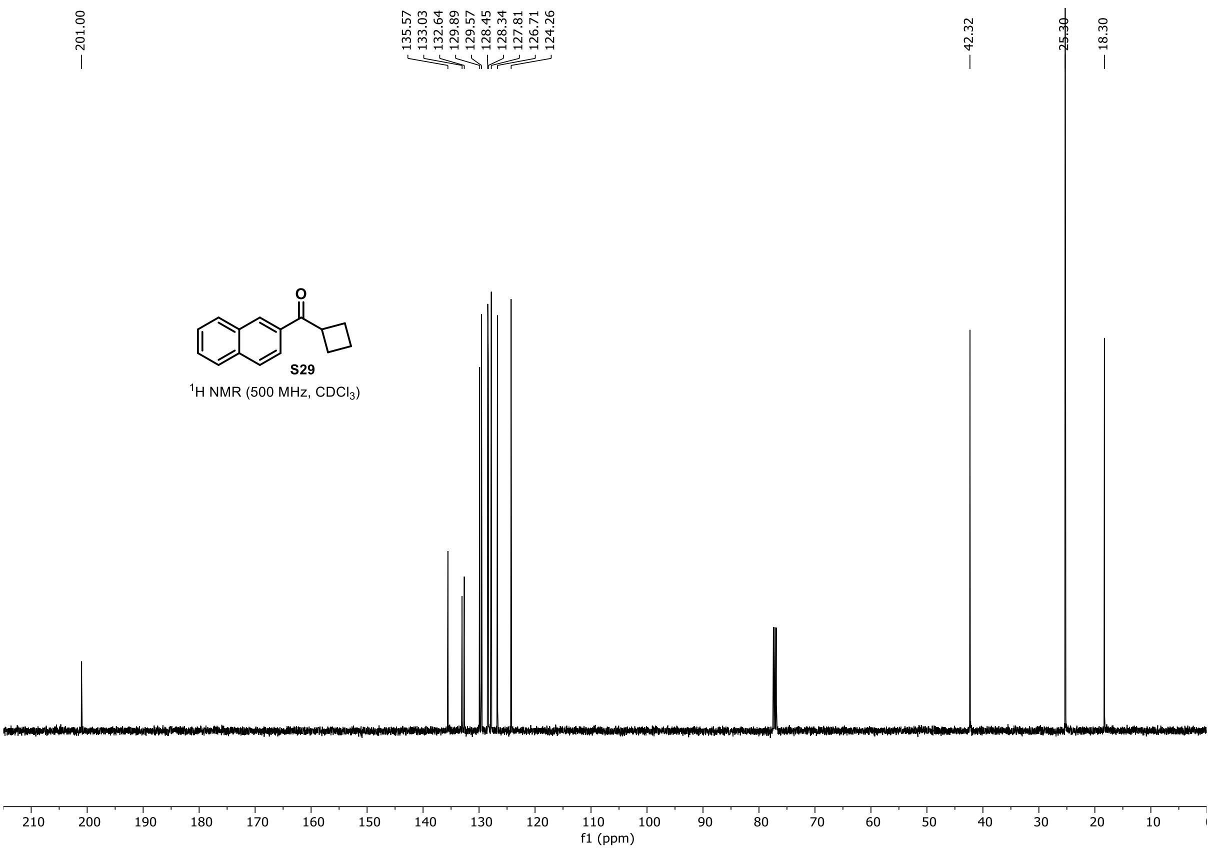


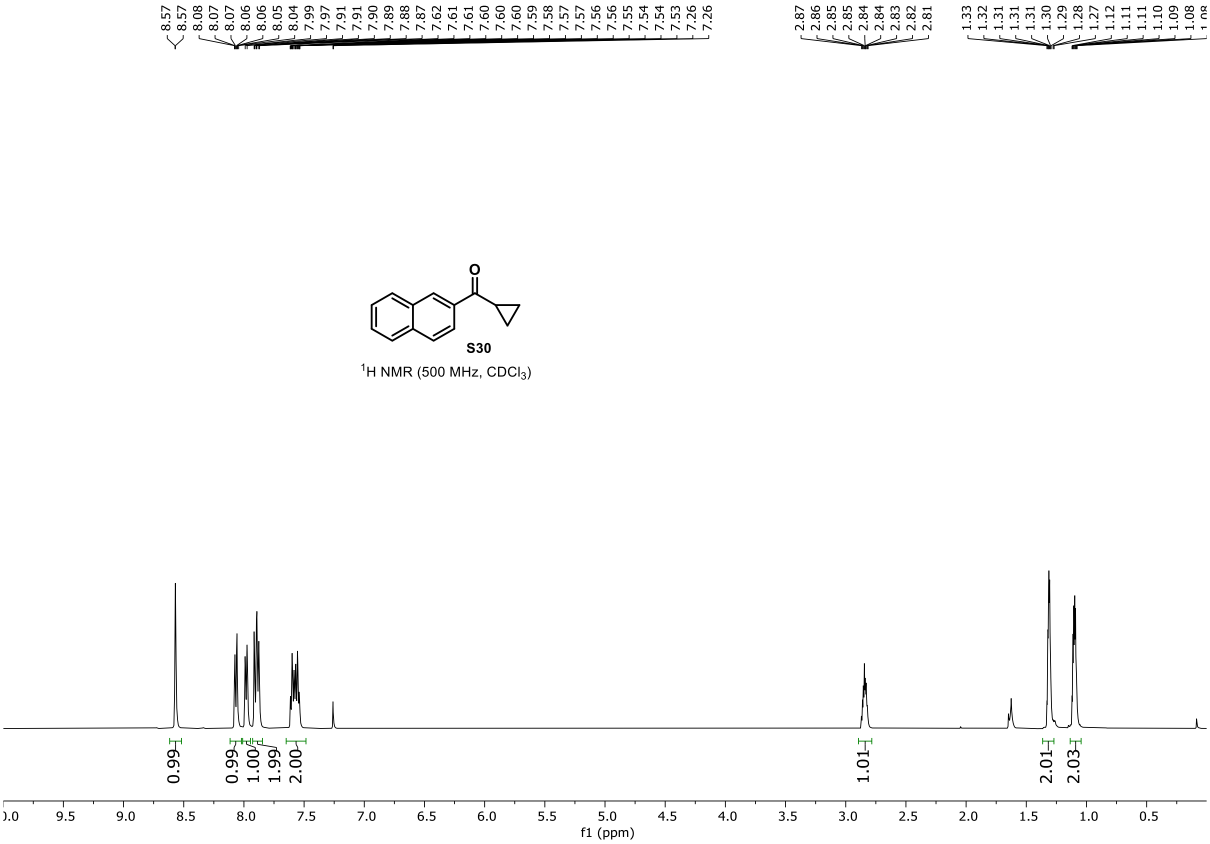
S28
^{1}H NMR (500 MHz, $CDCl_3$)

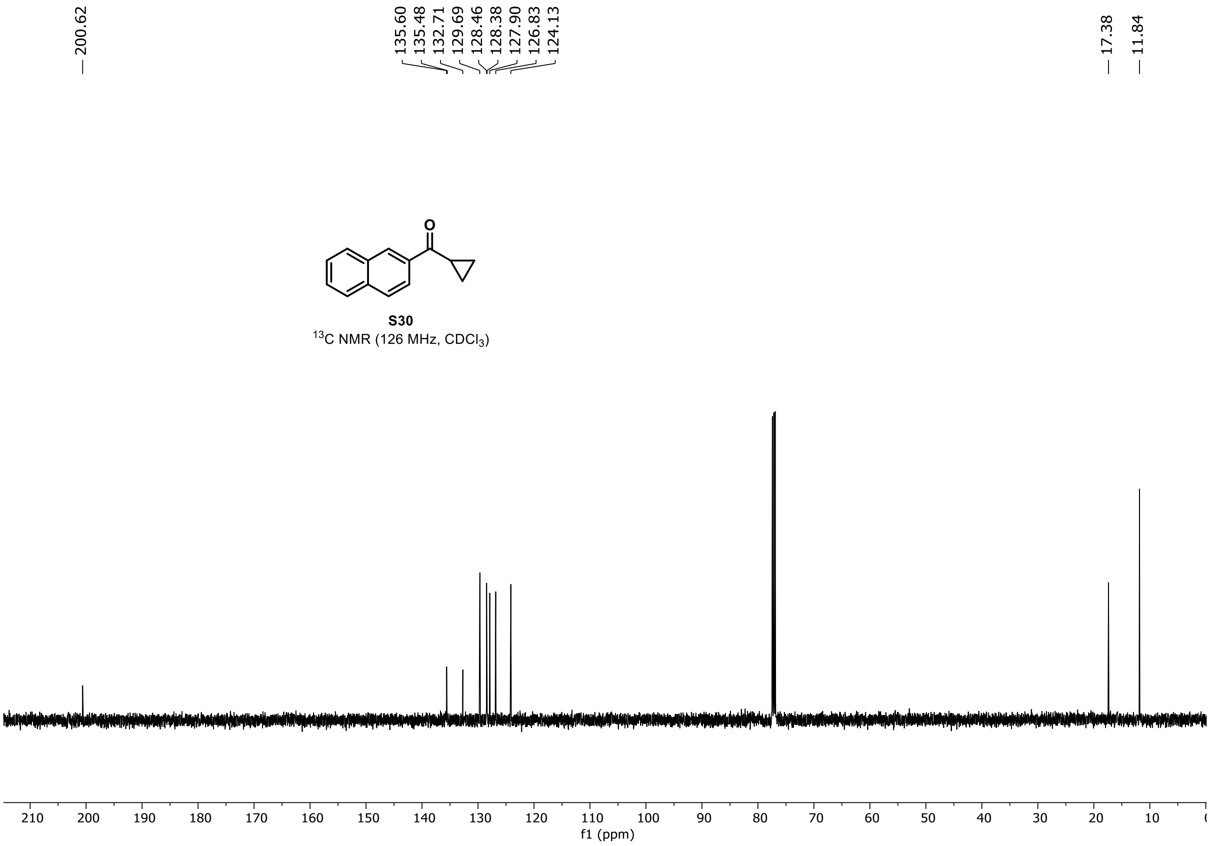


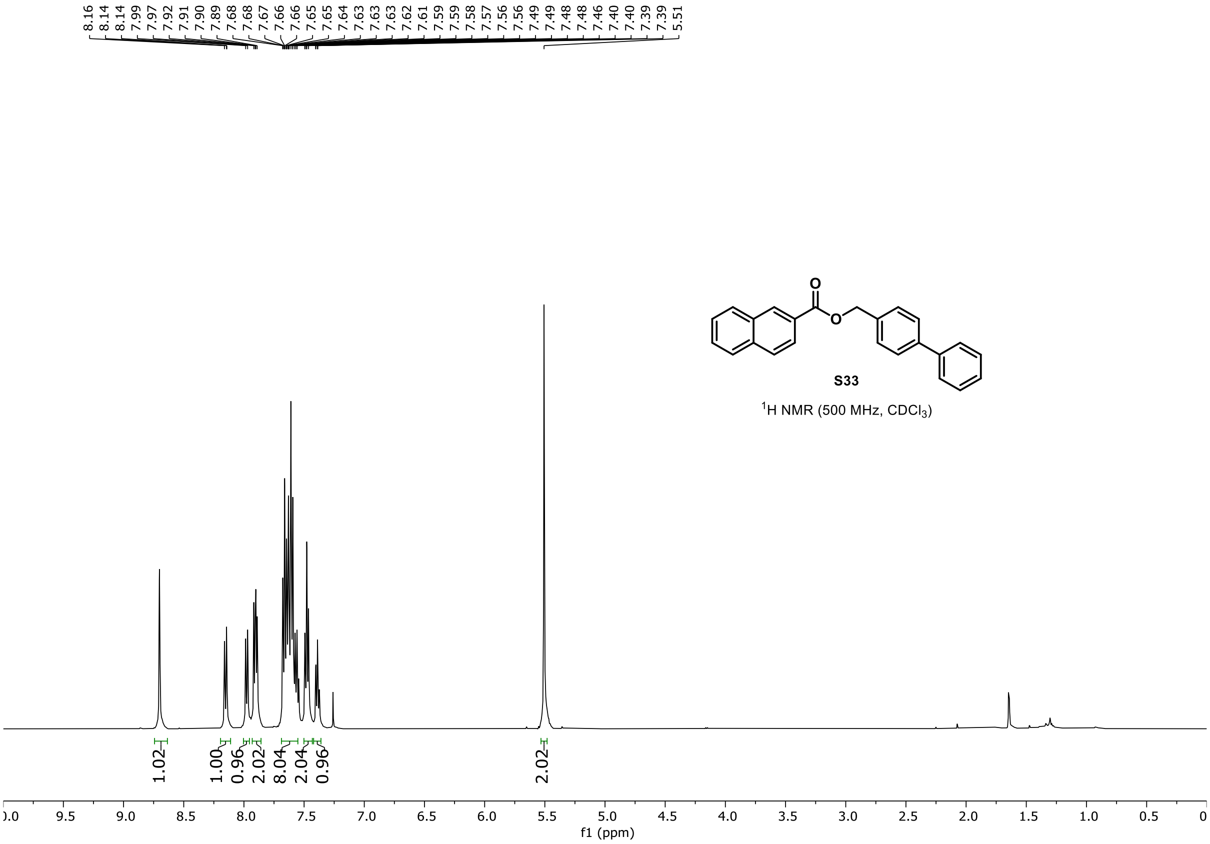
S28
^{13}C NMR (126 MHz, $CDCl_3$)

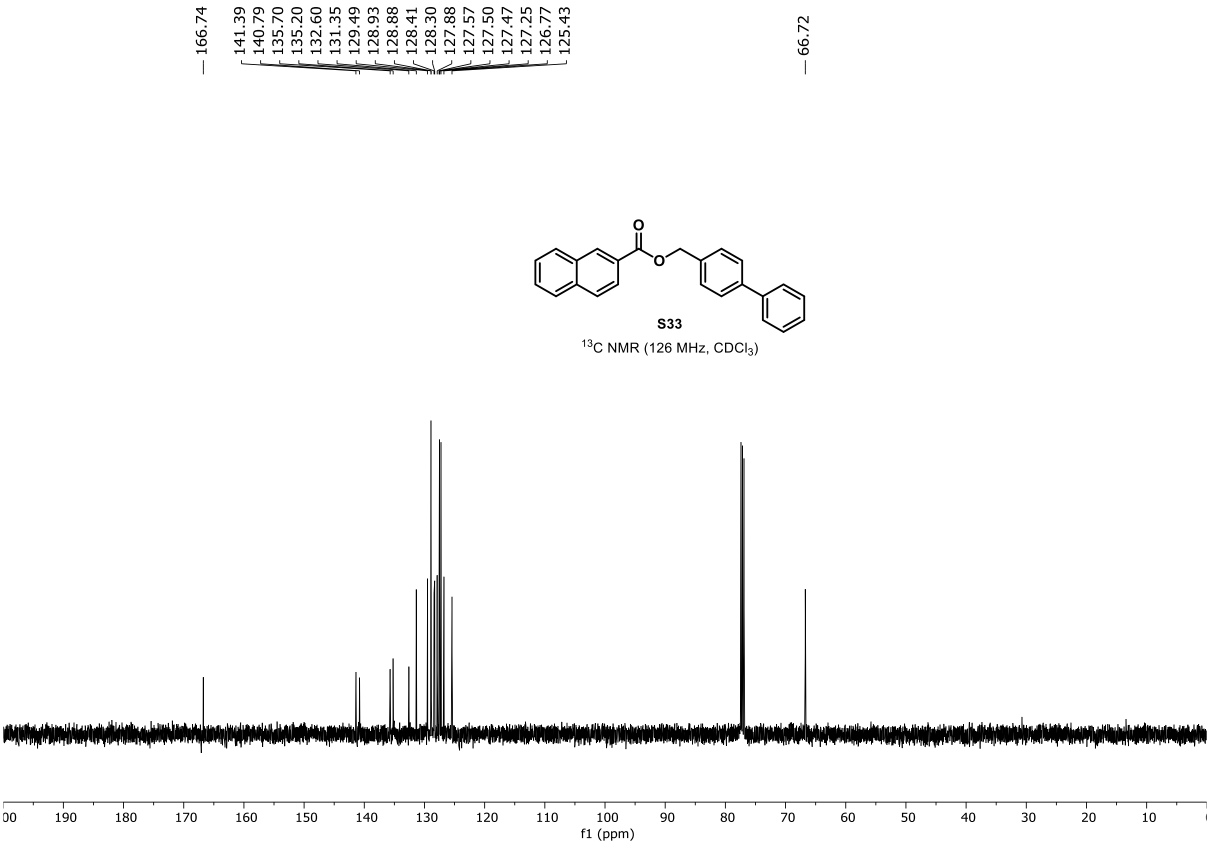

8.38 8.01 8.01 7.99 7.99 7.95 7.94 7.94 7.93 7.93 7.88 7.87 7.86 7.85 7.84 7.83 7.59 7.59 7.58 7.58 7.57 7.57 7.57 7.56 7.56 7.56 7.55 7.55 7.54 7.54 7.54 7.54 7.53 7.53 7.53 7.52 7.52 7.51 7.51 2.51 2.51 2.50 2.49 2.49 2.49 2.48 2.47 2.45 2.39 2.38 2.38 2.37 2.37 2.37 2.36 2.35 2.35 2.35 2.34 2.34 2.33 2.14 2.13 2.12 2.11 2.11 2.10 1.96 1.96 1.96 1.95 1.94 1.94
O
S29
^{13}C NMR (126 MHz, CDCl$_3$)
1.00 0.98 1.00 2.00 1.96 1.01 2.06 2.07 1.04 1.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

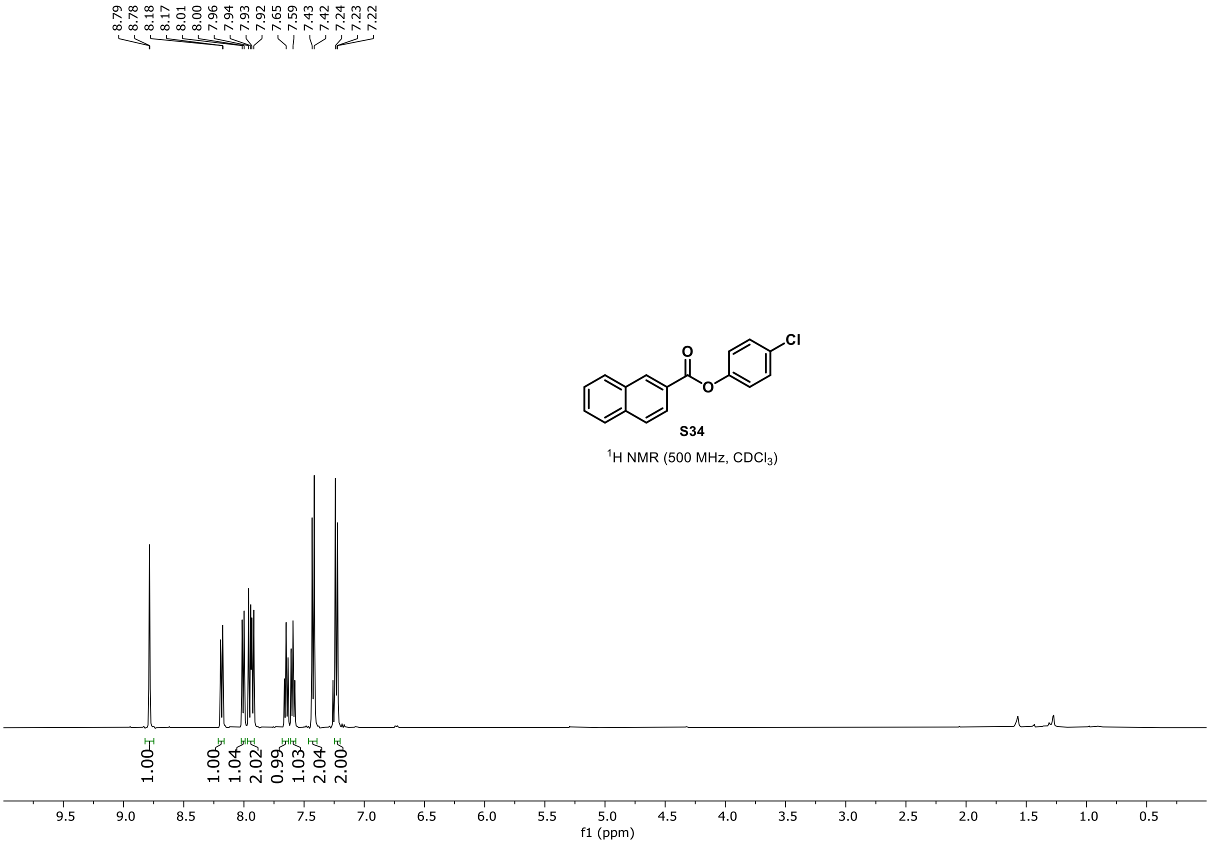

201.00
135.57 133.03 132.64 129.89 129.57 128.45 128.34 127.81 126.71 124.26
42.32
25.30
18.30
O
S29
^{1}H NMR (500 MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

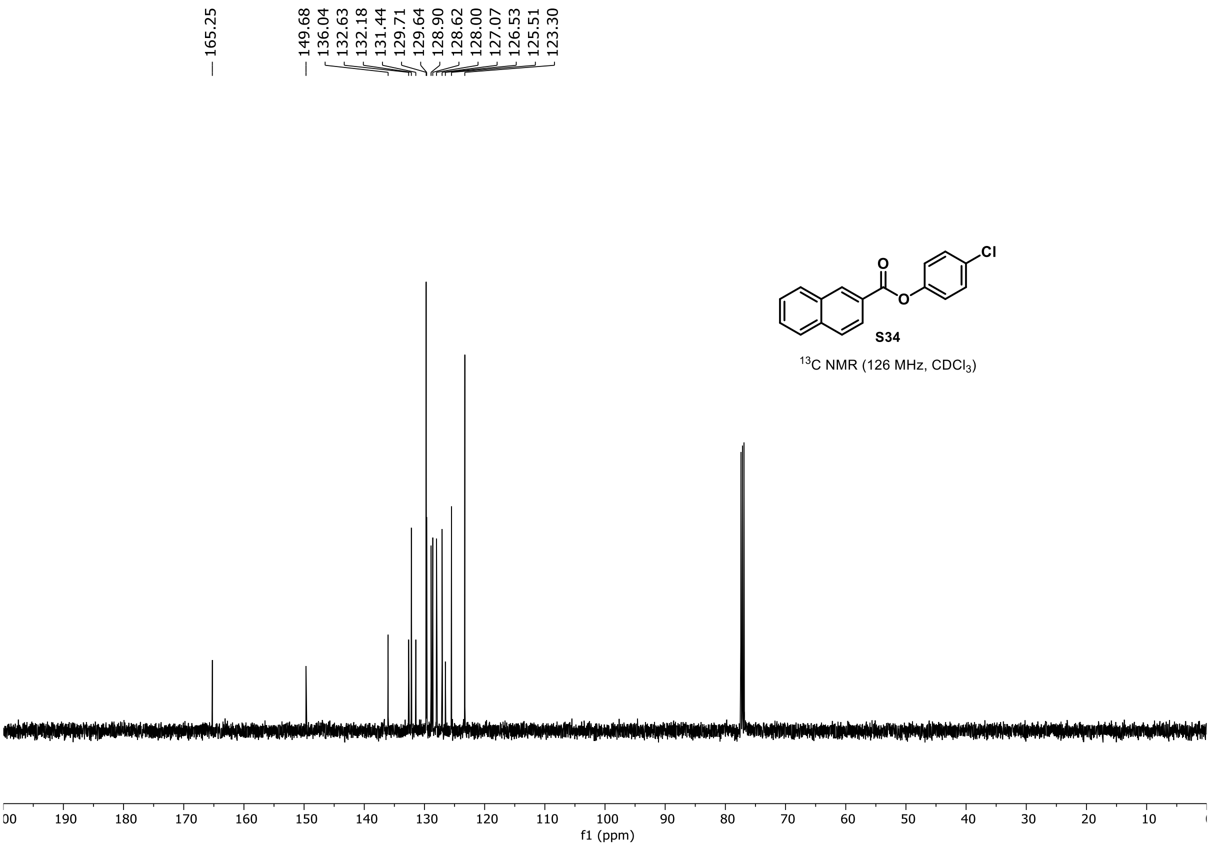

8.57 8.57 8.08 8.07 8.06 8.06 8.05 8.04 7.99 7.97 7.91 7.90 7.89 7.88 7.87 7.62 7.61 7.61 7.60 7.60 7.60 7.59 7.58 7.57 7.57 7.56 7.56 7.55 7.54 7.54 7.53 7.26 7.26
2.87 2.86 2.85 2.85 2.84 2.84 2.83 2.82 2.81
1.33 1.32 1.31 1.31 1.31 1.30 1.29 1.28 1.27 1.12 1.11 1.11 1.10 1.09 1.08
O
S30
1H NMR (500 MHz, CDCl3)
0.99 0.99 1.00 1.99 2.00 1.01 2.01 2.03
f1 (ppm)

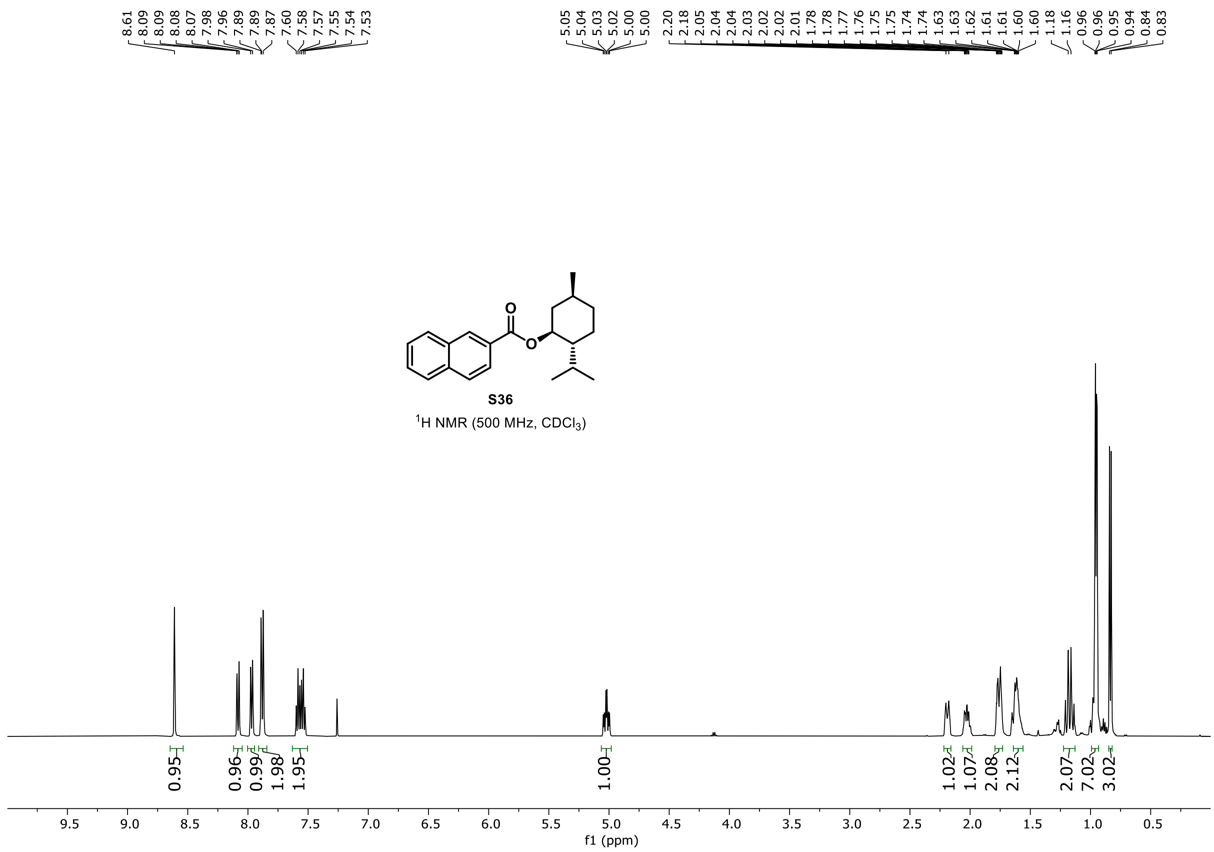

200.62
135.60 135.48 132.71 129.69 128.46 128.38 127.90 126.83 124.13
17.38 11.84
O
S30
13C NMR (126 MHz, CDCl3)
f1 (ppm)

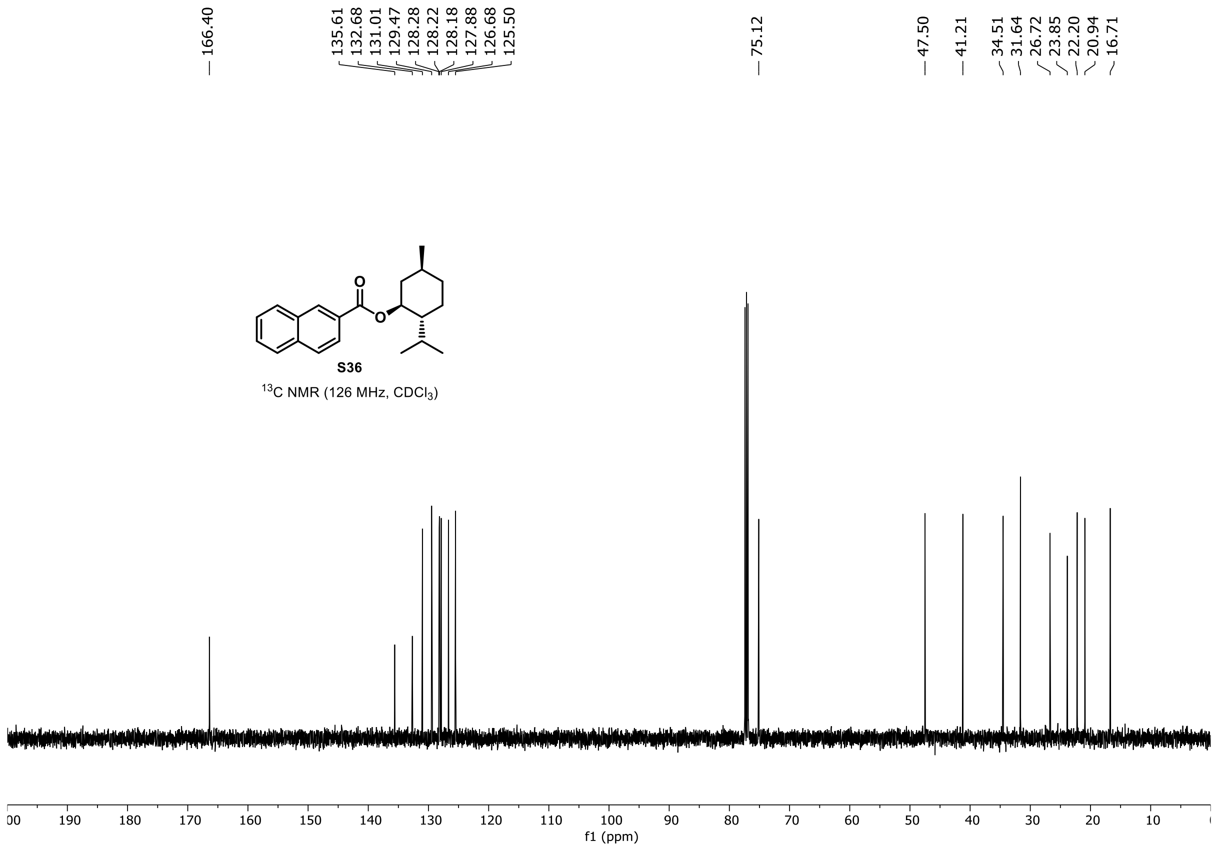

8.16
8.14
8.14
7.99
7.97
7.92
7.91
7.90
7.89
7.68
7.68
7.67
7.66
7.66
7.65
7.65
7.64
7.63
7.63
7.63
7.62
7.61
7.59
7.59
7.58
7.57
7.56
7.49
7.49
7.48
7.48
7.46
7.40
7.40
7.39
7.39
5.51
O
O
S33
^{1}H NMR (500 MHz, CDCl$_3$)
1.02
1.00
0.96
2.02
8.04
2.04
0.96
2.02
f1 (ppm)

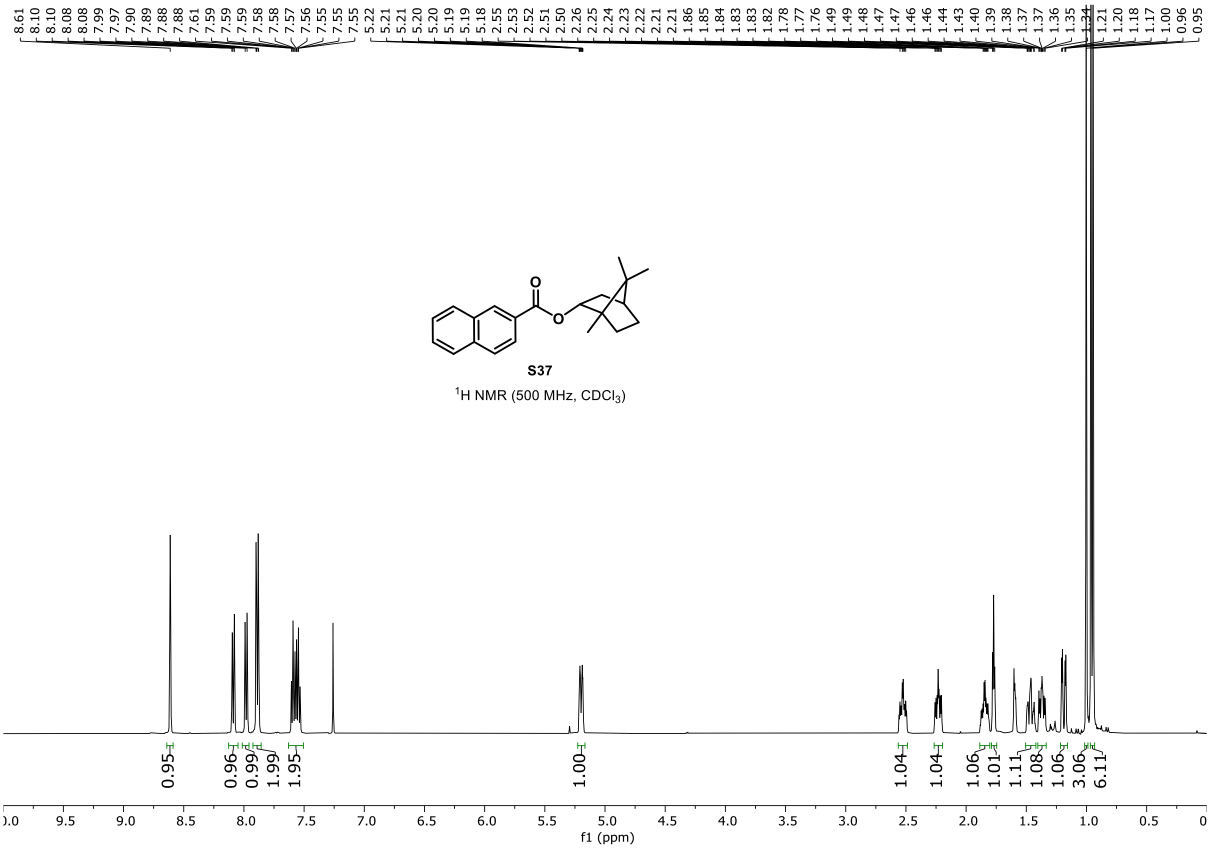

166.74
141.39
140.79
135.70
135.20
132.60
131.35
129.49
128.93
128.88
128.41
128.30
127.88
127.57
127.50
127.47
127.25
126.77
125.43
66.72
O
O
S33
^{13}C NMR (126 MHz, CDCl$_3$)
f1 (ppm)

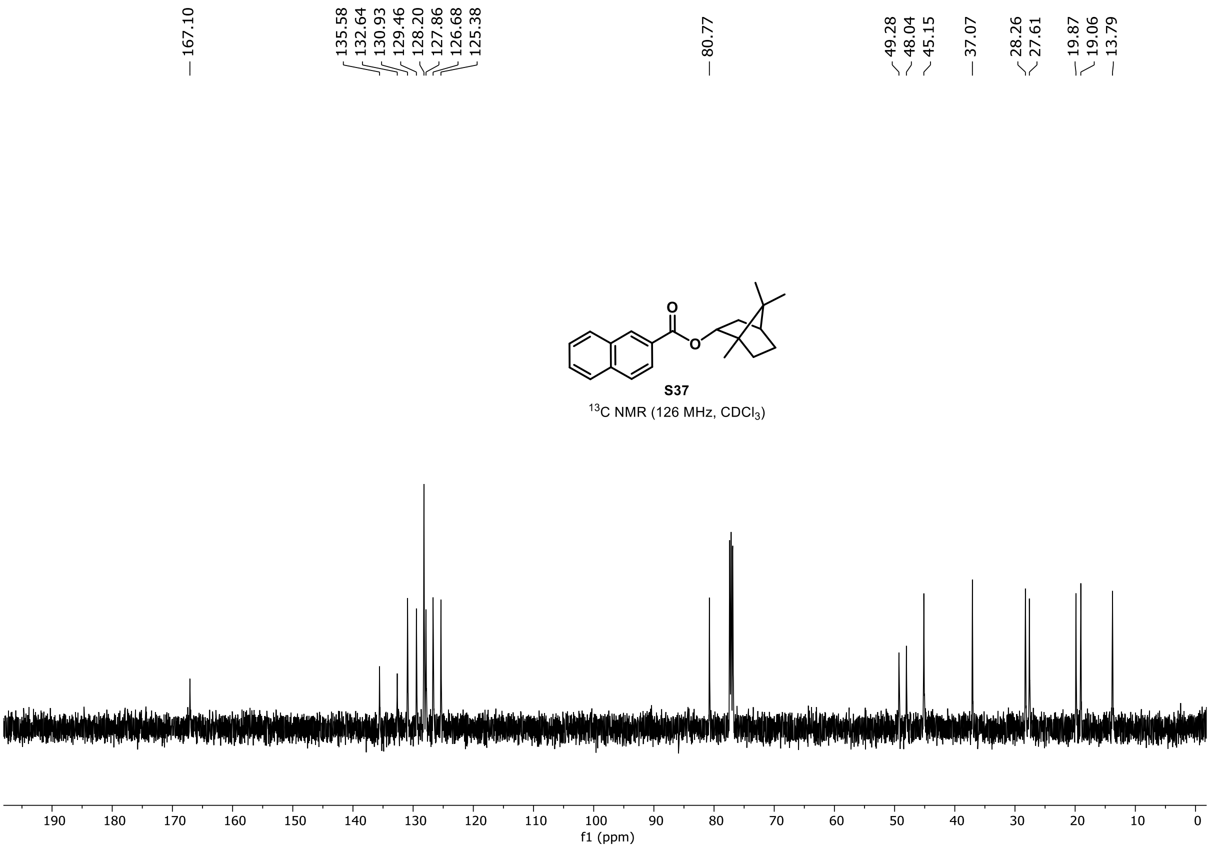

8.79
8.78
8.18
8.17
8.01
8.00
7.96
7.94
7.93
7.92
7.65
7.59
7.43
7.42
7.24
7.23
7.22
O
O
Cl
S34
1H NMR (500 MHz, CDCl3)
1.00
1.00
1.04
2.02
0.99
1.03
2.04
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

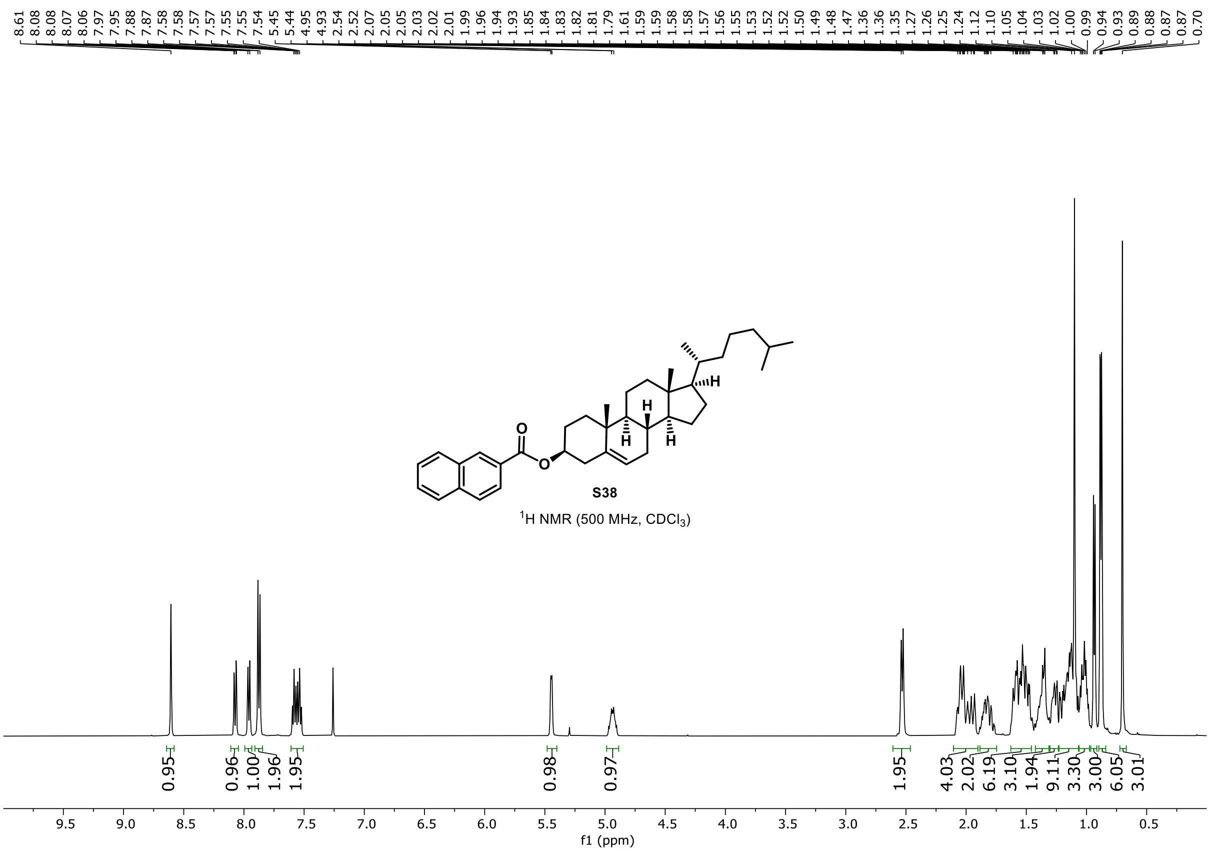

165.25
149.68
136.04
132.63
132.18
131.44
129.71
129.64
128.90
128.62
128.00
127.07
126.53
125.51
123.30
O
O
Cl
S34
13C NMR (126 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

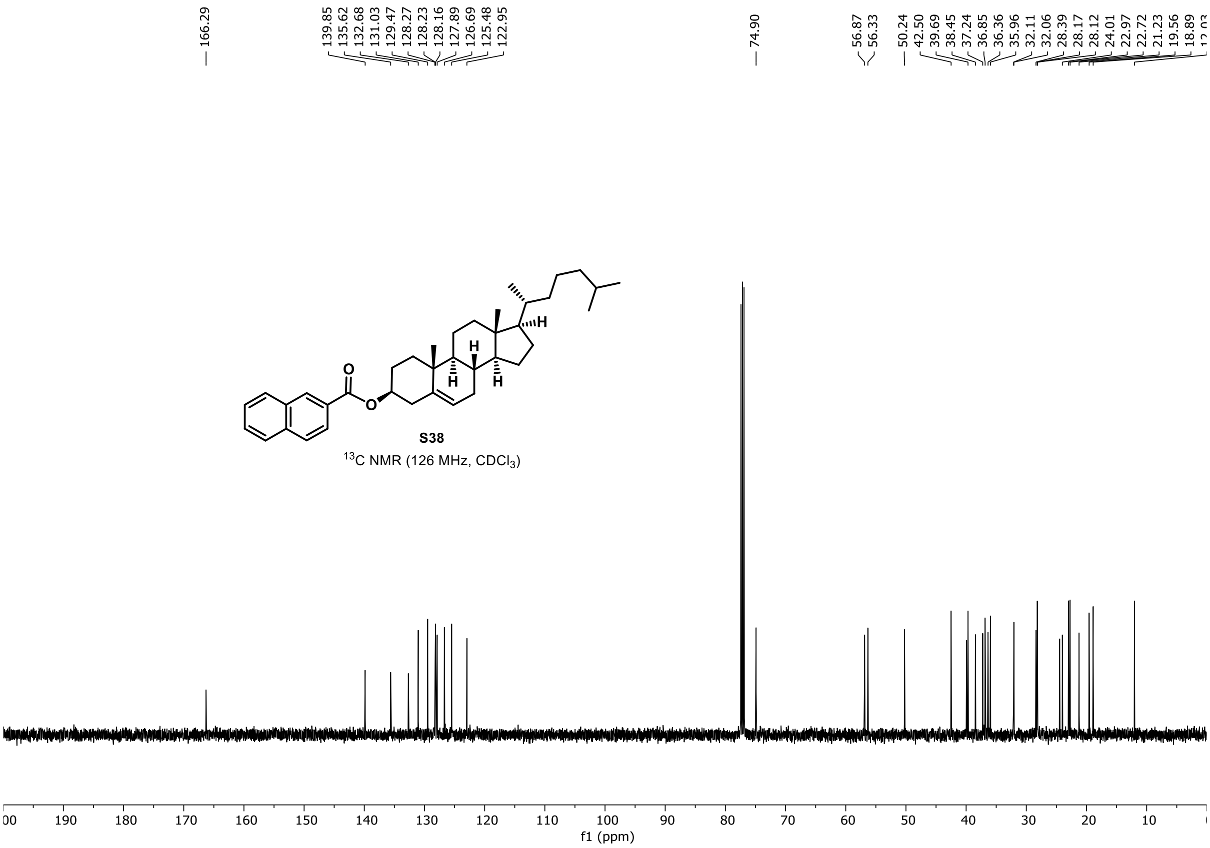

S36
1H NMR (500 MHz, CDCl3)
f1 (ppm)


S36
13C NMR (126 MHz, CDCl3)
f1 (ppm)


S37
[1]H NMR (500 MHz, CDCl3)
f1 (ppm)


S37
[13]C NMR (126 MHz, CDCl3)
167.10
135.58
132.64
130.93
129.46
128.20
127.86
126.68
125.38
80.77
49.28
48.04
45.15
37.07
28.26
27.61
19.87
19.06
13.79
f1 (ppm)


S38
^{1}H NMR (500 MHz, CDCl$_3$)
f1 (ppm)


S38
^{13}C NMR (126 MHz, CDCl$_3$)
f1 (ppm)