SUPPORTING INFORMATION

Annulation of Benzaldehydes with Norbornenes toward Indanones Assisted by Monodentate Transient Directing Groups via Double C–H Activation

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Contents:

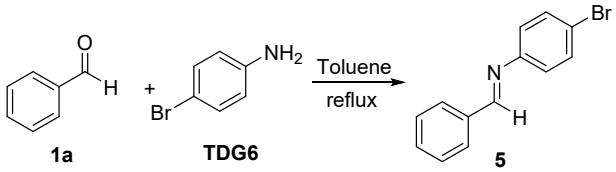
1. General Information

All reagents and solvents were obtained from commercial sources and used as received without further purification unless otherwise stated. The progress of the reactions was monitored by TLC (silica gel, Polygram SILG/UV 254 plates). Petroleum ether refers to the fraction boiling in the 60-90°C range. Reaction products were purified via column chromatography on silica gel (300-400 mesh). HPLC yields were determined on SHIMADZU LC-20A via standard curve method. ^{1}H NMR spectra were recorded on Bruker DPX-500 instrument (500 MHz) in Chloroform-*d* with tetramethylsilane (TMS) as an internal standard. Chemical shifts δ were quoted in parts per million (ppm) referenced to 0.0 ppm for tetramethylsilane. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Coupling constants, *J*, were reported in Hertz unit (Hz). ^{13}C NMR spectra were recorded on Bruker DRX-500 (126 MHz), and were fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.0 ppm of chloroform-*d*. ^{19}F NMR spectra were recorded on Bruker DPX-500 instrument (470 MHz) and chemical shifts were reported in ppm. High resolution mass spectra (HRMS) data were measured on an ESI-microTOF II spectrometer. X-ray intensity data were collected on a Bruker D8 CMOS detector employing graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Yield refers to isolated yield of analytically pure material unless otherwise noted. The known compounds were identified by comparison of their physical and spectral data with those reported in the literature.

2. Experimental Procedures

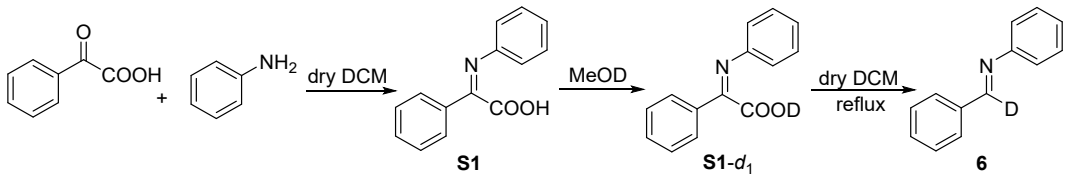
2.1 Synthesis of Starting Materials

2.1.1 Synthesis of Imine **5**



A mixture of benzaldehyde **1a** (1 mmol) and 4-bromoaniline **TDG6** (1 mmol) in toluene (25 mL) was heated to reflux for 12 h, after cooling to ambient temperature, no raw material detected by TLC. Evaporation of the solvent afforded the product **5** as an off-white solid and used for the following reaction without further purification.

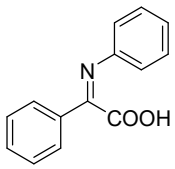
2.1.2 Synthesis of Deuterated Imine **6** [1]



A mixture of benzoylformic acid (5 mmol) and aniline (5 mmol) in dry DCM (25 mL) was stirred at room temperature for 30 min and during which time white solid precipitated gradually. Then, the reaction mixture was filtered and washed with dry DCM rapidly, and the *α*-imino acid **S1**

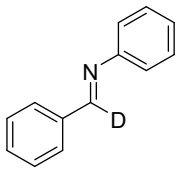
was gained in quantitative yield as a white powder (mp 151-153 ºC).

α-Imino acid **S1** (100 mg) was dissolved in methanol-d_1 and kept at room temperature for 2 h. The solvent was then removed under reduced pressure and the process repeated further four times to afford the deuterated product **S1**-d_1 as white solid. Subsequently, **S1**-d_1 was suspended in dry DCM (30 mL) and heated to reflux for 24 h, during which time the white solid would dissolved gradually. Evaporation of the solvent afforded the product **6** as a colorless oil. Based on ^{1}H NMR spectral data, the imine **6** contained 90% of the deuterium.



2-phenyl-2-(phenylimino)acetic acid (**S1**)

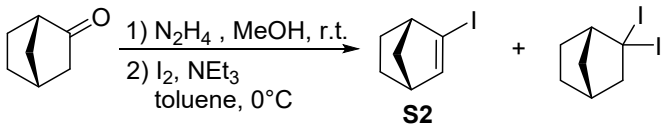
^{1}H NMR (500 MHz, DMSO-d_6) δ 7.86 (d, J = 7.2 Hz, 2H), 7.60 (d, J = 7.2 Hz, 1H), 7.56 (t, J = 7.3 Hz, 2H), 7.37 (t, J = 7.8 Hz, 2H), 7.16 (t, J = 7.4 Hz, 1H), 6.96 (d, J = 7.5 Hz, 2H).



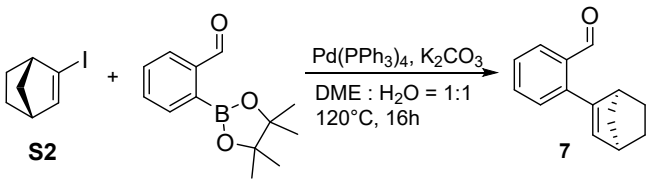
***N*,1-diphenylmethanimine-*d* (6)**

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.02–7.92 (m, 2H), 7.57–7.51 (m, 3H), 7.46 (t, J = 7.5 Hz, 2H), 7.34–7.26 (m, 3H).

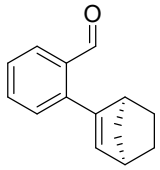
2.1.3 Synthesis of the Annulation Precursor **7** [2]



A solution of 2-norbornanone (770 mg, 7 mmol) and hydrazine monohydrate (0.8 mL, 14 mmol) in MeOH (40 mL) was stirred at ambient temperature overnight. Evaporation and addition of MeOH were repeated three times to remove the excess hydrazine. To a solution of crude hydrazone in toluene (40 mL) was added NEt_3 (3.4 mL, 24.5 mmol) at 0°C under argon atmosphere. Iodine (3.9 g, 15.4 mmol) in toluene (50 mL) was added gradually to the solution at 0°C. After stirring at 0°C for 1h, the reaction was quenched by aqueous $Na_2S_2O_3$ until the color of excess iodine disappeared. Water (50 mL) was added to the reaction mixture, and the mixture was extracted by *t*-BuOMe (50 mL×3). The combined extracts were washed with 1 M aq. HCl, aq. $NaHCO_3$ and brine successively, then dried over Na_2SO_4, filtered through celite, and evaporated. The residue was purified by silica gel column chromatography using hexane as the eluent to give a hardly separated mixture of the desired product **S2** and 2,2-diiodonorbornane.



A reaction tube (25 mL) with magnetic stir bar was charged with 2-formylphenylboronic acid pinacol ester (464 mg, 2 mmol), the mixture of **S2** and 2,2-diiodonorbornane (220 mg), $Pd(PPh_3)_4$ (57 mg, 5 mol%), K_2CO_3 (552 mg, 4 mmol), DME (5 mL), and H_2O (5 mL). The reaction mixture was heating to 120 °C for 16 h. After cooling to ambient temperature, water (20 mL) was added to the reaction mixture, and the mixture was extracted by DCM (20 mL×3). The combined extracts were dried over Na_2SO_4 and evaporated. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate as the eluent to afford the desired product **7** as a colorless oil.



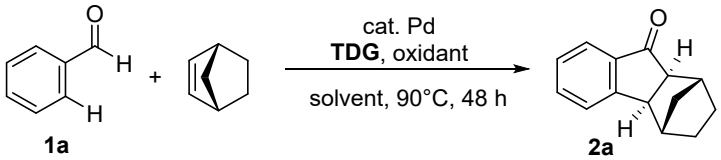
***o*-(norbornen-2-yl)benzaldehyde (7)**

^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.17 (s, 1H), 7.89 (d, *J* = 7.1 Hz, 1H), 7.53 (t, *J* = 6.9 Hz, 1H), 7.38 (d, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 5.98 (s, 1H), 3.23 (s, 1H), 3.10 (s, 1H), 1.85 (d, *J* = 7.8 Hz, 2H), 1.70 (d, *J* = 8.3 Hz, 1H), 1.34–1.28 (m, 2H), 1.23–1.18 (m, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 192.55, 144.49, 141.29, 139.09, 134.38, 133.33, 127.89, 127.73, 126.83, 48.79, 47.19, 44.15, 25.95, 25.22.

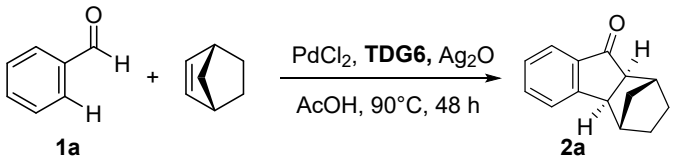
HRMS (ESI): *m/z* calculated for $C_{14}H_{15}O^+$ $[M+H]^+$ 199.1177; found 199.1175.

2.2 Optimization of the Reaction Conditions



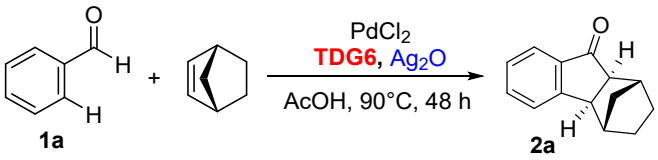
A reaction tube (4 mL) with magnetic stir bar was charged with benzaldehyde **1a** (21.2 mg, 0.2 mmol), palladium catalyst (0.02 mmol), **TDG** (0.2 mmol), oxidant (0.6 mmol), NBE (28.3 mg, 0.3 mmol) and solvent (2 mL) in air. The reaction mixture was stirred at room temperature for 10 min, followed by heating to 90°C for 48 h. After cooling to ambient temperature, 25 μL reaction mixture was extracted using a pipette gun and subsequently diluted into a 5 mL volumetric bottle with acetonitrile. The sample was analyzed by HPLC via standard curve method to calculate the yield.

Table S1 Screening of the Amount of NBE



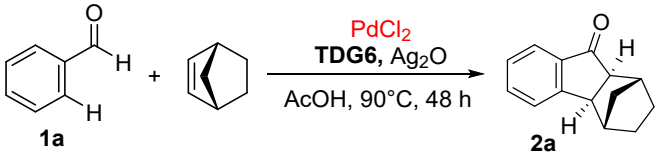
Entry	NBE(equiv.)	HPLC yield (%)
1	1.5	70
2	**2.0**	**77**
3	2.5	75
4	3.0	71

Table S2 Screening of the Amount of TDG and Oxidant



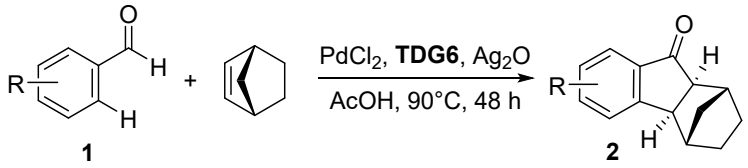
Entry	TDG6 (equiv.)	Ag_2O (equiv.)	HPLC yield (%)
1	1.0	3.0	77
2	0.5	3.0	65
3	1.5	3.0	77
4	**1.0**	**1.5**	**76**
5	1.0	4.5	35

Table S3 Screening of the Amount of Catalyst



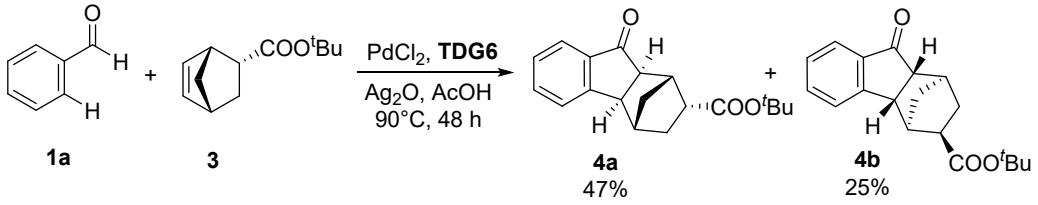
Entry	$PdCl_2$ (mol%)	HPLC yield (%)
1	10	76
2	20	88
3	**30**	**92**
4	40	92

2.3 General Procedure for the Synthesis of Indanones 2



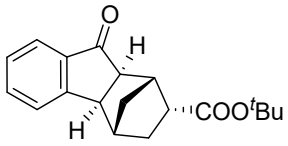
A reaction tube (4 mL) with magnetic stir bar was charged with benzaldehyde **1** (0.2 mmol), $PdCl_2$ (10.6 mg, 0.06 mmol), 4-bromoaniline (**TDG6**, 34.8 mg, 0.2 mmol), Ag_2O (69.5 mg, 0.3 mmol), NBE (37.6 mg, 0.4 mmol) and AcOH (2 mL) in air. The reaction mixture was stirred at room temperature for 10 min, followed by heating to 90°C for 48 h. After cooling to ambient temperature, the reaction mixture was filtered through a silica gel plug, and concentrated in *vacuo*. The crude reaction mixture was purified by flash silica gel column chromatography using petroleum ether/ethyl acetate as the eluent to afford the desired product.

2.4 Procedure for the Synthesis of Indanones 4a and 4b



t-Butyl 5-norbornene-2-carboxylate **3** was pre-purified by flash silica gel column chromatography using hexane as the eluent to afford the *endo*-isomer.

A reaction tube (4 mL) with magnetic stir bar was charged with benzaldehyde **1** (0.2 mmol), $PdCl_2$ (10.6 mg, 0.06 mmol), 4-bromoaniline (**TDG6**, 34.8 mg, 0.2 mmol), Ag_2O (69.5 mg, 0.3 mmol), **3** (77.6 mg, 0.4 mmol) and AcOH (2 mL) in air. The reaction mixture was stirred at room temperature for 10 min, followed by heating to 90°C for 48 h. After cooling to ambient temperature, the reaction mixture was filtered through a silica gel plug, and concentrated in *vacuo*. The crude reaction mixture was purified by flash silica gel column chromatography using petroleum ether/ethyl acetate (100:1) as the eluent to afford **4a** (28 mg, 47%) and **4b** (14.9 mg, 25%) as yellow oil respectively.

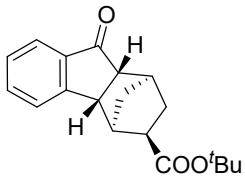


***t*-butyl (1*R*,2*R*,4*R*)-9-oxo-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanofluorene-2-carboxylate** (**4a**)

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 7.7 Hz, 1H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 7.4 Hz, 1H), 3.27 (d, *J* = 6.1 Hz, 1H), 2.87 (d, *J* = 4.3 Hz, 1H), 2.84–2.76 (m, 1H), 2.59 (d, *J* = 6.0 Hz, 1H), 2.44 (d, *J* = 3.6 Hz, 1H), 1.93–1.81 (m, 2H), 1.50 (s, 9H), 1.10 (d, *J* = 10.7 Hz, 1H), 0.94 (d, *J* = 10.4 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 208.33, 173.47, 156.79, 139.12, 135.04, 127.45, 126.19, 123.20, 80.67, 51.04, 47.40, 45.73, 43.98, 42.05, 34.02, 31.46, 28.21.

HRMS (ESI): *m/z* calculated for $C_{19}H_{23}O_3^+$ $[M+H]^+$ 299.1642; found 299.1641.



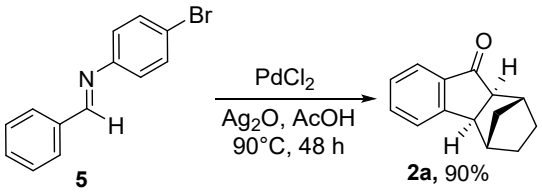
***t*-butyl (1*R*,3*R*,4*R*)-9-oxo-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanofluorene-3-carboxylate (4b)**

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 7.6 Hz, 1H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 3.29 (d, *J* = 6.0 Hz, 1H), 2.87 (dt, *J* = 10.3, 5.2 Hz, 1H), 2.71 (s, 1H), 2.65 (s, 1H), 2.60 (d, *J* = 6.0 Hz, 1H), 1.84–1.78 (m, 2H), 1.54 (s, 9H), 1.10 (d, *J* = 10.7 Hz, 1H), 0.93 (d, *J* = 10.7 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 208.28, 173.49, 156.63, 139.31, 135.10, 127.64, 125.96, 123.41, 80.55, 55.34, 46.28, 45.03, 42.98, 40.91, 33.83, 30.96, 28.34.

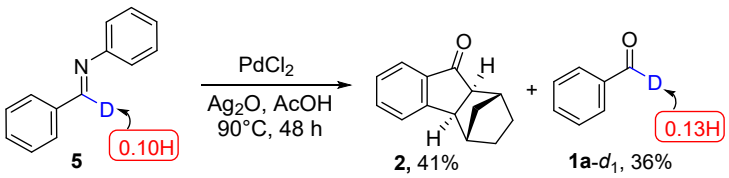
HRMS (ESI): *m/z* calculated for $C_{19}H_{23}O_3^+$ $[M+H]^+$ 299.1642; found 299.1641.

2.5 Procedure for the Synthesis of Indanones 2 by Imine 5



A reaction tube (4 mL) with magnetic stir bar was charged with imine **5** (0.2 mmol, 52 mg), $PdCl_2$ (10.6 mg, 0.06 mmol), Ag_2O (69.5 mg, 0.3 mmol), NBE (37.6 mg, 0.4 mmol) and AcOH (2 mL) in air. The reaction mixture was stirred at room temperature for 10 min, followed by heating to 90°C for 48 h. After cooling to ambient temperature, the reaction mixture was filtered through a silica gel plug, and concentrated in *vacuo*. The crude reaction mixture was purified by flash silica gel column chromatography using petroleum ether/ethyl acetate as the eluent to afford the desired product **2a** (35.5 mg, 90%).

2.6 Deuterium Labelling Experiment



The ^{1}H NMR spectra of staring material before reaction and recovered starting material after reaction are illustrated in Figure S1.

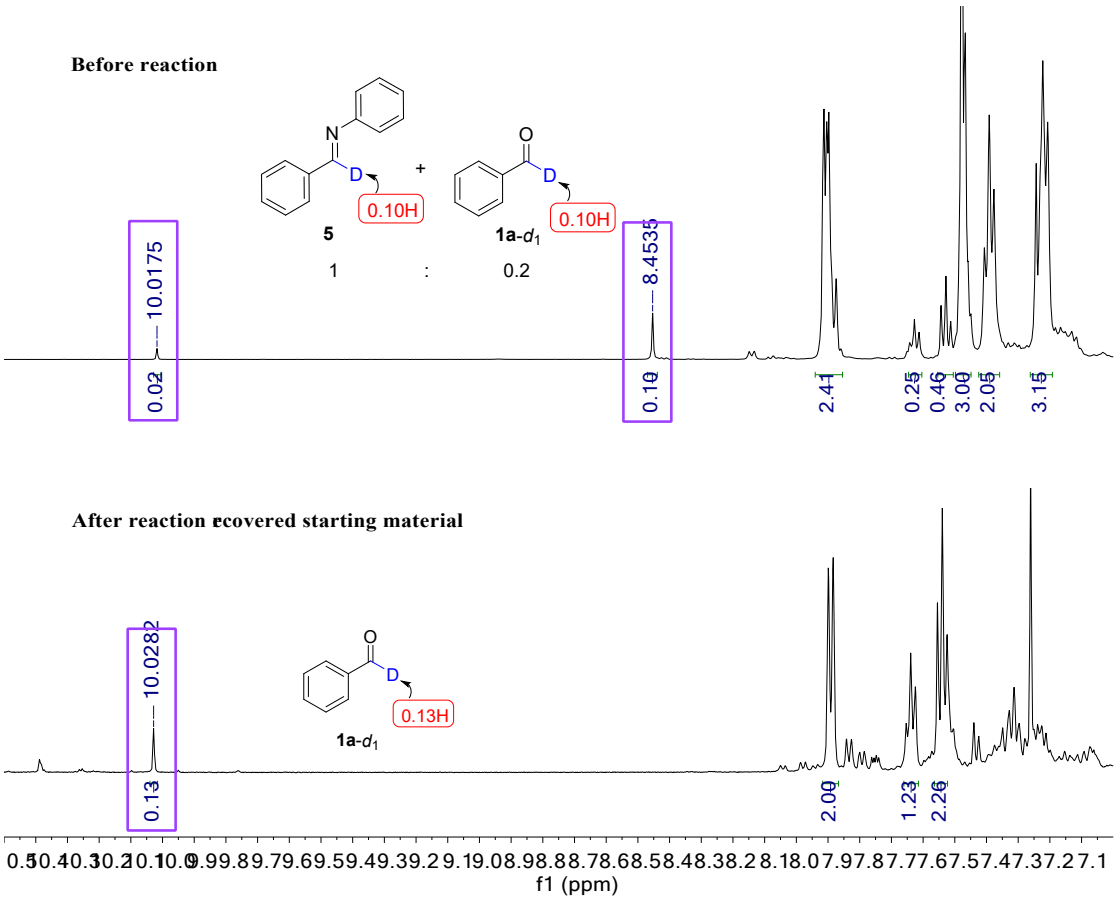
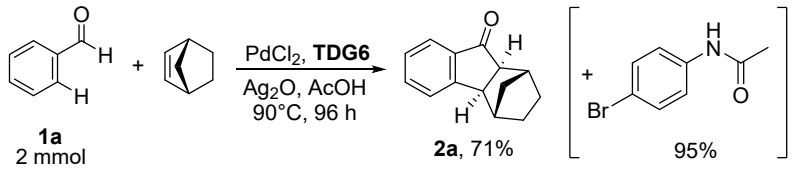


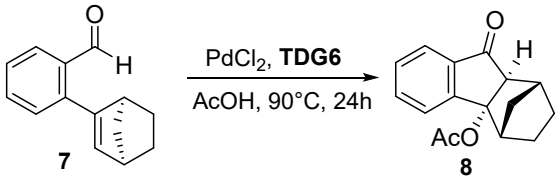
Figure S1: ^{1}H NMR spectra of staring material before reaction and recovered starting material after reaction.

2.7 Scale-up Experiment

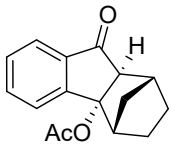


A reaction flask (50 mL) with magnetic stir bar was charged with benzaldehyde **1** (2 mmol), $PdCl_2$ (106 mg, 0.6 mmol), 4-bromoaniline (**TDG6**, 348 mg, 2 mmol), Ag_2O (695 mg, 3 mmol), NBE (376 mg, 4 mmol) and AcOH (20 mL) in air. The reaction mixture was stirred at room temperature for 10 min, followed by heating to 90°C for 96 h. After cooling to ambient temperature, the reaction mixture was filtered through a silica gel plug, and concentrated in *vacuo*. The crude reaction mixture was purified by flash silica gel column chromatography using petroleum ether/ethyl acetate as the eluent to afford the desired product **2a** (140.3 mg, 71%) and *N*-(4-bromophenyl)acetamide (203.1 mg, 95%).

2.8 Annulation Experiment of Precursor 7



A reaction tube (4 mL) with magnetic stir bar was charged with **7** (19.8 mg, 0.1 mmol), $PdCl_2$ (0.03 mmol), 4-bromoaniline (**TDG6**, 17.4 mg, 0.1 mmol), Ag_2O (0.15 mmol or no added) and AcOH (1 mL) in air. The reaction mixture was stirred at room temperature for 10 min, followed by heating to 90°C for 48 h. After cooling to ambient temperature, the reaction mixture was filtered throught a silica gel plug, and concentrated in *vacuo*. The crude reaction mixture was purified by flash silica gel column chromatography using petroleum ether/ethyl acetate as the eluent to afford the desired product **8** (22.7 mg, 86% or 3 mg, 11%) as a colorless oil.



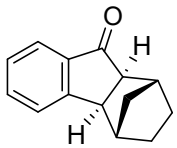
***(1R,4S,4aS)*-9-oxo-1,2,3,4,9,9a-hexahydro-4a*H*-1,4-methanofluoren-4a-yl acetate (8)**

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.72 (dd, *J* = 14.1, 7.7 Hz, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 1H), 2.91 (s, 1H), 2.63 (s, 1H), 2.57 (s, 1H), 2.01 (s, 3H), 1.96 (t, *J* = 9.2 Hz, 1H), 1.74 (t, *J* = 12.0 Hz, 1H), 1.66–1.59 (m, 1H), 1.46 (t, *J* = 10.6 Hz, 1H), 1.14 (d, *J* = 12.8 Hz, 1H), 0.89 (d, *J* = 10.9 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 204.93, 170.42, 153.34, 139.28, 135.46, 129.33, 124.73, 122.79, 90.12, 60.25, 45.03, 40.55, 34.24, 28.13, 22.61, 21.55.

HRMS (ESI): *m/z* calculated for $C_{16}H_{17}O^+$ $[M+H]^+$ 257.1172; found 257.1173.

3. Analytical Data of Products

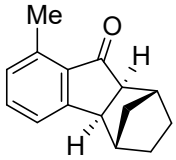


(1*R*,4*S*)-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (2a)

Following the general procedure, compound **2a** was isolated as a colorless oil (35.6 mg, 90% yield) by silica gel column chromatography (eluent: petroleum ether/ ethyl acetate = 150:1). The physical and spectral data are in accordance with literature values[3].

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 7.7 Hz, 1H), 7.61 (t, *J* = 7.8 Hz, 1H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 14.8 Hz, 1H), 3.15 (d, *J* = 6.1 Hz, 1H), 2.60 (d, *J* = 4.2 Hz, 1H), 2.50 (d, *J* = 6.1 Hz, 1H), 2.41 (d, *J* = 4.2 Hz, 1H), 1.72 (t, *J* = 11.8 Hz, 1H), 1.64 (t, *J* = 11.8 Hz, 1H), 1.47 (t, *J* = 10.9 Hz, 1H), 1.37 (t, *J* = 10.0 Hz, 1H), 0.94 (d, *J* = 10.6 Hz, 1H), 0.80 (d, *J* = 10.5 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 208.94, 157.28, 139.09, 135.00, 127.42, 126.20, 123.19, 55.87, 48.07, 41.30, 40.42, 32.25, 28.92, 28.71.

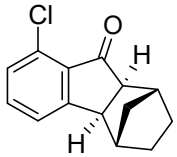


(1*R*,4*S*)-8-methyl-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (**2b**)

Following the general procedure, compound **2b** was isolated as a colorless oil (26.3 mg, 62% yield) by silica gel column chromatography (eluent: petroleum ether/ ethyl acetate = 400:1). The physical and spectral data are in accordance with literature values[3].

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.45 (t, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 7.3 Hz, 1H), 3.08 (d, *J* = 6.2 Hz, 1H), 2.63 (s, 3H), 2.58 (d, *J* = 4.1 Hz, 1H), 2.45 (d, *J* = 6.2 Hz, 1H), 2.38 (d, *J* = 4.1 Hz, 1H), 1.71 (tt, *J* = 10.8, 3.9 Hz, 1H), 1.67–1.60 (m, 1H), 1.46 (t, *J* = 10.0 Hz, 1H), 1.37 (t, *J* = 9.8 Hz, 1H), 0.93 (d, *J* = 10.5 Hz, 1H), 0.84 (d, *J* = 10.5 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 209.93, 158.16, 138.34, 136.51, 134.22, 129.20, 123.52, 56.06, 47.41, 41.52, 40.50, 32.15, 28.98, 28.73, 18.42.



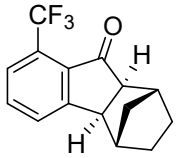
(1*R*,4*S*)-8-chloro-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (**2c**)

Following the general procedure, compound **2c** was isolated as a colorless oil (23.7 mg, 51% yield) by silica gel column chromatography (eluent: petroleum ether/ ethyl acetate = 200:1).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 1H), 3.10 (d, *J* = 6.2 Hz, 1H), 2.64 (d, *J* = 4.1 Hz, 1H), 2.53 (d, *J* = 6.3 Hz, 1H), 2.41 (d, *J* = 4.2 Hz, 1H), 1.73 (t, *J* = 11.8 Hz, 1H), 1.64 (t, *J* = 11.8 Hz, 1H), 1.47 (t, *J* = 10.6 Hz, 1H), 1.38 (t, *J* = 10.9 Hz, 1H), 0.97 (d, *J* = 10.7 Hz, 1H), 0.85 (d, *J* = 10.7 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 205.81, 159.78, 135.29, 134.82, 131.41, 129.09, 124.68, 56.28, 47.15, 41.61, 40.80, 32.23, 28.90, 28.60.

HRMS (ESI): *m/z* calculated for $C_{14}H_{14}ClO^+$ $[M+H]^+$ 233.0728; found 233.0729.



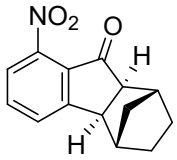
(1*R*,4*S*)-8-(trifluoromethyl)-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (**2d**)

Following the general procedure, compound **2d** was isolated as a white solid (23.4 mg, 44% yield) by silica gel column chromatography (eluent: petroleum ether/ ethyl acetate = 50:1). The physical and spectral data are in accordance with literature values[3].

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.74–7.63 (m, 3H), 3.17 (d, *J* = 6.3 Hz, 1H), 2.66 (s, 1H), 2.55 (d, *J* = 6.3 Hz, 1H), 2.43 (s, 1H), 1.75 (t, *J* = 11.8 Hz, 1H), 1.66 (t, *J* = 11.8 Hz, 1H), 1.53–1.47 (m, 1H), 1.43–1.36 (m, 1H), 0.99 (d, *J* = 10.6 Hz, 1H), 0.83 (d, *J* = 10.6 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 204.78, 159.43, 135.76, 134.18, 130.17, 126.39 (d, *J* = 34.6 Hz), 125.15 (q, *J* = 6.0 Hz), 122.72 (d, *J* = 273.9 Hz), 55.70, 47.66, 41.53, 40.90, 32.15, 28.90, 28.47.

^{19}F NMR (470 MHz, Chloroform-d_3) δ -61.38.



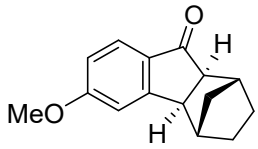
(1*R*,4*S*)-8-nitro-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (**2e**)

Following the general procedure, compound **2e** was isolated as a yellow oil (18 mg, 37% yield) by silica gel column chromatography (eluent: petroleum ether/ ethyl acetate = 50:1). m.p. = 99.5 ºC.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 3.5 Hz, 2H), 7.59 (s, 1H), 3.21 (d, *J* = 6.2 Hz, 1H), 2.68 (s, 1H), 2.61 (d, *J* = 6.2 Hz, 1H), 2.46 (s, 1H), 1.76 (t, *J* = 11.8 Hz, 1H), 1.67 (t, *J* = 12.0 Hz, 1H), 1.50 (t, *J* = 10.4 Hz, 1H), 1.43–1.36 (m, 1H), 1.02 (d, *J* = 10.8 Hz, 1H), 0.86 (d, *J* = 10.7 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 202.53, 159.02, 145.57, 135.20, 130.09, 130.03, 121.78, 77.30, 77.04, 76.79, 56.09, 47.64, 41.57, 40.87, 32.35, 28.83, 28.37.

HRMS (ESI): *m/z* calculated for $C_{14}H_{14}NO_3^+$ $[M+H]^+$ 244.0968; found 244.0969.

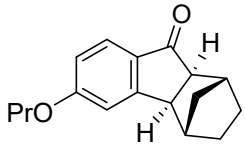


(1*R*,4*S*)-6-methoxy-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (**2f**)

Following the general procedure, compound **2f** was isolated as a colorless oil (29.2 mg, 64% yield) by silica gel column chromatography (eluent: petroleum ether/ ethyl acetate = 100:1). The physical and spectral data are in accordance with literature values[3].

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 8.4 Hz, 1H), 6.91 (s, 1H), 6.89 (dd, *J* = 8.4, 2.2 Hz, 1H), 3.89 (s, 3H), 3.08 (d, *J* = 6.1 Hz, 1H), 2.58 (s, 1H), 2.49 (d, *J* = 6.1 Hz, 1H), 2.39 (s, 1H), 1.71 (t, *J* = 11.7 Hz, 1H), 1.68–1.63 (m, 1H), 1.45 (t, *J* = 11.6 Hz, 1H), 1.40–1.35 (m, 1H), 0.95 (d, *J* = 10.5 Hz, 1H), 0.85 (d, *J* = 10.4 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 207.01, 165.61, 160.23, 132.51, 124.93, 115.38, 109.23, 56.28, 55.66, 48.05, 41.32, 40.19, 32.25, 28.92, 28.74.

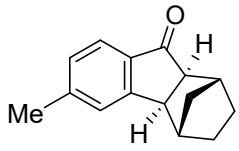


(1*R*,4*S*)-6-propoxy-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (**2g**)

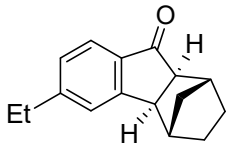
Following the general procedure, compound **2g** was isolated as a colorless oil (29.3 mg, 57% yield) by silica gel column chromatography (eluent: petroleum ether/ ethyl acetate = 75:1).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 8.4 Hz, 1H), 6.90 (s, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 4.00 (t, *J* = 6.6 Hz, 2H), 3.07 (d, *J* = 6.0 Hz, 1H), 2.58 (d, *J* = 4.1 Hz, 1H), 2.48 (d, *J* = 6.1 Hz, 1H), 2.39 (d, *J* = 4.2 Hz, 1H), 1.85 (q, *J* = 7.0 Hz, 2H), 1.75–1.67 (m, 1H), 1.67–1.60 (m, 1H), 1.47–1.41 (m, 1H), 1.40–1.35 (m, 1H), 1.06 (t, *J* = 7.4 Hz, 3H), 0.94 (d, *J* = 10.4 Hz, 1H), 0.85 (d, *J* = 10.4 Hz, 1H).

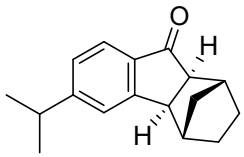
^{13}C NMR (126 MHz, Chloroform-*d*) δ 207.00, 165.24, 160.22, 132.26, 124.90, 115.73, 109.73, 69.95, 56.27, 48.04, 41.31, 40.17, 32.24, 28.92, 28.76, 22.50, 10.52.
HRMS (ESI): *m/z* calculated for $C_{17}H_{21}O_2^+$ $[M+H]^+$ 257.1536; found 257.1537.



(1*R*,4*S*)-6-methyl-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (**2h**)
Following the general procedure, compound **2h** was isolated as a yellow solid (30.1 mg, 71% yield) by silica gel column chromatography (eluent: petroleum ether/ ethyl acetate = 150:1). The physical and spectral data are in accordance with literature values[3].
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 7.8 Hz, 1H), 7.29 (s, 1H), 7.16 (d, *J* = 7.8 Hz, 1H), 3.09 (d, *J* = 6.0 Hz, 1H), 2.58 (d, *J* = 4.1 Hz, 1H), 2.48 (d, *J* = 6.1 Hz, 1H), 2.44 (s, 3H), 2.39 (d, *J* = 4.1 Hz, 1H), 1.71 (t, *J* = 11.7 Hz, 1H), 1.63 (t, *J* = 11.8 Hz, 1H), 1.48–1.42 (m, 1H), 1.39–1.34 (m, 1H), 0.93 (d, *J* = 10.5 Hz, 1H), 0.81 (d, *J* = 10.5 Hz, 1H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 208.40, 157.81, 146.15, 136.89, 128.75, 126.52, 123.04, 56.11, 47.91, 41.27, 40.30, 32.23, 28.93, 28.74, 22.15.



(1*R*,4*S*)-6-ethyl-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (**2i**)
Following the general procedure, compound **2i** was isolated as a colorless oil (28.1 mg, 62% yield) by silica gel column chromatography (eluent: petroleum ether/ ethyl acetate = 150:1).
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 7.8 Hz, 1H), 7.31 (s, 1H), 7.19 (d, *J* = 7.9 Hz, 1H), 3.10 (d, *J* = 6.0 Hz, 1H), 2.74 (q, *J* = 7.6 Hz, 2H), 2.59 (d, *J* = 4.1 Hz, 1H), 2.49 (d, *J* = 6.0 Hz, 1H), 2.40 (d, *J* = 4.2 Hz, 1H), 1.71 (t, *J* = 11.7 Hz, 1H), 1.65–1.60 (m, 1H), 1.45 (t, *J* = 10.5 Hz, 1H), 1.40–1.34 (m, 1H), 1.28 (t, *J* = 7.6 Hz, 3H), 0.94 (d, *J* = 10.6 Hz, 1H), 0.82 (d, *J* = 10.6 Hz, 1H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 208.53, 157.92, 152.39, 137.09, 127.69, 125.22, 123.16, 56.16, 47.99, 41.29, 40.32, 32.27, 29.43, 28.95, 28.74, 15.32.
HRMS (ESI): *m/z* calculated for $C_{16}H_{19}O^+$ $[M+H]^+$ 227.1430; found 227.1429.

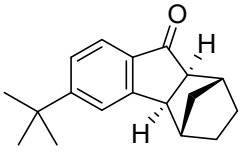


(1*R*,4*S*)-6-isopropyl-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (**2j**)
Following the general procedure, compound **2j** was isolated as a colorless oil (27.9 mg, 58% yield) by silica gel column chromatography (eluent: petroleum ether/ ethyl acetate = 150:1).
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 7.9 Hz, 1H), 7.33 (s, 1H), 7.22 (dd, *J* = 8.0, 1.5 Hz, 1H), 3.11 (d, *J* = 6.0 Hz, 1H), 2.99 (p, *J* = 6.9 Hz, 1H), 2.59 (d, *J* = 4.1 Hz, 1H), 2.48 (d, *J* =

6.0 Hz, 1H), 2.41 (d, *J* = 4.2 Hz, 1H), 1.71 (t, *J* = 11.7 Hz, 1H), 1.66–1.60 (m, 1H), 1.46 (t, *J* = 10.6 Hz, 1H), 1.40–1.35 (m, 1H), 1.29 (d, *J* = 6.8 Hz, 6H), 0.94 (d, *J* = 10.5 Hz, 1H), 0.83 (d, *J* = 10.4 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 208.54, 157.92, 157.00, 137.23, 126.35, 123.74, 123.18, 56.18, 48.06, 41.31, 40.32, 34.74, 32.29, 28.96, 28.73, 23.89, 23.80.

HRMS (ESI): *m/z* calculated for $C_{17}H_{21}O^+$ $[M+H]^+$ 241.1587; found 241.1589.

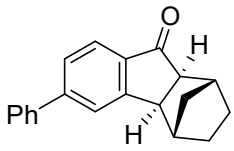


(1*R*,4*S*)-6-(*tert*-butyl)-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (**2k**)

Following the general procedure, compound **2k** was isolated as a white solid (27.5 mg, 54% yield) by silica gel column chromatography (eluent: petroleum ether/ ethyl acetate = 150:1). The physical and spectral data are in accordance with literature values[3].

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 8.2 Hz, 1H), 7.49 (s, 1H), 7.41 (d, *J* = 8.1 Hz, 1H), 3.12 (d, *J* = 6.0 Hz, 1H), 2.60 (d, *J* = 4.1 Hz, 1H), 2.49 (d, *J* = 6.1 Hz, 1H), 2.42 (d, *J* = 4.2 Hz, 1H), 1.76–1.69 (m, 1H), 1.67–1.60 (m, 1H), 1.49–1.44 (m, 1H), 1.36 (s, 10H), 0.94 (d, *J* = 10.6 Hz, 1H), 0.84 (d, *J* = 10.4 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 208.60, 159.22, 157.63, 136.74, 125.27, 122.79, 122.55, 56.22, 48.19, 41.33, 40.32, 35.56, 32.31, 31.30, 28.97, 28.74.



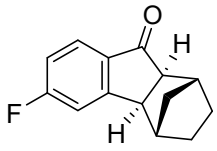
(1*R*,4*S*)-6-phenyl-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (**2l**)

Following the general procedure, compound **2l** was isolated as a white solid (36.2 mg, 66% yield) by silica gel column chromatography (eluent: petroleum ether/ ethyl acetate = 200:1). m.p. = 82 ºC.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 8.0 Hz, 1H), 7.69 (s, 1H), 7.64 (d, *J* = 7.4 Hz, 2H), 7.59 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.41 (t, *J* = 7.3 Hz, 1H), 3.20 (d, *J* = 6.1 Hz, 1H), 2.63 (d, *J* = 4.1 Hz, 1H), 2.55 (d, *J* = 6.0 Hz, 1H), 2.47 (d, *J* = 4.2 Hz, 1H), 1.74 (t, *J* = 11.7 Hz, 1H), 1.70–1.62 (m, 1H), 1.52–1.45 (m, 1H), 1.42–1.36 (m, 1H), 0.98 (d, *J* = 10.6 Hz, 1H), 0.89 (d, *J* = 6.7 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 208.56, 158.02, 148.05, 140.32, 138.00, 129.00, 128.37, 127.54, 126.92, 124.68, 123.60, 56.28, 48.16, 41.42, 40.49, 32.37, 28.96, 28.75.

HRMS (ESI): *m/z* calculated for $C_{20}H_{19}O^+$ $[M+H]^+$ 275.1430; found 275.1429.



(1*R*,4*S*)-6-fluoro-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (**2m**)

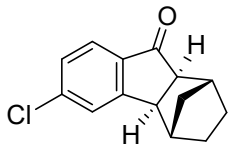
Following the general procedure, compound **2m** was isolated as a colorless oil (25.1 mg, 58% yield)

by silica gel column chromatography (eluent: petroleum ether/ ethyl acetate = 100:1). The physical and spectral data are in accordance with literature values[3].

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.71 (dd, *J* = 8.5, 5.3 Hz, 1H), 7.15 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.05 (td, *J* = 8.6, 2.3 Hz, 1H), 3.13 (d, *J* = 6.1 Hz, 1H), 2.60 (d, *J* = 4.1 Hz, 1H), 2.53 (d, *J* = 6.1 Hz, 1H), 2.40 (d, *J* = 4.2 Hz, 1H), 1.73 (t, *J* = 11.8 Hz, 1H), 1.65 (t, *J* = 11.8 Hz, 1H), 1.46 (t, *J* = 10.9 Hz, 1H), 1.41–1.34 (m, 1H), 0.98 (d, *J* = 10.6 Hz, 1H), 0.82 (d, *J* = 10.6 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.87, 167.50 (d, *J* = 256.3 Hz), 160.13 (d, *J* = 9.7 Hz), 135.54, 125.49 (d, *J* = 10.4 Hz), 115.75 (d, *J* = 23.9 Hz), 112.70 (d, *J* = 21.8 Hz), 56.22, 47.92 (d, *J* = 2.2 Hz), 41.30, 40.40, 32.28, 28.85, 28.62.

^{19}F NMR (470 MHz, Chloroform-*d*) δ -103.43.

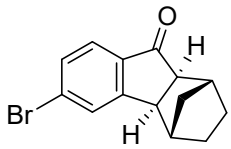


(1*R*,4*S*)-6-chloro-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (**2n**)

Following the general procedure, compound **2n** was isolated as a colorless oil (25.6 mg, 55% yield) by silica gel column chromatography (eluent: petroleum ether/ ethyl acetate = 100:1). The physical and spectral data are in accordance with literature values[3].

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 8.1 Hz, 1H), 7.49 (s, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 3.13 (d, *J* = 6.1 Hz, 1H), 2.60 (d, *J* = 4.1 Hz, 1H), 2.52 (d, *J* = 6.1 Hz, 1H), 2.41 (d, *J* = 4.3 Hz, 1H), 1.73 (t, *J* = 11.8 Hz, 1H), 1.65 (t, *J* = 11.8 Hz, 2H), 1.46 (t, *J* = 10.7 Hz, 1H), 1.40–1.34 (m, 1H), 0.98 (d, *J* = 10.9 Hz, 1H), 0.81 (d, *J* = 10.7 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 207.41, 158.69, 141.49, 137.55, 128.25, 126.46, 124.36, 56.06, 47.83, 41.30, 40.50, 32.33, 28.84, 28.63.

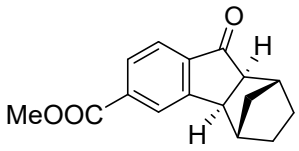


(1*R*,4*S*)-6-bromo-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (**2o**)

Following the general procedure, compound **2o** was isolated as a colorless oil (24.4 mg, 44% yield) by silica gel column chromatography (eluent: petroleum ether/ ethyl acetate = 100:1). The physical and spectral data are in accordance with literature values[3].

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.67 (s, 1H), 7.57 (d, *J* = 8.2 Hz, 1H), 7.49 (dd, *J* = 8.1, 1.6 Hz, 1H), 3.13 (d, *J* = 6.1 Hz, 1H), 2.60 (d, *J* = 4.0 Hz, 1H), 2.50 (d, *J* = 6.1 Hz, 1H), 2.41 (d, *J* = 4.2 Hz, 1H), 1.73 (t, *J* = 11.8 Hz, 1H), 1.69–1.63 (m, 1H), 1.46 (t, *J* = 11.0 Hz, 1H), 1.40–1.34 (m, 1H), 0.98 (d, *J* = 10.7 Hz, 1H), 0.80 (d, *J* = 10.7 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 207.58, 158.81, 137.92, 131.06, 130.36, 129.56, 124.45, 55.96, 47.81, 41.30, 40.50, 32.33, 28.84, 28.62.

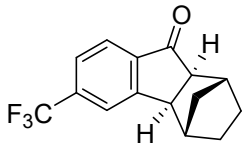


Methyl (1*R*,4*S*)-9-oxo-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanofluorene-6-carboxylate (2p)

Following the general procedure, compound **2p** was isolated as a white solid (23.1 mg, 45% yield) by silica gel column chromatography (eluent: petroleum ether/ ethyl acetate = 50:1). The physical and spectral data are in accordance with literature values[3].

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.19 (s, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 7.9 Hz, 1H), 3.96 (s, 3H), 3.21 (d, *J* = 6.1 Hz, 1H), 2.62 (d, *J* = 4.1 Hz, 1H), 2.56 (d, *J* = 6.1 Hz, 1H), 2.47 (d, *J* = 4.2 Hz, 1H), 1.75 (t, *J* = 11.9 Hz, 1H), 1.66 (t, *J* = 11.9 Hz, 1H), 1.49 (t, *J* = 10.6 Hz, 1H), 1.42–1.35 (m, 1H), 0.98 (d, *J* = 10.7 Hz, 1H), 0.78 (d, *J* = 10.7 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 208.40, 166.49, 156.98, 142.22, 135.80, 128.68, 127.67, 123.09, 56.23, 52.57, 48.03, 41.33, 40.72, 32.33, 28.84, 28.65.



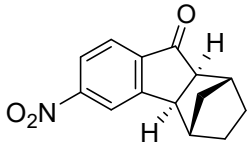
(1*R*,4*S*)-6-(trifluoromethyl)-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (2q)

Following the general procedure, compound **2q** was isolated as a white solid (22.9 mg, 43% yield) by silica gel column chromatography (eluent: petroleum ether/ ethyl acetate = 300:1). The physical and spectral data are in accordance with literature values[3].

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 8.0 Hz, 1H), 7.78 (s, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 3.22 (d, *J* = 6.1 Hz, 1H), 2.64 (d, *J* = 4.2 Hz, 1H), 2.58 (d, *J* = 6.1 Hz, 1H), 2.47 (d, *J* = 4.3 Hz, 1H), 1.76 (t, *J* = 11.9 Hz, 1H), 1.67 (t, *J* = 11.9 Hz, 1H), 1.54–1.46 (m, 1H), 1.44–1.36 (m, 1H), 1.00 (d, *J* = 10.7 Hz, 1H), 0.79 (d, *J* = 10.7 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 207.87, 157.29, 141.64, 136.27 (d, *J* = 31.8 Hz), 124.60 (q, *J* = 3.6 Hz), 123.76, 123.74 (d, *J* = 273.3 Hz), 123.45 (q, *J* = 4.0 Hz), 56.11, 48.08, 41.38, 40.72, 32.38, 28.84, 28.59.

^{19}F NMR (470 MHz, Chloroform-*d*) δ -63.37.

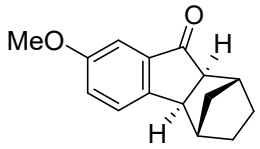


(1*R*,4*S*)-6-nitro-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (2r)

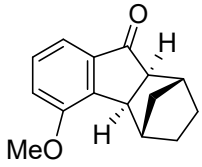
Following the general procedure, compound **2r** was isolated as a white solid (21.5 mg, 44% yield) by silica gel column chromatography (eluent: petroleum ether/ ethyl acetate = 50:1). M.p. = 114.5 ^{o}C

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.37 (s, 1H), 8.21 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.84 (d, *J* = 8.3 Hz, 1H), 3.28 (d, *J* = 6.1 Hz, 1H), 2.65 (dd, *J* = 14.0, 5.2 Hz, 2H), 2.51 (d, *J* = 4.3 Hz, 1H), 1.78 (t, *J* = 12.0 Hz, 1H), 1.68 (t, *J* = 12.0 Hz, 1H), 1.52 (t, *J* = 10.6 Hz, 1H), 1.42 (t, *J* = 9.7 Hz, 1H), 1.04 (d, *J* = 10.8 Hz, 1H), 0.78 (d, *J* = 10.8 Hz, 1H).

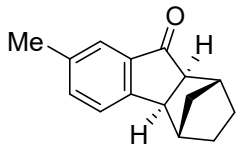
^{13}C NMR (126 MHz, Chloroform-*d*) δ 207.15, 157.91, 152.21, 143.19, 124.19, 122.97, 121.68, 56.43, 48.07, 41.46, 40.97, 32.47, 28.80, 28.53.
HRMS (ESI): *m/z* calculated for $C_{14}H_{14}NO_3^+$ $[M+H]^+$ 244.0968; found 244.0967.



(1*R*,4*S*)-7-methoxy-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (**2s**)
Following the general procedure, compound **2s** was isolated along with **2ss** as a yellow oil (16.5 mg, 36% yield) by silica gel column chromatography (eluent: petroleum ether/ ethyl acetate = 300:1). The physical and spectral data are in accordance with literature values[3].
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 8.3 Hz, 1H), 7.21 (dd, *J* = 8.4, 2.5 Hz, 1H), 7.14 (d, *J* = 2.6 Hz, 1H), 3.83 (s, 3H), 3.08 (d, *J* = 5.9 Hz, 1H), 2.58 (d, *J* = 4.1 Hz, 1H), 2.52 (d, *J* = 5.9 Hz, 1H), 2.36 (d, *J* = 4.2 Hz, 1H), 1.71 (t, *J* = 11.6 Hz, 1H), 1.63 (t, *J* = 11.8 Hz, 1H), 1.48–1.41 (m, 1H), 1.39–1.34 (m, 1H), 0.94 (d, *J* = 10.5 Hz, 1H), 0.81 (d, *J* = 10.5 Hz, 1H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 208.82, 159.46, 150.24, 140.32, 126.86, 124.43, 104.29, 56.65, 55.61, 47.44, 41.04, 40.35, 32.09, 28.81, 28.68.

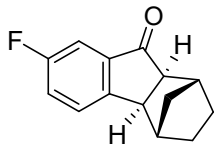


(1*R*,4*S*)-5-methoxy-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (**2ss**)
Following the general procedure, compound **2ss** was isolated along with **2s** as a yellow oil (8.8 mg, 19% yield) by silica gel column chromatography (eluent: petroleum ether/ ethyl acetate = 300:1). The physical and spectral data are in accordance with literature values[4].
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.36–7.28 (m, 2H), 7.04 (dd, *J* = 6.8, 1.9 Hz, 1H), 3.92 (s, 3H), 3.16 (d, *J* = 6.0 Hz, 1H), 2.59 (dd, *J* = 13.9, 4.2 Hz, 1H), 2.47 (d, *J* = 6.0 Hz, 1H), 1.71 (t, *J* = 11.6 Hz, 1H), 1.63 (t, *J* = 11.8 Hz, 1H), 1.50–1.41 (m, 1H), 1.40–1.33 (m, 1H), 0.94 (d, *J* = 10.5 Hz, 1H), 0.81 (d, *J* = 10.5 Hz, 1H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 209.15, 157.19, 145.49, 140.81, 129.03, 115.28, 114.90, 55.86, 55.44, 45.64, 40.30, 38.68, 32.37, 29.06, 28.64.

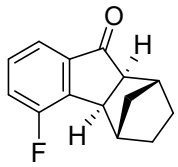


(1*R*,4*S*)-7-methyl-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (**2t**)
Following the general procedure, compound **2t** was isolated as a yellow oil (26.9 mg, 63% yield) by silica gel column chromatography (eluent: petroleum ether/ ethyl acetate = 300:1). The physical and spectral data are in accordance with literature values[3].

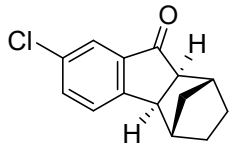
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.51 (s, 1H), 7.43 (d, *J* = 7.9 Hz, 1H), 7.38 (d, *J* = 7.8 Hz, 1H), 3.10 (d, *J* = 6.1 Hz, 1H), 2.58 (d, *J* = 4.1 Hz, 1H), 2.49 (d, *J* = 6.0 Hz, 1H), 2.40 (s, 3H), 2.38 (d, *J* = 4.4 Hz, 1H), 1.71 (t, *J* = 11.7 Hz, 1H), 1.63 (t, *J* = 11.7 Hz, 1H), 1.45 (t, *J* = 10.7 Hz, 1H), 1.39–1.33 (m, 1H), 0.93 (d, *J* = 10.4 Hz, 1H), 0.80 (d, *J* = 10.6 Hz, 1H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 209.10, 154.76, 139.27, 137.38, 136.29, 125.85, 123.15, 56.24, 47.73, 41.23, 40.36, 32.19, 28.89, 28.72, 21.15.



(1*R*,4*S*)-7-fluoro-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (**2u**)
Following the general procedure, compound **2u** was isolated along with **2uu** as a yellow oil (14.3 mg, 33% yield) by silica gel column chromatography (eluent: petroleum ether/ ethyl acetate = 200:1). The physical and spectral data are in accordance with literature values[5].
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.46 (dd, *J* = 8.1, 4.6 Hz, 1H), 7.35–7.30 (m, 2H), 3.12 (d, *J* = 5.9 Hz, 1H), 2.63–2.59 (m, 1H), 2.56–2.53 (m, 1H), 2.39 (d, *J* = 4.0 Hz, 1H), 1.77–1.69 (m, 1H), 1.69–1.59 (m, 1H), 1.54–1.42 (m, 1H), 1.42–1.34 (m, 1H), 1.03–0.93 (m, 1H), 0.84–0.77 (m, 1H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 207.81, 162.29 (d, *J* = 248.2 Hz), 152.66, 140.82 (d, *J* = 7.2 Hz), 127.50 (d, *J* = 8.0 Hz), 122.61 (d, *J* = 23.8 Hz), 108.88 (d, *J* = 21.6 Hz), 56.60, 47.50, 41.15, 40.49, 32.13, 28.74, 28.52.
^{19}F NMR (470 MHz, Chloroform-*d*) δ -114.43.



(1*R*,4*S*)-5-fluoro-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (**2uu**)
Following the general procedure, compound **2uu** was isolated along with **2u** as a yellow oil (12.6 mg, 29% yield) by silica gel column chromatography (eluent: petroleum ether/ ethyl acetate = 200:1). The physical and spectral data are in accordance with literature values[5].
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.52 (d, *J* = 7.5 Hz, 1H), 7.38–7.33 (m, 1H), 7.30–7.24 (m, 1H), 3.27 (d, *J* = 6.1 Hz, 1H), 2.64–2.58 (m, 2H), 2.57–2.51 (m, 1H), 1.77–1.69 (m, 1H), 1.68–1.60 (m, 1H), 1.51–1.43 (m, 1H), 1.42–1.33 (m, 1H), 1.04–0.94 (m, 1H), 0.85–0.75 (m, 1H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 207.64, 160.24 (d, *J* = 250.8 Hz), 142.65 (d, *J* = 19.1 Hz), 142.05 (d, *J* = 4.7 Hz), 129.49 (d, *J* = 6.3 Hz), 121.11 (d, *J* = 20.3 Hz), 119.05 (d, *J* = 3.9 Hz), 55.83, 44.64, 40.43, 39.46, 32.42, 28.83, 28.46.
^{19}F NMR (470 MHz, Chloroform-d_3) δ -118.80.



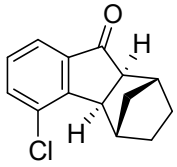
(1*R*,4*S*)-7-chloro-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (**2v**)

Following the general procedure, compound **2v** was isolated along with **2vv** as a yellow oil (25.6 mg, 55% yield) by silica gel column chromatography (eluent: petroleum ether/ ethyl acetate = 200:1). The physical and spectral data are in accordance with literature values[6].

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 1.9 Hz, 1H), 7.56 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 1H), 3.12 (d, *J* = 6.0 Hz, 1H), 2.60 (d, *J* = 3.7 Hz, 1H), 2.53 (d, *J* = 6.0 Hz, 1H), 2.40 (d, *J* = 3.9 Hz, 1H), 1.73 (t, *J* = 11.8 Hz, 1H), 1.64 (t, *J* = 11.9 Hz, 1H), 1.50–1.42 (m, 1H), 1.41–1.33 (m, 1H), 0.97 (d, *J* = 10.6 Hz, 1H), 0.80 (d, *J* = 10.6 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 207.39, 155.26, 140.61, 134.96, 133.90, 127.40, 123.03, 56.35, 47.70, 41.25, 40.55, 32.25, 28.84, 28.59.

HRMS (ESI): *m/z* calculated for $C_{14}H_{14}ClO^+$ $[M+H]^+$ 233.0728; found 233.0726.



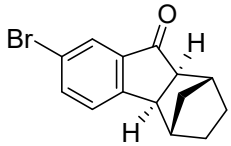
(1*R*,4*S*)-5-chloro-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (**2vv**)

Following the general procedure, compound **2vv** was isolated along with **2v** as a yellow oil (5.1 mg, 11% yield) by silica gel column chromatography (eluent: petroleum ether/ ethyl acetate = 200:1).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 7.6 Hz, 1H), 7.59 (d, *J* = 7.4 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 3.22 (d, *J* = 6.1 Hz, 1H), 2.76 (d, *J* = 3.8 Hz, 1H), 2.64 (d, *J* = 3.8 Hz, 1H), 2.53 (d, *J* = 6.0 Hz, 1H), 1.73 (t, *J* = 11.8 Hz, 1H), 1.64 (t, *J* = 11.9 Hz, 1H), 1.50–1.42 (m, 1H), 1.41–1.32 (m, 1H), 0.97 (d, *J* = 10.6 Hz, 1H), 0.80 (d, *J* = 10.6 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 207.39, 153.76, 141.17, 134.93, 132.90, 129.05, 121.61, 55.98, 47.43, 40.66, 38.64, 32.45, 29.04, 28.41.

HRMS (ESI): *m/z* calculated for $C_{14}H_{14}ClO^+$ $[M+H]^+$ 233.0728; found 233.0726.

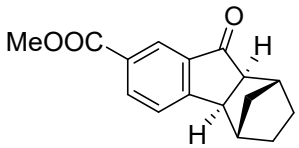


(1*R*,4*S*)-7-bromo-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (**2w**)

Following the general procedure, compound **2w** was isolated as a yellow solid (24.9 mg, 45% yield) by silica gel column chromatography (eluent: petroleum ether/ ethyl acetate = 150:1). The physical and spectral data are in accordance with literature values[3].

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 1.8 Hz, 1H), 7.70 (dd, *J* = 8.1, 1.9 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 1H), 3.10 (d, *J* = 6.0 Hz, 1H), 2.60 (d, *J* = 4.1 Hz, 1H), 2.52 (d, *J* = 6.0 Hz, 1H), 2.39 (d, *J* = 4.2 Hz, 1H), 1.72 (t, *J* = 11.8 Hz, 1H), 1.64 (t, *J* = 11.9 Hz, 1H), 1.49–1.42 (m, 1H), 1.40–1.34 (m, 1H), 0.97 (d, *J* = 10.6 Hz, 1H), 0.80 (d, *J* = 10.7 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 207.38, 155.75, 140.92, 137.74, 127.78, 126.21, 121.78, 56.22, 47.76, 41.21, 40.55, 32.28, 28.85, 28.59.



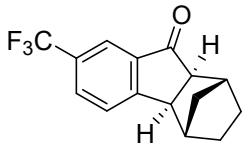
Methyl (1*R*,4*S*)-9-oxo-2,3,4,4a,9,9a-hexahydro-1*H*-1,4-methanofluorene-7-carboxylate (2x)

Following the general procedure, compound **2x** was isolated as a yellow solid (21 mg, 41% yield) by silica gel column chromatography (eluent: petroleum ether/ ethyl acetate = 150:1). m.p. = 122.5 ºC.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.37 (d, *J* = 1.7 Hz, 1H), 8.29 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 3.94 (s, 3H), 3.20 (d, *J* = 6.1 Hz, 1H), 2.64 (d, *J* = 4.2 Hz, 1H), 2.57 (d, *J* = 6.1 Hz, 1H), 2.45 (d, *J* = 4.2 Hz, 1H), 1.74 (t, *J* = 11.9 Hz, 1H), 1.66 (t, *J* = 11.9 Hz, 1H), 1.49 (t, *J* = 10.5 Hz, 1H), 1.42–1.36 (m, 1H), 0.98 (d, *J* = 10.7 Hz, 1H), 0.79 (d, *J* = 10.7 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 207.92, 166.38, 161.53, 139.36, 135.76, 129.85, 126.37, 124.75, 56.21, 52.39, 48.25, 41.40, 40.61, 32.42, 28.96, 28.62.

HRMS (ESI): *m/z* calculated for $C_{16}H_{17}O_3^+$ $[M+H]^+$ 257.1172; found 257.1173.



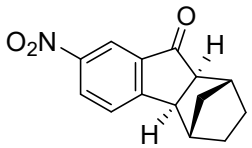
(1*R*,4*S*)-7-(trifluoromethyl)-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (2y)

Following the general procedure, compound **2y** was isolated as a colorless oil (24.5 mg, 46% yield) by silica gel column chromatography (eluent: petroleum ether/ ethyl acetate = 150:1). The physical and spectral data are in accordance with literature values[3].

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.98 (s, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 3.22 (d, *J* = 6.2 Hz, 1H), 2.65 (d, *J* = 4.1 Hz, 1H), 2.58 (d, *J* = 6.2 Hz, 1H), 2.46 (d, *J* = 4.3 Hz, 1H), 1.76 (t, *J* = 11.9 Hz, 1H), 1.67 (t, *J* = 11.9 Hz, 1H), 1.49 (d, *J* = 11.2 Hz, 1H), 1.44–1.37 (m, 1H), 1.00 (d, *J* = 10.6 Hz, 1H), 0.79 (d, *J* = 10.3 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 207.46, 160.27, 139.46, 131.43, 130.37 (d, *J* = 28.7 Hz), 126.96, 123.72 (d, *J* = 241.2 Hz), 120.52, 56.12, 48.15, 41.37, 40.65, 32.38, 28.92, 28.58.

^{19}F NMR (470 MHz, Chloroform-*d*) δ -62.30.

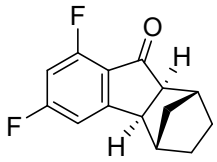


(1*R*,4*S*)-7-nitro-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (2z)

Following the general procedure, compound **2z** was isolated as a yellow oil (20 mg, 41% yield) by silica gel column chromatography (eluent: petroleum ether/ ethyl acetate = 75:1). The physical and spectral data are in accordance with literature values[4].

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.52 (s, 1H), 8.47 (d, *J* = 8.3 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 3.27 (d, *J* = 6.1 Hz, 1H), 2.68 (s, 1H), 2.64 (d, *J* = 6.2 Hz, 1H), 2.49 (s, 1H), 1.78 (t, *J* = 11.8 Hz, 1H), 1.68 (t, *J* = 11.9 Hz, 1H), 1.55–1.48 (m, 1H), 1.41 (t, *J* = 9.8 Hz, 1H), 1.04 (d, *J* = 10.8 Hz, 1H), 0.79 (d, *J* = 10.8 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.50, 162.67, 147.98, 140.16, 129.21, 127.28, 118.61, 56.52, 48.30, 41.53, 40.85, 32.52, 28.94, 28.48.



(1*R*,4*S*)-6,8-*d*ifluoro-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (**2aa**)

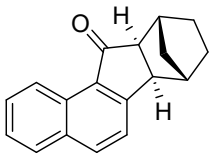
Following the general procedure, compound **2z** was isolated as a yellow solid (19.7 mg, 42% yield) by silica gel column chromatography (eluent: petroleum ether/ ethyl acetate = 75:1). M.p. = 59.8 ^{o}C.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.98 (d, *J* = 7.7 Hz, 1H), 6.73 (t, *J* = 9.0 Hz, 1H), 3.14 (d, *J* = 6.2 Hz, 1H), 2.64 (d, *J* = 4.2 Hz, 1H), 2.55 (d, *J* = 6.2 Hz, 1H), 2.42 (d, *J* = 4.2 Hz, 1H), 1.73 (t, *J* = 11.8 Hz, 1H), 1.65 (t, *J* = 11.8 Hz, 1H), 1.45 (t, *J* = 10.5 Hz, 1H), 1.40–1.34 (m, 1H), 1.02 (d, *J* = 10.7 Hz, 1H), 0.90 (d, *J* = 10.6 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 203.51, 167.79 (dd, *J* = 258.8, 11.0 Hz), 161.42 (dd, *J* = 10.9, 3.3 Hz), 159.11 (dd, *J* = 266.4, 13.9 Hz), 123.63 (d, *J* = 11.0 Hz), 109.06 (dd, *J* = 21.7, 4.0 Hz), 103.60 (dd, *J* = 26.8, 23.2 Hz), 56.63, 48.24, 41.61, 40.57, 32.34, 28.74, 28.49.

^{19}F NMR (470 MHz, Chloroform-*d*) δ -98.43–-98.55 (m), -110.28 (dd, *J* = 12.8, 9.4 Hz).

HRMS (ESI): *m/z* calculated for $C_{14}H_{13}F_2O^+$ $[M+H]^+$ 235.0929; found 235.0930.

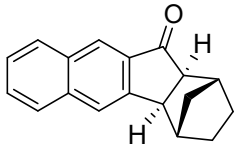


(7*S*,10*R*)-6b,7,8,9,10,10a-hexahydro-11*H*-7,10-methanobenzo[a]fluoren-11-one (**2ab**)

Following the general procedure, compound **2ab** was isolated as a white solid (24.4 mg, 49% yield) by silica gel column chromatography (eluent: petroleum ether/ ethyl acetate = 100:1). The physical and spectral data are in accordance with literature values[5].

^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.18 (d, *J* = 8.4 Hz, 1H), 8.06 (d, *J* = 8.3 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.70 – 7.64 (m, 1H), 7.56 (t, *J* = 7.3 Hz, 2H), 3.21 (d, *J* = 5.7 Hz, 1H), 2.66 (d, *J* = 4.1 Hz, 1H), 2.60 (d, *J* = 5.8 Hz, 1H), 2.47 (d, *J* = 4.2 Hz, 1H), 1.77 (t, *J* = 11.7 Hz, 1H), 1.68 (t, *J* = 11.8 Hz, 1H), 1.52 (t, *J* = 11.0 Hz, 1H), 1.46–1.39 (m, 1H), 0.95 (d, *J* = 10.6 Hz, 1H), 0.87 (d, *J* = 10.3 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 209.19, 160.05, 136.09, 133.23, 132.67, 129.05, 128.93, 128.07, 126.68, 124.19, 123.46, 56.38, 48.09, 40.62, 40.27, 31.84, 29.18, 28.72.



(1*R*,4*S*)-1,2,3,4,4a,11a-hexahydro-11*H*-1,4-methanobenzo[b]fluoren-11-one (**2ac**)

Following the general procedure, compound **2ac** was isolated as a white solid (30.3 mg, 61% yield) by silica gel column chromatography (eluent: petroleum ether/ ethyl acetate = 100:1). The physical

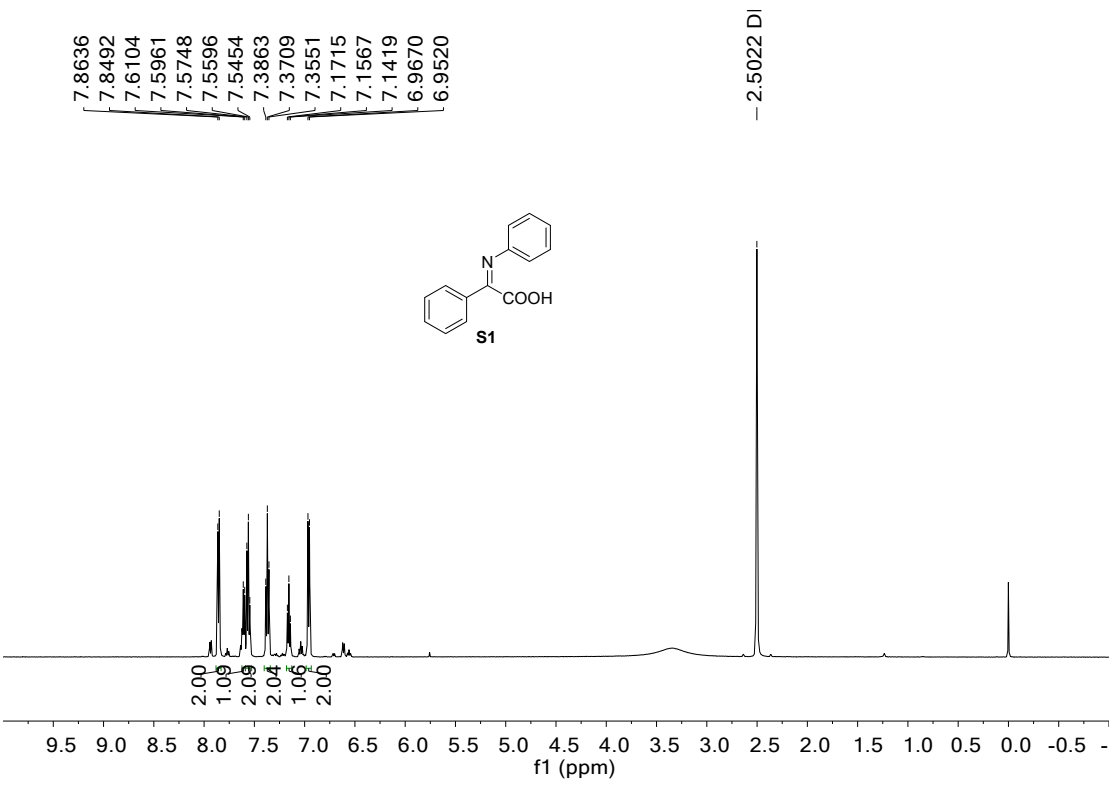
and spectral data are in accordance with literature values[5].

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.27 (s, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.92 (s, 1H), 7.89 (d, *J* = 8.3 Hz, 1H), 7.62–7.55 (m, 1H), 7.53–7.46 (m, 1H), 3.34 (d, *J* = 6.5 Hz, 1H), 2.68 (d, *J* = 4.0 Hz, 1H), 2.62 (d, *J* = 6.5 Hz, 1H), 2.54 (d, *J* = 4.1 Hz, 1H), 1.78–1.71 (m, 1H), 1.71–1.64 (m, 1H), 1.53 (t, *J* = 10.6 Hz, 1H), 1.42 (t, *J* = 9.9 Hz, 1H), 0.97 (d, *J* = 10.5 Hz, 1H), 0.84 (d, *J* = 10.5 Hz, 1H).

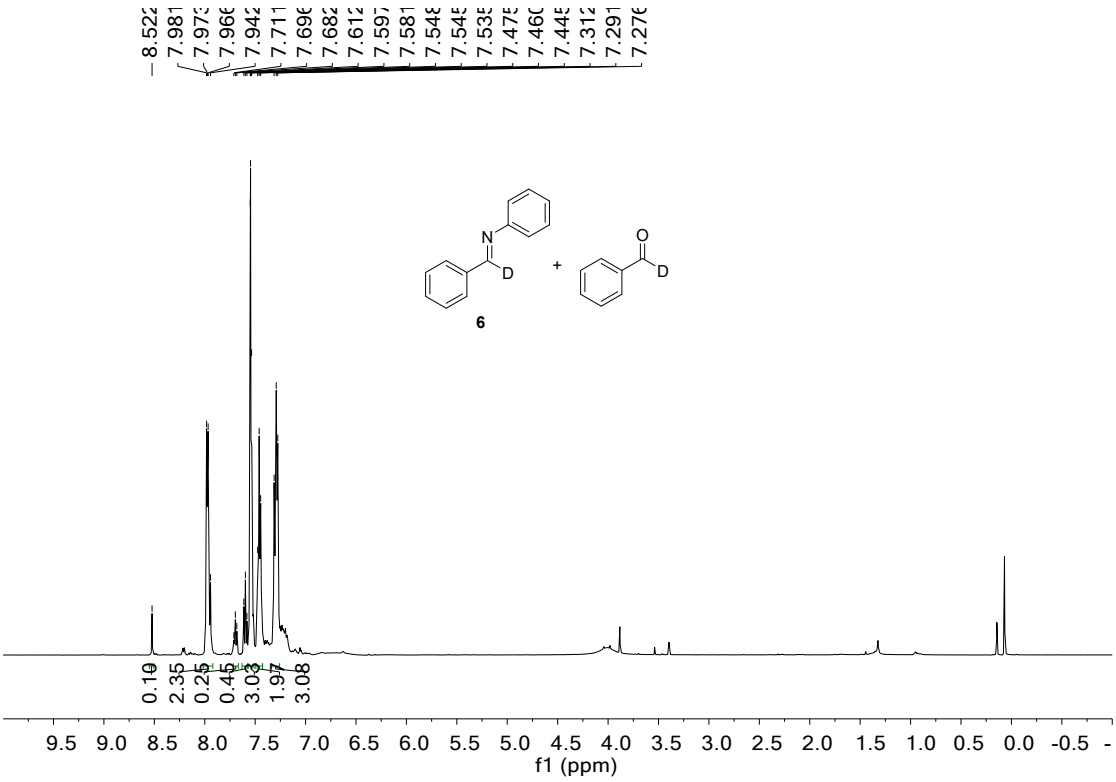
^{13}C NMR (126 MHz, Chloroform-*d*) δ 209.48, 150.74, 137.53, 136.62, 132.42, 130.47, 128.51, 127.93, 126.20, 124.59, 123.77, 56.57, 47.76, 42.73, 41.04, 32.84, 28.84, 28.83.

4. ^{1}H, ^{13}C, and ^{19}F NMR Spectra of Compounds

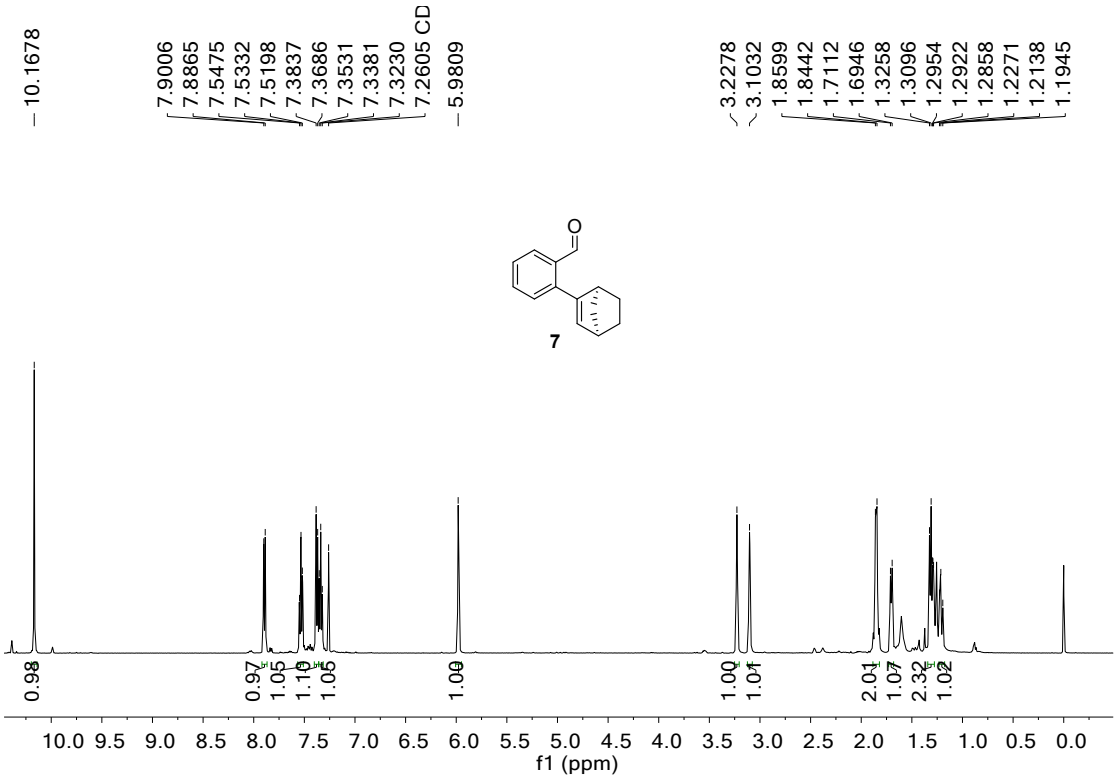
^{1}H NMR spectrum of compound S1 (DMSO-d_6, 500 MHz)



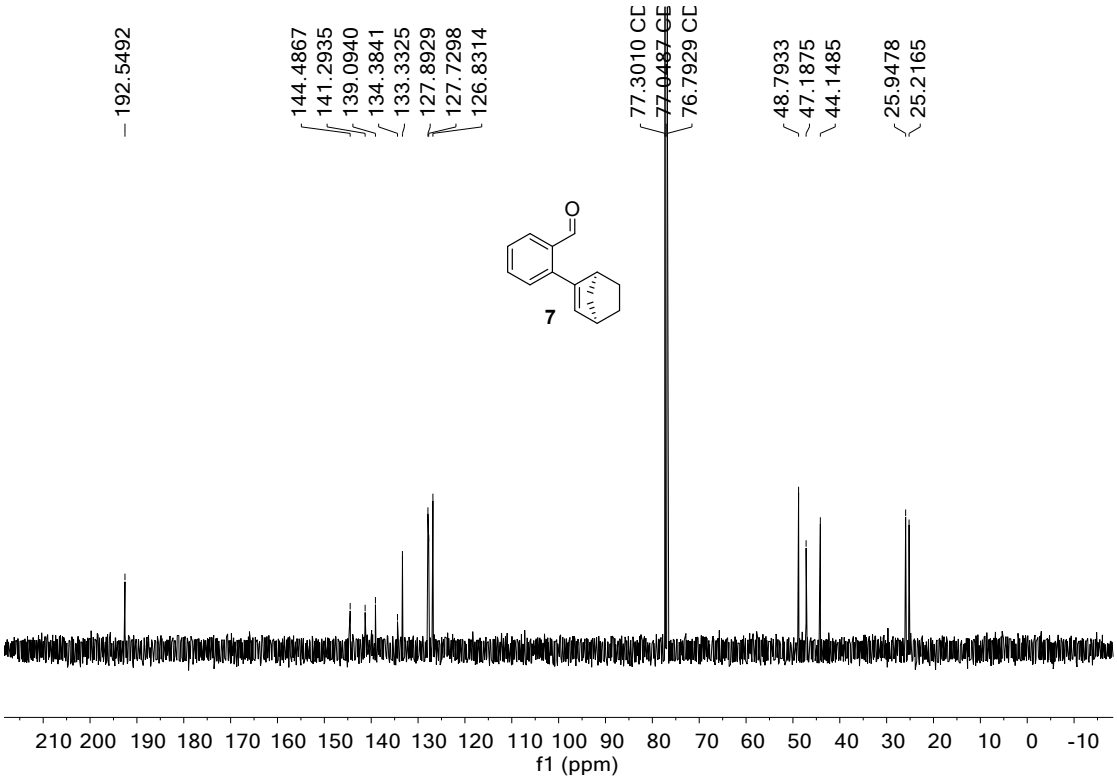
^{1}H NMR spectrum of compound 6 ($CDCl_3$, 500 MHz)



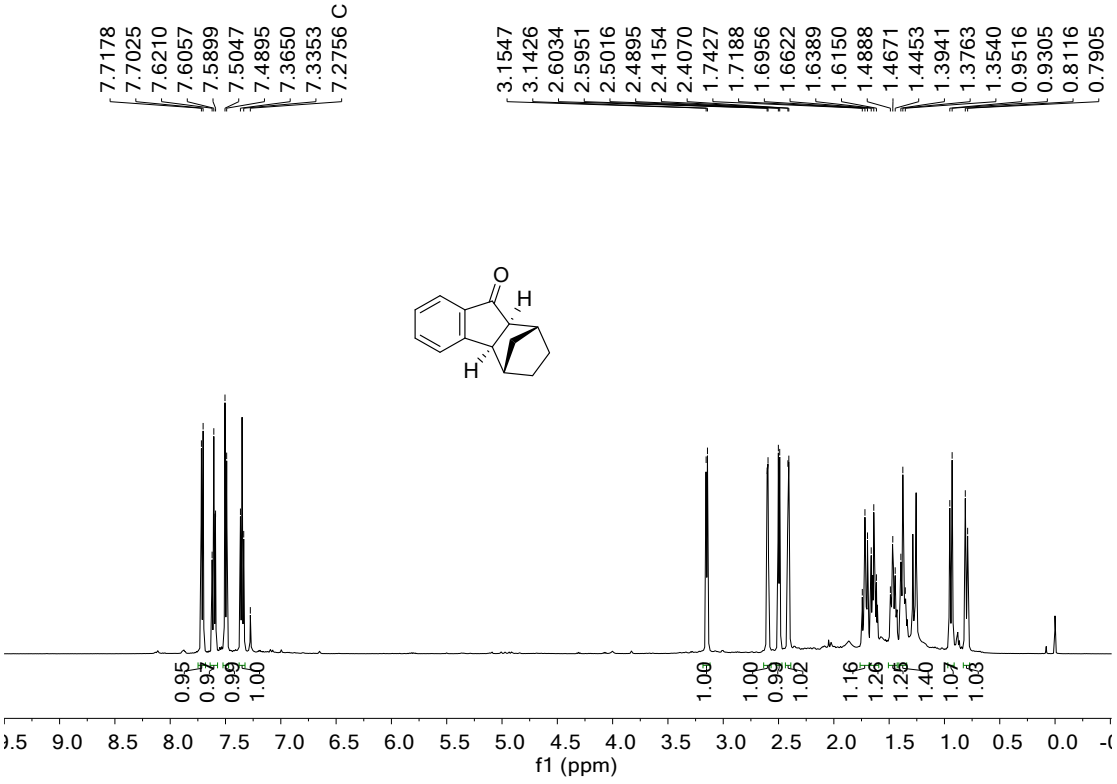
^{1}H NMR spectrum of compound 7 ($CDCl_3$, 500 MHz)



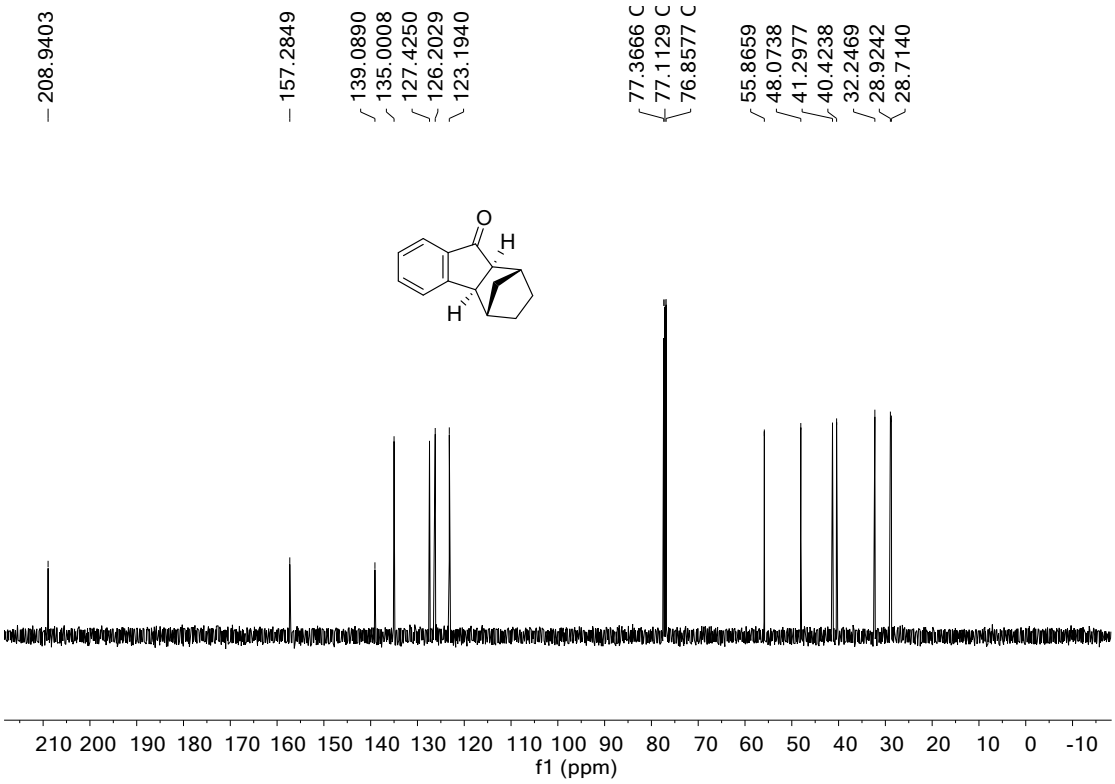
^{13}C NMR spectrum of compound 7 ($CDCl_3$, 126 MHz)



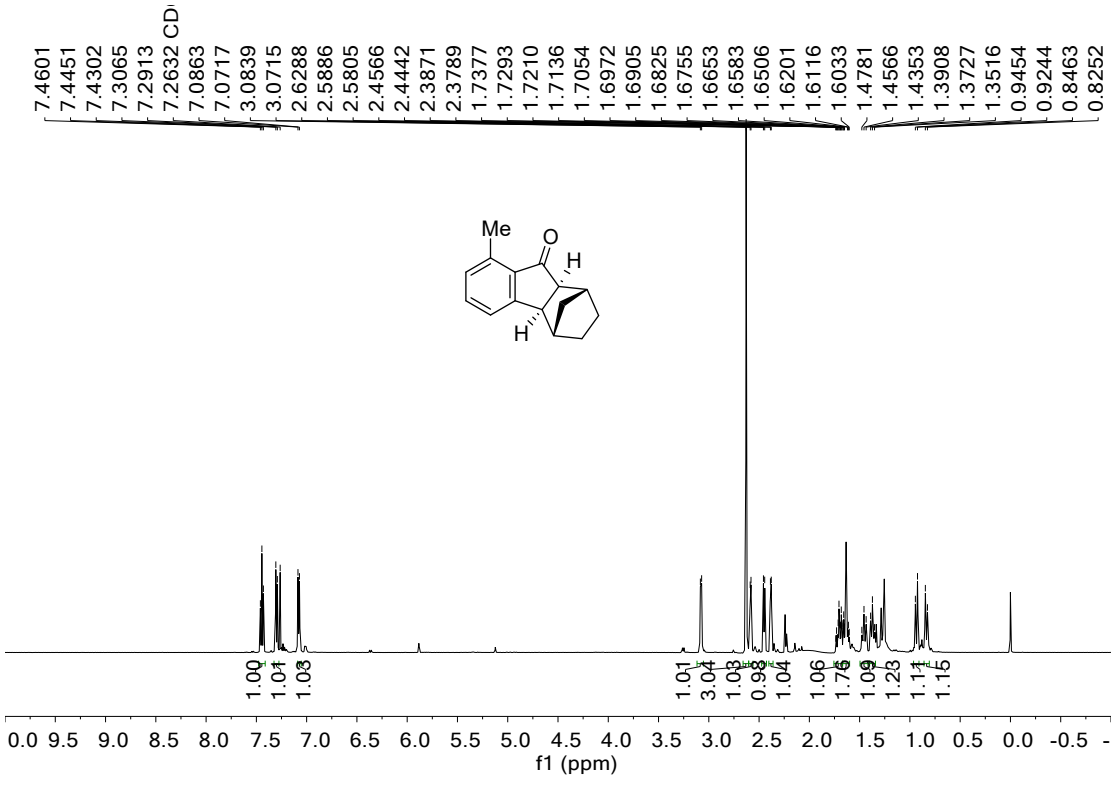
^{1}H NMR spectrum of compound 2a ($CDCl_3$, 500 MHz)



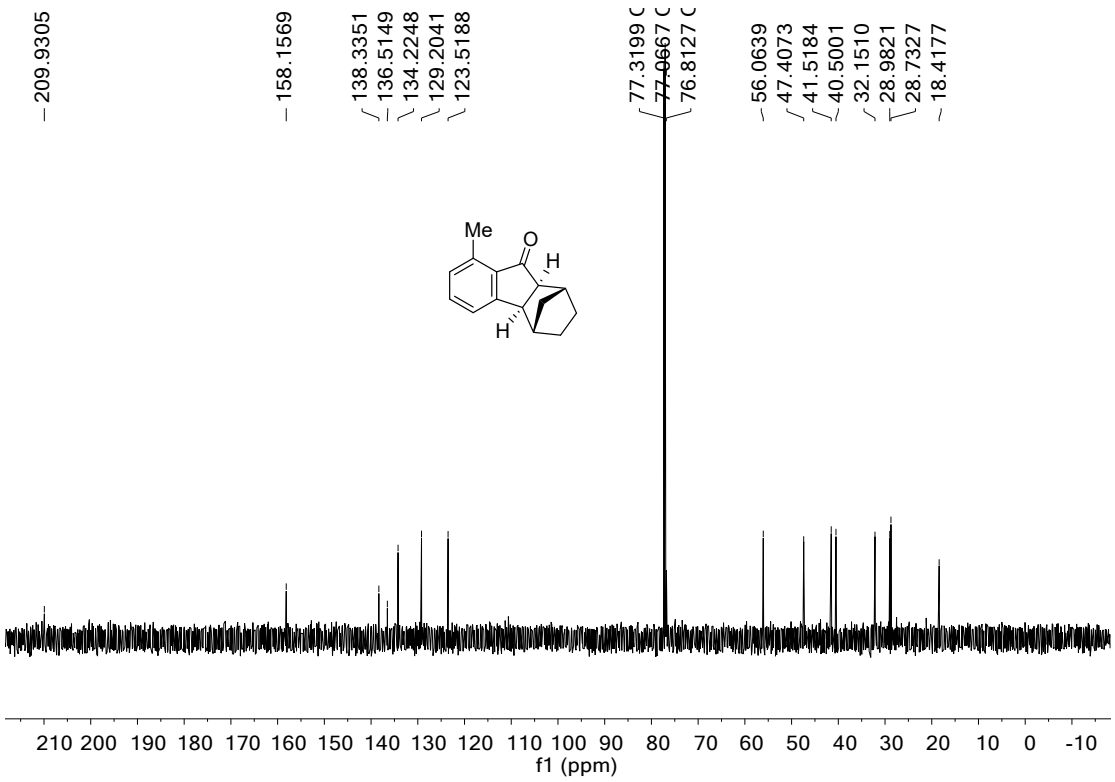
^{13}C NMR spectrum of compound 2a ($CDCl_3$, 126 MHz)



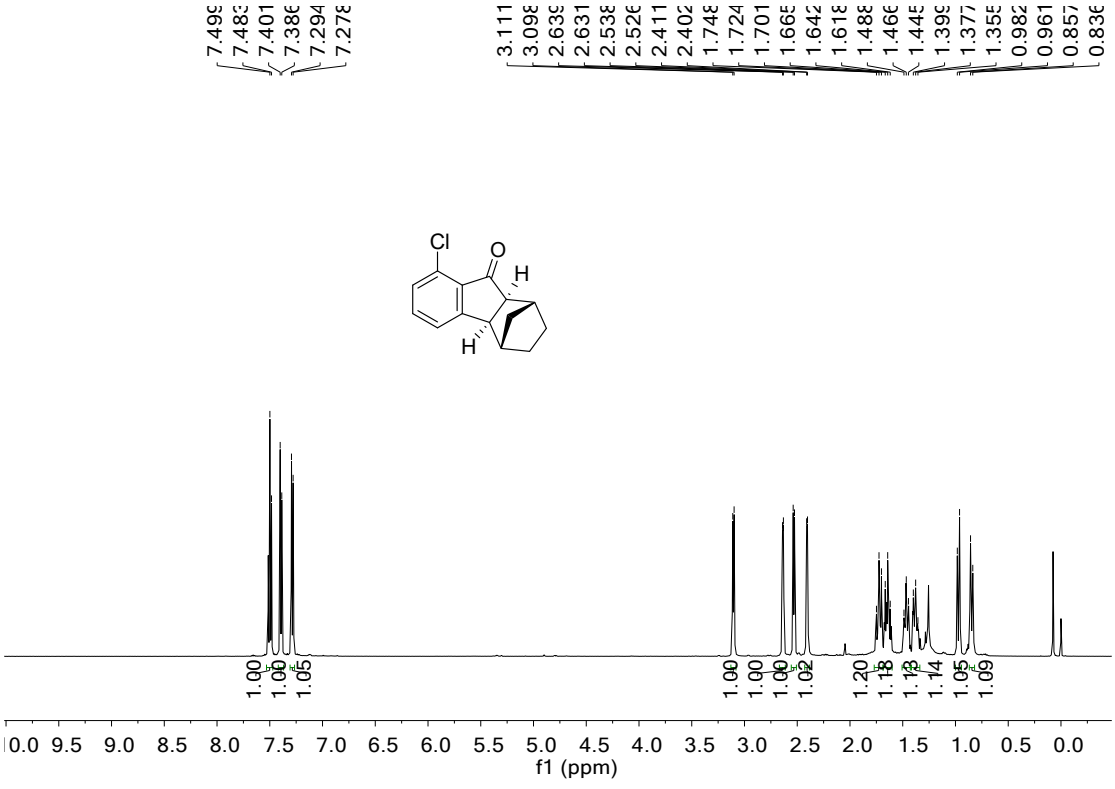
^{1}H NMR spectrum of compound 2b ($CDCl_3$, 500 MHz)



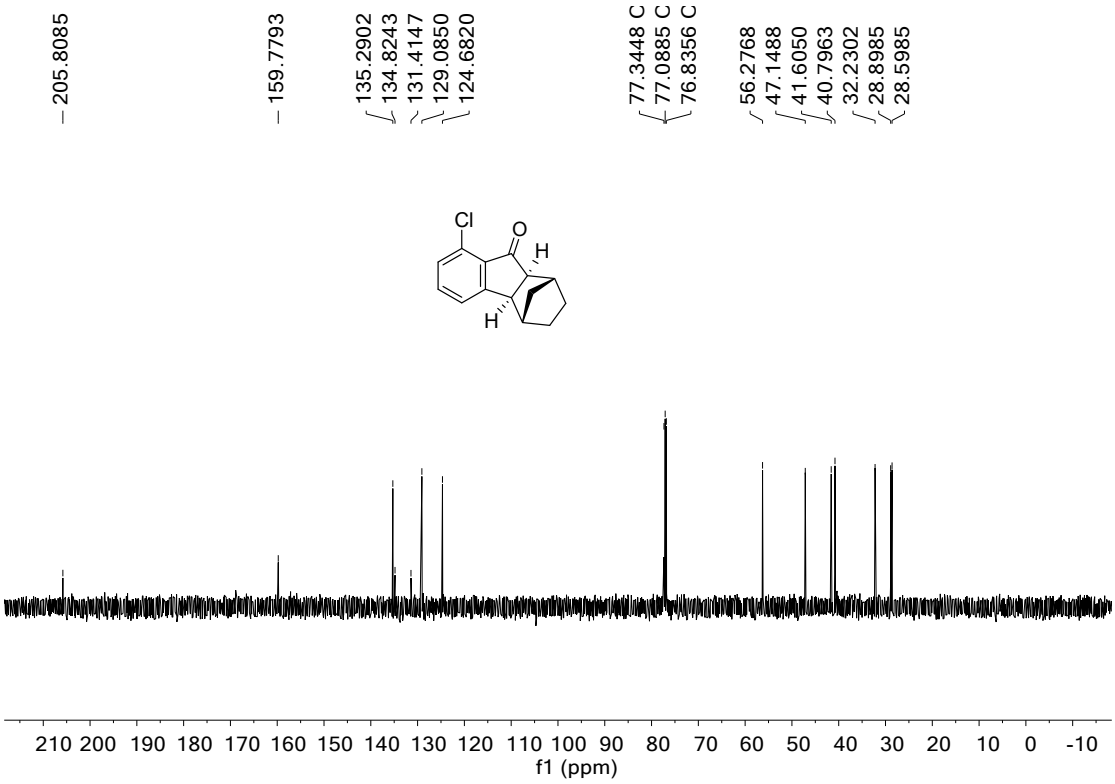
^{13}C NMR spectrum of compound 2b ($CDCl_3$, 126 MHz)



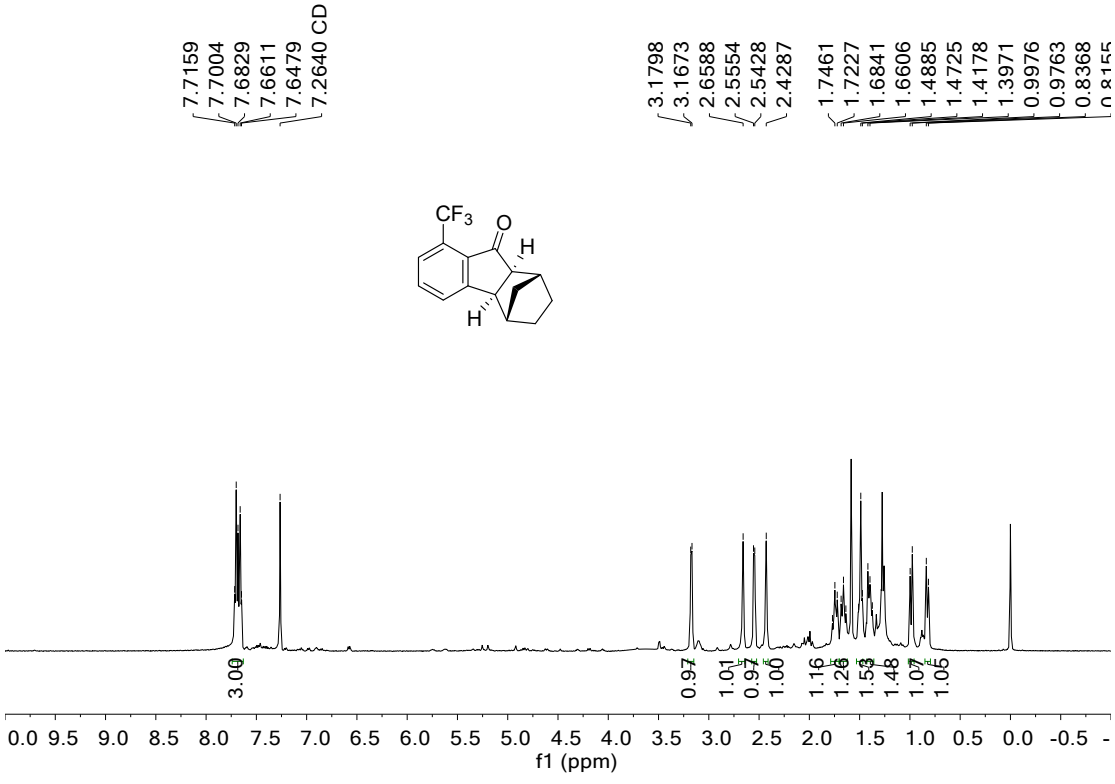
^{1}H NMR spectrum of compound 2c ($CDCl_3$, 500 MHz)



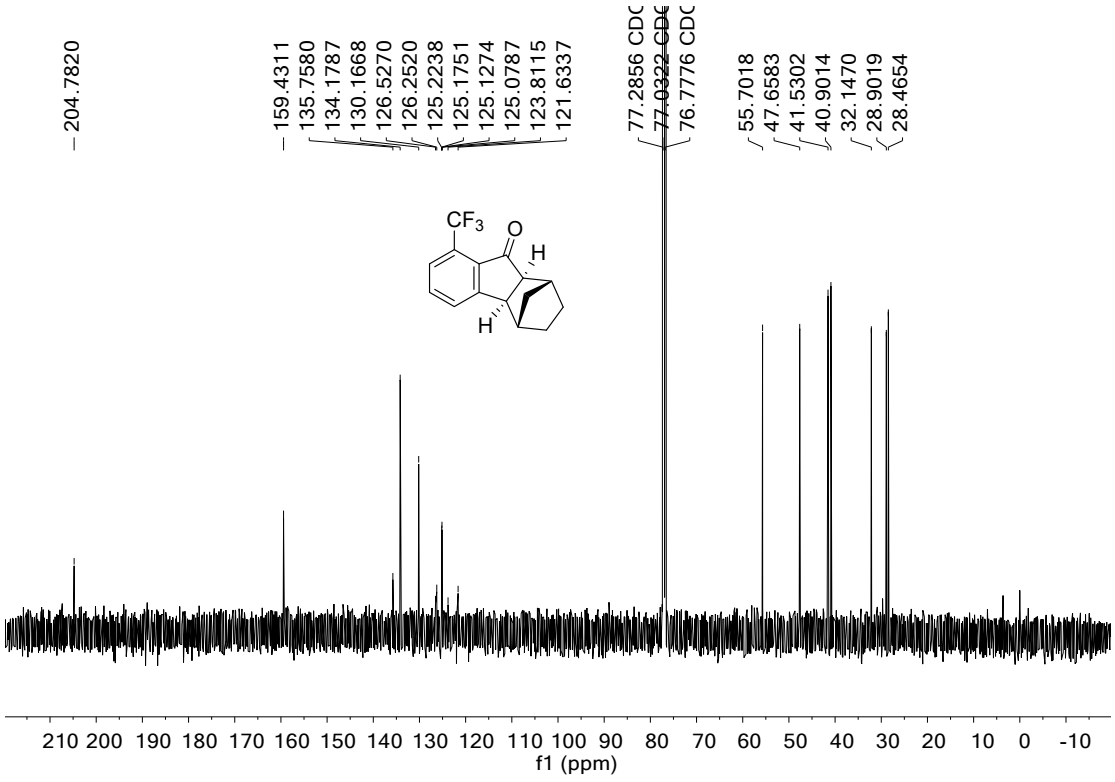
^{13}C NMR spectrum of compound 2c ($CDCl_3$, 126 MHz)



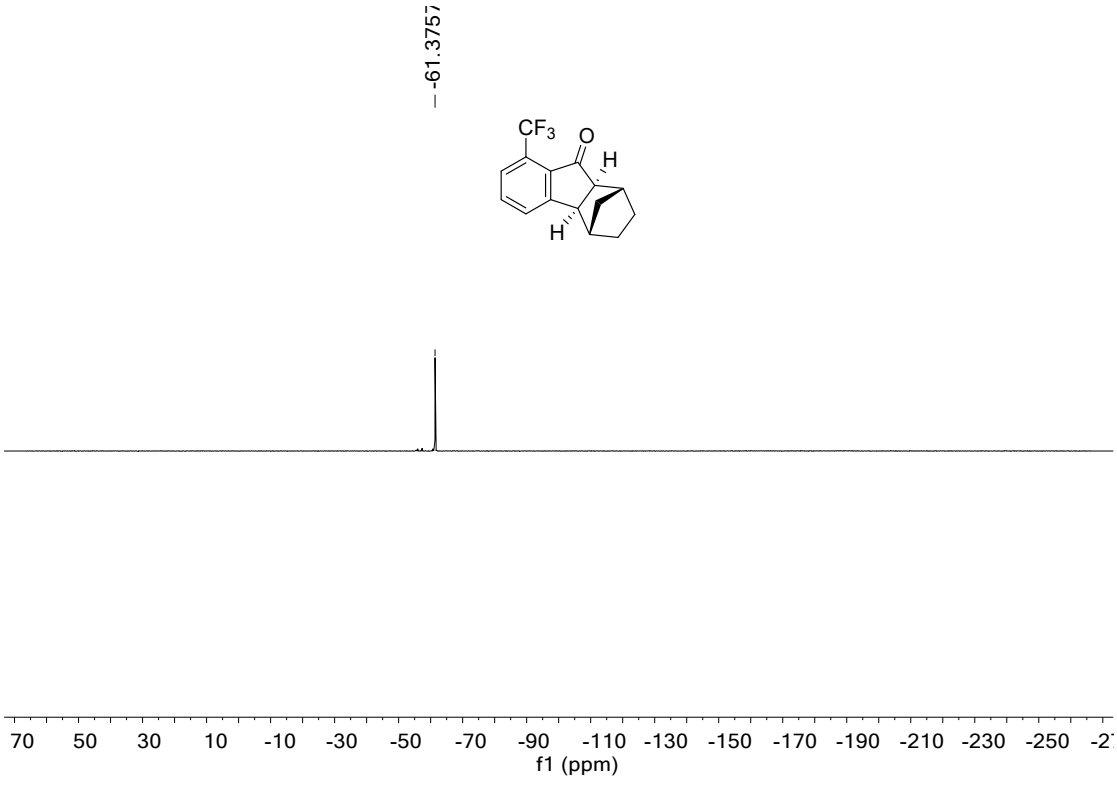
^{1}H NMR spectrum of compound 2d ($CDCl_3$, 500 MHz)



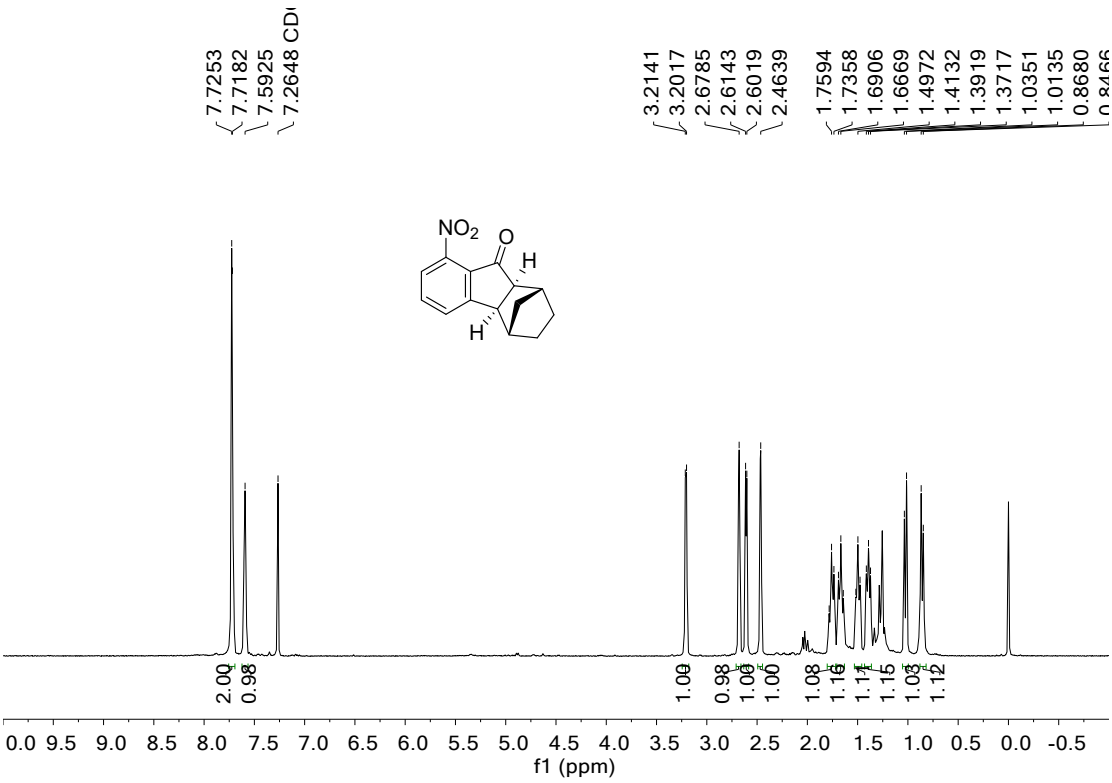
^{13}C NMR spectrum of compound 2d ($CDCl_3$, 126 MHz)



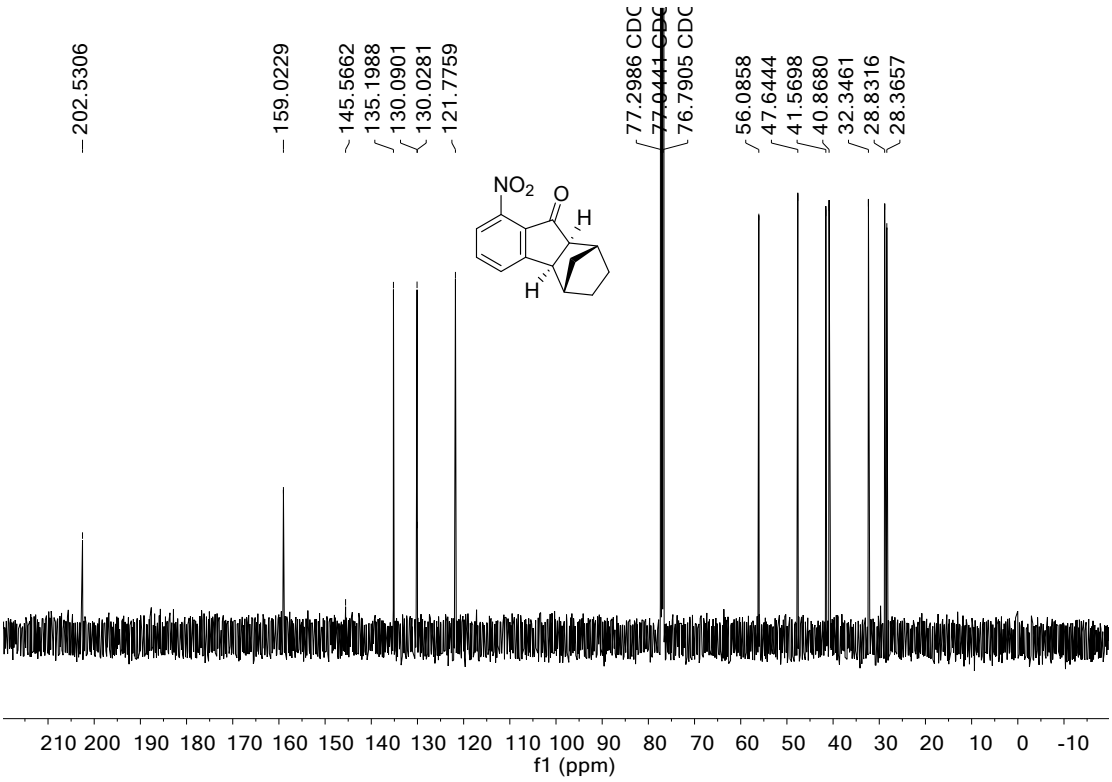
^{19}F NMR spectrum of compound 2d ($CDCl_3$, 470 MHz)



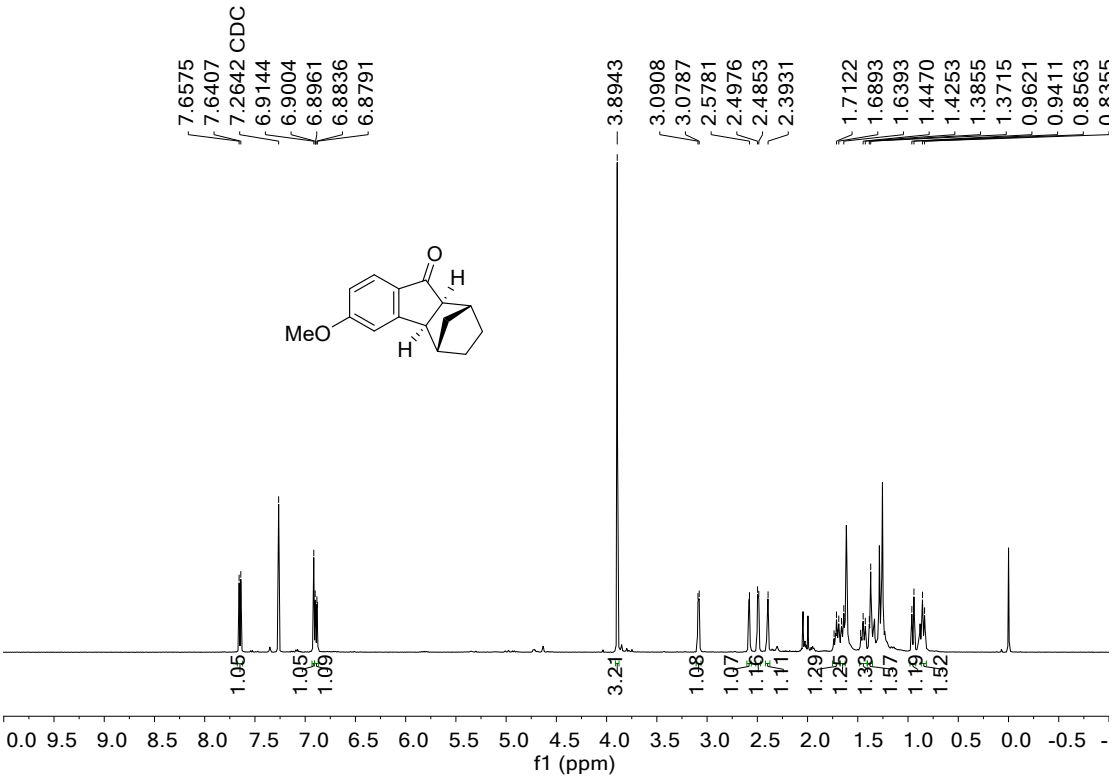
^{1}H NMR spectrum of compound 2e ($CDCl_3$, 500 MHz)



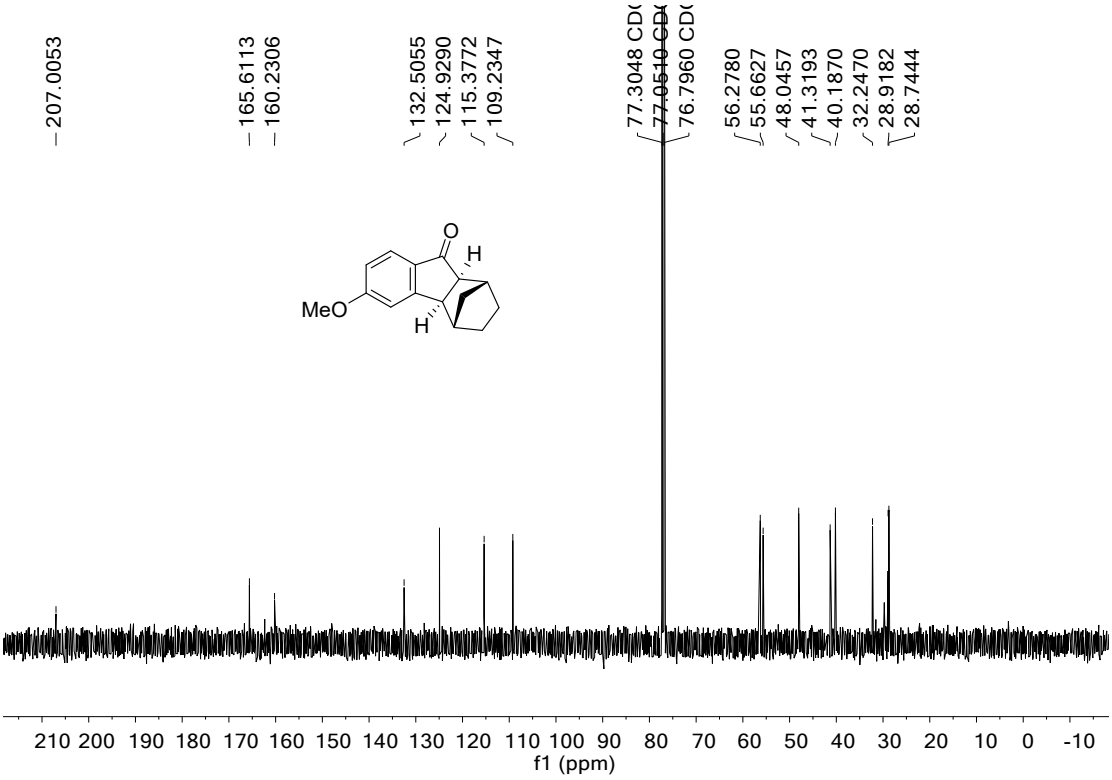
^{13}C NMR spectrum of compound 2e ($CDCl_3$, 126 MHz)



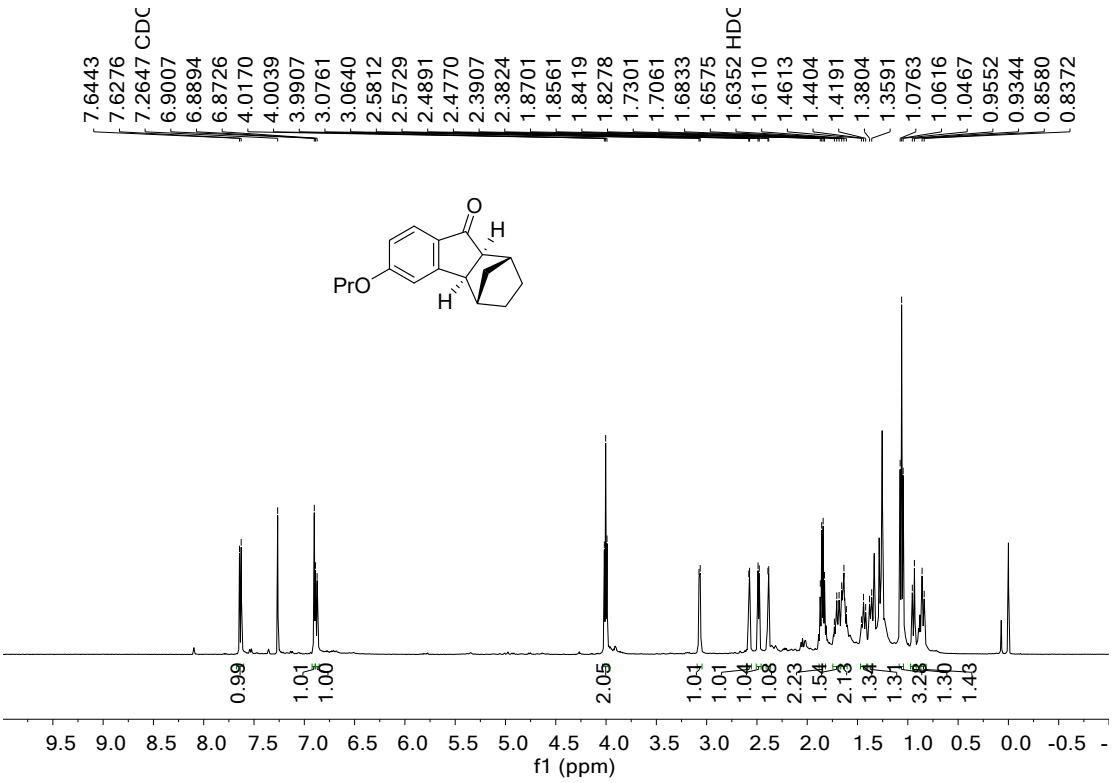
^{1}H NMR spectrum of compound 2f ($CDCl_3$, 500 MHz)



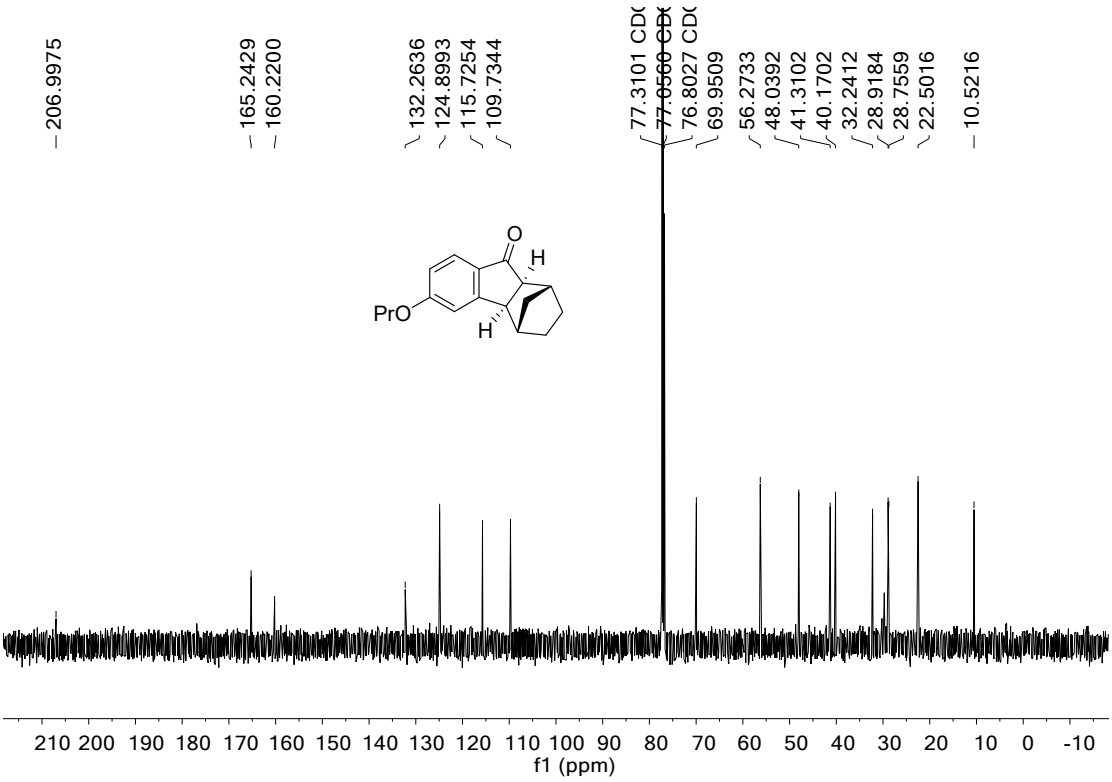
^{13}C NMR spectrum of compound 2f ($CDCl_3$, 126 MHz)



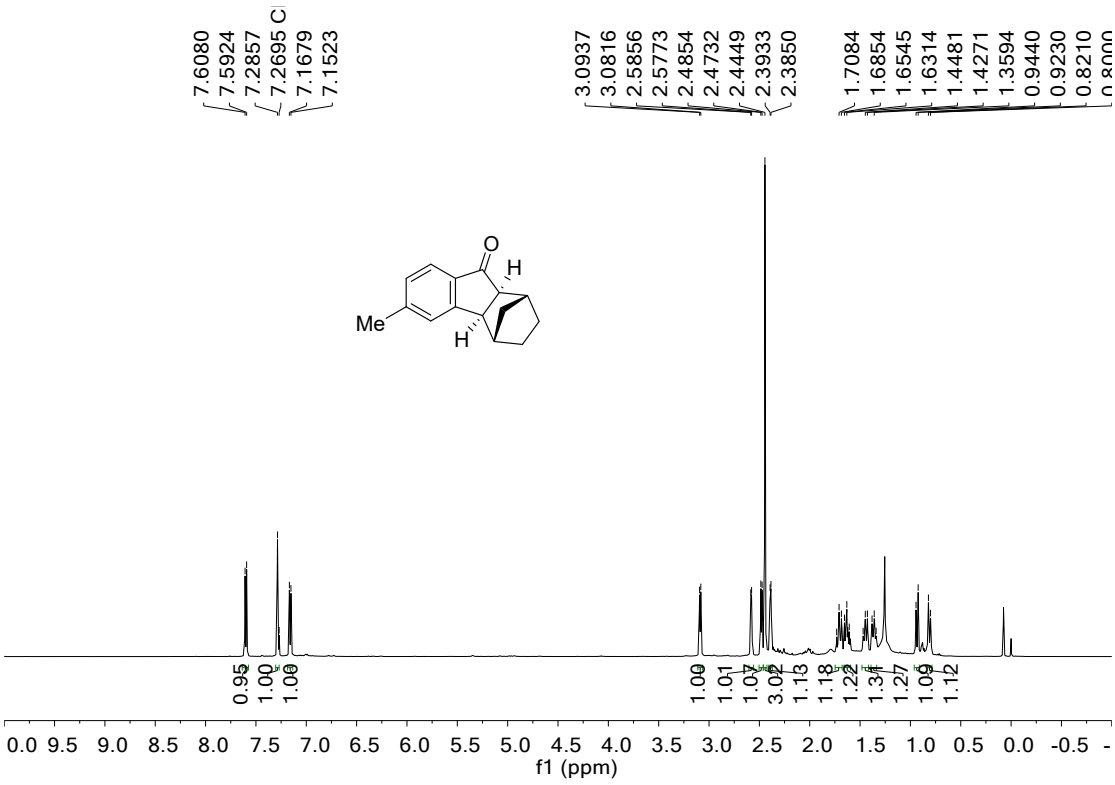
^{1}H NMR spectrum of compound 2g ($CDCl_3$, 500 MHz)



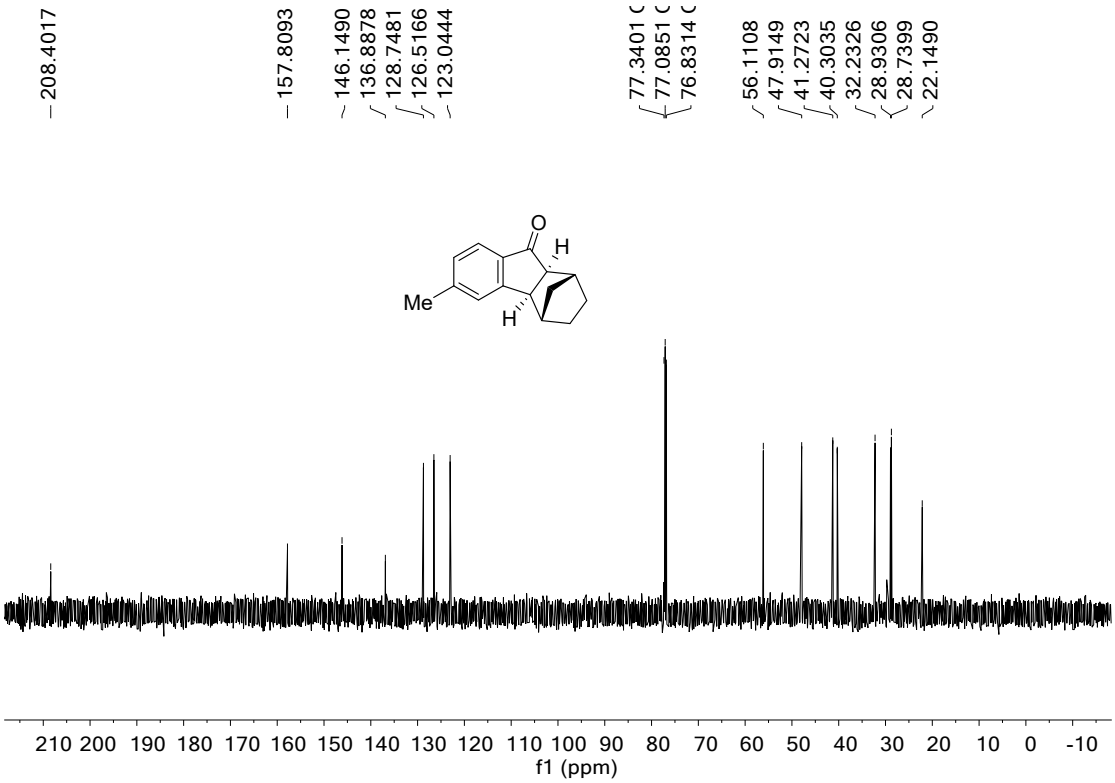
^{13}C NMR spectrum of compound 2g ($CDCl_3$, 126 MHz)



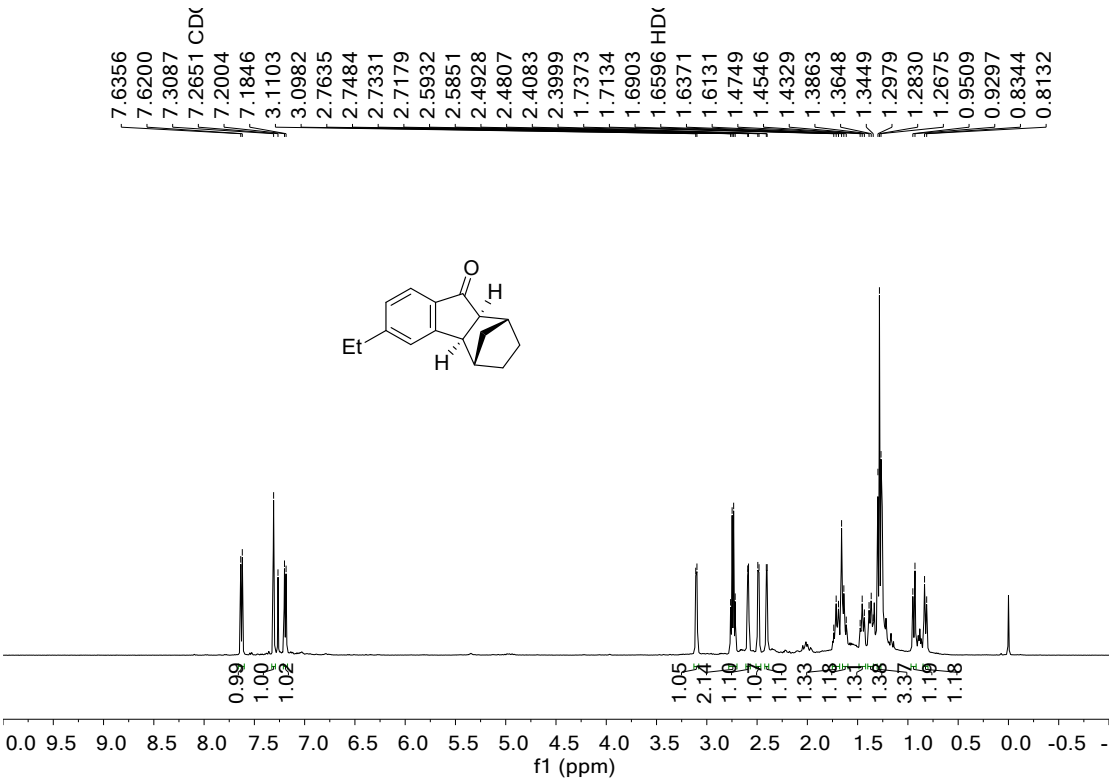
^{1}H NMR spectrum of compound 2h ($CDCl_3$, 500 MHz)



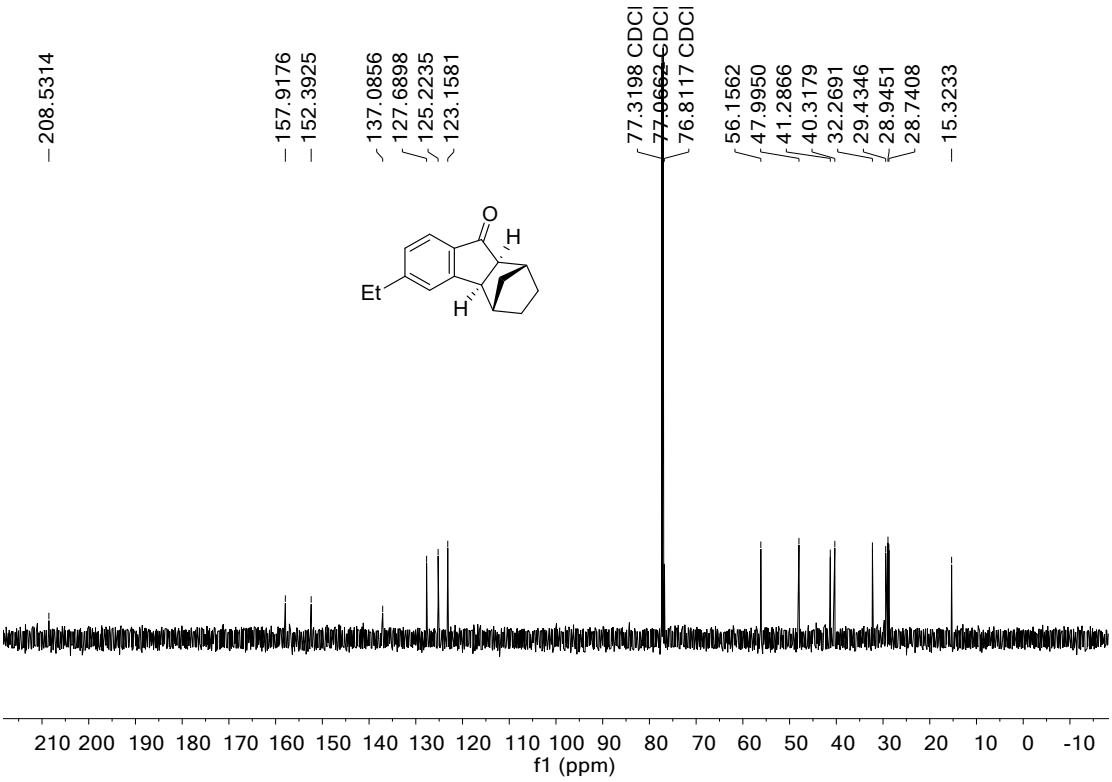
^{13}C NMR spectrum of compound 2h ($CDCl_3$, 126 MHz)



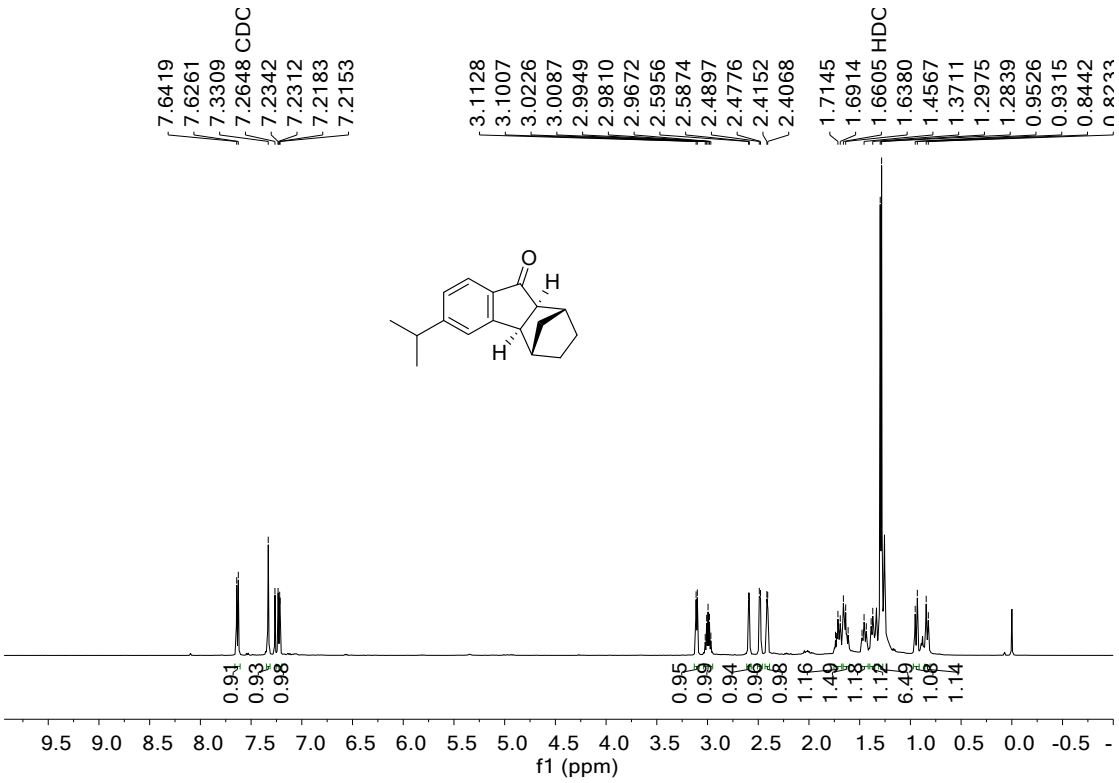
^{1}H NMR spectrum of compound 2i ($CDCl_3$, 500 MHz)



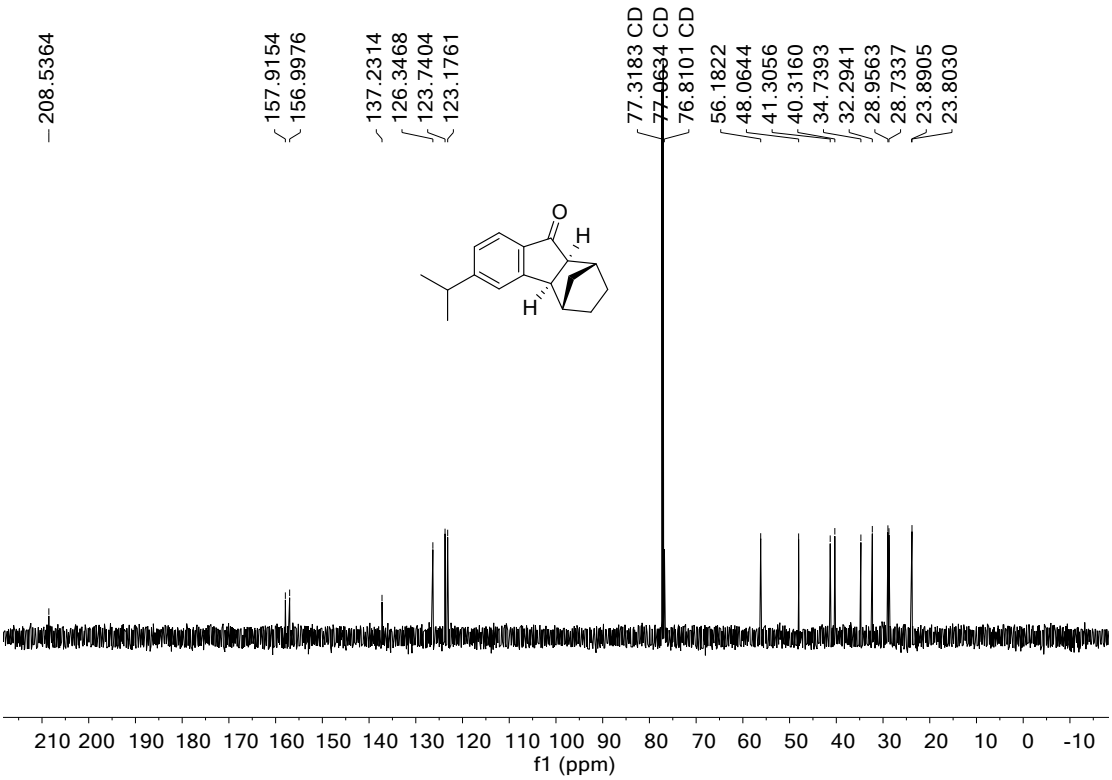
^{13}C NMR spectrum of compound 2i ($CDCl_3$, 126 MHz)



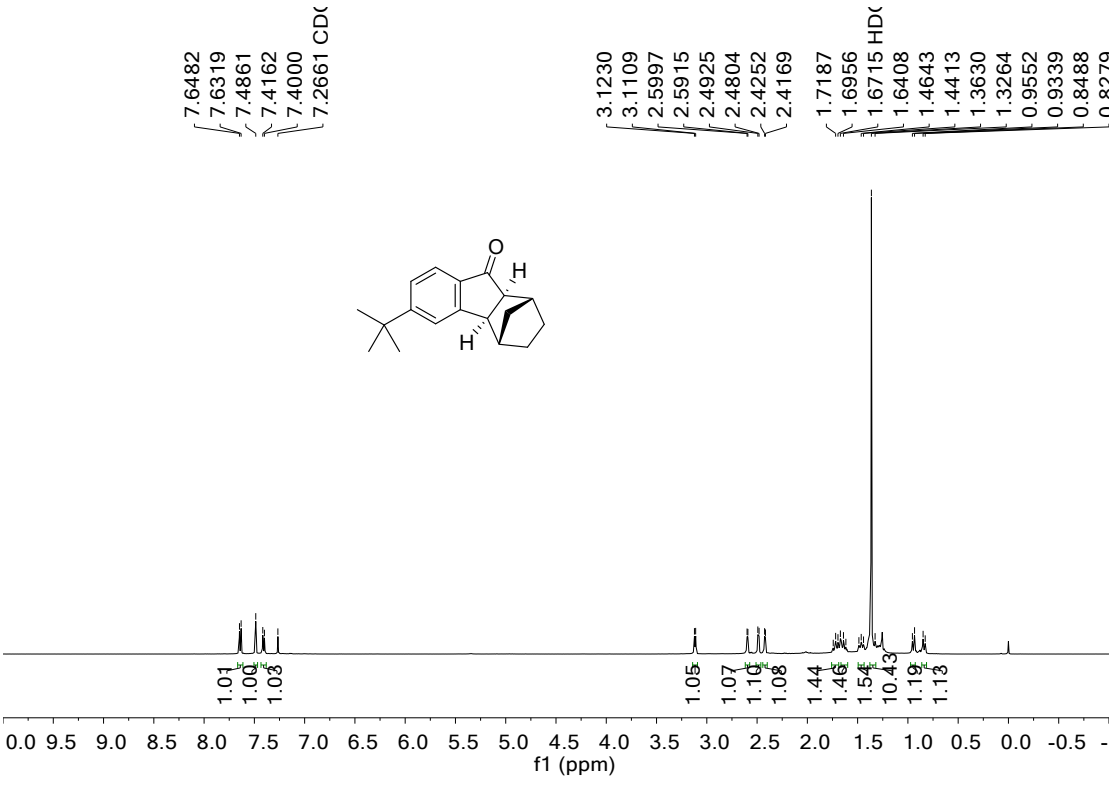
^{1}H NMR spectrum of compound 2j ($CDCl_3$, 500 MHz)



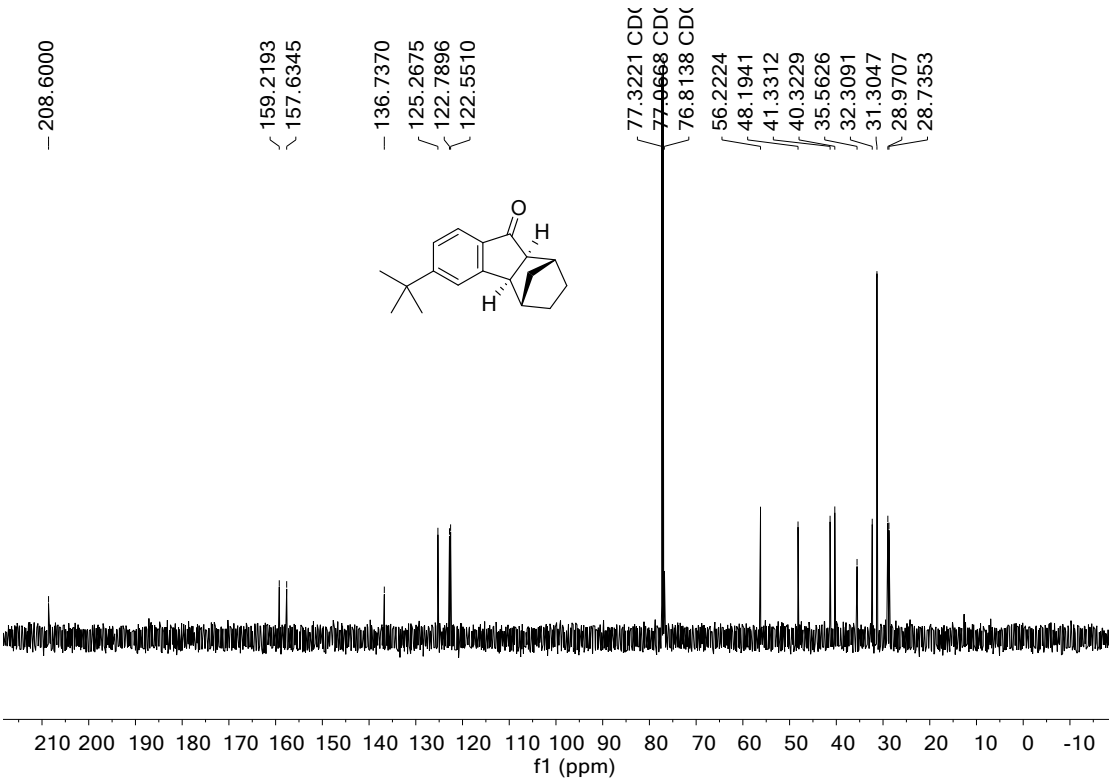
^{13}C NMR spectrum of compound 2j ($CDCl_3$, 126 MHz)



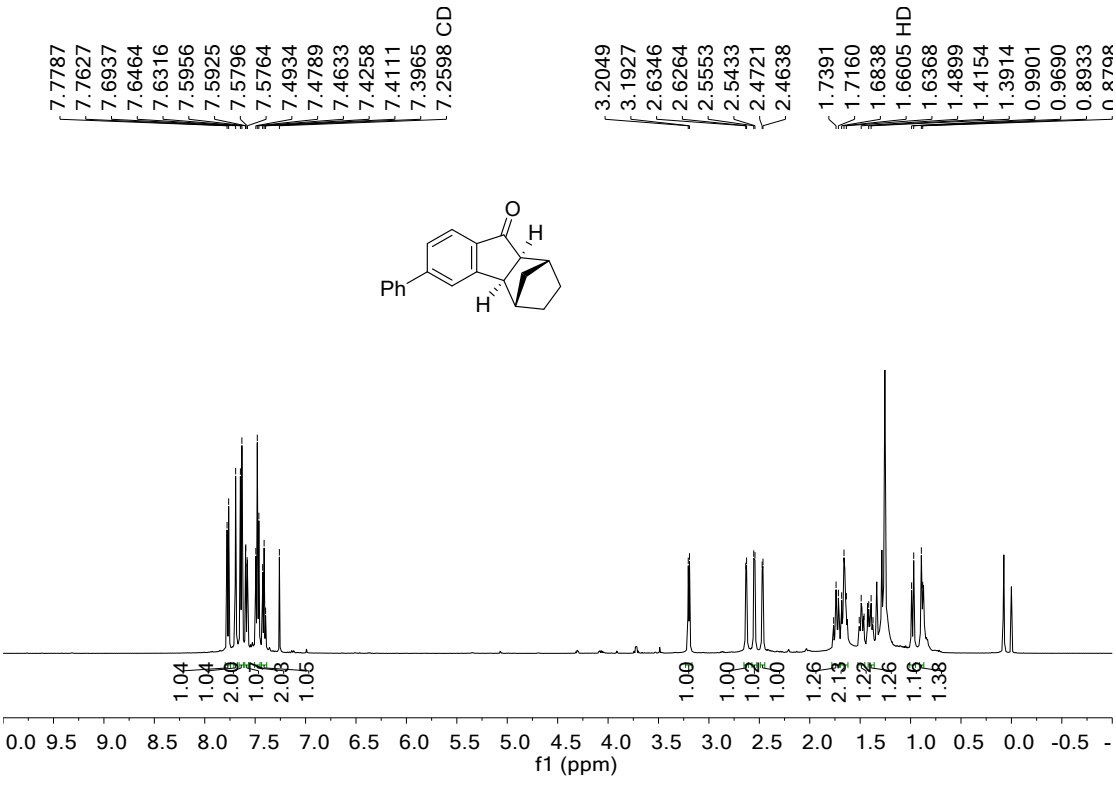
^{1}H NMR spectrum of compound 2k ($CDCl_3$, 500 MHz)



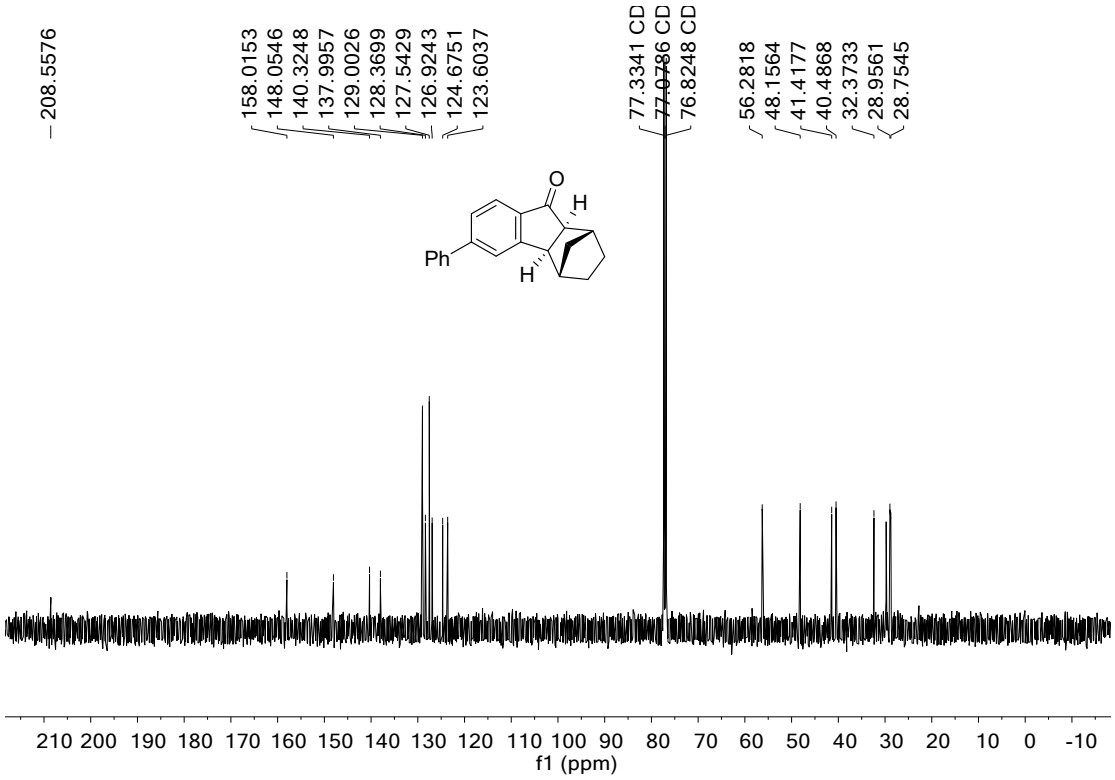
^{13}C NMR spectrum of compound 2k ($CDCl_3$, 126 MHz)



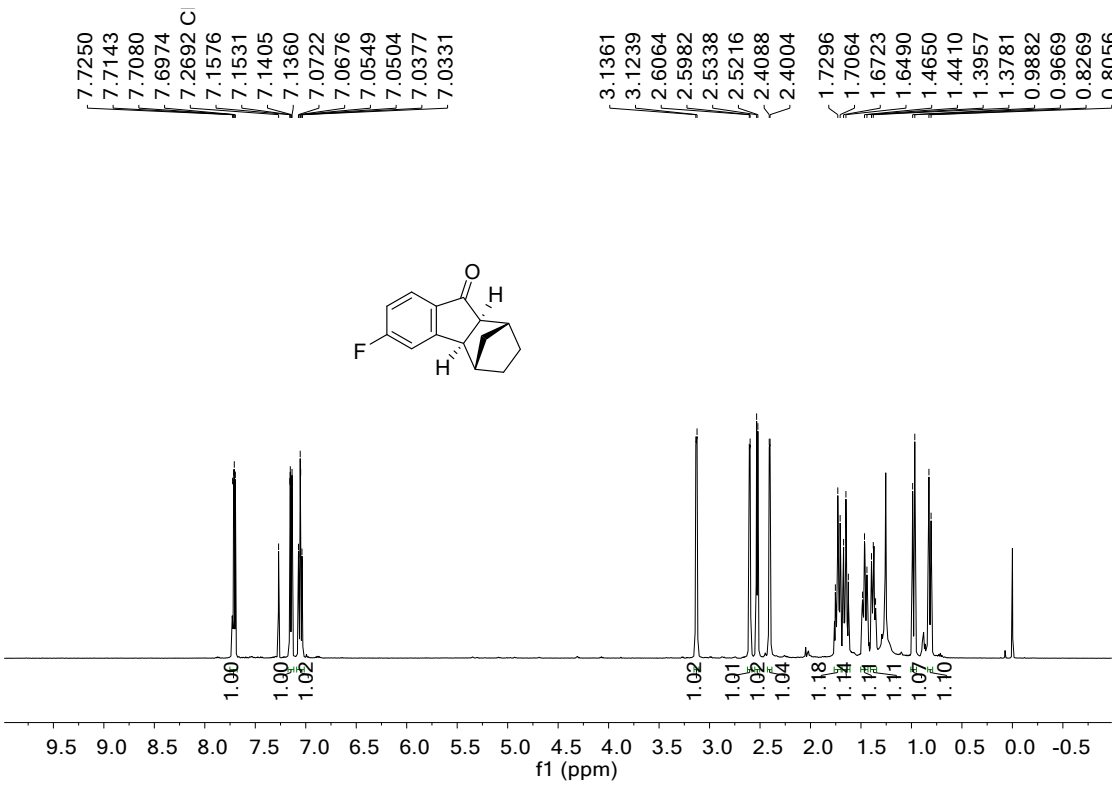
^{1}H NMR spectrum of compound 2l ($CDCl_3$, 500 MHz)



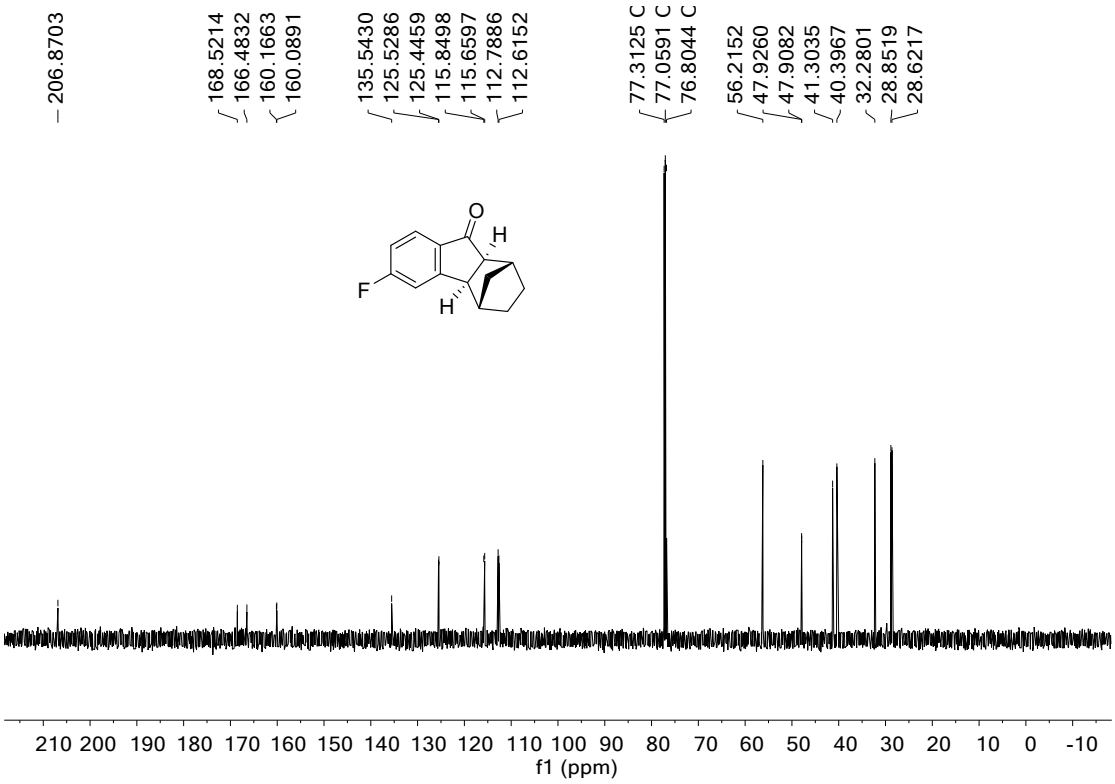
^{13}C NMR spectrum of compound 2l ($CDCl_3$, 126 MHz)



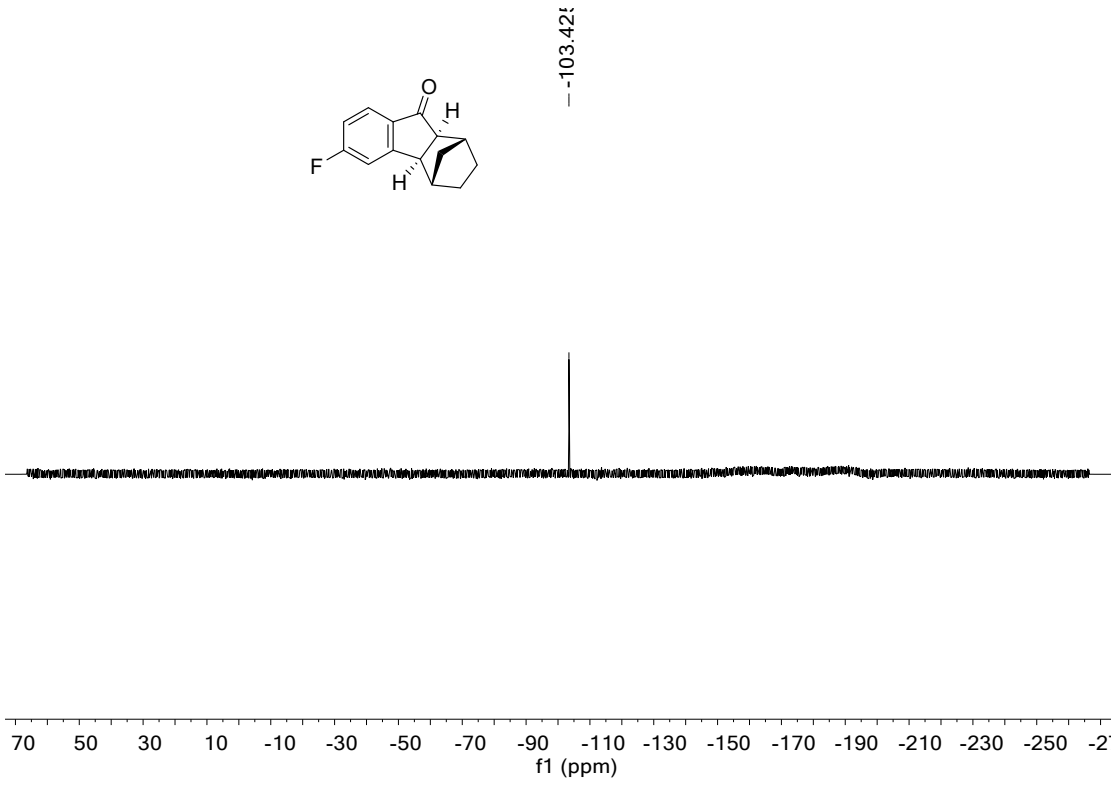
^{1}H NMR spectrum of compound 2m ($CDCl_3$, 500 MHz)



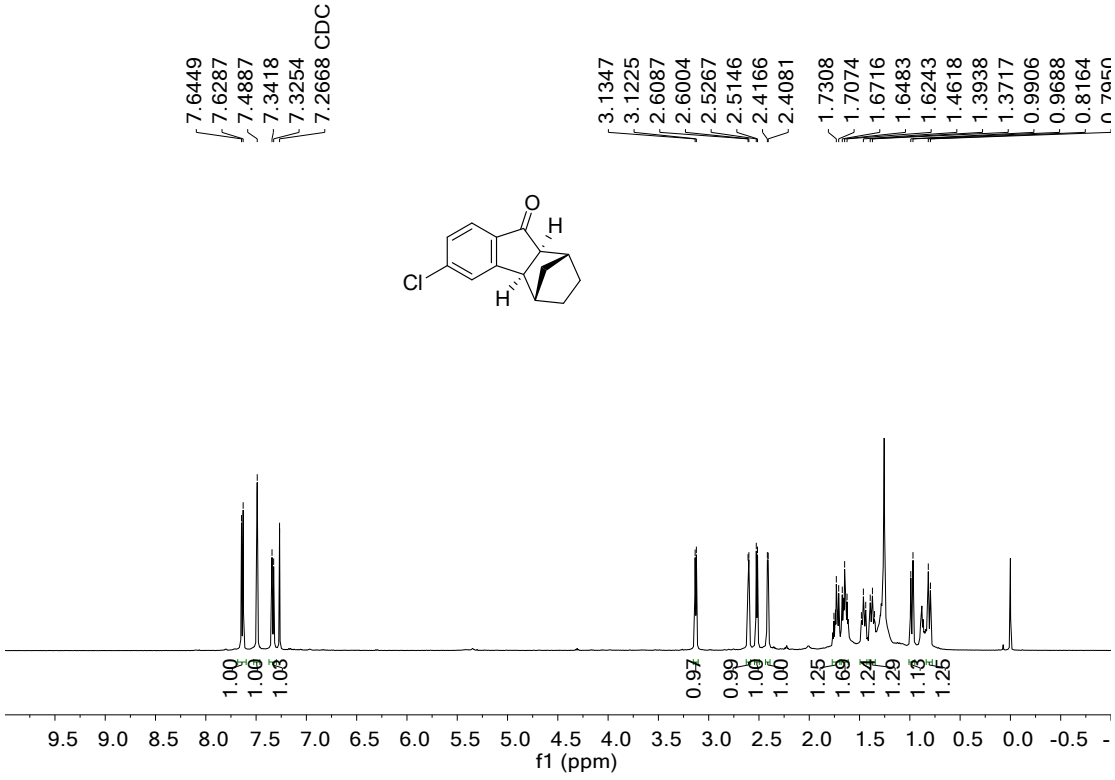
^{13}C NMR spectrum of compound 2m ($CDCl_3$, 126 MHz)



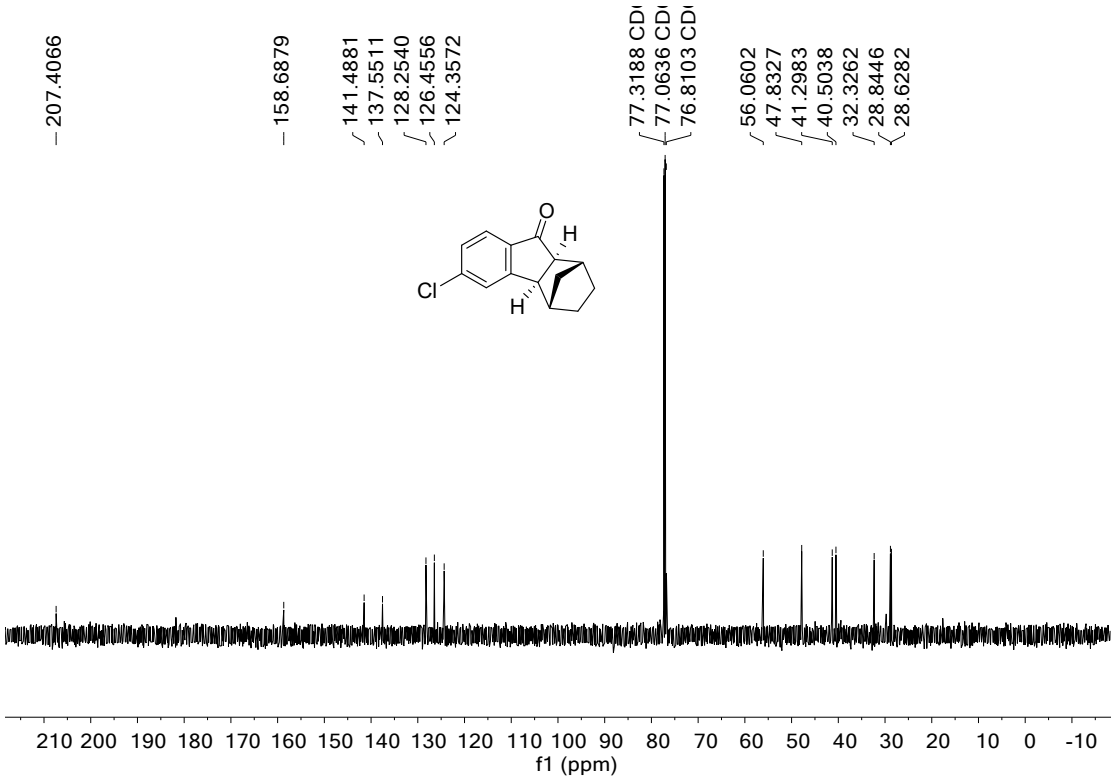
^{19}F NMR spectrum of compound 2m ($CDCl_3$, 470 MHz)



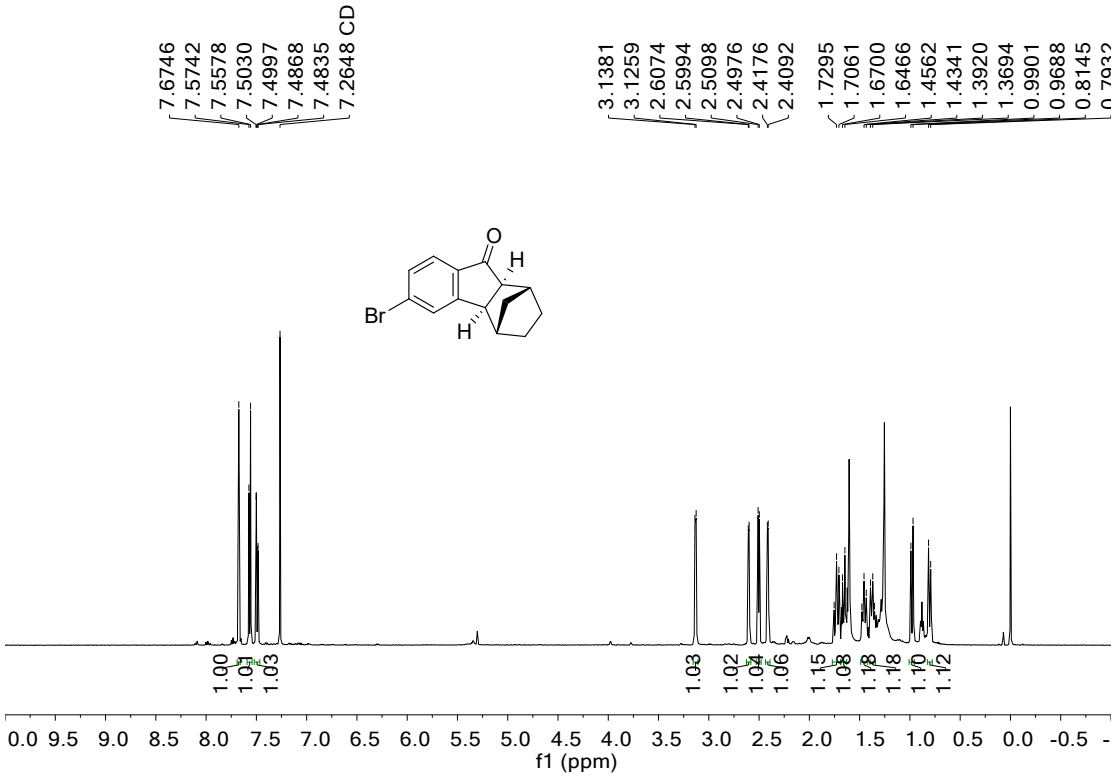
^{1}H NMR spectrum of compound 2n ($CDCl_3$, 500 MHz)



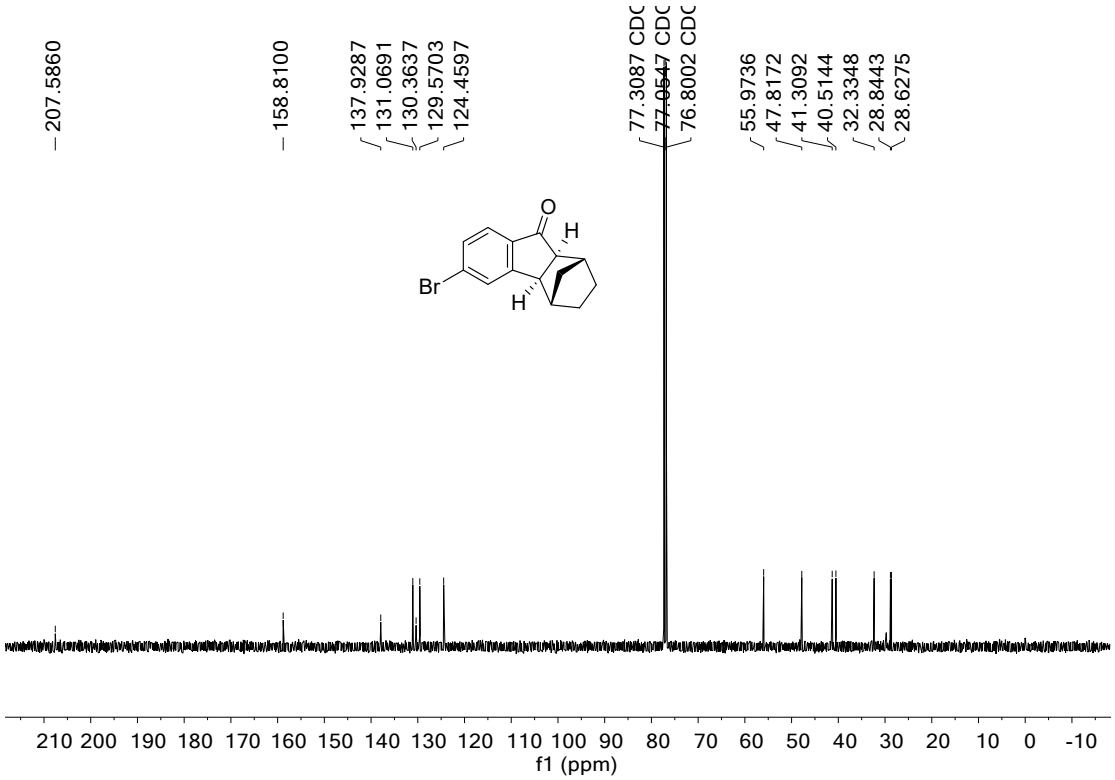
^{13}C NMR spectrum of compound 2n ($CDCl_3$, 126 MHz)



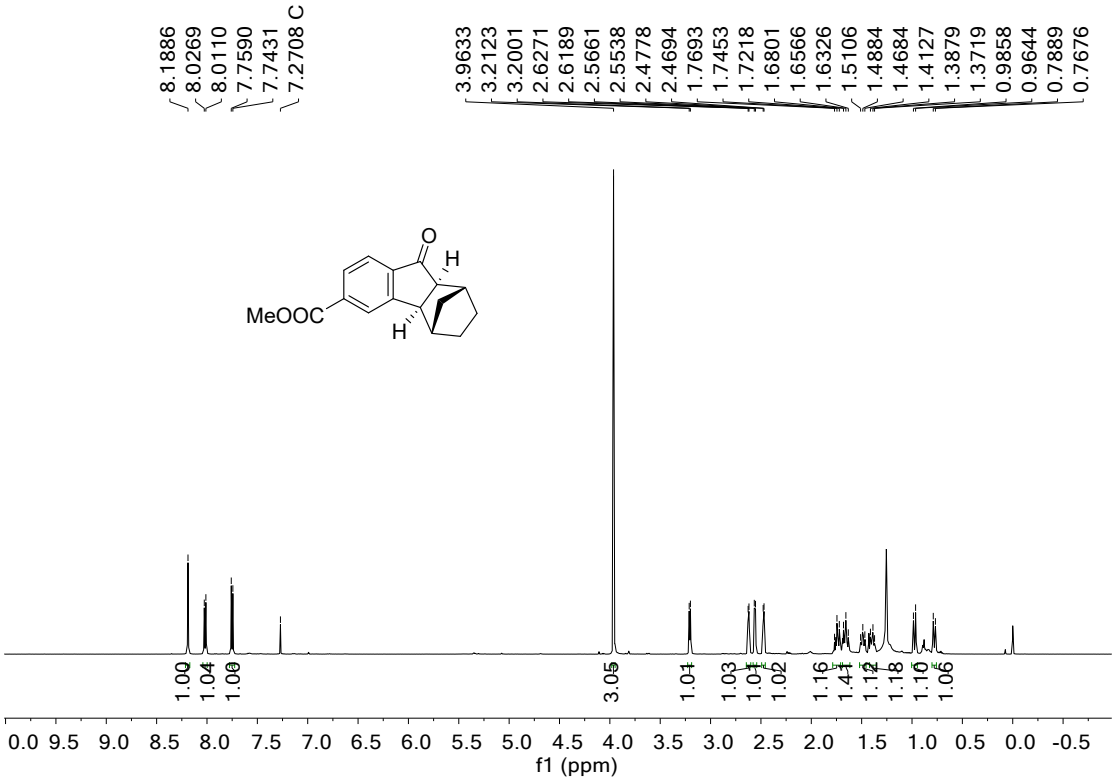
^{1}H NMR spectrum of compound 2o ($CDCl_3$, 500 MHz)



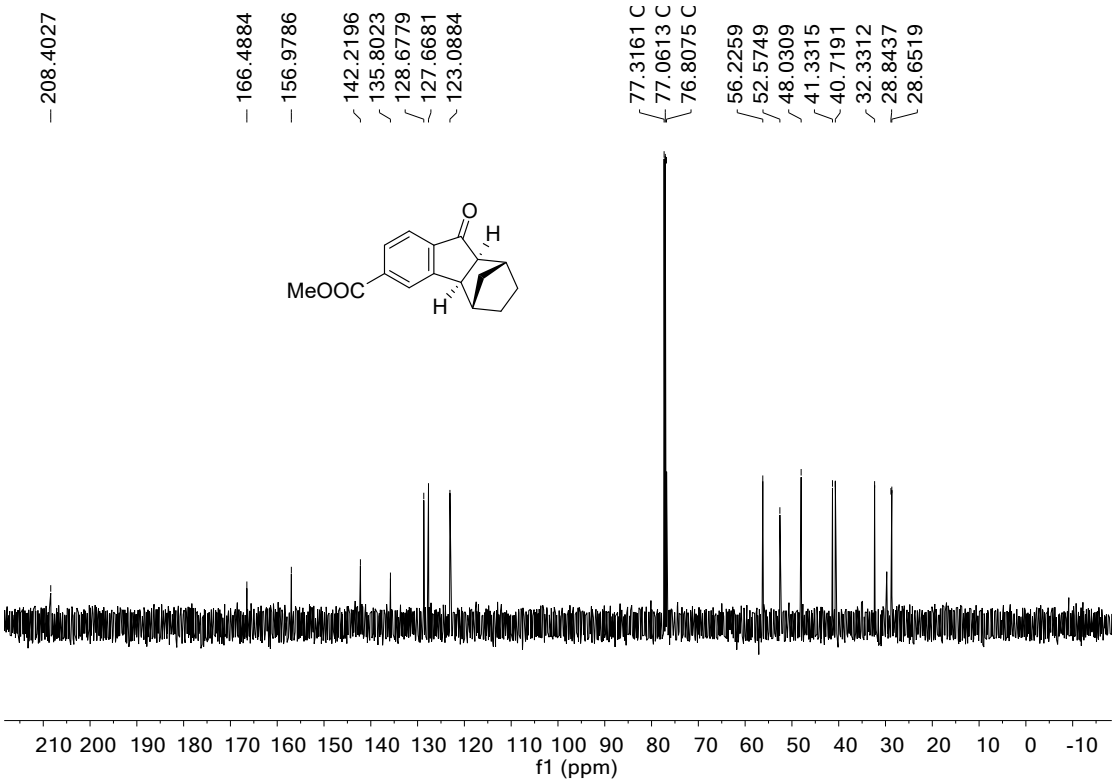
^{13}C NMR spectrum of compound 2o ($CDCl_3$, 126 MHz)



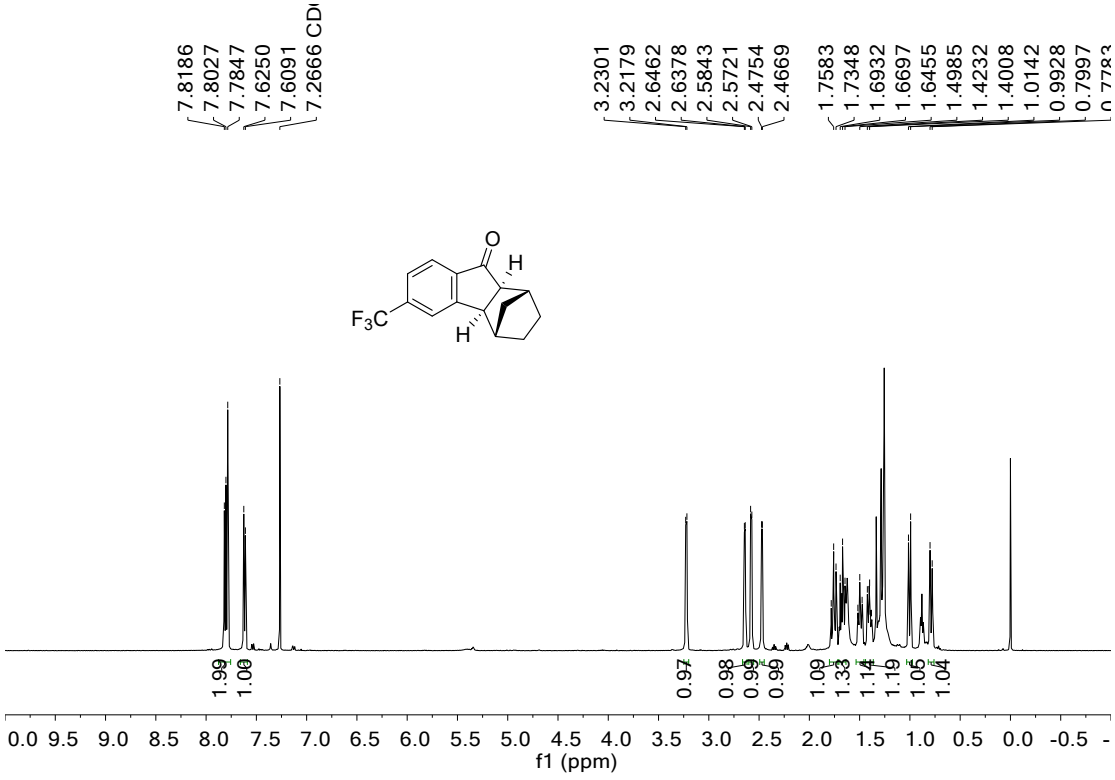
^{1}H NMR spectrum of compound 2p ($CDCl_3$, 500 MHz)



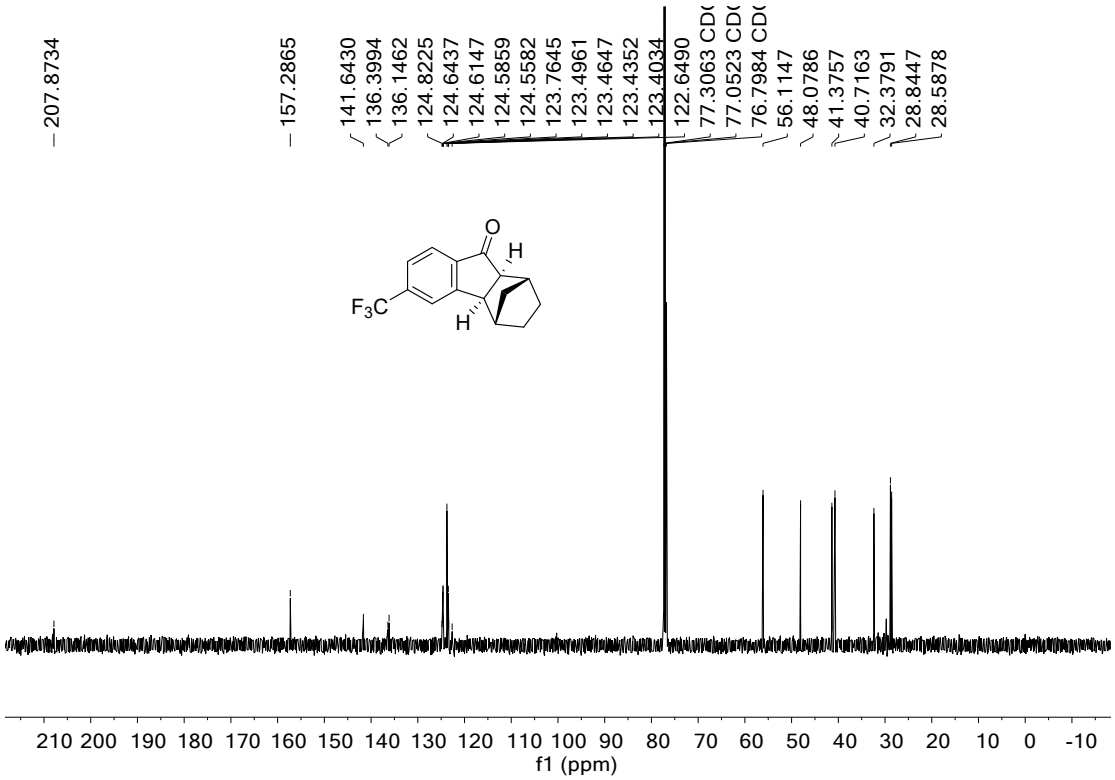
^{13}C NMR spectrum of compound 2p ($CDCl_3$, 126 MHz)



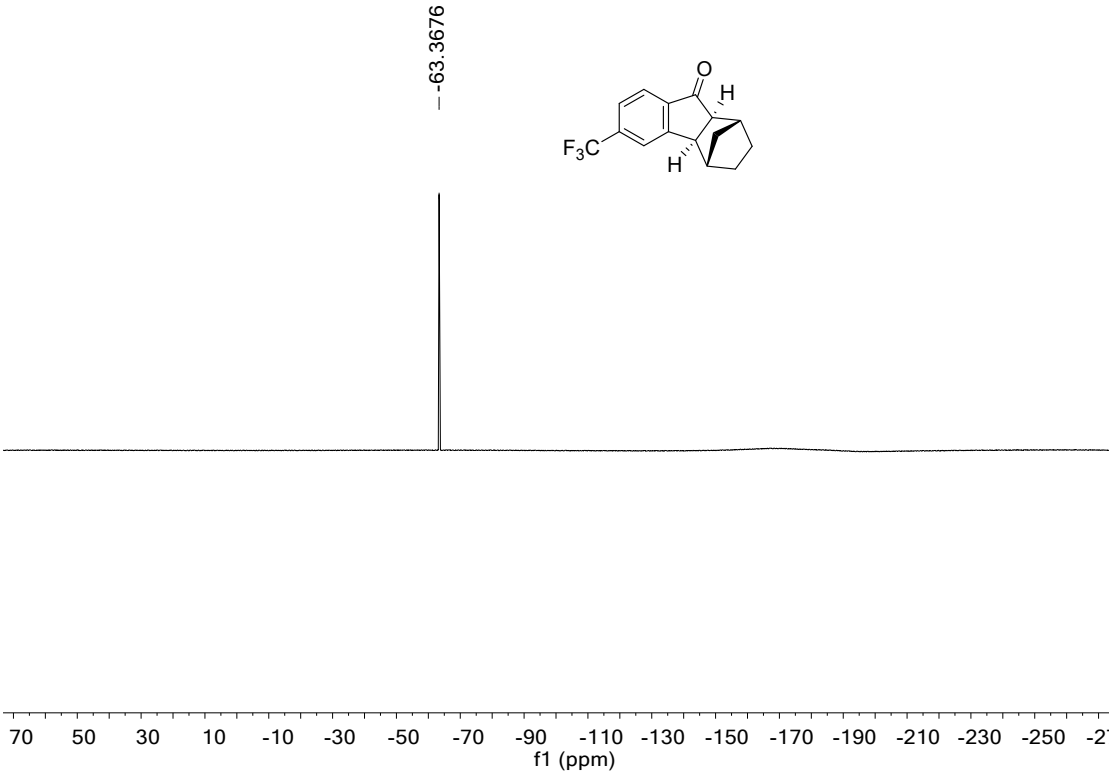
^{1}H NMR spectrum of compound 2q ($CDCl_3$, 500 MHz)



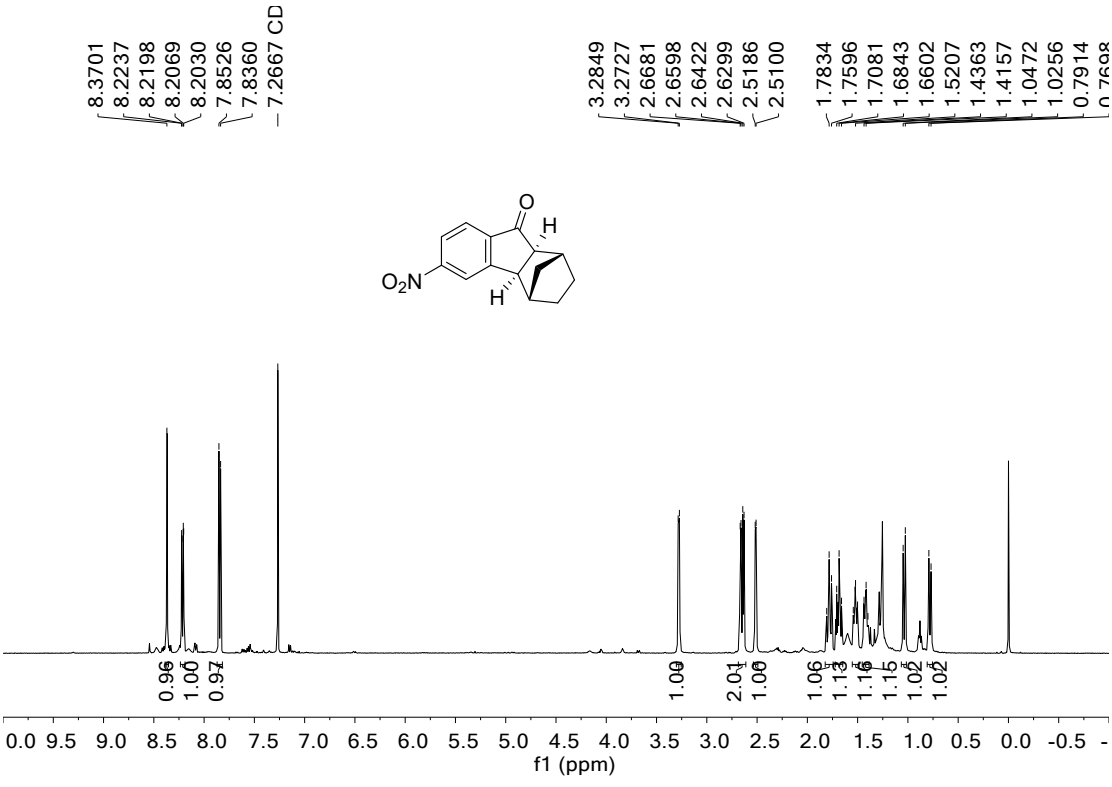
^{13}C NMR spectrum of compound 2q ($CDCl_3$, 126 MHz)



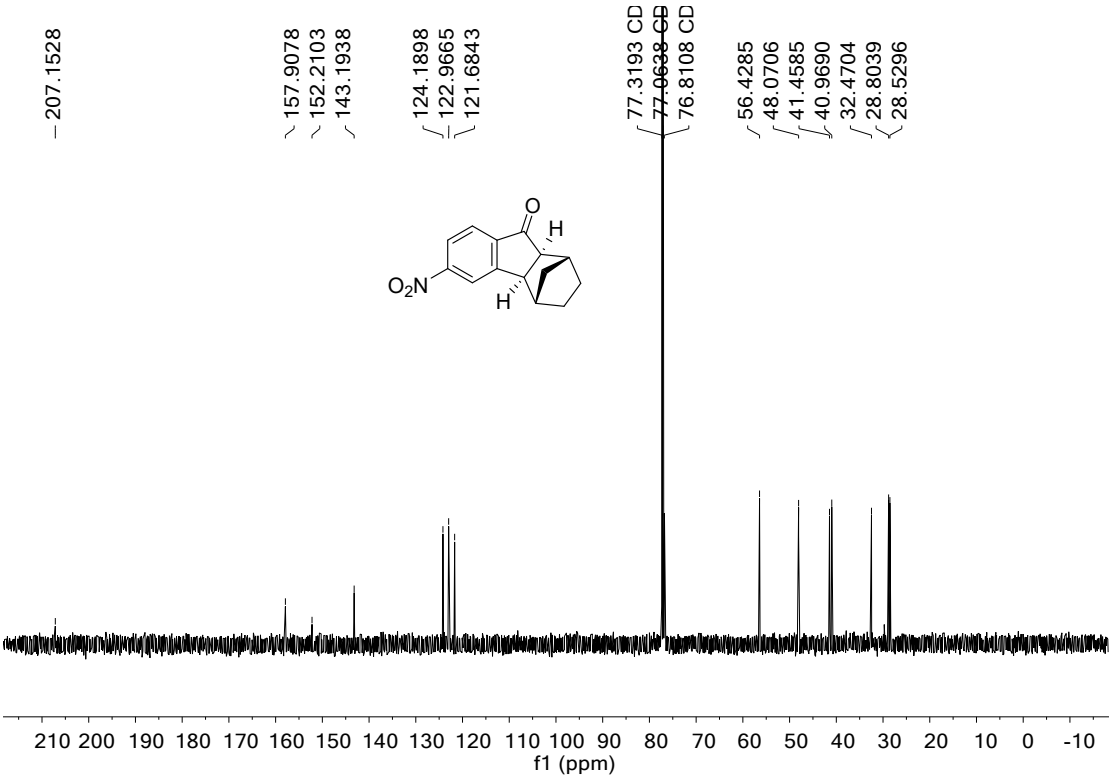
^{19}F NMR spectrum of compound 2q ($CDCl_3$, 470 MHz)



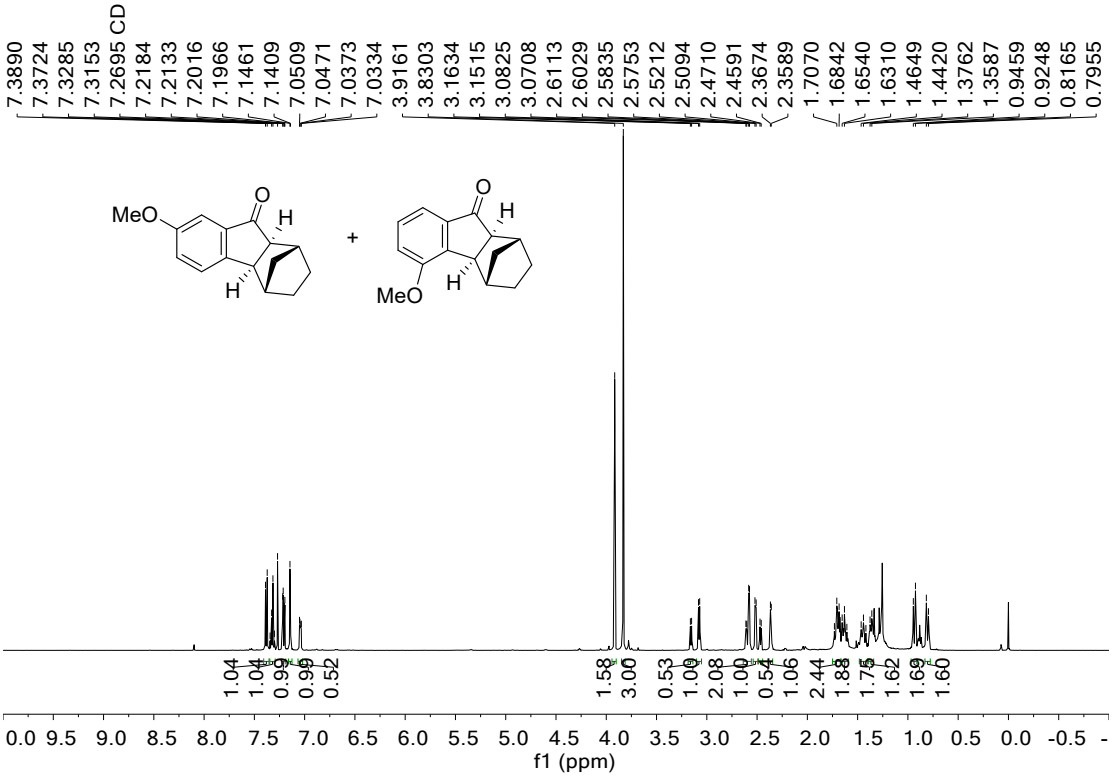
^{1}H NMR spectrum of compound 2r ($CDCl_3$, 500 MHz)



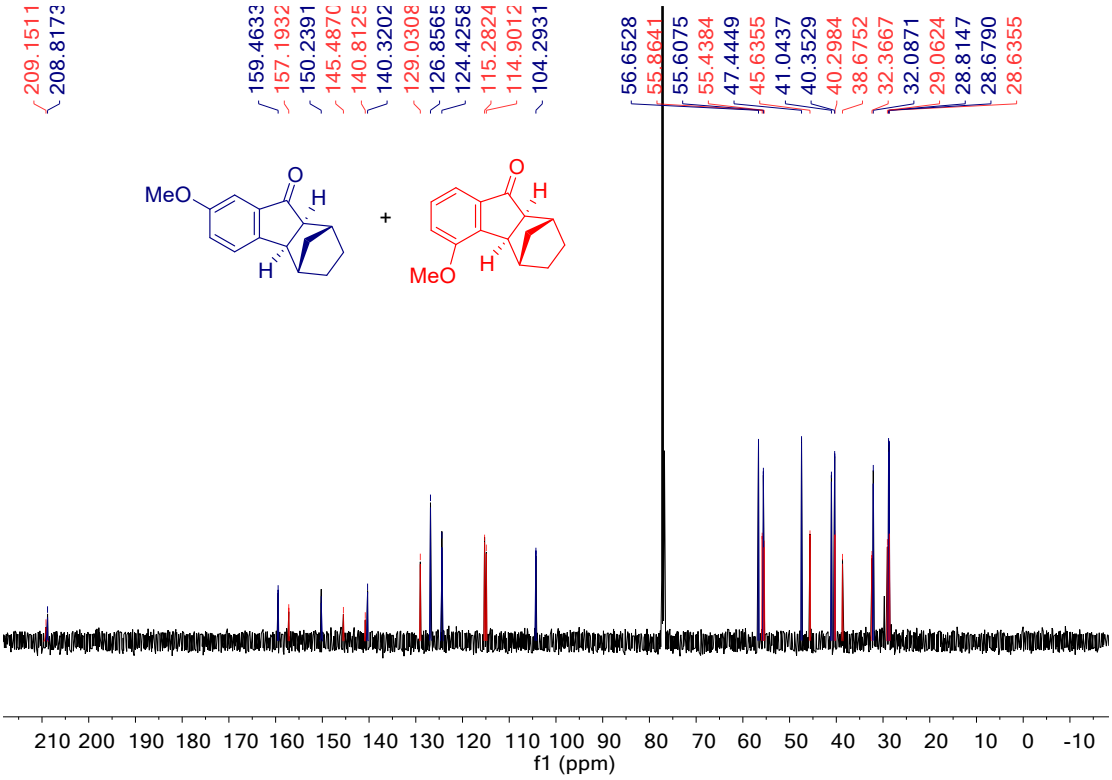
^{13}C NMR spectrum of compound 2r ($CDCl_3$, 126 MHz)



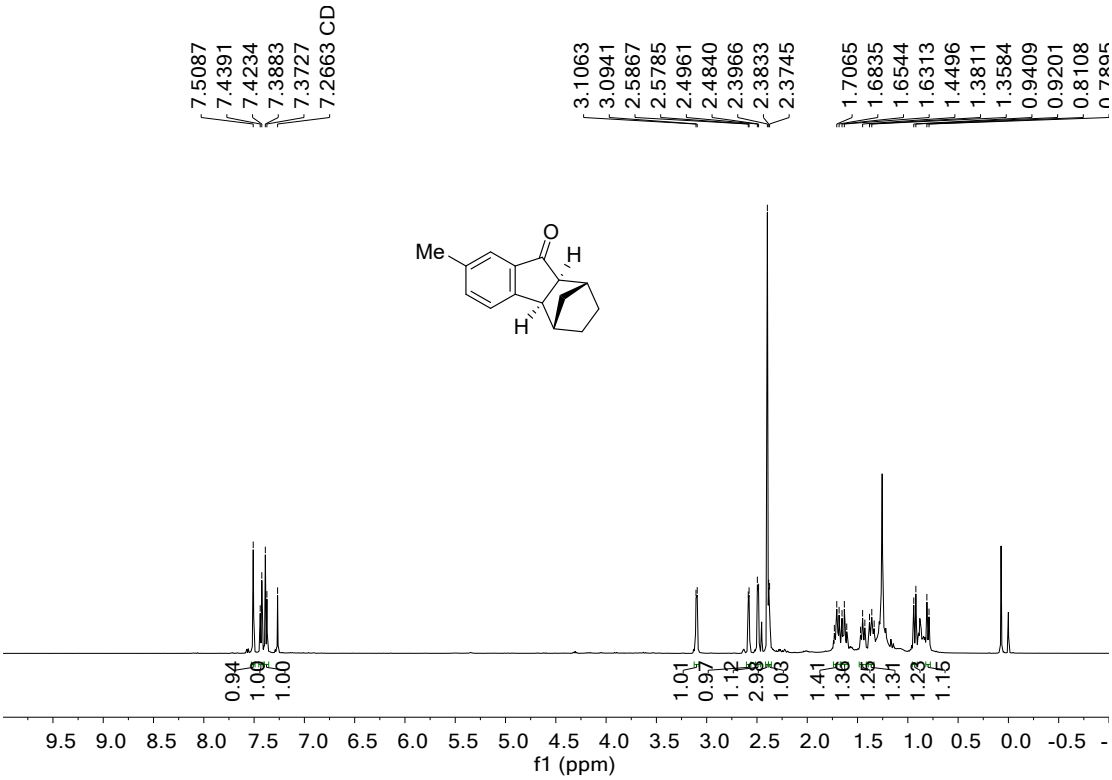
^{1}H NMR spectrum of compound 2s and 2ss ($CDCl_3$, 500 MHz)



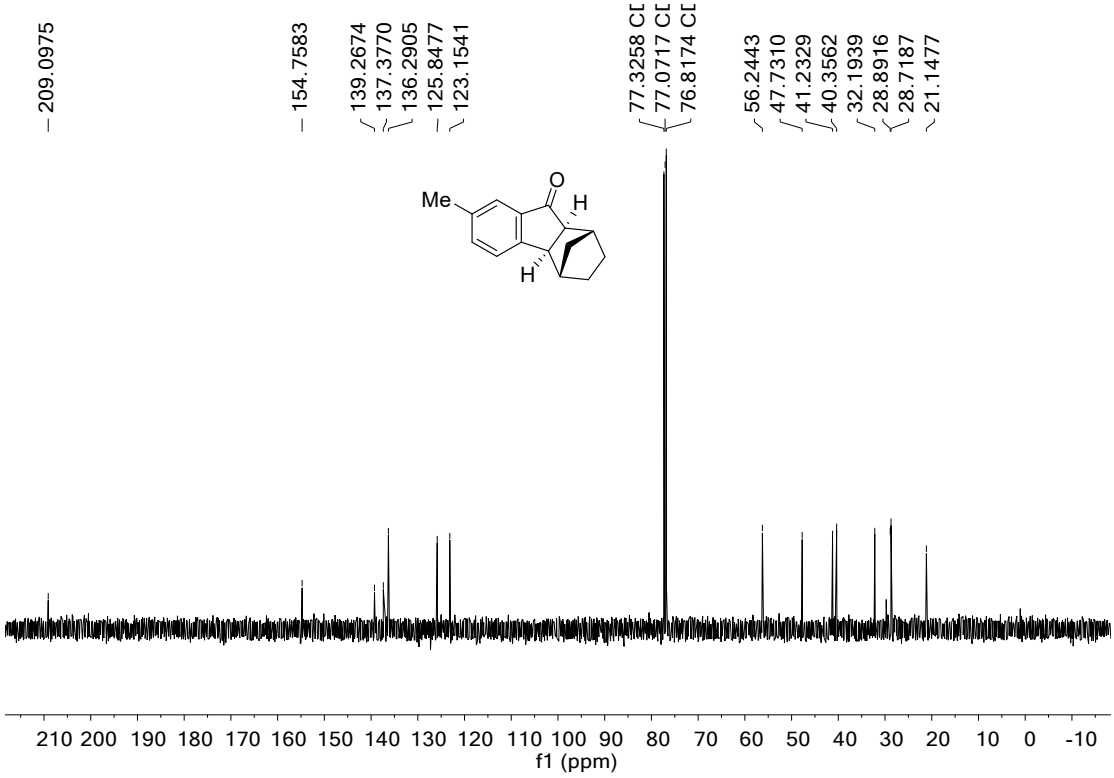
^{13}C NMR spectrum of compound 2s and 2ss ($CDCl_3$, 126 MHz)



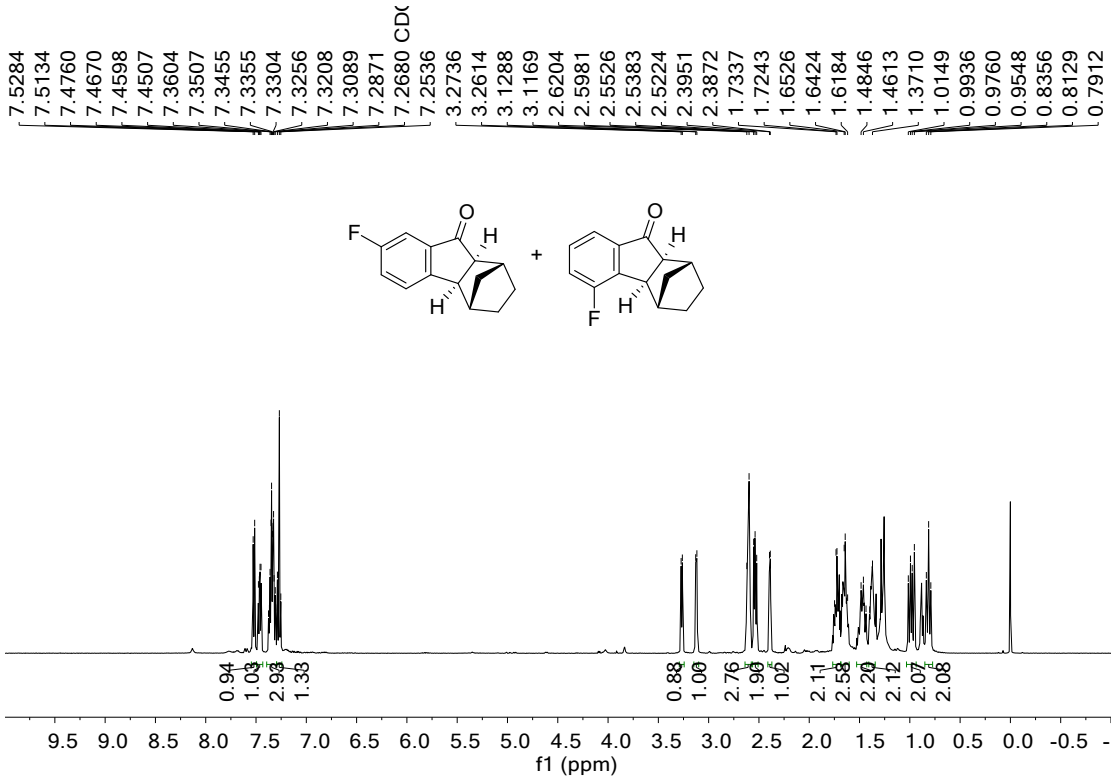
^{1}H NMR spectrum of compound 2t ($CDCl_3$, 500 MHz)



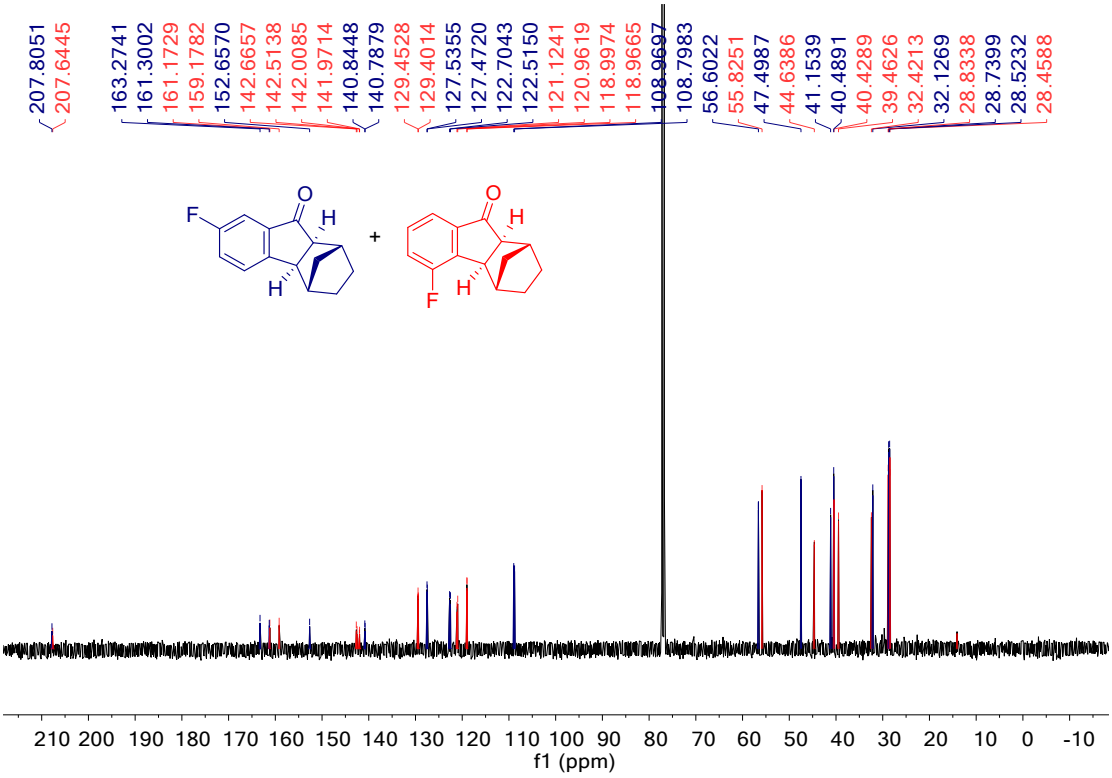
^{13}C NMR spectrum of compound 2t ($CDCl_3$, 126 MHz)



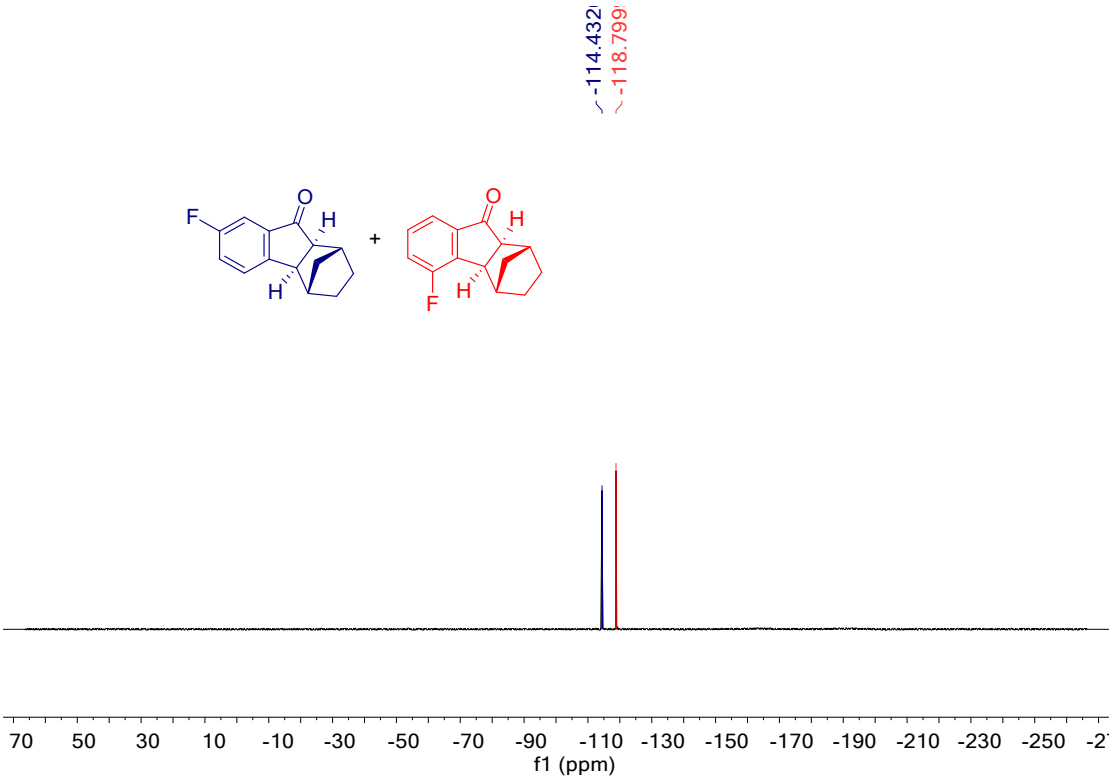
^{1}H NMR spectrum of compound 2u and 2uu ($CDCl_3$, 500 MHz)



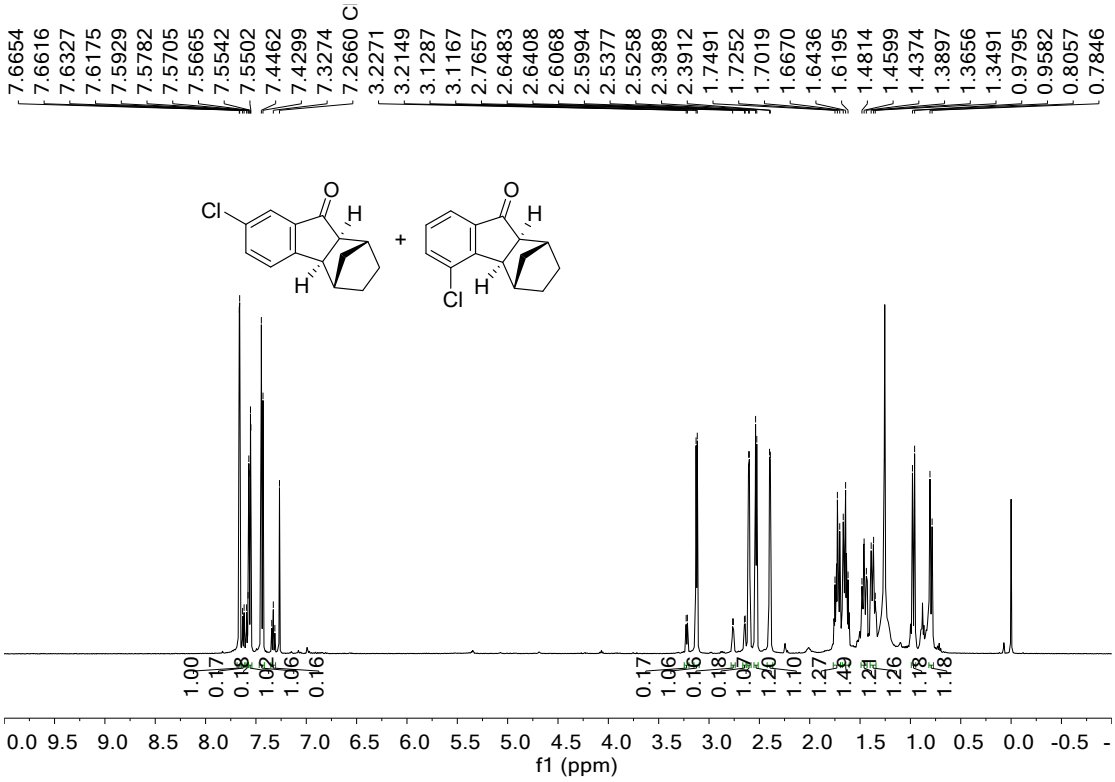
^{13}C NMR spectrum of compound 2u and 2uu ($CDCl_3$, 126 MHz)



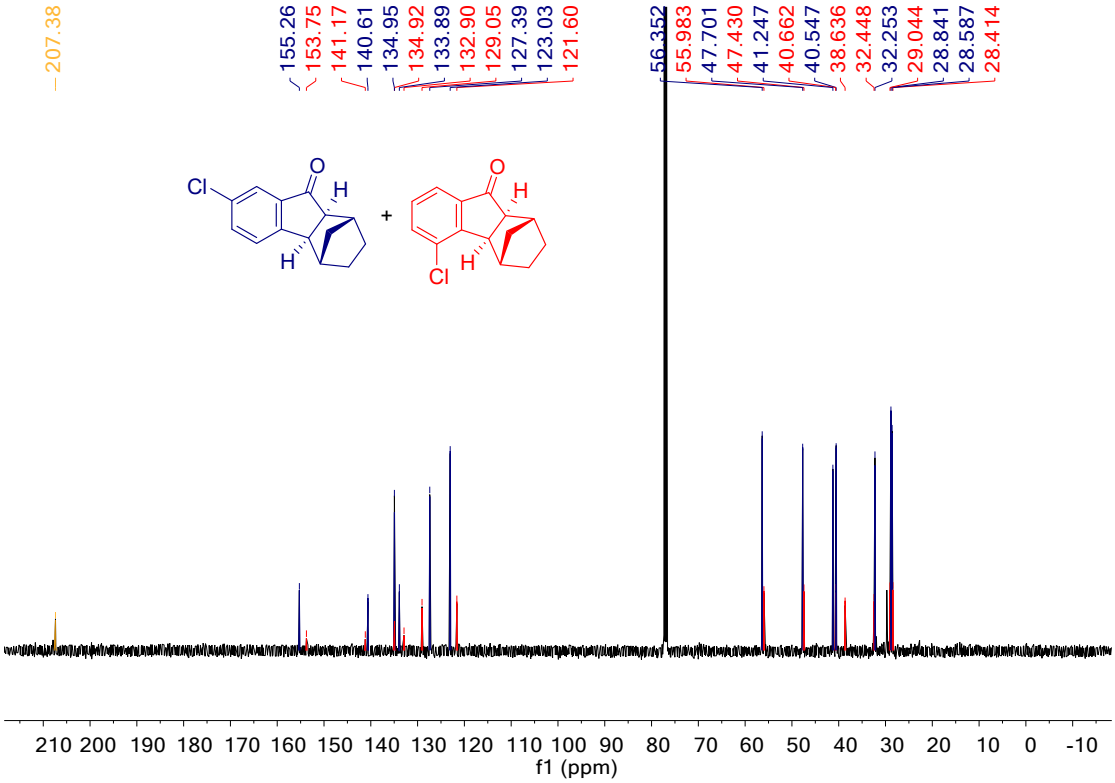
^{19}F NMR spectrum of compound 2u and 2uu ($CDCl_3$, 470 MHz)



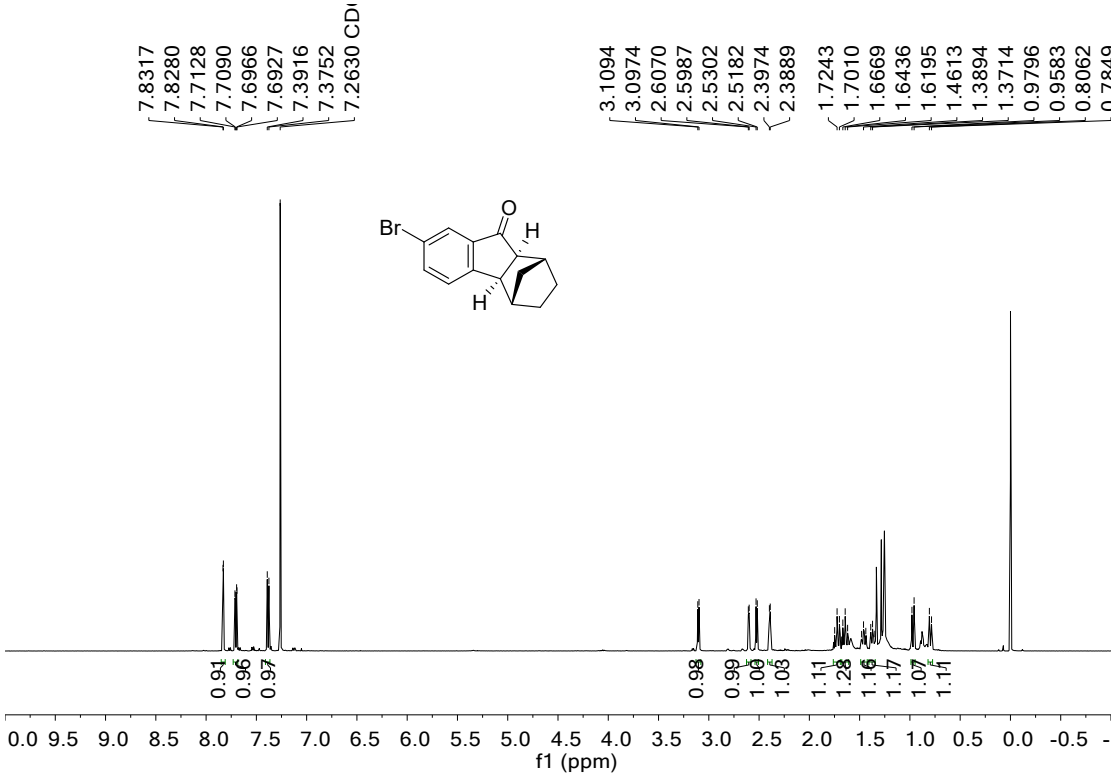
^{1}H NMR spectrum of compound 2v and 2vv ($CDCl_3$, 500 MHz)



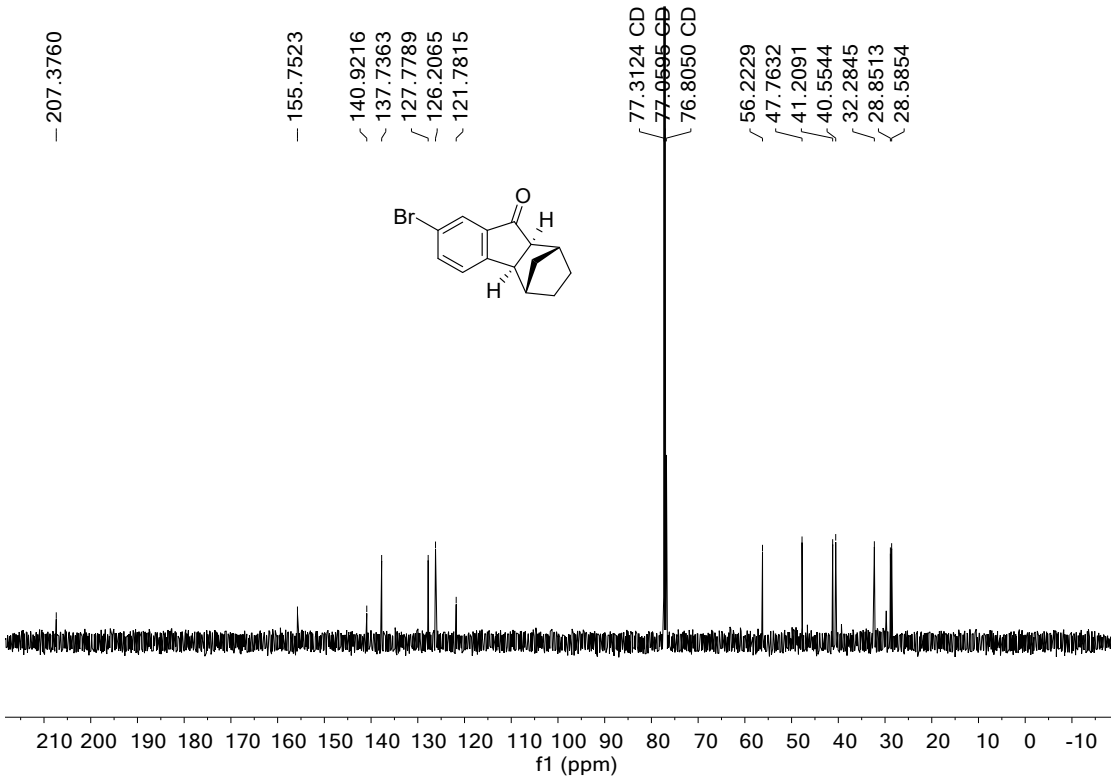
^{13}C NMR spectrum of compound 2v and 2vv ($CDCl_3$, 126 MHz)



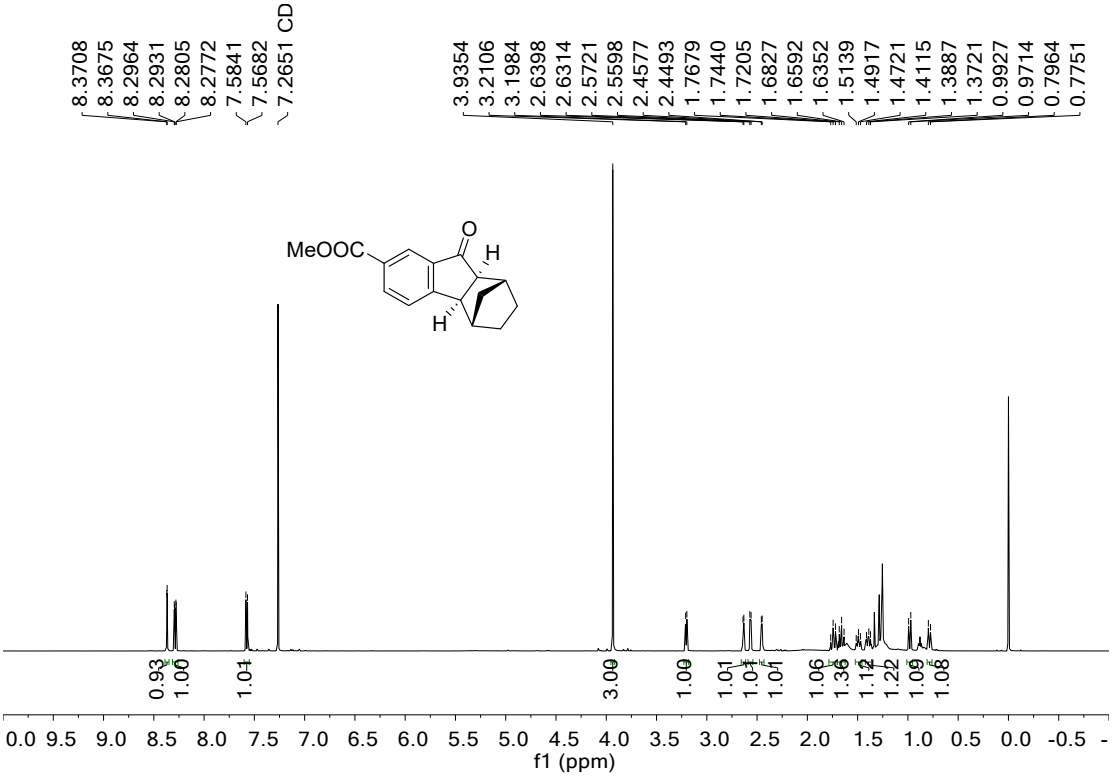
^{1}H NMR spectrum of compound 2w ($CDCl_3$, 500 MHz)



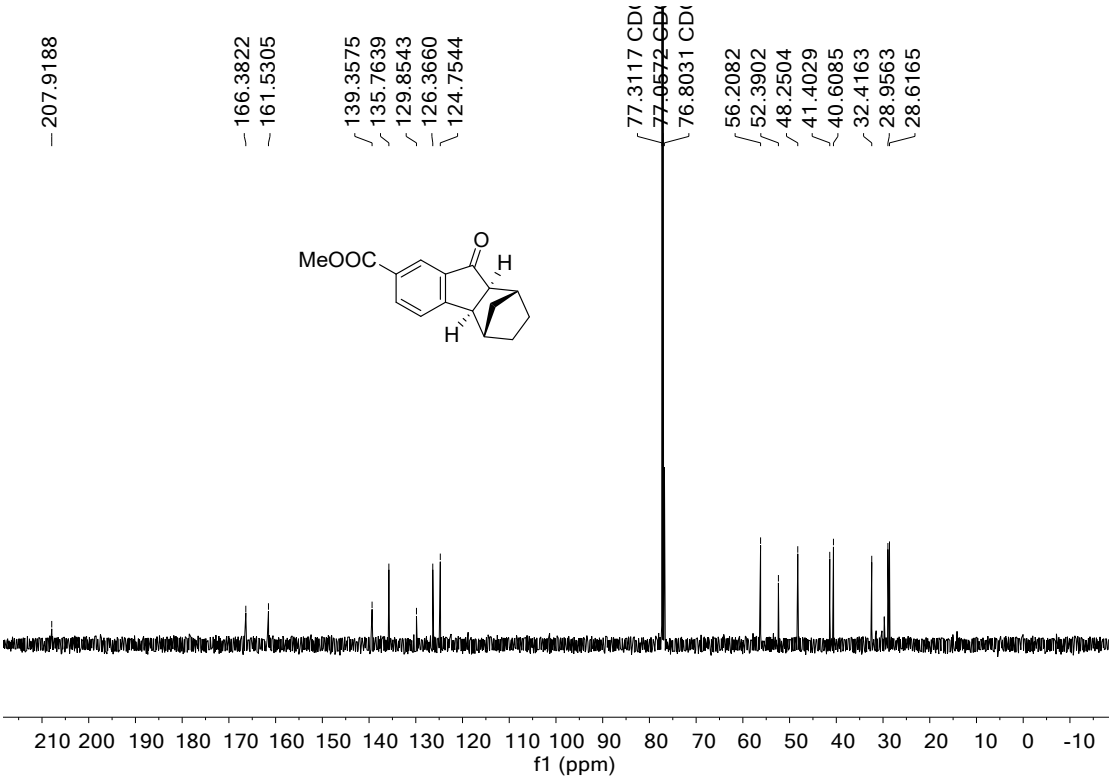
^{13}C NMR spectrum of compound 2w ($CDCl_3$, 126 MHz)



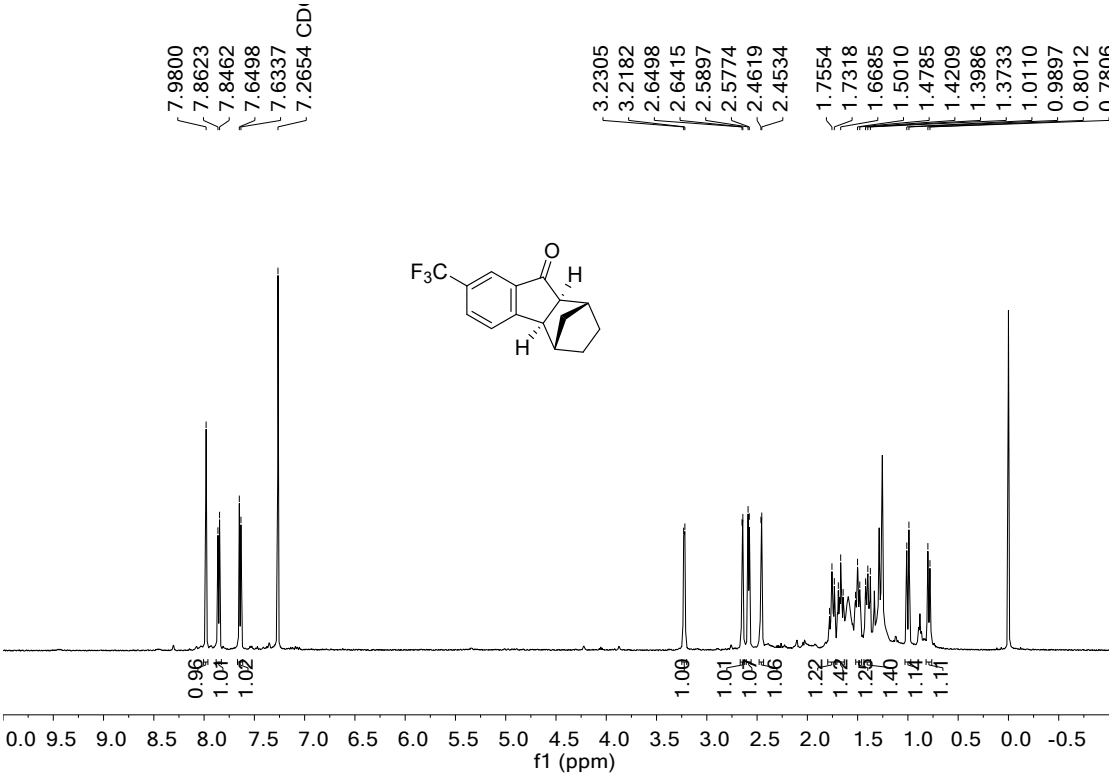
^{1}H NMR spectrum of compound 2x ($CDCl_3$, 500 MHz)



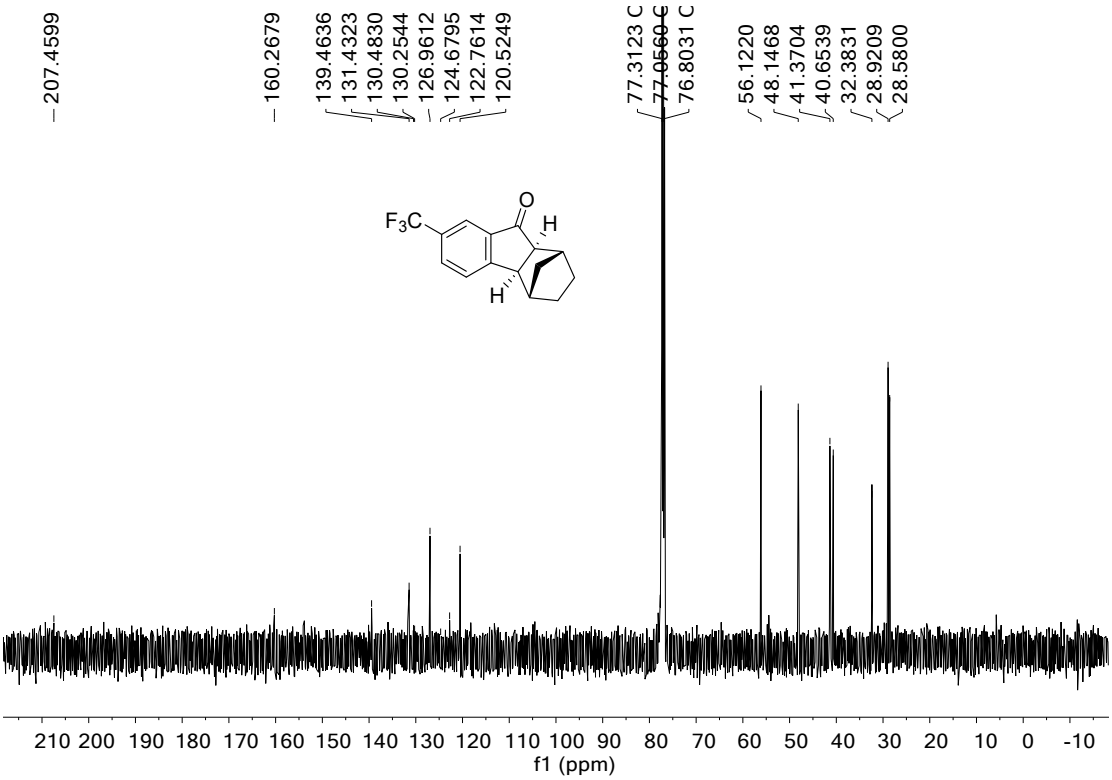
^{13}C NMR spectrum of compound 2x ($CDCl_3$, 126 MHz)



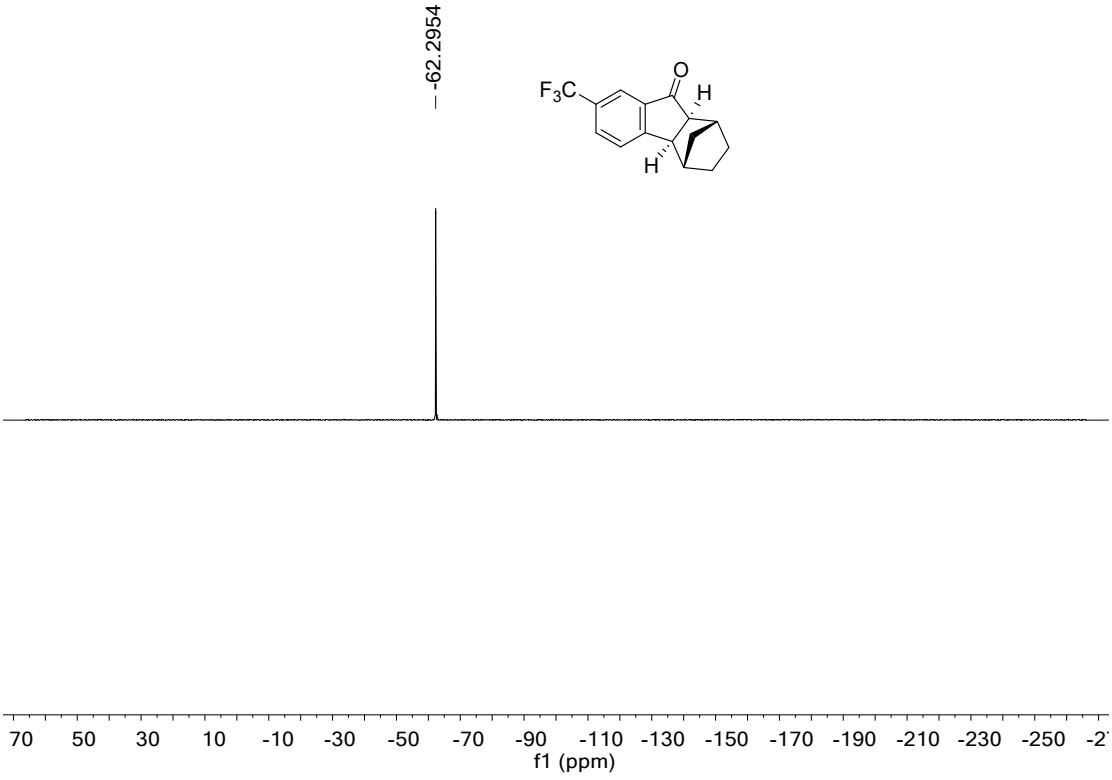
^{1}H NMR spectrum of compound 2y ($CDCl_3$, 500 MHz)



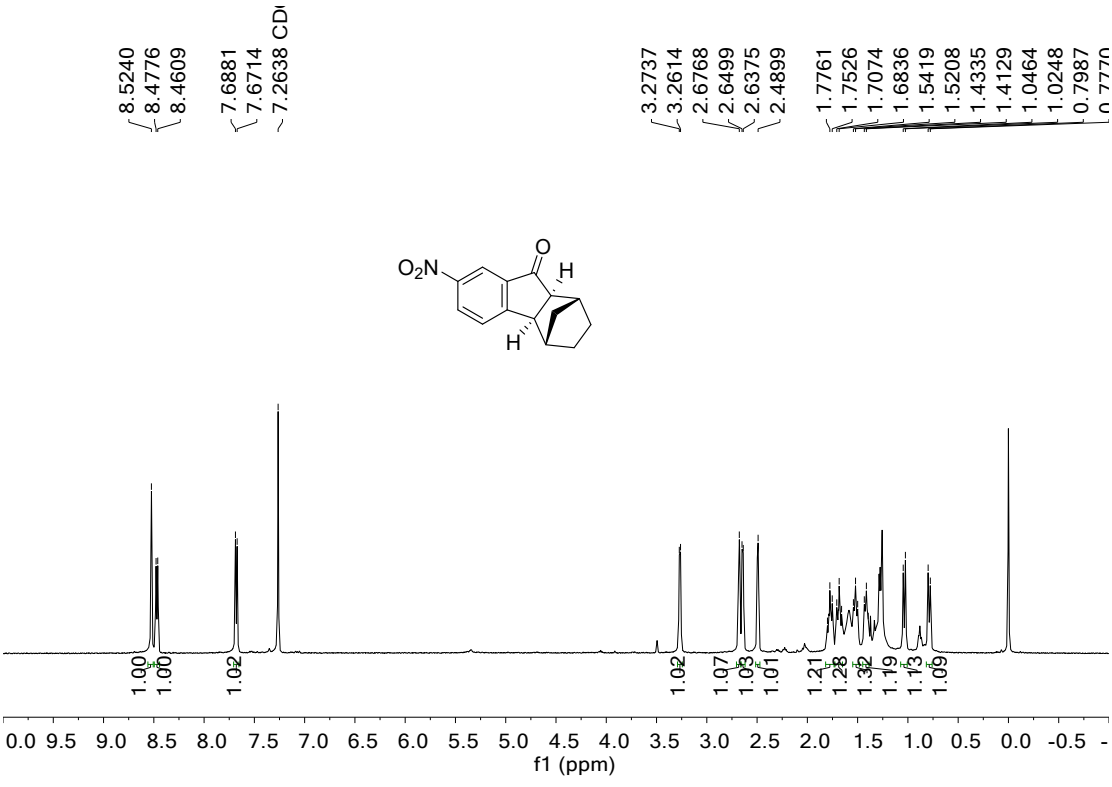
^{13}C NMR spectrum of compound 2y ($CDCl_3$, 126 MHz)



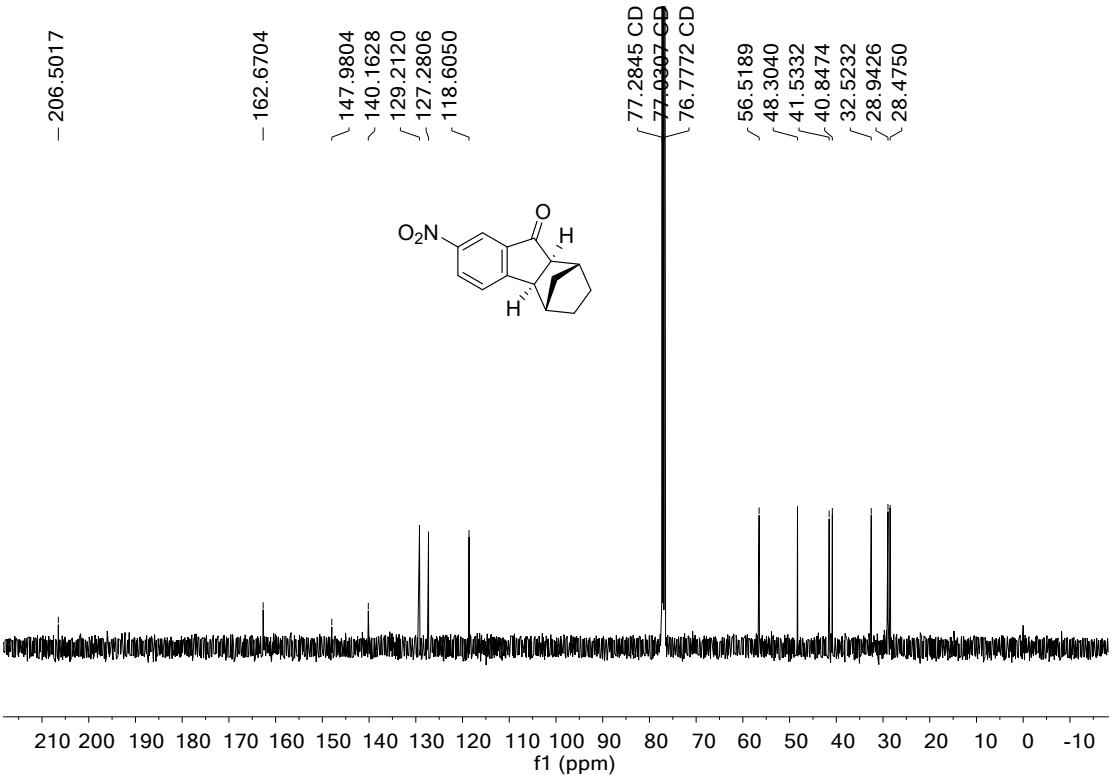
^{19}F NMR spectrum of compound 2y ($CDCl_3$, 470 MHz)



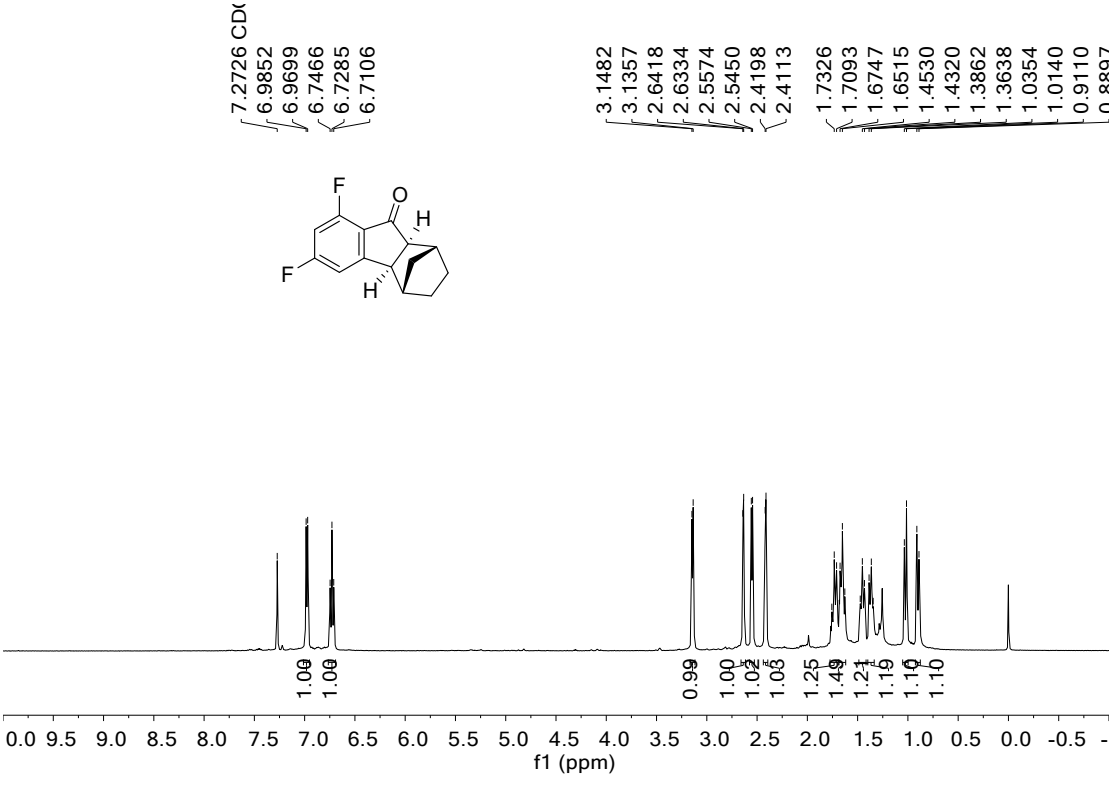
^{1}H NMR spectrum of compound 2z ($CDCl_3$, 500 MHz)



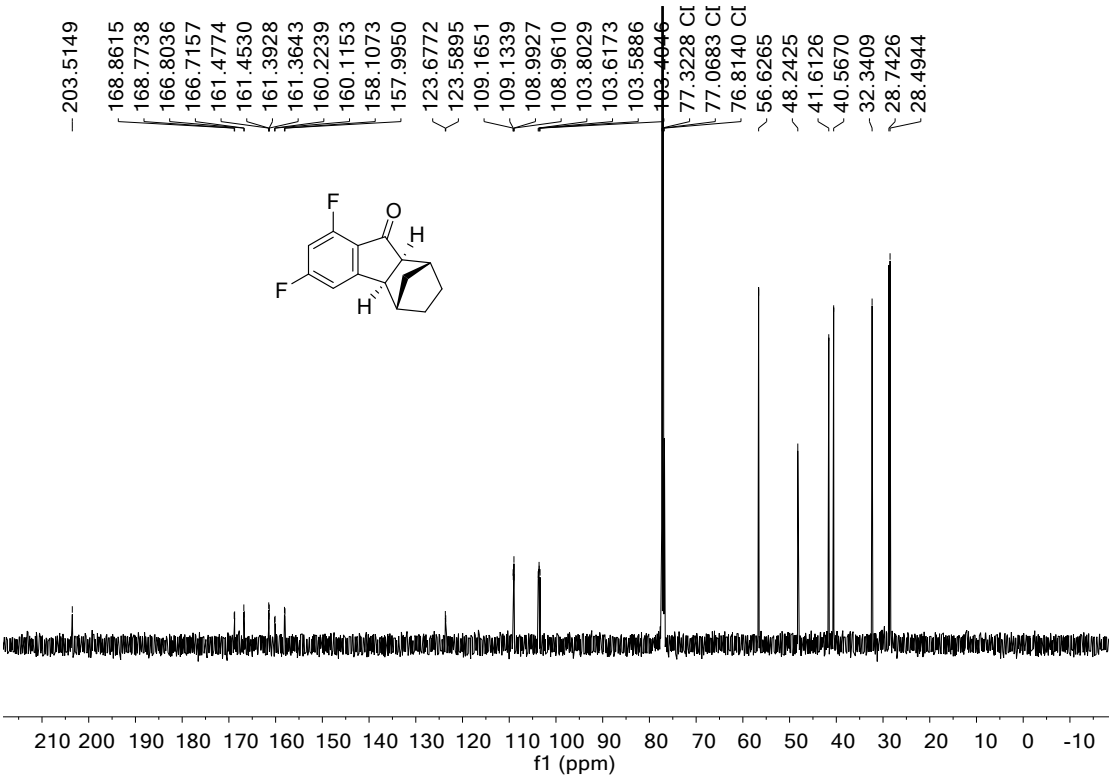
^{13}C NMR spectrum of compound 2z ($CDCl_3$, 126 MHz)



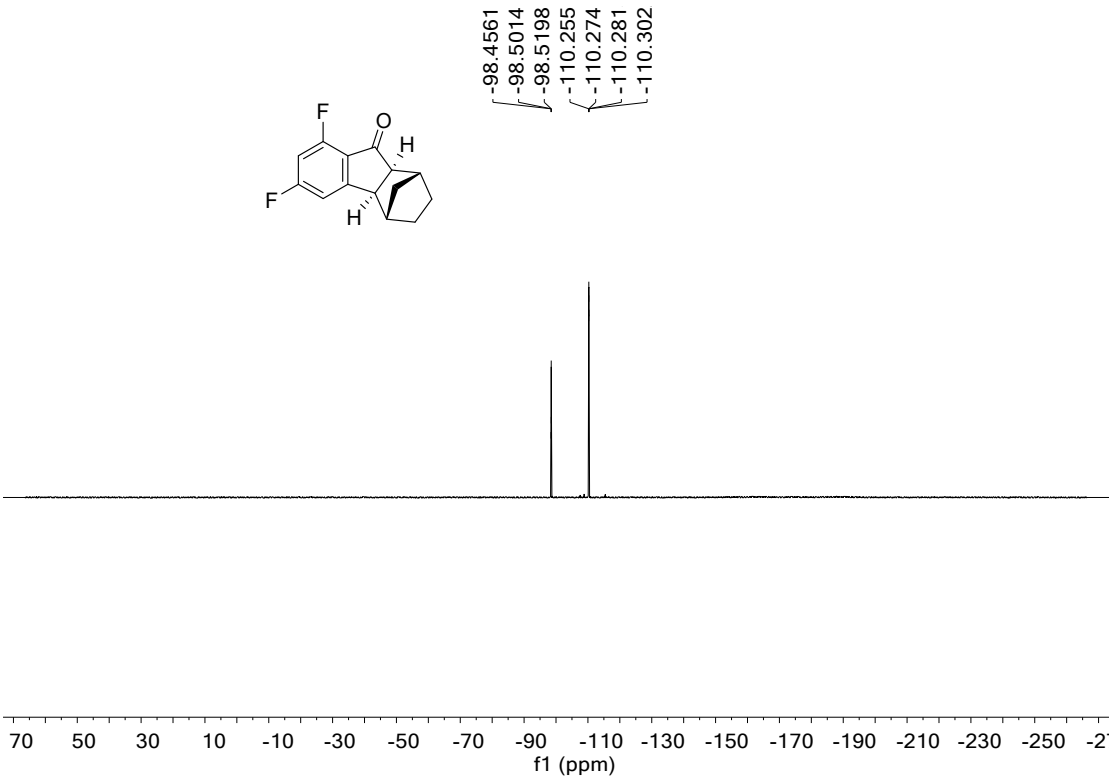
^{1}H NMR spectrum of compound 2aa ($CDCl_3$, 500 MHz)



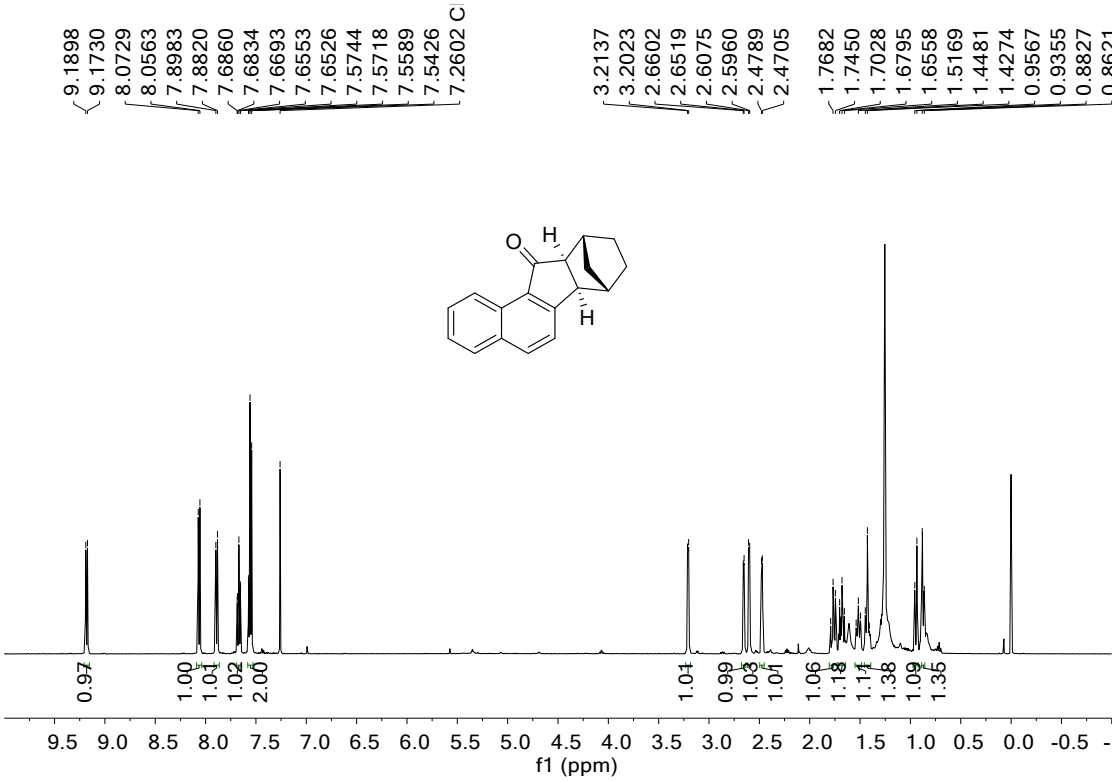
^{13}C NMR spectrum of compound 2aa ($CDCl_3$, 126 MHz)



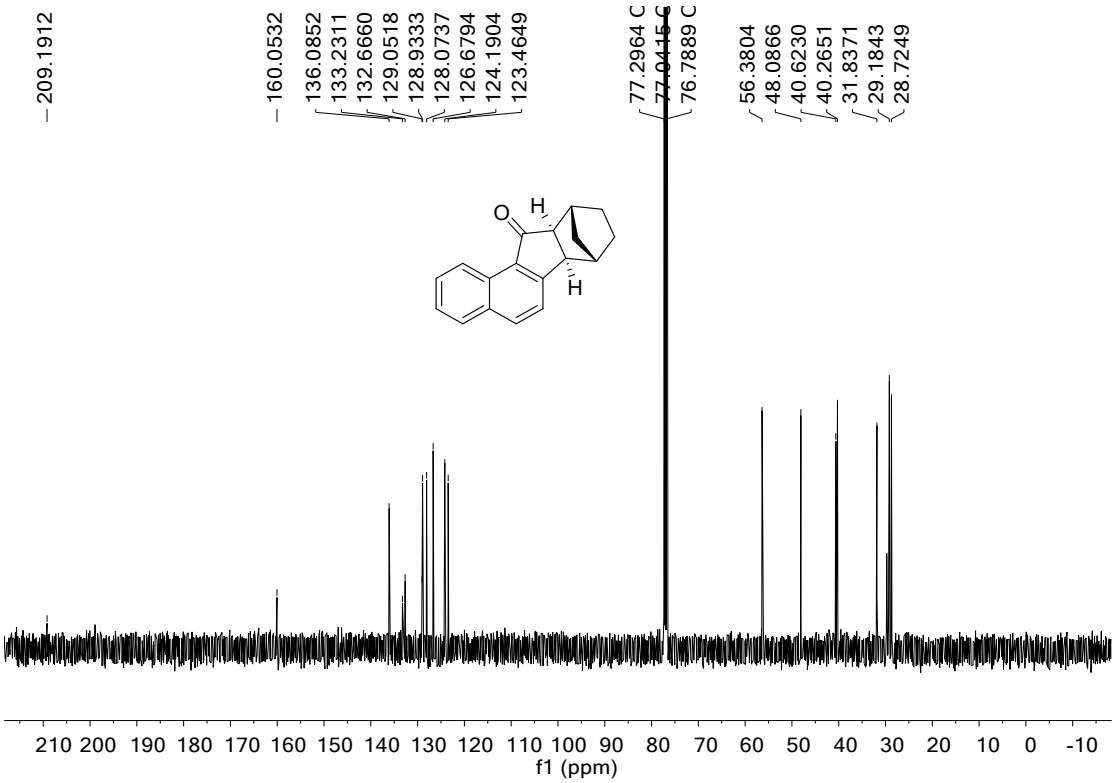
^{19}F NMR spectrum of compound 2aa ($CDCl_3$, 470 MHz)



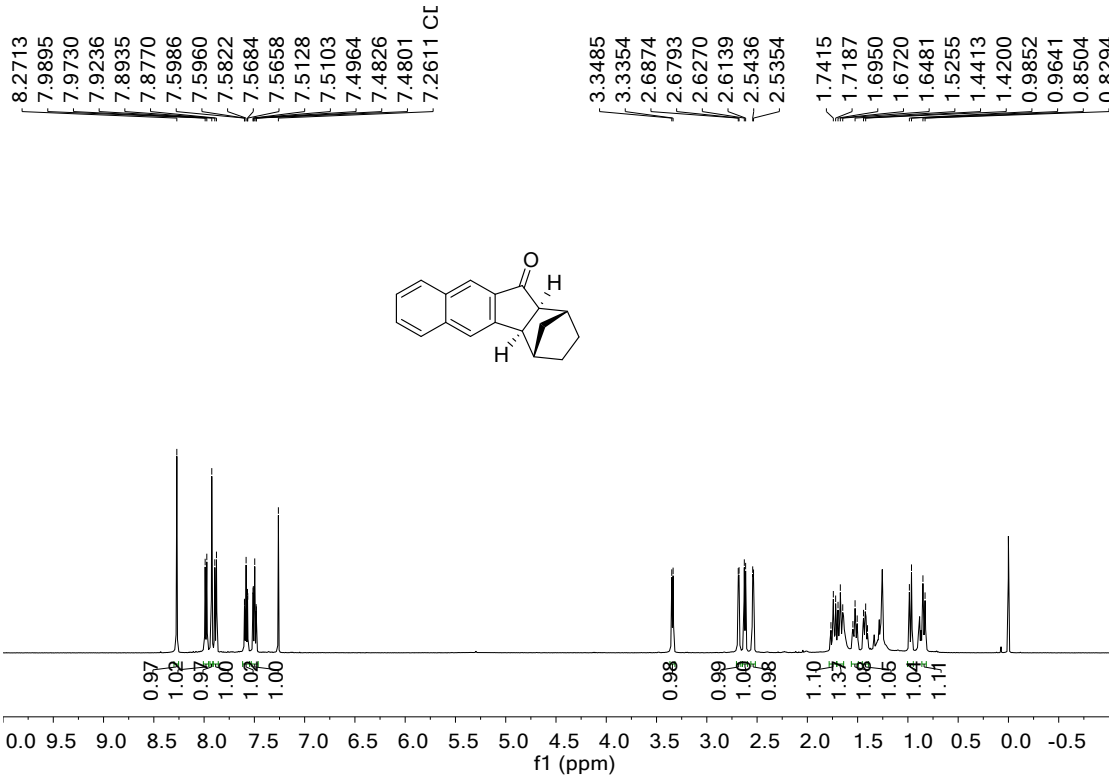
^{1}H NMR spectrum of compound 2ab ($CDCl_3$, 500 MHz)



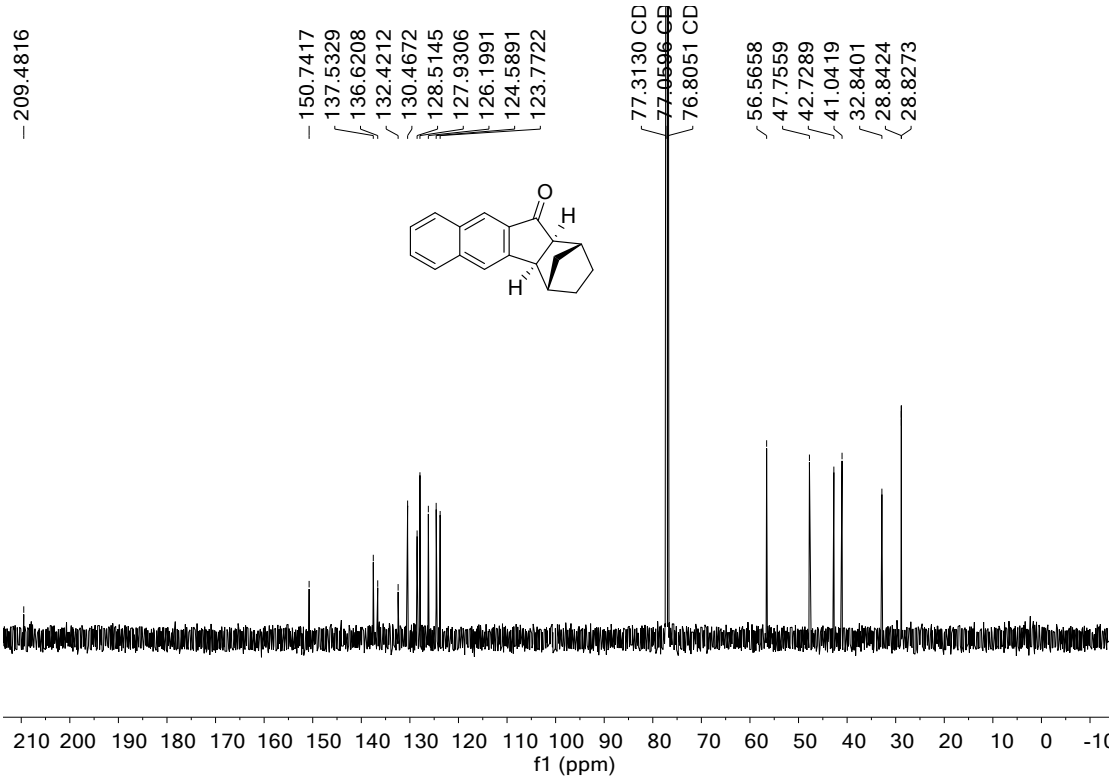
^{13}C NMR spectrum of compound 2ab ($CDCl_3$, 126 MHz)



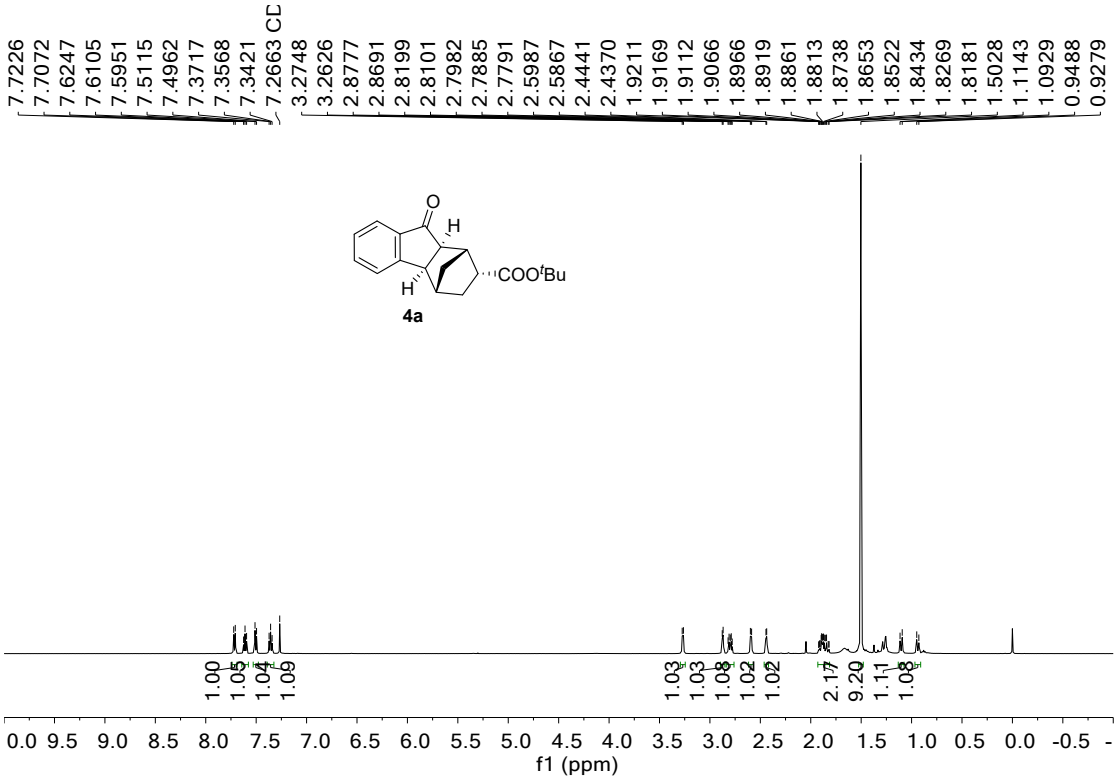
^{1}H NMR spectrum of compound 2ac ($CDCl_3$, 500 MHz)



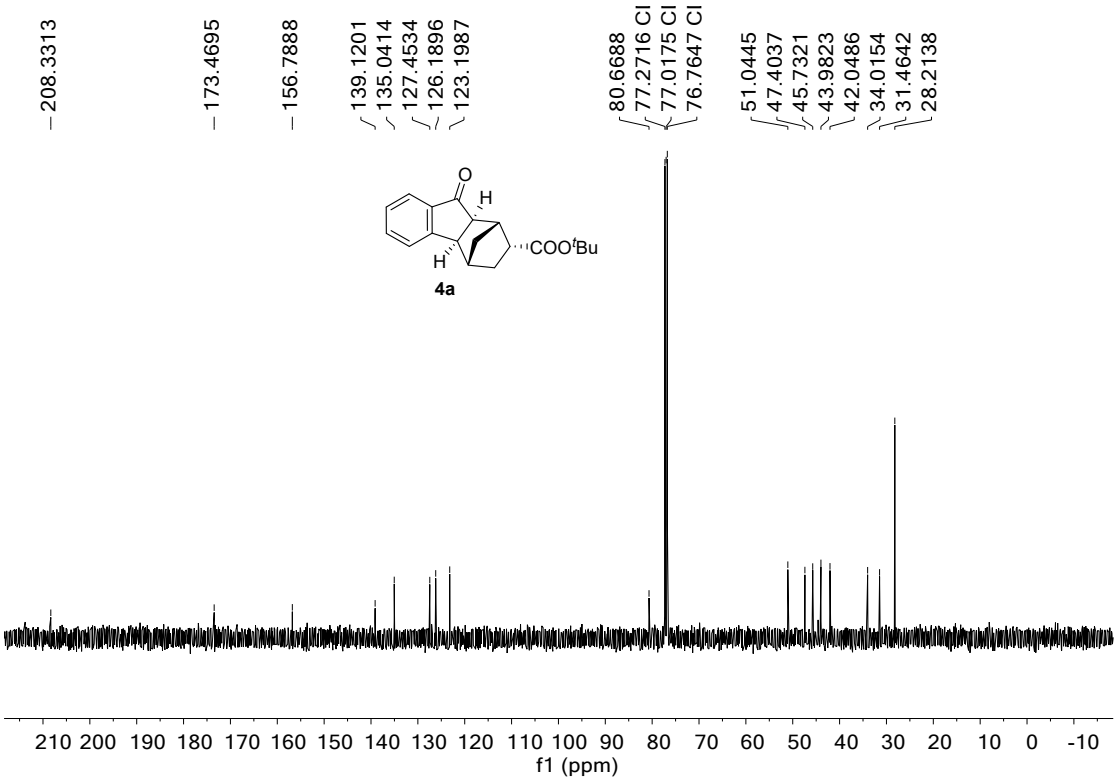
^{13}C NMR spectrum of compound 2ac ($CDCl_3$, 126 MHz)



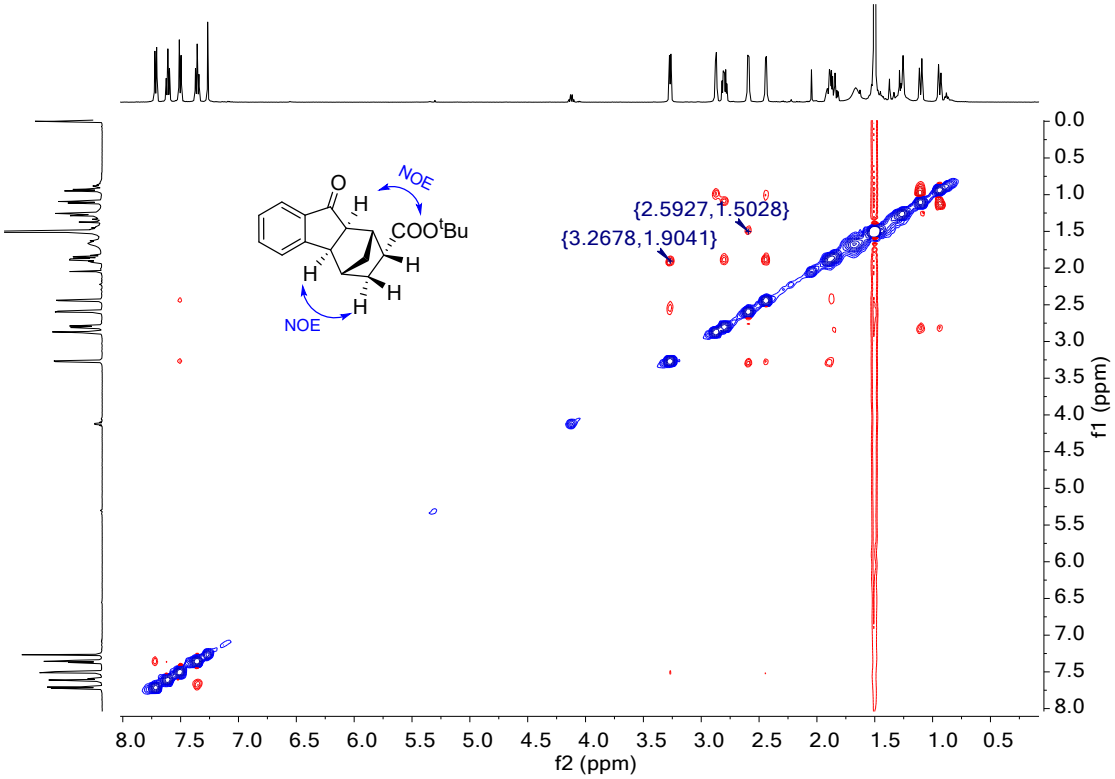
^{1}H NMR spectrum of compound 4a ($CDCl_3$, 500 MHz)



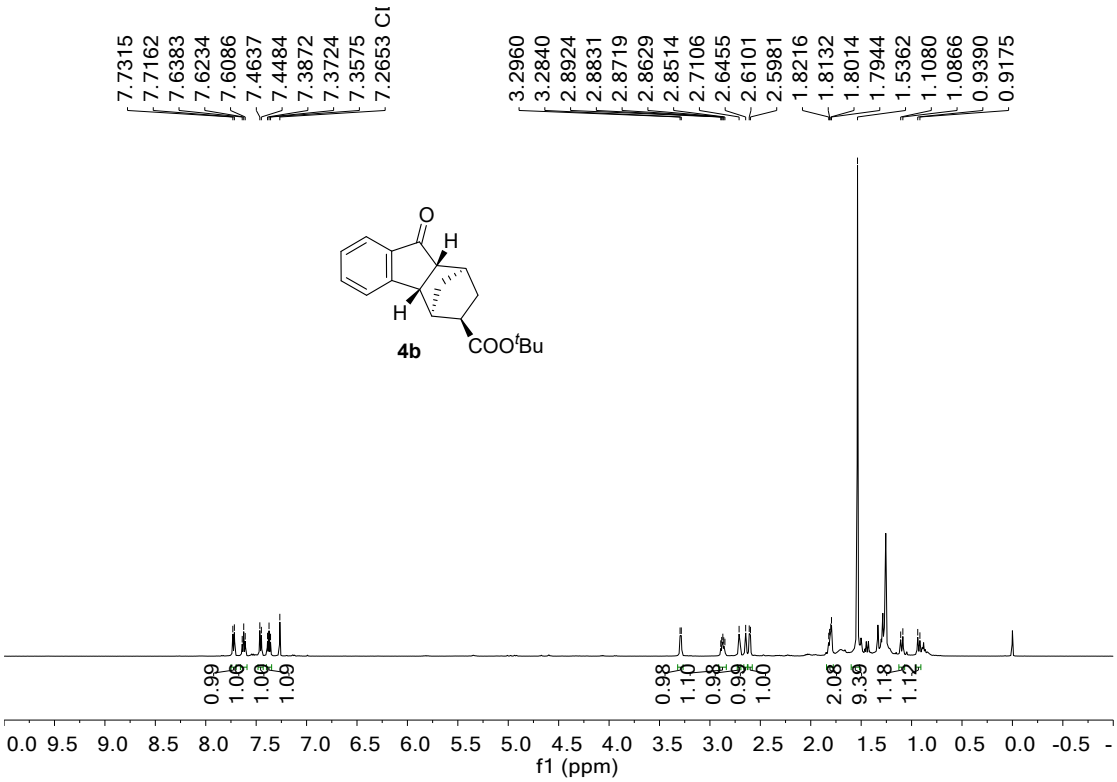
^{13}C NMR spectrum of compound 4a ($CDCl_3$, 126 MHz)



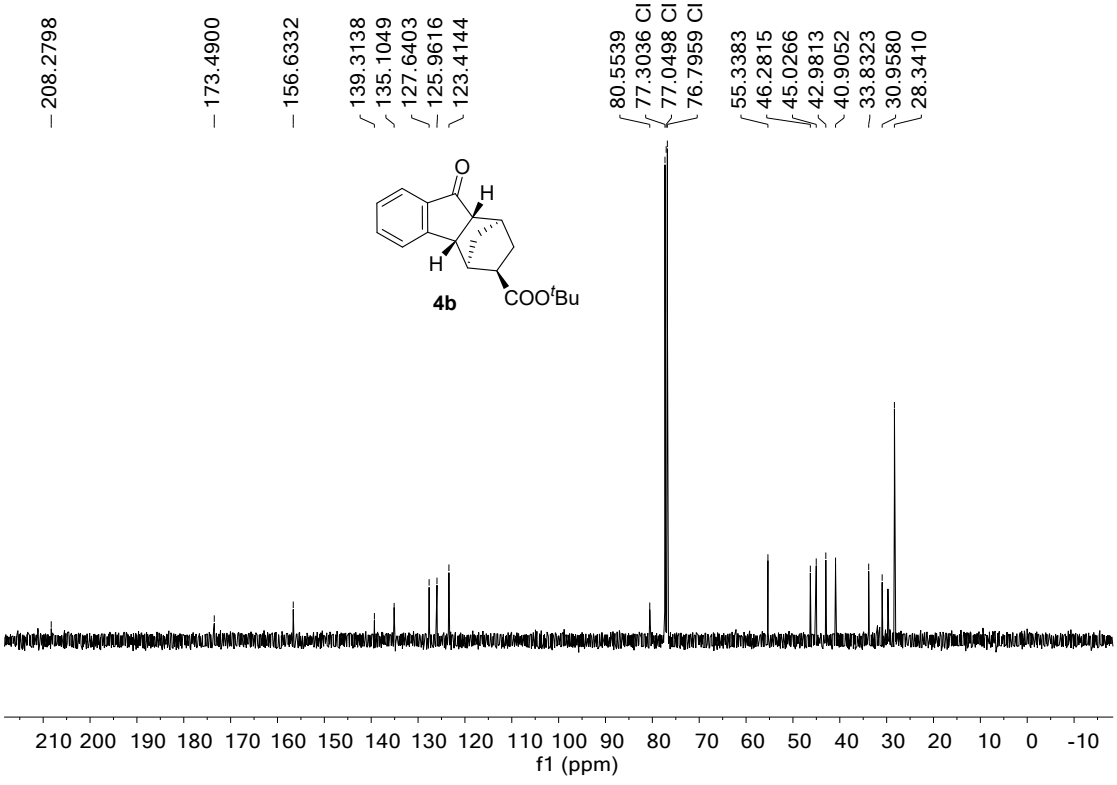
NOSEY spectrum of compound 4a ($CDCl_3$, 500 MHz)



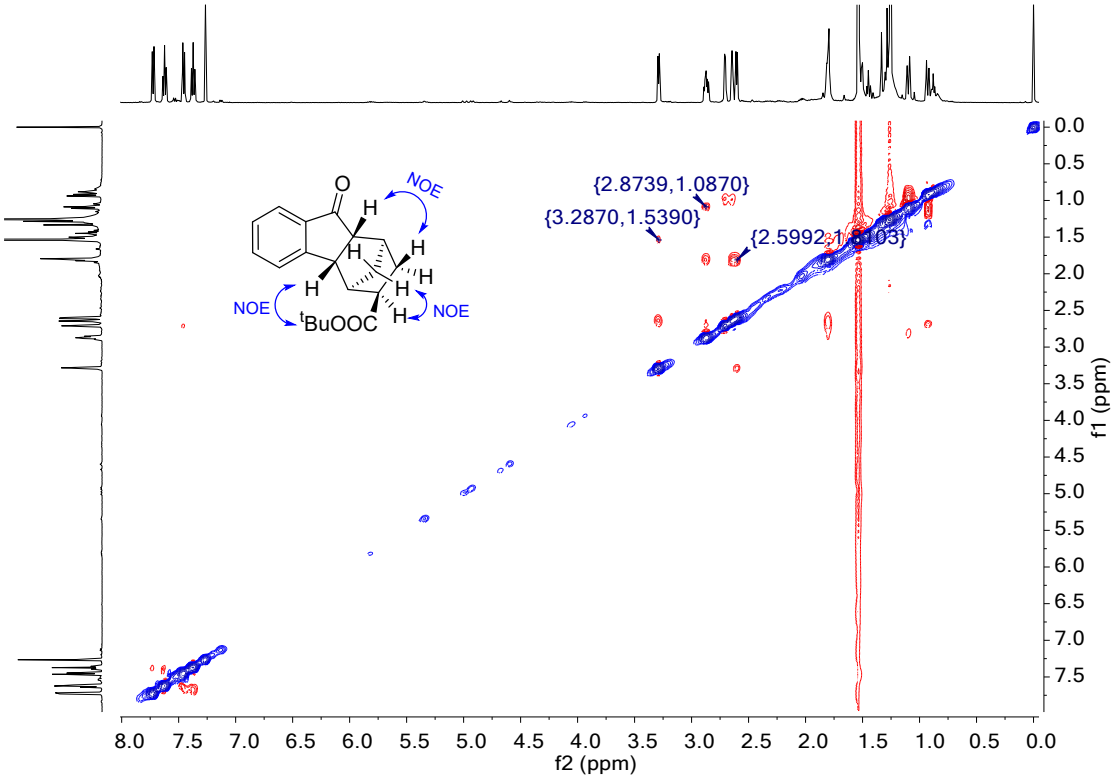
^{1}H NMR spectrum of compound 4b ($CDCl_3$, 500 MHz)



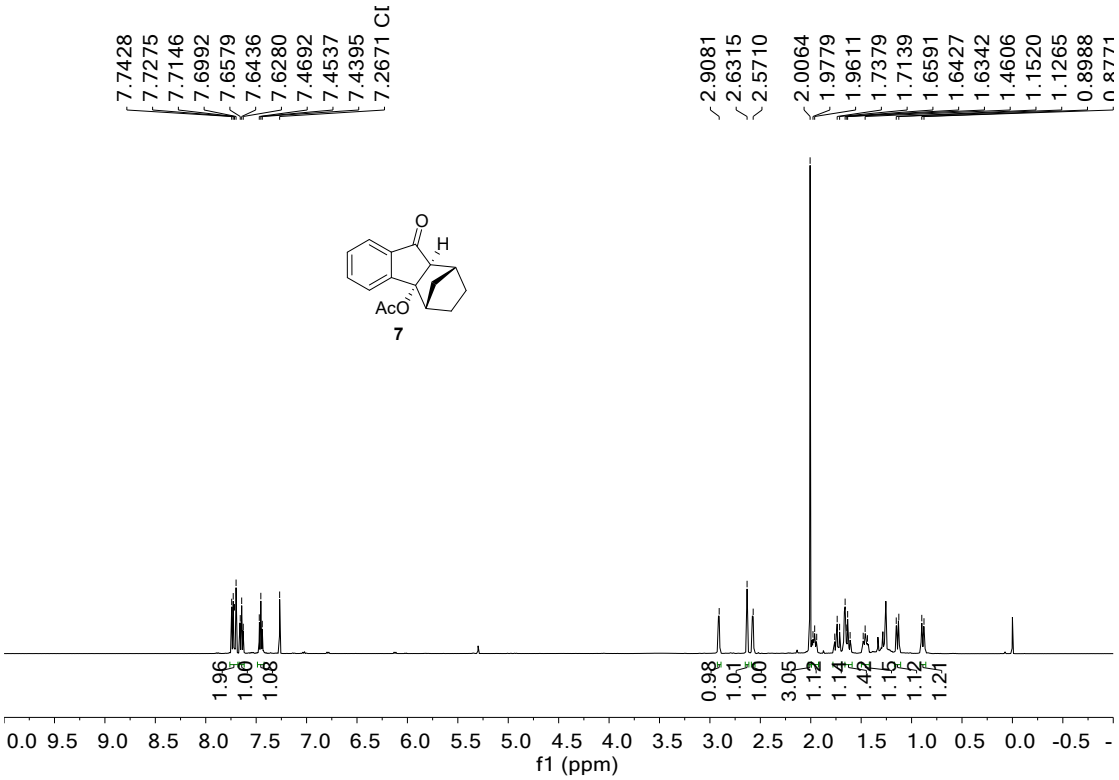
^{13}C NMR spectrum of compound 4b ($CDCl_3$, 126 MHz)



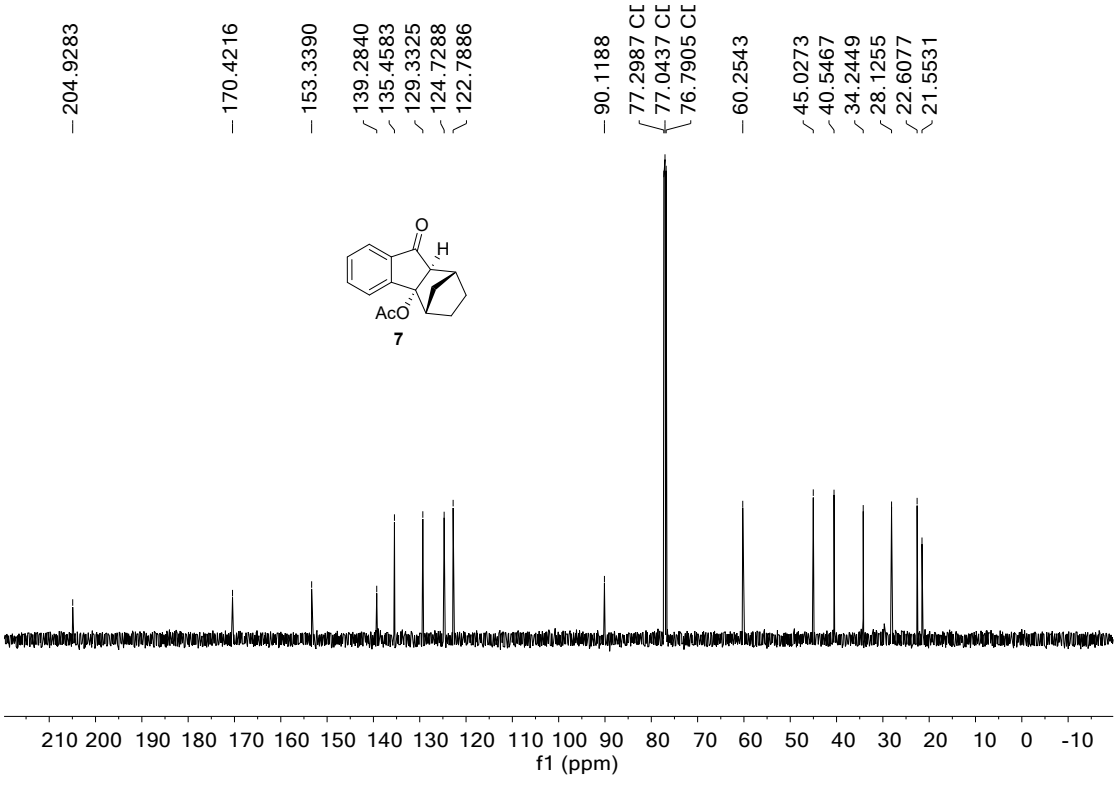
NOSEY spectrum of compound 4b ($CDCl_3$, 500 MHz)



^{1}H NMR spectrum of compound 8 ($CDCl_3$, 500 MHz)



^{13}C NMR spectrum of compound 8 ($CDCl_3$, 126 MHz)



5. X-Ray Crystallographic Data of 2n

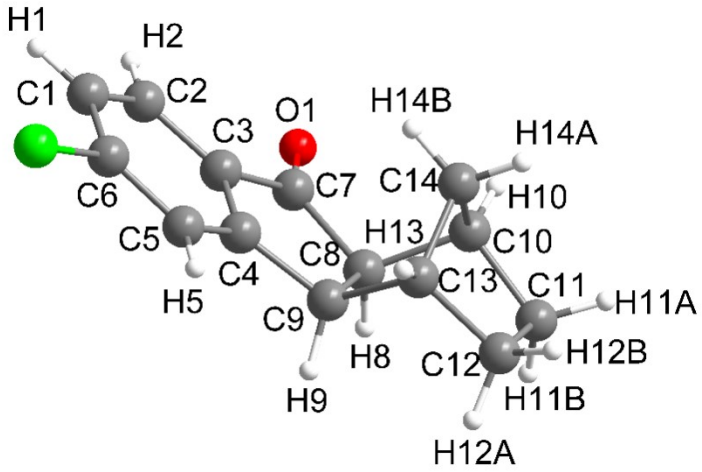


Table S3 Crystallographic data for the compound 2n

Compound	**2n**
Empirical formula	$C_{14}H_{13}ClO$
Formula weight	232.69
Crystal system	Triclinic
Space group	*P*-1
a (Å)	6.9459(11)
b (Å)	9.3739(15)
c (Å)	9.7165(15)
α (°)	66.321(2)
β (°)	76.356(2)
γ (°)	88.872(2)
V (Å^3)	561.03(15)
Z	2
D_c (g·cm^{-3})	1.377
μ (mm^{-1})	0.314
F (000)	244
Crystal size (mm^3)	0.18 × 0.17 × 0.16
θ Range (°)	2.363-27.180
Reflections collected	4371
Independent reflections	2205 [R_{int} = 0.0255]
Reflections observed [$I > 2\sigma(I)$]	1828
Data/restraints/parameters	2205/0/145
Goodness-of-fit on F^2	1.006
R_1/wR_2 [$I > 2\sigma(I)$]	0.0386/0.0942
R_1/wR_2 (all data)	0.0473/0.0993
Max., Min. Δ*ρ* (e·Å^{-3})	0.180, -0.208

6. References

(1) Aly, M. F.; Grigg, R., X= Y-ZH systems as potential 1, 3-dipoles: Part 20. Decarboxylation of α-imino acids. Mechanism and applications to thioamide synthesis. *Tetrahedron* **1988,** *44*, 7271-7282.

(2) Higashibayashi, S.; Reza, A. F. G. M.; Sakurai, H., Stereoselective Cyclotrimerization of Enantiopure Iodonorbornenes Catalyzed by Pd Nanoclusters for C_3 or C_{3v} Symmetric *syn*-Tris(norborneno)benzenes. *J. Org. Chem.* **2010,** *75*, 4626-4628.

(3) Skhiri, A.; Chatani, N., Nickel-Catalyzed Reaction of Benzamides with Bicylic Alkenes: Cleavage of C–H and C–N Bonds. *Org. Lett.* **2019,** *21*, 1774-1778.

(4) Pletnev, A. A.; Tian, Q.; Larock, R. C., Carbopalladation of Nitriles: Synthesis of 2,3-Diarylindenones and Polycyclic Aromatic Ketones by the Pd-Catalyzed Annulation of Alkynes and Bicyclic Alkenes by 2-Iodoarenenitriles. *J. Org. Chem.* **2002,** *67*, 9276-9287.

(5) Sakurai, Y.; Ogiwara, Y.; Sakai, N., Palladium-Catalyzed Annulation of Acyl Fluorides with Norbornene via Decarbonylation and CO Reinsertion. *Chem. Eur. J.* **2020,** *26*, 12972-12977.

(6) Lu, W.-X.; Xing, J.; Sun, Y.; Huang, Q.; Deng, Z.; Mao, J.-G., Palladium-catalyzed and alcohol-enabled transformation to synthesize benzocyclic ketones. *Org. Biomol. Chem.* **2021,** *19*, 10210-10214.